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Brent St. Onge  
*University of Windsor*

James R. Green  
*University of Windsor*

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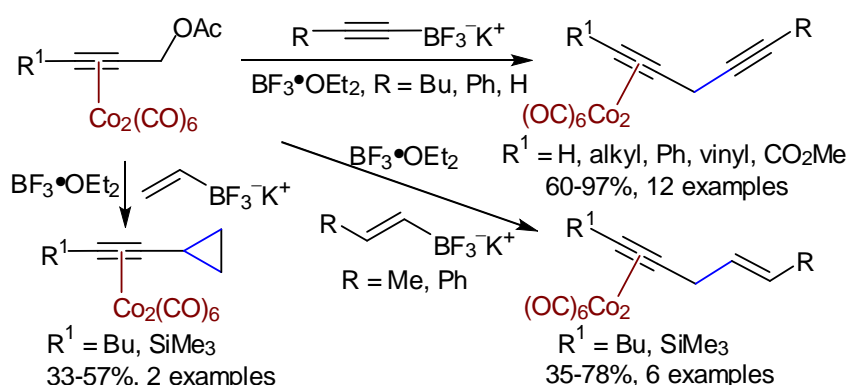
# Nicholas Reactions of Alkynyl- and Alkenyltrifluoroborates

Brent St. Onge<sup>a</sup>  
James R. Green<sup>\*a</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Ave., Windsor, ON, Canada, N9B 3P4.

jgreen@uwindsor.ca

This paper is dedicated to Prof. Victor Snieckus, in consideration of his many years of mentorship and friendship, and for his tireless and continuing dedication to progress in synthetic aromatic chemistry.

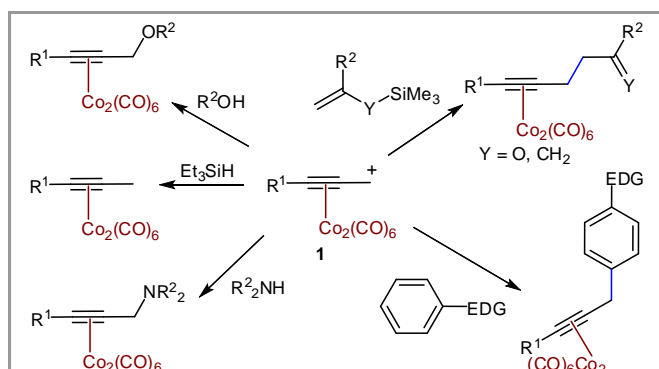


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**Abstract** The Lewis acid mediated Nicholas reaction of potassium alkynyltrifluoroborates and propargyl acetate-hexacarbonyldicobalt complexes affords 1,4-diyne dicobalt hexacarbonyl complexes in good yields. The analogous Nicholas reactions of potassium alkenyltrifluoroborates give 1,3-enyne dicobalt hexacarbonyl complexes in most cases, although the initial site of reaction can vary. Potassium vinyltrifluoroborate itself affords alkynylcyclopropane complexes.

**Key words** alkyne complexes, boron, carbocation, coupling, Lewis acids, alkynes, enynes

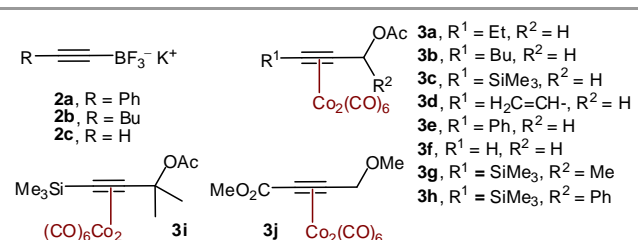
The generation and reaction of hexacarbonyldicobalt complexes of propargylic carbocations (**1**), or Nicholas reaction, has achieved a place of prominence in metal-organic chemistry due to high reaction site selectivity, good cation stability and reactivity, ease of handling of the alkynedicobalt complexes, and ready decomplexation of the organic unit. Many of the requirements for participation of the nucleophile are well-understood,<sup>1</sup> and a wide range of heteroatom-based nucleophiles, hydride sources, and carbon-based nucleophiles are compatible (Scheme 1). For carbon-carbon bond formation processes, electron-rich arenes, enol derivatives, and allylmetals are particularly reliable reaction participants.



**Scheme 1** Nicholas reactions of heteroatom, hydride, and carbon nucleophiles.

Nevertheless, some classes of carbon based nucleophiles remain problematic for the Nicholas reaction. Alkynyl nucleophiles are known, but solely as the trialkynylaluminums;<sup>2</sup> there is little further work reported based on this transformation, perhaps due to reactivity issues with some of the alanes involved.<sup>3</sup> Similarly, there are limited reports of intermolecular reactions with alkene nucleophiles that are not activated as either enol ethers or allylmetals. For simple alkene nucleophiles, modest yields of isomeric alkene mixtures are the norm, with pendant cation-trapping nucleophiles substituted on the alkene ameliorating the situation only somewhat.<sup>4,5</sup> Simple vinylsilanes have not been reported to be reliable nucleophiles in this process.

In this context, our attention has been drawn to the chemistry of potassium organotrifluoroborates. Arguably most prominent as boronic acid equivalents for cross coupling procedures,<sup>6,7</sup> the alkynyl- and alkenyltrifluoroborates recently have been shown to enter into reactions with carbocations or related electrophilic carbon centres.<sup>8</sup> These trifluoroborates are water-stable and have good long-term storage capability, and they would appear to be useful in addressing the limitations with alkynyl- and alkenyl nucleophiles in Nicholas reaction chemistry. This letter reports our preliminary work on these reactions.

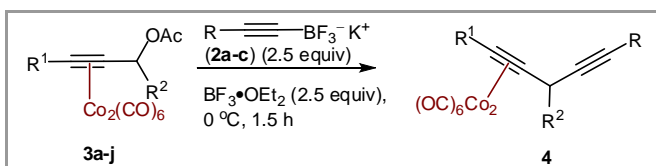


**Figure 1** Starting potassium alkynyltrifluoroborates (**2**), propargyl acetate hexacarbonyldicobalt complexes (**3**).

Our initial experiments involved use of phenylalkynyltrifluoroborate **2a** and 1-acetoxy-2-pentyne complex **3a** (Figure 1). In the presence of  $BF_3 \cdot OEt_2$  (2.5 equiv) in  $CH_2Cl_2$  at 0 °C (1.5 equiv **3a**), a reaction occurred that ceased

progressing after 1.5 h, giving **4aa** (65% yield). Reversing the stoichiometry (1.5 equiv  $\text{BF}_3 \cdot \text{OEt}_2$ , 2.5 equiv **2a**) improved the yield significantly (**4aa**, 86%), while use of 2.5 equiv each of  $\text{BF}_3 \cdot \text{OEt}_2$  and **2a** gave **4aa** in 91% yield.<sup>9</sup> This latter procedure was adopted as standard conditions for subsequent experiments.

Using these standard conditions, the reactions of three potassium alkynyltrifluoroborates (**2a**, butyl- substituted **2b**, and unsubstituted **2c**) were investigated, with a number of cobalt hexacarbonyl complexes of propargyl acetates **3** (Equation 1, Table 1).<sup>10</sup> The alkynyltrifluoroborates successfully reacted with ethyl substituted complex **3a** (**4aa**, 91% yield; **4ba**, 73% yield; **4ca**, 67% yield), butyl substituted complex **3b** (**4ab**, 73%), trimethylsilyl substituted complex **3c** (**4ac**, 65% yield; **4bc**, 77% yield), vinyl substituted complex **3d** (**4bd**, 65% yield), phenyl substituted complex **3e** (**4be**, 60% yield) and unsubstituted complex **3f** (**4bf**, 63% yield). Monosubstitution at the propargylic site of the alkynedicobalt complex was well tolerated, as methyl substituted complex **3g** (**4ag**, 90% yield) and phenyl substituted **3h** (**4ah**, 97% yield) each gave high yields of condensation product with **2a**. Conversely, tertiary acetate **3i** gave only elimination product **5** (54% yield) with **2a** to the exclusion of any C-C bond forming product. Finally, a remote ester function on the propargyl ether complex (**3j**) was tolerated, giving  $\gamma$ -carbonyl cation reaction product **4aj** (65% yield) employing  $\text{Bu}_2\text{BOTf}$  in place of  $\text{BF}_3 \cdot \text{OEt}_2$ .<sup>11</sup>



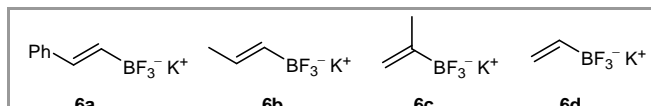
**Equation 1** Lewis acid mediated reaction of potassium alkynyltrifluoroborates (**2**) and propargyl acetate hexacarbonyldicobalt complexes (**3**).

**Table 1** Reactions of alkynyltrifluoroborates (**2**) and propargyl acetate hexacarbonyldicobalt complexes (**3**).

<b>2</b>	<b>3</b>	<b>4</b>	Product Structure	Yield (%) <sup>a</sup>
<b>2a</b>	<b>3a</b>	<b>4aa</b>		91
<b>2b</b>	<b>3a</b>	<b>4ba</b>		73
<b>2c</b>	<b>3a</b>	<b>4ca</b>		67 (77)
<b>2a</b>	<b>3b</b>	<b>4ab</b>		73
<b>2a</b>	<b>3c</b>	<b>4ac</b>		65
<b>2b</b>	<b>3c</b>	<b>4bc</b>		77
<b>2b</b>	<b>3d</b>	<b>4bd</b>		65 (72)
<b>2b</b>	<b>3e</b>	<b>4be</b>		60 (67)
<b>2b</b>	<b>3f</b>	<b>4bf</b>		63 (72)

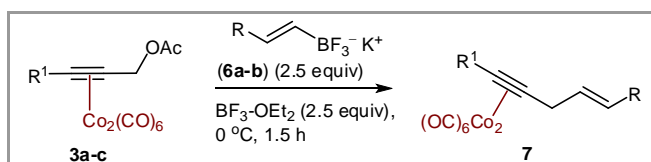
<b>2a</b>	<b>3g</b>	<b>4ag</b>		90
<b>2a</b>	<b>3h</b>	<b>4ah</b>		97
<b>2a</b>	<b>3i</b>	<b>5</b>		54
<b>2a</b>	<b>3j</b>	<b>4aj</b>		65 <sup>b</sup>

<sup>a</sup> Yields in parentheses based on recovered starting **3** (brsm). <sup>b</sup> Lewis acid  $\text{Bu}_2\text{BOTf}$ .



**Figure 2** Potassium alkenyltrifluoroborates (**6**).

Four potassium alkenyltrifluoroborates were chosen for investigation with propargyl acetate complexes (**3**), including styryltrifluoroborate **6a**, *n*-propenyltrifluoroborate **6b**, isopropenyltrifluoroborate **6c**, and vinyltrifluoroborate **6d** (Figure 2). The styryl substituted trifluoroborates, reacted in a quite straightforward manner under the standard conditions, as **6a** with **3b** afforded **7ab** (68% yield), and **6a** with **3c** gave **7ac** (71% yield), each as (*E*)- isomers to the limits of detection by <sup>1</sup>H NMR spectroscopy (Equation 2, Table 2).<sup>12</sup> *n*-Propenyltrifluoroborate **6b** reacted analogously with **3a** to give (*E*)- **7ba** (51% yield, 58% brsm) and with **3c** to give (*E*)- **7bc** (35% yield, 69% brsm), but the reactions suffered from incomplete conversion under the standard conditions. Increasing the amounts of  $\text{BF}_3 \cdot \text{OEt}_2$  and **6c** to 4.0 equiv raised the yield of (*E*)- **7bc** to 42% (65% brsm).



**Equation 2** Lewis acid mediated reaction of potassium alkenyltrifluoroborates (**6**) and propargyl acetate hexacarbonyldicobalt complexes (**3**).

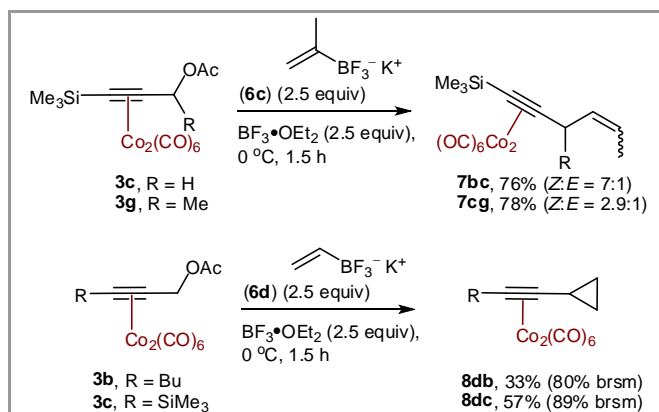
**Table 2** Reactions of alkenyltrifluoroborates (**6**) and propargyl acetate hexacarbonyldicobalt complexes (**3**).

<b>3</b>	<b>6</b>	<b>7</b>	Product Structure	Yield (%) <sup>a</sup>
<b>3b</b>	<b>6a</b>	<b>7ab</b>		68
<b>3c</b>	<b>6a</b>	<b>7ac</b>		71
<b>3a</b>	<b>6b</b>	<b>7ba</b>		51 (58)
<b>3c</b>	<b>6b</b>	<b>7bc</b>		35 (69)

<sup>a</sup> Yields in parentheses based on recovered starting **3** (brsm).

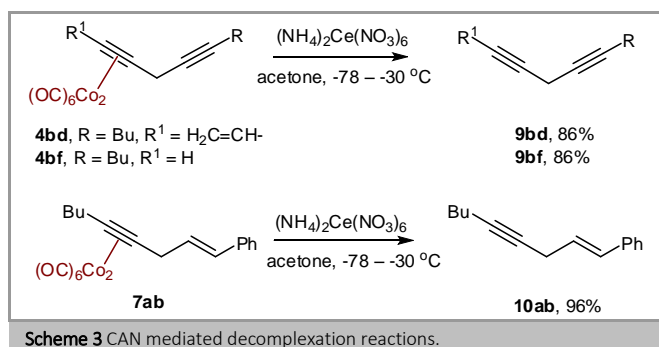
In contrast, **6c** and **6d** gave unexpected reaction patterns (Scheme 2). Isopropenylborate **6c** afforded 1-propenyl adducts as the sole regioisomers, predominantly as (*Z*)- isomers, with **3c** giving **7bc** (76% yield, *Z*:*E* = 7.1:1) and **3g** giving **7cg** (78% yield, *Z*:*E* = 2.9:1).<sup>13</sup> Vinylborate **6d**, on the other hand, gave incomplete

conversion to cyclopropane products with only traces (ca. 7%) of alkene isomers evident by NMR spectroscopy; **3b** afforded **8db** (33% yield, 80% brsm), and **3c** provided **8dc** (57% yield, 89% brsm). An increase in the amounts of  $\text{BF}_3 \cdot \text{OEt}_2$  and **6d** (to 4.0 equiv each) with **3b** gave somewhat improved yields of **8db**, but still incomplete conversion (49% yield, 78% brsm).



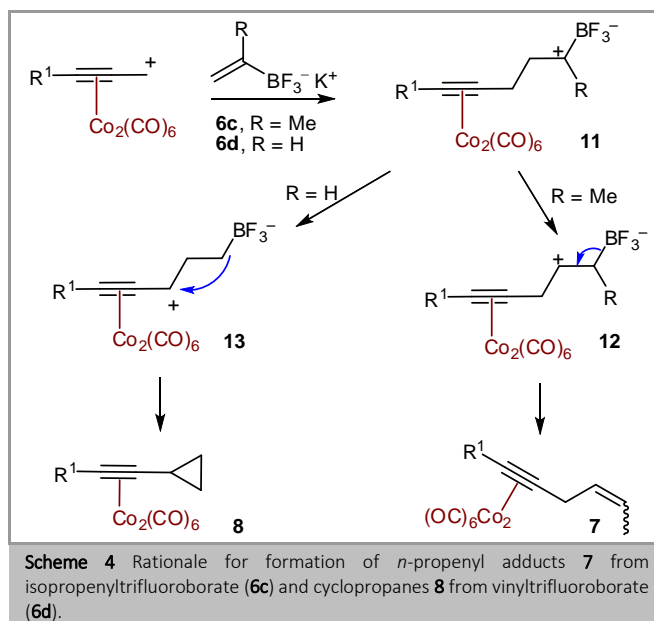
**Scheme 2** Reactions of isopropenyltrifluoroborate (**6c**) and vinyltrifluoroborate (**6d**) with propargyl acetate hexacarbonyldicobalt complexes (**3**).

Three Nicholas reaction products were selected for decomplexation, for illustration of the viability of the process for these substrates (Scheme 3). Employing ceric ammonium nitrate (CAN) in acetone, under carefully controlled conditions, skipped diyne complexes **4bd** and **4bf**, and enyne complex **7ab** each afforded their metal-free counterparts in good to excellent yields (**9bd**, 86% yield; **9bf**, 86% yield; **10ab**, 96% yield).<sup>14</sup>



**Scheme 3** CAN mediated decomplexation reactions.

The Nicholas reactions with alkynyltrifluoroborates are quite successful in the anticipated manner. They give reasonable to excellent chemical yields in all cases except the elimination-prone tertiary case (**3i**), with the higher yielding cases generally coincident with the more stabilized propargyldicobalt cationic species. The modest amounts of starting propargyl acetate recovered in a few cases likely stems from a competitive defluorination reaction by  $\text{BF}_3 \cdot \text{OEt}_2$  of the alkynyltrifluoroborate salt.<sup>15</sup>



**Scheme 4** Rationale for formation of *n*-propenyl adducts **7** from isopropenyltrifluoroborate (**6c**) and cyclopropanes **8** from vinyltrifluoroborate (**6d**).

For the alkenyltrifluoroborates, it is our belief that the reaction is being driven by attack of the propargyldicobalt cation by the most nucleophilic carbon of the alkene function, with ultimate alkene re-formation by way of  $\text{BF}_3$  loss from a  $\beta$ -boryl cation. This results in straightforward substitution at boron-substituted site with styryltrifluoroborate **6a**, and less efficiently for *n*-propenyltrifluoroborate **6b**. For isopropenylborate **6c**, attack at the terminal alkene carbon results in formation of carbocation **11**, followed by hydride migration to give **12**, which in turn undergoes  $\text{BF}_3$  loss to give **7bc/7cg** (Scheme 4).<sup>16</sup> There are rare examples of reactions involving isopropenyltrifluoroborate that afford a 1-propenyl adduct;<sup>17</sup> however, they likely are not proceeding by way of a carbocation.<sup>18</sup> Finally, the reaction of vinyltrifluoroborate **6d** is consistent with initial formation carbocation **11**, a 1,3-hydride shift to give propargyl cation **13**, and nucleophilic attack on the cation to give **8db/8dc**. It is likely that **6d** is a less nucleophilic trifluoroborate and that  $\text{BF}_3$  induced defluorination competes more substantially in these cases. The reasons for the change in pattern of **6d** from **6c** are not clear at this time.

Future work will involve investigating other protocols<sup>19</sup> for generation of the propargyldicobalt cation for the purpose of obtaining complete conversion in the more difficult cases, determining the borderline between divergent reaction processes with the alkenyltrifluoroborates, and exploration of aryl- and alkyltrifluoroborates as potential Nicholas reaction partner. These are in progress and will be reported in due course.

## Funding Information

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## Acknowledgment

We are indebted to Prof. Yuri Bolshan (University of Ontario Institute of Technology, UOIT) for helpful discussions on the chemistry of potassium organotrifluoroborates.

## Supporting Information

YES (this text will be updated with links prior to publication)

## Primary Data

NO (this text will be deleted prior to publication)

## References and Notes

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- (9) **Experimental Procedure.** To a solution of **3a** (89.7 mg, 0.218 mmol) and **2a** (0.113 g, 0.544 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) at 0 °C was added BF<sub>3</sub>•OEt<sub>2</sub> (67 µL, 0.54 mmol). After 1.5 h, saturated NH<sub>4</sub>Cl(aq) was added and the mixture subjected to conventional extractive workup (CH<sub>2</sub>Cl<sub>2</sub>). Flash chromatography (petroleum ether : Et<sub>2</sub>O, 50:1) afforded **4aa** (90.3 mg, 91%) as a viscous red oil.
- (10) **Representative Characterization Data (4aa):** <sup>1</sup>H NMR: δ 7.30-7.44 (m, 5H), 4.00 (s, 2H), 2.92 (q, J = 7.3 Hz, 2H), 1.35 (t, J = 7.3 Hz, 3H); <sup>13</sup>C: 199.7, 131.5, 128.3, 128.0, 123.3, 101.6, 93.7, 86.5, 82.3, 26.9, 25.0, 15.6; IR ν<sub>max</sub>: 2971, 2088, 2043, 1989, 1600, 1490 cm<sup>-1</sup>; HRMS m/e for C<sub>19</sub>H<sub>12</sub>Co<sub>2</sub>O<sub>6</sub> calcd (M<sup>+</sup>-CO+H) 454.9376 found 454.9367. **(4ba):** <sup>1</sup>H NMR: δ 3.72 (t, J = 2.3 Hz, 2H), 2.87 (q, J = 7.4 Hz, 2H), 2.17 (m, 2H), 1.31 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H); <sup>13</sup>C: 200.0, 101.5, 95.3, 82.6, 76.7, 30.6, 26.8, 24.3, 21.9, 18.3, 15.5, 13.5; IR ν<sub>max</sub>: 2964, 2874, 2087, 2043, 1990, 1457; HRMS m/e for C<sub>17</sub>H<sub>16</sub>Co<sub>2</sub>O<sub>6</sub> calcd (M<sup>+</sup>-CO+H) 406.9740 found 406.9733. **(4ca):** <sup>1</sup>H NMR: δ 3.76 (d, J = 2.6 Hz, 2H), 2.88 (q, J = 7.4 Hz, 2H), 2.19 (t, J = 2.6 Hz, 1H), 1.32 (t, J = 7.4 Hz, 3H); <sup>13</sup>C: 200.2, 128.7, 128.0, 101.3, 98.9, 37.0, 27.1, 17.5, 15.6. IR ν<sub>max</sub>: 3314, 2972, 2877, 2089, 2044, 1994 cm<sup>-1</sup>; HRMS m/e for C<sub>13</sub>H<sub>8</sub>Co<sub>2</sub>O<sub>6</sub> calcd (M<sup>+</sup>+ H) 378.9063, found 378.9063.
- (11) Nicholas reactions for γ- carbonyl cation equivalents routinely give more rapid reaction with Bu<sub>2</sub>BOTf as Lewis acid relative to BF<sub>3</sub>•OEt<sub>2</sub>. See: Taj, R.; Green, J. R. *J. Org. Chem.* **2010**, *75*, 8258.
- (12) **Representative Characterization Data. 7ab:** <sup>1</sup>H NMR: δ 7.29 – 7.44 (m, 5H), 6.61 (d, J = 15.7 Hz, 1H), 6.31 – 6.41 (dt, J = 15.7, 7.2 Hz, 1H), 3.77 – 3.79 (d, J = 7.2 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 1.48 – 1.77 (m, 4H), 1.00 (t, J = 7.2 Hz, 3H); <sup>13</sup>C: 200.3, 137.0, 132.3, 128.6, 127.5, 127.4, 126.2, 99.4, 97.7, 37.4, 33.8, 22.8, 13.9; IR ν<sub>max</sub>: 3084, 3062, 3028, 2960, 2874, 2085, 2040, 1994, 1495 cm<sup>-1</sup>; HRMS m/e for C<sub>21</sub>H<sub>18</sub>Co<sub>2</sub>O<sub>6</sub> calcd (M<sup>+</sup>-CO+H) 456.9896, found 456.9907.
- (13) **Representative Characterization Data. ((Z)-7bc):** <sup>1</sup>H NMR: δ 5.50 – 5.67 (m, 2H), 3.68 (d, J = 6.7 Hz, 2H), 1.70 (d, J = 5.9 Hz, 3H), 0.31 (s, 9H); resonances from the minor isomer were observed at 3.56 (d, J = 5.9 Hz, 2H), 0.30 (s, 9H); <sup>13</sup>C NMR (major isomer only): 200.4, 128.0, 125.9, 111.2, 78.7, 32.3, 12.9, 0.6; IR ν<sub>max</sub>: 3025, 2959, 2984, 2085, 2041, 2000, 1581; HRMS m/e for C<sub>15</sub>H<sub>16</sub>Co<sub>2</sub>O<sub>6</sub>Si calcd (M<sup>+</sup>-CO+H) 410.9509, found 410.9501. **(8db):** δ 2.78 (t, J = 8.0 Hz, 2H), 2.15 (tt, J = 7.4, 4.2 Hz, 1H), 1.43 – 1.67 (m, 4H), 1.11 (ddd, J = 7.4, 6.6, 4.3 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H), 0.72 – 0.77 (ddd, J = 6.6, 4.3, 4.2 Hz, 2H); <sup>13</sup>C: 200.1, 103.8, 98.4, 33.9, 33.6, 22.7, 15.2, 13.8, 12.5; IR ν<sub>max</sub>: 2962, 2876, 2086, 2040, 2005, 1450 cm<sup>-1</sup>; HRMS m/e for C<sub>16</sub>H<sub>14</sub>Co<sub>2</sub>O<sub>6</sub> calcd (M<sup>+</sup>-CO+H) 380.9583 found 380.9589.
- (14) **Experimental Procedure.** Complex **4bd** (47.6 mg, 0.110 mmol) was dissolved in acetone (8 mL), and the solution cooled to -78 °C. Ceric ammonium nitrate (0.302 g, 0.551 mmol, 5 equiv) was added and the solution allowed to warm to -30 °C (2 h), with monitoring by TLC. A saturated sodium chloride solution was added and the mixture subjected to a conventional extractive workup (Et<sub>2</sub>O). The product was filtered through a silica plug using Et<sub>2</sub>O and concentrated under reduced pressure to give **9bd** (13.9 mg, 86%).
- (15) (a) Bir, G.; Schacht, W.; Kaufmann, D. *J. Organomet. Chem.* **1988**, *340*, 267. (b) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020. (c) For a comparison of BF<sub>3</sub>•OEt<sub>2</sub> with other common Lewis acids in aldehyde-allyltrifluoroborate reactions, see reference 8g.
- (16) Our operating hypothesis for the predominant (Z)- isomer formation comes from the proposed larger size of the BF<sub>3</sub>-unit relative to a methyl group. Initial reaction consequently gives a cation **11** with the methyl nearly eclipsed to the homopropargyl-Co<sub>2</sub>(CO)<sub>6</sub> unit (Scheme 4); subsequent hydride migration then gives a cation **12** where rotation of the C-B bond to a co-linear orientation relative to the empty p- orbital of the cation is lower energy than a rotation of the methyl group *anti*- to the homopropargyl-Co<sub>2</sub>(CO)<sub>6</sub> group.
- (17) (a) Corey, E. J.; Lallie, G. *Tetrahedron Lett.* **2008**, *49*, 4894. (b) Zhang, Y.; Fu, Z.; Wang, J.; Li, J.; Chen, S.; Wei, Y.; Yu, L.; Tao, X. PCT Int. Appl. WO 2016045587, Sep 23, 2015; *Chem. Abstr.* **2016**, 511177.
- (18) For analogous reactivity of vinylsilanes with more electrophilic carbocations, see: Laub, H. A.; Mayr, H. *Chem. – Eur. J.* **2014**, *20*, 1103.
- (19) El-Amouri, H.; Gruselle, M.; Jaouen, G.; Daran, J. C.; Vaissermann, J. *Inorg. Chem.* **1990**, *29*, 3238.

