philicities in these complexes, with vanadium in complexes **4** and **5** exhibiting greater electrophilicity.

Given the inclination of other 17-electron metal carbonyl complexes to undergo associative ligand displacement reactions, it seems ironic that the incorporation of a pentadienyl ligand, which would be expected to promote associative attack via $\eta^5 \rightarrow \eta^3$ coordination changes, should lead instead to a series of compounds for which much lower rates of substitution are observed and for which the substitutions also take place via dissociative means. Additional kinetic, EPR, and structural studies are under way in attempts to better understand the unexpected behavior of these 17-electron complexes.

Acknowledgment. We thank the National Science Foundation for support of this research. Two of us (R.M.K. and F.B.) thank Dr. Robin Perutz for helpful discussions and R. W. Gedridge and T. D. Newbound for samples of the phosphine complexes.

Supplementary Material Available: Table of rate constants and CO concentration dependence for CO exchange in complex **1** (1 page). Ordering information is given on any current masthead page.

Reactions of Alkenylchromium Reagents Prepared from Alkenyl Trifluoromethanesulfonates (Triflates) with Chromium(II) Chloride under Nickel Catalysis

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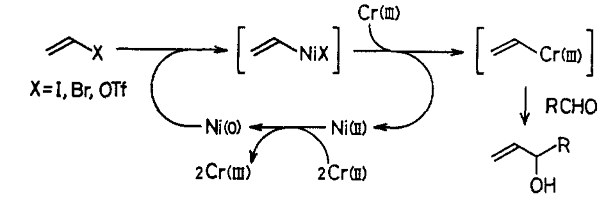
Nucleophilic substitution of an enolate oxygen with an organometallic compound under $C(sp^2)$–O bond fission has been recently achieved.[1] However, there are few examples of the production of alkenyl anion equivalents from such enolate derivatives as alkenyl triflates.[2] We disclose here reactions of alkenylchromium reagents[3] prepared from alkenyl triflates[4] by reduction with chromium(II) chloride under nickel catalysis.

After our report in 1983 about Grignard-type carbonyl addition of alkenyl halides mediated by $CrCl_2$,[3] we noticed that the success of the reaction heavily depended on the nature of the $CrCl_2$. A certain specimen of $CrCl_2$ purchased[5] was effective and the others[6] failed to give reproducible results. This trouble prompted us to seek a second metal catalyst which might be contained in the effective crop of chromium(II) salt.[7] Analysis of fluorescent

Scheme I



X-rays of the special lots revealed that nickel was the major contaminant.[5] Addition of a catalytic amount of $NiCl_2$ to a commercial lot of $CrCl_2$[6] has shown reproducible results as we reported.[3] Moreover, the system has proved to promote the Grignard-type reaction between alkenyl triflates and aldehydes under mild conditions.

A mixture of anhydrous $CrCl_2$ (0.49 g, 4.0 mmol)[6] and a catalytic amount of $NiCl_2$ (2.6 mg, 0.020 mmol) in dry, oxygen-free dimethylformamide (DMF, 10 mL) was stirred at 25 °C for 10 min under argon atmosphere. To the reagent at 25 °C was added a solution of benzaldehyde (0.11 g, 1.0 mmol) in DMF (5 mL) and a solution of alkenyl triflate **1** (0.63 g, 2.0 mmol) in DMF (5 mL) successively. After stirring at 25 °C for 1 h, the reaction mixture was diluted with ether (20 mL), poured into water (20 mL), and extracted with ether repeatedly. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica gel column chromatography provided 0.23 g (83%) of the desired allylic alcohols **2** as a colorless oil. Under the same conditions, 1-iodo-1-cyclohexene also reacted with the aldehyde to give the adduct in 74% yields (Table I, run 11), while 1-(trimethylsiloxy)-1-cyclohexene and 1-cyclohexenyl diethyl phosphate remained unchanged with 83%[8] and 98% recovery, respectively. Yields of the coupling reaction between triflate **1** and benzaldehyde with such potential catalysts[9] (5 mol % of $CrCl_2$) in DMF at 25 °C for 12 h are as follows: $MnCl_2$, <1%; $FeCl_3$, 9%; $CoCl_2$, 16%; CuCl, <1%; $PdCl_2$,[10] <1%.[11] In general, high solubility of $CrCl_2$ is essential to promote the reaction smoothly. Little or no reaction occurs in ether or THF. DMF is the most effective solvent.

The examples of the Grignard-type addition of alkenyl triflates to aldehydes with the combination of $CrCl_2$ and $NiCl_2$ are shown in Table I. In the case of α,β-unsaturated aldehyde, 1,2-addition products are produced mainly (runs 4 and 10).[3,12] The alkenylchromium reagents have aldehyde-selectivity[13] (runs 5–7) similarly to allyl-[14] and alkynylchromium ones.[15] Steric factors of double bonds influence the reaction markedly. Triflates **4** and **6**, whose substituents of double bonds possess trans position of OTf group, reacted smoothly (runs 14 and 17). In contrast, treatment of a triflate having a cis substituent with the $CrCl_2$–$NiCl_2$ system resulted in recovery of the starting triflate even at 60 °C (run 13) or in cis–trans isomerization–coupling reaction sequence (run 15).[16] As seen in Table I, regiochemistry of double bonds is maintained during the coupling reaction. Since alkenyl triflates can be obtained regioselectively from ketones,[1b,17] the new

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(1) (a) For organoalanes–Pd(0) system, see: Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 2531. (b) For organostannanes–Pd(0) system, see: Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (c) For the combination of Grignard reagents and Ni(0), see: Wenkert, E.; Michelotti, E. L.; Swindel, C. S. *Ibid.* **1979**, *101*, 2246. Hayashi, T.; Katsura, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (d) For organocopper reagents, see: McMurry, J. E.; Scott, W. J. *Ibid.* **1980**, *21*, 4313.

(2) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271.

(3) Takai, K.; Kimura, K.; Kuroda, T.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 5281.

(4) For general reviews of triflate chemistry, see: (a) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85. (b) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.

(5) In 1983 we purchased anhydrous $CrCl_2$ from ROC/RIC Corp (Belleville, NJ) and used it without further purifications. The effective lots have been proved to contain ca. 0.5 mol % of Ni on the basis of Cr.

(6) Anhydrous $CrCl_2$ free from nickel salts[9] was purchased from either Aldrich Co. (90% purity) or Rare Metallic Co. (99.99% purity).

(7) Professor Yoshito Kishi kindly informed us that he also encountered the problem and found the same effect of nickel independently. He employed the combination of chromium and nickel in the total synthesis of palytoxin. See, Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.*, in press.

(8) GLPC (3% Silicone OV-17, 1.5 m) yield.

(9) The absence of Ni was confirmed by fluorescent X-rays analysis.

(10) Reduction of triflate **1** to 1-dodecene took place in 64% yield based on the triflate **1**.

(11) Decomposition of triflate **1** leading to 1-dodecyne and/or 1,2-dodecadiene proceeded at the same time with these catalysts.

(12) In nickel-catalyzed 1,4-addition reaction of organoaluminum or -zirconium compounds, the transformation of Ni(I) → Ni(III) → Ni(I) is postulated for an efficient catalytic cycle. Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3976.

(13) (a) For organotitanium reagents, see: Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1. Seebach, D. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Salle & Sauererlaender, Aarau, and Wiley: New York; 1983; Vol. 3, p 217. (b) For methylenation reaction, see: Okazoe, T.; Hibino, J.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5581.

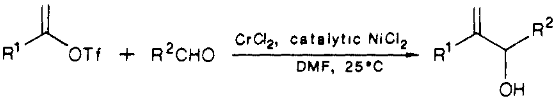
(14) Hiyama, T.; Okude, Y.; Kimura, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 561 and references cited therein.

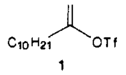
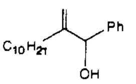
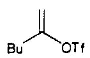
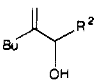
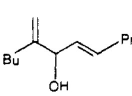
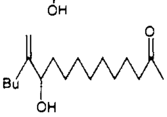
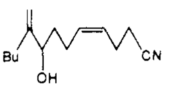
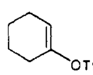
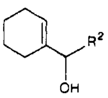
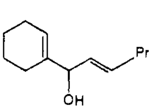
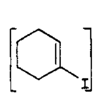
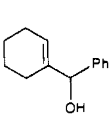
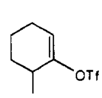
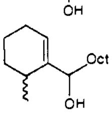
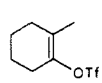
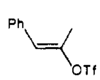
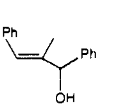
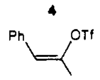
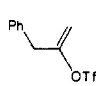
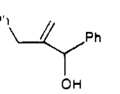
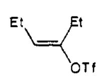
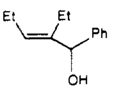
(15) Takai, K.; Kuroda, K.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5585.

(16) The cis–trans isomerization of double bond could occur during oxidative addition of triflate **4** to nickel(0). See ref 18a.

0002-7863/86/1508-6048$01.50/0

Table I. Grignard-Type Reaction between Alkenyl Triflates and Aldehydes Mediated by $CrCl_2$–$NiCl_2$ System[a]



run	alkenyl triflate	aldehyde	time, h	product	isolated yield, %
1	 1	PhCHO	1	 2	83
2		PhCHO	1		72
3		OctCHO	3		81
4		*t*-PrCH=CHCHO	4		64
5			1		87[b]
6			2		78
7		(PhCOMe)	6	(recovery of PhCOMe, 87%)[c]	
8		PhCHO	1		74
9		OctCHO	4		83
10		*t*-PrCH=CHCHO	4		41
11		PhCHO	1		74[d]
12		OctCHO	4		76[e]
13	 3	OctCHO			*f*
14	 4	PhCHO	1		92
15	 5	PhCHO	3		46
16		PhCHO	1		85
17	 6	PhCHO	2		72

[a] A mixture of an alkenyl triflate (2.0 mmol) and an aldehyde (1.0 mmol) was treated at 25 °C with $CrCl_2$ (4.0 mmol) and $NiCl_2$ (0.02 mmol) in DMF. [b] See ref 21. [c] The reaction mixture was heated at 60 °C. [d] See ref 3. [e] Almost 1:1 mixture of diastereomers was produced. [f] Triflate **3** was recovered unchanged in 79% yield after being heated at 60 °C for 6 h.

method provides an effective tool for the crossed pinacol-type coupling of the two carbonyl carbon with regiospecific dehydration.

We are tempted to assume the following mechanism (Scheme I). Nickel(II) chloride is first reduced to nickel(0) with 2 equiv of chromium(II) chloride. Oxidative addition of alkenyl triflates to the nickel(0) takes place.[1c,18] Then transmetalation reaction between the resulting alkenylnickel species and chromium(III) salt occurs to afford alkenylchromium reagents, which react with

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(18) (a) Semmelhack, M. F.; Helquist, P. M.; Gorzynski, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 9234. (b) Tsou, T. T.; Kochi, J. K. *Ibid.* **1979**, *101*, 7547.

aldehydes to produce the desired allylic alcohols.[19] Presence of a donor ligand on nickel such as triphenylphosphine proved to accelerate the homo-coupling of alkenyl triflates.[20] For example, addition of a catalytic amount of $NiCl_2(PPh_3)_2$ (5 mol % of $CrCl_2$) instead of $NiCl_2$ in the reaction of triflate **1** and benzaldehyde under the same condition described above provided 2,3-didecyl-1,3-butadiene (**7**) in 37% yield along with the desired alcohol **2** (35%).

Acknowledgment. We are grateful to Professor Yoshito Kishi at Harvard University for valuable discussions.

(19) Attempt to complete the Grignard-type reaction between triflate **1** (1.0 equiv) and benzaldehyde (0.5 equiv) with $NiCl_2$ (0.2) and zinc (2.0) in DMF at 25 °C for 6 h resulted in recovery of the starting materials.

(20) (a) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375. (b) Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089.

(21) Bp 112 °C (bath temperature, 2 torr); IR (neat) 3434, 2926, 2854, 1714, 1646, 1459, 1359, 1047, 718 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (t, 3, J = 7 Hz), 1.15–1.75 (m, 18), 1.90–2.15 (m, 3), 2.13 (s, 3), 2.42 (t, 2, J = 7 Hz), 4.06 (t, 1, J = 6 Hz), 4.84 (s, 1), 5.00 (s, 1). Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 75.97; H, 12.26.

Synthesis and Structure of 2,2′,3,3′-Tetrakis(trimethylsilyl)[1,1′-*commo*-bis(2,3-dicarba-1-germa-*closo*-heptaborane)] (12): A Germanocene Analogue?

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Recent theoretical calculations[1,2] coupled with synthetic[3] and structural investigations, unambiguously show that the lone pair of electrons on the divalent tin in stannocene[4,5] and stannacarborane derivatives[6] is chemically inactive and the metal does not act as a donor atom. But the stannocinium cations[7] and the stannacarboranes behave as Lewis acids when forming complexes with tetrahydrofuran and 2,2′-bipyridine.[8,9] Although a similar study in the analogous germanocene,[10,11] germacarboranes,[6,12] and germaboranes[13] began in early 1970, convenient synthetic methods and crystal structures of $(\eta^5\text{-}C_5H_5)_2Ge$,[14] $(\eta^5\text{-}CH_3C_5H_4)_2Ge$,[15] $(\eta^5\text{-}C_5Me_5)_2Ge$,[16] and $(\eta^5\text{-}C_5CH_2Ph_5)_2Ge$[17] were reported only during the last few years. To date, a stannocene or a germanocene analogue in the stanna- or germacarboranes, in which the heteroatom is sandwiched by two carborane cages, has not been reported. We report herein the synthesis, characterization, and crystal structure of $[2,3\text{-}(Me_3Si)_2C_2B_4H_4]_2Ge^{IV}$ (I) which may be the first example of a germanocene analogue.

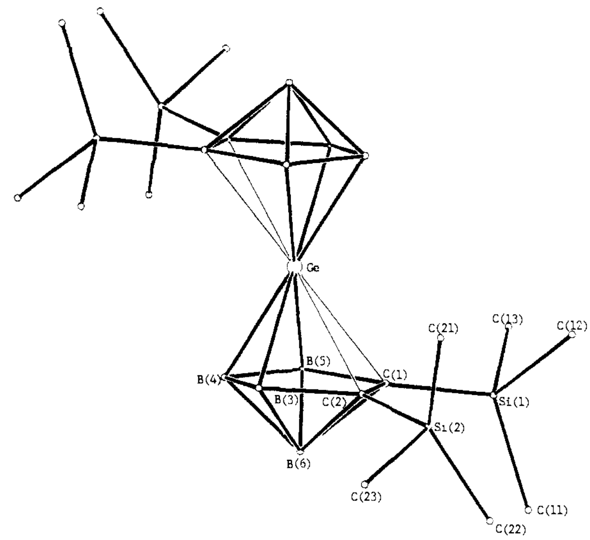

Figure 1. Side view of I; atoms are represented as circles of arbitrary radii. The central Ge atom lies at a center of symmetry. The weaker Ge–C interactions are shown by thinner lines.

Table I. Selected Bond Lengths (Å) with Standard Deviations in Parentheses

Ge–C(1)	2.38 (2)	C(2)–Si(2)	1.88 (2)
Ge–C(2)	2.39 (2)	C(2)–B(3)	1.63 (4)
Ge–B(3)	2.14 (3)	C(2)–B(6)	1.72 (3)
Ge–B(4)	2.08 (3)	B(3)–B(4)	1.56 (4)
Ge–B(5)	2.15 (2)	B(3)–B(6)	1.73 (4)
C(1)–C(2)	1.43 (3)	B(4)–B(5)	1.56 (3)
C(1)–B(5)	1.61 (3)	B(4)–B(6)	1.72 (3)
C(1)–B(6)	1.72 (2)	B(5)–B(6)	1.71 (3)
C(1)–Si(1)	1.89 (2)		

A 6.60-mmol sample of $Li^+[(Me_3Si)_2C_2B_4H_5]^-$ in tetrahydrofuran (50 mL) was allowed to react with anhydrous $GeCl_4$ (0.71 g; 3.3 mmol), in a procedure identical with that employed in the synthesis of stannacarboranes,[6] to produce ca. 0.338 g (collected at 0 °C; 0.67 mmol, 20% yield based on $GeCl_4$ consumed; mp 107 °C) of colorless $[(Me_3Si)_2C_2B_4H_4]_2Ge^{IV}$ (I) as a pure sublimed crystalline product.[18] In addition, neutral *nido*-carborane $(Me_3Si)_2C_2B_4H_6$ (II)[19] (0.69 g, 3.14 mmol) and *closo*-germacarborane $[(Me_3Si)_2C_2B_4H_4]Ge^{II}$ (III) (pale yellow liquid, 0.26 g, 0.90 mmol, 27% yield based on $GeCl_4$ consumed; bp 205 °C) were collected in traps held at −23 and −15 °C, respectively.

The electron-impact (EI) mass spectrum of I (supplementary material, Table IV) exhibited a parent grouping $[^{76}Ge(^{12}CH_3)_{12}{}^{28}Si_4{}^{12}C_4{}^{11}B_8H_8]^+$ with the major cutoff at m/z 512.

The most significant features in both the infrared spectrum[20] and ^1H pulse Fourier-transform NMR spectrum[21] of I are the

(1) Jutzi, P.; Kohl, F.; Hoffmann, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757.
(2) (a) Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharnn, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064. (b) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6773.
(3) (a) Dory, T. S.; Zuckerman, J. J.; Barnes, C. L., *J. Organomet. Chem.*, **1985**, *281*, C1. (b) Dory, T. S.; Zuckerman, J. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *281*, C8.
(4) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 921.
(5) Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259.
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