angles and bond lengths. This is clearly justified on the basis of the constancy exhibited in Figure 4.

The energetics for reactions 1-3 are summarized in Table II. Particularly at the 3-21G level of computation, all three measures of delocalization stabilization of the ions agree that systematic vinylization successively increases the stability of the silicon ion more than the carbon ion. The differences are primarily quantitative due to the different reference points as discussed above. For the bond separation reactions (1) the ratio R steadily increases as the number of vinyl groups is increased. In fact, according to the 3-21G results trivinylsilylenium ion is more stable relative to its isolated component bonds than is its carbon analogue. This may well be a result of the strain introduced by the presence of three coplanar vinyl groups. Because the C-Vi bond length is shorter than its Si-Vi counterpart, this is likely to be more of a problem for C than for Si. To investigate the possibility that this strain may cause the vinyl groups be non-coplanar, the three vinyls were rotated out of coplanarity for both trivinyl ions. In each case the 10° rotation caused a substantial energy increase (4.2 and 2.5 kcal/mol for carbon and silicon, respectively).

The results for the bond replacement reaction 2 may be directly compared with the earlier results of Apeloig and co-workers.[5] These authors, using STO-3G[9] wave functions, find Li and planar NH_2 to be the most effective substituents for stabilizing both SiH_3^+ and CH_3^+. According to our STO-2G results, ΔE for reaction 2 is about the same for vinyl and planar NH_2 when X = Si. In contrast, vinyl is only about two-thirds as effective as planar NH_2 when X = C. Similar results apply for 3-21G wave functions, although here planar NH_2 has a slightly larger ΔE. The addition of three vinyl groups produces the greatest stabilization yet calculated. Finally, the predictions of reaction 3 are qualitatively similar to those of (1) and (2).

Conclusions

Successive vinylization of carbenium and silylenium ions provides increasing stabilization of these ions, suggesting that these substituents may lead to isolable silylenium ions, an approach now under investigation in our laboratories. Each additional vinyl group provides less additional stabilization than the last. The latter is more true for carbon than for silicon, so that successive vinylization preferentially stabilizes the silicon. The bond separation reactions, in particular, predict the trivinyl silylenium ion to be more stable than its carbenium analogue. This is likely to be due, at least in part, to the strain of having three coplanar vinyl groups and will have a greater effect for carbon than for silicon due to the shorter C-Vi bond lengths.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Grant No. AFOSR-80-239 from the Air Force Office of Scientific Research. The computer time made available by the North Dakota State University Computer Center is greatly appreciated.

Registry No. $^+CH_2(CH{=}CH_2)$, 1724-44-3; $^+CH(CH{=}CH_2)_2$, 54963-17-6; $^+C(CH{=}CH_2)_3$, 54963-18-7; $^+SiH_2(CH{=}CH_2)$, 64840-94-4; $^+SiH(CH{=}CH_2)_2$, 87999-58-4; $^+Si(CH{=}CH_2)_3$, 87999-59-5.

Communications

Alkylidenebis(perthiolates): A New Class of Organosulfur Ligands Prepared from $(RC_5H_4)_2TiS_5$

Dean M. Giolando and Thomas B. Rauchfuss*

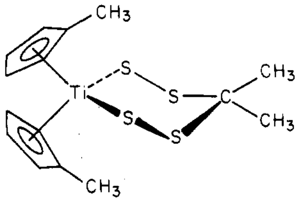
School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

Received September 28, 1983

Summary: In the presence of $(NH_4)_2S$, $(RC_5H_4)_2TiS_5$ (R = H, Me, *i*-Pr) reacts with aliphatic ketones and CH_2Br_2 to give 1,4-$(RC_5H_4)_2TiS_4CR_2$ (R_2 = Me_2; Me, Et; c-C_6H_{10}; H_2) and 1,3-$(RC_5H_4)_2TiS_4CH_2$. The new compounds were purified chromatographically and were characterized spectroscopically including DNMR spectroscopy. Single-crystal X-ray crystallography confirmed the structure of $(i\text{-}PrC_5H_4)_2TiS_4CH_2$.

Bis(cyclopentadienyl)titanium pentasulfide (1) is the most thoroughly studied metal polysulfido chelate.[1-3] According to the method described by Köpf and Schmidt, 1 is prepared from the reaction of Cp_2TiCl_2 (Cp = η^5-C_5H_5) and ammonium polysulfide in acetone.[1] Close examination of one such preparation employing $(MeCp)_2TiCl_2$ revealed two previously unnoticed products, a small amount of a red compound, and a substantial quantity of a colorless species. This paper describes our characterization of these compounds and their bearing on the chemistry of Cp_2TiS_5.[4]

The red product **3b** was found to have the formula $(MeCp)_2TiS_4CMe_2$.[5] Its ^1H NMR spectrum featured



3b

---

[1] Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968,** *101,* 272.

[2] Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982,** *21,* 3947.

[3] (a) Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* **1968,** *7,* 632. (b) Sandow, T.; Steidel, J.; Steudel, R. *Ibid.* **1982,** *21,* 794. (c) Schmidt, M.; Wilhelm, E. *J. Chem. Soc., Chem. Commun.* **1970,** 1111.

[4] For the compound numbers in this paper, the letters **a**, **b** and **c** indicate the Cp, MeCp, and *i*-PrCp derivatives, respectively. The nomenclature for these compounds has been questioned by a reviewer. The staff at Chemical Abstracts suggests naming these compounds as derivatives of sulfenic acids. For example, 1,4-$(C_5H_5)_2TiS_4C(CH_3)_2$ (**3a**) and 1,3-$(C_5H_5)_2TiS_4CH_2$ (**7a**) would be named bis(η^5-2,4-cyclopentadien-1-yl)[2,2-propanedisulfenothioato(2−)]titanium and bis(η^5-2,4-cyclopentadien-1-yl)[1-mercapto-1-methanosulfeno(dithioperoxoate)(2−)]titanium, respectively.

0276-7333/84/2303-0487$01.50/0

singlets for each methyl group and four ring proton multiplets. These data require that the molecule contain nonequivalent MeCp groups with a time-averaged plane of symmetry bisecting the MeCp rings. The nonequivalency of the methyl resonances indicates that **3b** exists in the chair but not the twist conformation although the sterically unfavorable boat conformation is also consistent with these data. The colorless product obtained in good yields from the synthesis of **3b** is also formed in the absence of titanium and proved to be 1,4-$(Me_2C)_2S_4$ otherwise known as 3,3,6,6-tetramethyl-*s*-tetrathiane or duplodithioacetone (**2**).[6] With this information in hand, an improved synthesis of this class of unusual TiS_4C cycles was developed.

Attempts to prepare **3b** from the reaction of **2** with $(MeCp)_2TiS_5$ or $(MeCp)_2Ti(SH)_2$[7] were unsuccessful. It was found, however, that the dropwise addition of aqueous $(NH_4)_2S$ to an acetone slurry of **1** followed by chromatography on silica gel gave **3a** in 42–50% yields as red-black crystals from CH_2Cl_2–hexanes. Our procedure appears to be general for unhindered aliphatic ketones; using methyl ethyl ketone and cyclohexanone, we obtained the corresponding derivatives **4a**,**b** and **5a** in 20–40% yields (eq 1) an analytically pure crystals from hexane.[8] The ^1H NMR spectrum for **4a** was particularly informative as it revealed the presence of two conformers in a ~2:1 ratio.[9]

$$(RCp)_2TiS_5 + 2(NH_4)_2S + R'C(O)R'' \rightarrow \underset{\mathbf{3-5}}{(RCp)_2TiS_4CR'R''} + H_2O + 2NH_3 + (NH_4)_2S_3 \quad (1)$$

3 (R′ = R″ = CH_3), **a**, R = H, **b**, R = CH_3, **c**, R = $CH(CH_3)_2$; **4** (R′ = CH_3, R″ = CH_2CH_3), **a**, R = H, **b**, R = CH_3; **5** (R′, R″ = $(CH_2)_5$), **a**, R = H

The procedure indicated in eq 1 is not applicable to aldehydes, and we were unsuccessful in our attempts to prepare methylene derivatives of **1** from aqueous formaldehyde, paraformaldehyde, or *s*-trithiane. It was found, however, that slurries of **1** in CH_2Br_2 did react with aqueous ammonium sulfide to afford two new red products that were purified by chromatography on silica gel. Both new compounds have the formula $(MeCp)_2TiS_4CH_2$,[8] but while the more abundant (19% yield) isomer appeared to be analogous to the aforementioned derivatives, the ^1H NMR spectrum of the minor product (4% yield), consisting of eight cyclopentadienyl resonances, revealed that this species lacks any time-averaged plane of symmetry.[10] These data suggest that in the case of the sterically unhindered CH_2 moiety, both the 1,4-**6b** and the 1,3-**7b** isomers of $(MeCp)_2TiS_4CH_2$ (eq 2) were obtained.

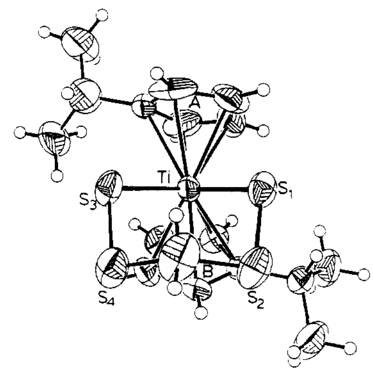
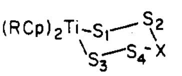


Figure 1. ORTEP plots of 1,4-$(i\text{-}PrCp)_2TiS_4CH_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are represented by arbitrary spheres.

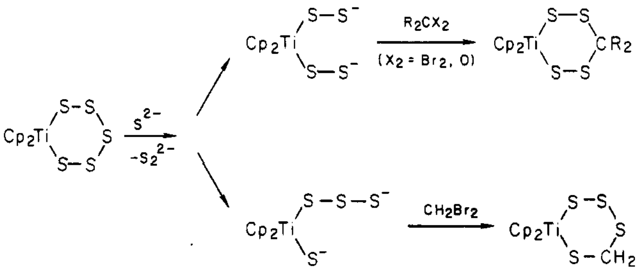
Table I. Selected Bond Distances (Å) and Angles (deg) for[a]



parameter	R = *i*-Pr, X = CH_2	R = H, X = S[13]
TiS_1	2.438 (1)	2.448 (1)
S_1-S_2	2.055 (2)	2.059 (2)
S_2-X	1.818 (3)	2.067 (2)
RCp-Ti-RCp	130.1	133.7
Ti-S_1-S_2	109.4 (1)	108.6 (1)
S_1-Ti-S_3	91.6 (1)	94.6 (1)
S_2-X-S_4	118.3 (4)	106.7 (1)
$S_1 \cdots S_3$	3.489 (1)	3.58
$S_2 \cdots S_4$	3.117 (1)	3.29

[a] Both molecules possess approximately C_s symmetry.

Scheme I



$$(RCp)_2TiS_5 + 2(NH_4)_2S + CH_2Br_2 \rightarrow \underset{\mathbf{6,\,7}}{(RCp)_2TiS_4CH_2} + 2NH_4Br + (NH_4)_2S_3 \quad (2)$$

6 (1,4-$(RCp)_2TiS_4CH_2$), **a**, R = H, **b**, R = CH_3, **c**, R = $CH(CH_3)_2$; **7** (1,3-$RCp)_2TiS_4CH_2$), **a**, R= H, **b**, R = CH_3, **c**, R = $CH(CH_3)_2$

The structure of 1,4-$(i\text{-}PrCp)_2TiS_4CH_2$[11] was established by single-crystal X-ray diffraction.[12] The molecule is well behaved in the lattice, all atoms were located, an ORTEP plot is depicted in Figure 1, and important parameters are

---

(5) Anal. Calcd for $C_{15}H_{20}TiS_4$ (**3b**): C, 47.88; H, 5.36; Ti, 21.73; S, 34.02. *Found:* C, 47.69; H, 5.50; Ti, 12.59; S, 33.75. **3b**: ^1H NMR (toluene-d_8, −33 °C) δ 6.090 (2 H, t), 5.670 (2 H, t), 5.648 (2 H, t), 5.323 (2 H, t), 2.172 (3 H, s), 1.796 (3 H, s), 1.695 (3 H, s), 1.264 (3 H, s); FDMS (0 ma) 376 (100, M^+).

(6) Magnusson, B. *Acta Chem. Scand.* **1959**, *13*, 1031.

(7) Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223.

(8) Molecular ions were observed in the field desorption mass spectra for the new compounds. Analyses for the C_5H_5 derivatives are given below. Calcd for $C_{13}H_{16}TiS_4$ (**3a**): C, 44.84; H, 4.63; Ti, 13.76; S, 36.76. Found: C, 44.84; H, 4.68; Ti, 13.58; S, 36.52. Calcd for $C_{14}H_{18}TiS_4$ (**4a**): C, 46.42; H, 5.01; Ti, 13.22; S, 35.34. Found: C, 45.54; H, 5.08; Ti, 13.08; S, 36.18. Calcd for $C_{16}H_{20}TiS$ (**5a**): C, 49.49; H, 5.19; Ti, 12.34; S, 32.97. Found: C, 49.26; H, 5.03; Ti, 12.42; S, 32.73. Calcd for $C_{11}H_{12}TiS_4$ (**6a**): C, 41.27; H, 3.78; Ti, 14.96; S, 39.99. Found: C, 41.39; H, 3.63; Ti, 14.90; S, 38.60.

(9) 1,4-$(C_5H_5)_2TiS_4C(CH_3)(CH_2CH_3)$ (**4a**): ^1H NMR ($CHCl_3$-d_1, 20 °C) δ 6.335 (s), 6.328 (s), 6.253 (s), 6.215 (s), 2.133 (q, 2 H), 1.614 (s, 6 H), 1.247 (t, 3 H), 1.066 (q, 4 H), 0.909 (s, 3 H), 0.743 (t, 6 H).

(10) The coalescence temperatures of the cyclopentadienyl, methylene, and methyl protons are −4, 20 and 20 °C, respectively. A slow-exchange spectrum was obtained at −33 °C. 1,3-$(CH_3C_5H_4)_2TiS_4CH_2$ (**7b**): ^1H NMR (THF-d_8, −33 °C) δ 6.255 (2 H, m), 6.196 1 H, m), 6.156 (1 H, m), 6.068 (1 H, m), 6.040 (1 H, m), 5.971 (1 H, m), 5.784 (1 H, m), 5.439 (1 H, d), J_{HH} = 13.7 Hz), 4.638 (1 H, d, J_{HH} = 13.7 Hz), 2.832 (3 H, s), 2.226 (3 H, s).

(11) These preparations work well for the Cp, MeCp, and *i*-PrCp derivatives; the latter tend to give higher quality single crystals.

(12) The structure was solved by Dr. C. S. Day of the Crystalytics Co. $(C_5H_4CH(CH_3)_2)_2TiS_4CH_2$ (**4a**) crystallizes in the monoclinic space group $p2_1/c—C_{2h}^5$ (no. 14) with a = 11.584 (5) Å, b = 11.044 (4) Å, c = 15.252 (8) Å, β = 102.95 (4)°, V = 1901 (1) Å^3 Z = 4, μ = 9.9 cm^{-1} (Mo Kα, λ = 0.71073 Å). A total of 4366 independent reflections (3° ≥ 2θ ≥ 55°) were collected on a Nicolet autodiffractometer. The final discrepancy factors are 4.7 and 4.5% for R_F and R_w, respectively.

presented in Table I. Structurally, **6c** closely resembles Cp_2TiS_5[13] and S_5CH_2.[14] In contrast, the most stable conformer of **2** in solution and as a solid[15] is the twist boat which is stabilized by minimization of unfavorable transannular S···S contacts.[16] In **6c** the transannular S···S distances are longer as the result of the Ti–S bonds being ca. 0.6 Å longer than typical C–S bonds offsetting the effect of the S–Ti–S angle (91°) which is 26° more acute than for typical S–C–S angles.[17]

The pathway for insertion of CR_2 unit into the *cyclo*-TiS_5 moiety is proposed to proceed via initial cleavage of the TiS_5 ring by an anionic sulfur nucleophile. The intermediate $Cp_2TiS_x^{2-}$ species would be capable of nucleophilic addition to ketones or alkyl halides (Scheme I). We have previously shown that **1** is reactive toward phosphine nucleophiles,[7,20] and it is well-known that S–S bonds are readily cleaved by RS^- reagents.[21] It should be noted that our procedures work optimally with aqueous $(NH_4)_2S$; aqueous Na_2S and anhydrous Li_2S (in THF) were found not to be useful.

The TiS_4CR_2 ring inversion barriers for **3a**, **6a**, and **7a** were measured in toluene-d_8 by DNMR spectroscopy.[22] The results reveal the following ordering in the free energies of activation for ring inversion: $Cp_2TiS_4CMe_2$ (83.6 kJ/mol) > Cp_2TiS_5[24] (76 kJ/mol) > 1,4-$Cp_2TiS_4CH_2$ (59.2 kJ/mol) ≈ 3-$(C_5H_5)_2TiS_4CH_2$ (57 kJ/mol). We suggest that the lone pair–methyl and lone pair–lone pair repulsions strongly influence the ease of TiS_4X ring inversion.

In summary, the reactivity of **1** toward sulfur nucleophiles establishes a route to novel Ti–S–C rings. By virtue of the stability of the Ti–S bonds toward nucleophiles, **1** reacts in a more controlled manner with S^{2-} than S_8 itself. It will be of interest to test the generality of this reaction with other polysulfide chelates and to examine the utility of these compounds in organic synthetic applications.

Acknowledgment. This research was supported by the National Science Foundation (NSF CHE 81-06781). The 360-MHz NMR spectra were obtained through the Regional NMR Facility at the University of Illinois (CHE 79-16100). T.B.R. is a fellow of the A. P. Sloan and Camille and Henry Dreyfus Foundations.

Registry No. **1a**, 12116-82-4; **1b**, 78614-86-5; **1c**, 88510-17-2; **2**, 4475-72-3; **3a**, 88510-18-3; **3b**, 88510-19-4; **3c**, 88510-20-7; **4a**, 88510-21-8; **4b**, 88510-22-9; **5a**, 88510-23-0; **6a**, 88510-24-1; **6b**, 88510-25-2; **6c**, 88510-26-3; **7a**, 88510-27-4; **7b**, 88524-89-4; **7c**, 88510-28-5; $(NH_4)_2S$, 12135-76-1; CH_2Br_2, 74-95-3; methyl ethyl ketone, 78-93-3; cyclohexanone, 108-94-1.

Supplementary Material Available: A full structure analysis report, including tables of atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, intramolecular contacts, and observed and calculated structure factor amplitudes (31 pages). Ordering information is given on any masthead page.

---

(13) Muller, E. G.; Peterson, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91. Epstein, E. F.; Bernal, I. *J. Organomet. Chem.* **1971**, *26*, 229.

(14) Fehér, R.; Lex, J. *Z. Anorg. Allg. Chem.* **1976**, *423*, 103.

(15) Fredga, A. *Acta Chem. Scand.* **1958**, *12*, 891.

(16) Bushweller, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 6019.

(17) The average C–S distance and S–C–S angle for 3,3:6,6-bis(pentamethylene)-*s*-tetrathiane,[18] pentathiane, and 1,4-$(i\text{-}PrCp)_2TiS_4CH_2$ are 1.82 Å and 114°, respectively. The average Ti–S distance for Cp_2TiS_5, 1,4-$(i\text{-}PrCp)_2TiS_4CH_2$, 1,4-$(i\text{-}PrCp)_4Ti_2S_4$[19] and 1,5-$(MeCp)_4TiS_6$[20] is 2.40 Å.

(18) Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65.

(19) Giolando, D. M.; Rauchfuss, T. B.; Wilson, S. R., unpublished results.

(20) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.

(21) Davis, R. E. In "Survey of Progress in Chemistry"; Scott, A., Ed.; Academic Press: New York, 1964; Vol. II, pp 189–238.

(22) Values were calculated from[23] $k = \pi\delta\nu^2/[2(W^* - W_0)]$ and $\Delta G^* = 1.914 \times 10^{-2})T[10.319 + \log(T/k)]$. Assuming an uncertainty of 4 K in the coallescence temperature, ΔG^* will differ by 0.5 kJ/mol.

(23) Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982.

(24) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1978**, *160*, 75.

Mechanistic and Synthetic Implications of the Reactions of Aroyl Chlorides with Chlorocarbonylbis(triphenylphosphine)rhodium(I). A Catalytic Procedure for the Preparation of Carbonyl-Labeled Aroyl Chlorides

J. A. Kampmeier* and Sankaran Mahalingam

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received December 16, 1983

Summary: The reaction of chlorocarbonylbis(triphenylphosphine)rhodium, $RhCl(CO)(PPh_3)_2$, with aroyl chlorides in the presence of free ^{13}CO in $CDCl_3$ or C_6H_6 solvent at 100 °C gives a statistical distribution of the label over all of the "CO" sites in the system. The reaction is catalytic in rhodium complex and constitutes a simple synthesis of aroyl chlorides labeled with ^{13}C in the carbonyl position. $Ph^{13}COCl$, 2-$ClC_6H_4{}^{13}COCl$, 3-$NO_2C_6H_4{}^{13}COCl$, 4-$NO_2C_6H_4{}^{13}COCl$, 4-$Cl^{13}COC_6H_4{}^{13}COCl$, 4-$CH_3OC_6H_4{}^{13}COCl$, 4-$CH_3COC_6H_4{}^{13}COCl$, and *trans*-$C_6H_5CH{=}CH^{13}COCl$ were successfully prepared by this procedure. $Ph^{14}COCl$ was prepared by exchange with $CH_3{}^{14}COCl$ in the presence of $RhCl(CO)(PPh_3)_2$. Control experiments show that the labeling does not proceed via aryl chlorides. The labeling, by equilibrium of organometallic intermediates, shows that $RhCl(CO)(PPh_3)_2$ reacts with aroyl chlorides at 100 °C and that the equilibration reactions are faster than formation of aryl chlorides.

Acid chlorides are decarbonylated to give aryl chlorides by catalytic amounts of chlorotris(triphenylphosphine)rhodium, **1**, at temperatures of the order of 180 °C.[1] At temperatures of the order of 100 °C, the reaction of aroyl chlorides with complex **1** is stoichiometric and was thought[2] to give aryl chlorides and chlorocarbonylbis(triphenylphosphine)rhodium, **4**. The difference between the catalytic and stoichiometric reactions was attributed to a high barrier to further reaction of complex **4** with the aroyl chloride.[3]

We recently reported[4] that the stoichiometric decarbonylation of aroyl chlorides by $RhCl(PPh_3)_3$ does not give aryl chlorides[5] and that the actual decarbonylation product is $RhCl_2(Ar)(PPh_3)_2$, **5**. We also presented evidence for

---

(1) The literature has been summarized and reviewed several times, most recently and thouroughly by Baird (Baird, M. C. In "The Chemistry of Acid Derivatives"; Patai, S., Ed., Wiley: New York, 1979, Supplement B, part 2, pp 825–857. See also: Tsuji, J. In "Organic Synthesis by Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977, Vol. 2, pp 595–654.

(2) (a) Blum, J. *Tetrahedron Lett.* **1966**, 1605–1608. (b) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508–1514.

(3) (a) Ohno, K.; Tsuji J. J. Am. Chem. Soc. **1968**, *90*, 99–107. (b) Stille, J. K.; Huang, F.; Regan, M. T. *Ibid.* **1974**, *96*, 1518–1522. (c) Strohmeier, W.; Pfohler, P. *J. Organomet. Chem.* **1967**, *89*, 2338–2341.

(4) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 1847–49.

(5) Ehrenkaufer, R. E.; MacGregor, R. R.; Wolf, R. P. *J. Org. Chem.* **1982**, *47*, 2489–91, subsequently reported that benzoyl fluoride is not converted to fluorobenzene as claimed in the literature.[6]