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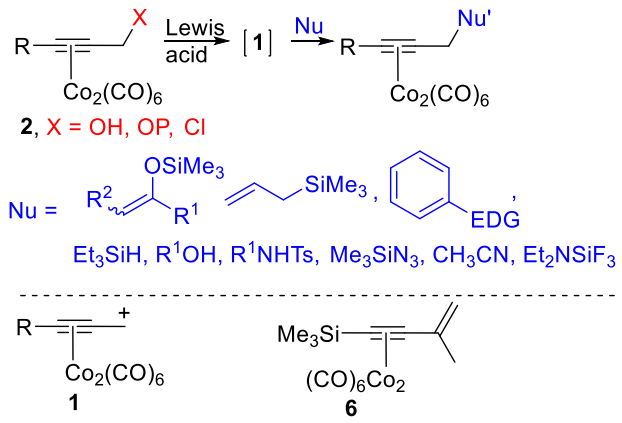
Abstract: The Lewis acid mediated Nicholas reactions of propargyl acetate-$Co_2(O)_6$ complexes with a series of potassium alkynyltrifluoroborates and potassium alkenyltrifluoroborates are described. Alk**yn**yltrifluoroborates directly alkynylate the intermediate propargyldicobalt cations. In contrast, alk**en**yltrifluoroborates proceed through one of three modes of dominant reactivity: C-2 substituted alkenyltrifluorobrates directly alkenylate, predominantly with retention of stereochemistry. C-1 substituted alkenyltrifluoroborates alkenylate at C-2. Potassium vinyltrifluoroborate incorporates a cyclopropane at the site propargyl to the alkynedicobalt. Computational analysis of these systems explains the differential modes of reactivity of the alkenyltrifluoroborates and outlines probable mechanisms for the formation of each product.

Introduction: The Nicholas reaction, the nucleophilic attack at propargyldicobalt cations (**1**), is among the most reliable metal-mediated organic transformations.[1] The cations are readily generated from the dicobalt hexacarbonyl complexes of propargyl alcohols (**2**), their derivatives, or from analogous enyne complexes and an electrophile. The ions are highly stabilized, on the order of trityl cation, yet low steric congestion ensures electrophilic reactivity remains high. Numerous inter- and intramolecular examples of enolic derivatives,[2] allylmetals,[3] electron rich arenes and heteroarenes,[4] hydrides,[5] and group 15[6] and group 16[7] nucleophiles react well with these cations; fluoride nucleophiles are also compatible (**Scheme 1**).[8] Nucleophilic regioselectivity is readily predicted in most cases, and allenic byproducts are not observed.

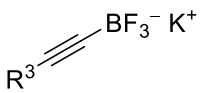
Scheme 1. The Nicholas reaction.



However, a remaining limitation of Nicholas chemistry involves difficulties when alkynyl and alkenyl nucleophiles are introduced. Historically, the only way an alkynylmetal nucleophile could participate in the Nicholas reaction was as the organoaluminum.[9] The transformations are acceptably efficient, but the pyrophoric, and water-sensitive nature of triorganoaluminum reagents renders them less than ideal substrates. Alkene nucleophiles are inherently sufficiently nucleophilic but, excepting specialized cases such as enol ethers or allylsilanes, tend to provide only modest yields of regioisomeric mixtures.[10] Vinylsilanes have not been reported as successful nucleophiles, and in our hands have always generated only low yields of condensation products.

Organotrifluoroborates might offer a solution; their alkynyltrifluoroborate and alkenyltrifluoroborate manifestations react well with carbocations.[11] Consequently, we are reporting on our investigation into whether these two classes of organotrifluoroborates can efficiently and cleanly conduct Nicholas chemistry. The expected products, 1,4- (skipped) diynes and enynes, are valuable both as synthetic intermediates,[12] and for their presence as extant motifs in natural products.[13] In 2017 we communicated a preliminary report on their reactivity,[14] and we now wish to provide a more detailed description of the experimental reactivity patterns of alkynyl- and alkenyltrifluoroborates with propargyldicobalt cations, supported by a DFT-based computational evaluation of the most likely reaction pathways.

Results and Discussion: Studies of reactivity were initiated with alkynyltrifluoroborates **3** (Figure 1) and propargyl acetate-$Co_2(CO)_6$ complexes **4** (Figure 2). To determine the stoichiometries to be used in the screen, we conducted the reaction of phenyl- substituted alkynyltrifluoroborate **3a** with complex **4a** over 1.5 h at 0 °C, in CH_2Cl_2. The reaction provided better yields of **5aa** in the presence of excesses of either BF_3-OEt_2 or **3a** (2.5 equiv BF_3-OEt_2, 1. 5 equiv **3a**, 67% yield; 1.5 equiv BF_3-OEt_2, 2.5 equiv **3a**, 86% yield; 2.5 equiv BF_3-OEt_2, 2.5 equiv **3a**, 91% yield). The latter conditions were consequently adopted as standard for all subsequent substrates (Table 1).



3a, R^3 = Ph
3b, R = Bu
3c, R^3 = H
3d, R^3 = $(CH_2)_4Cl$

Figure 1. Potassium alkynyltrifluoroborates employed

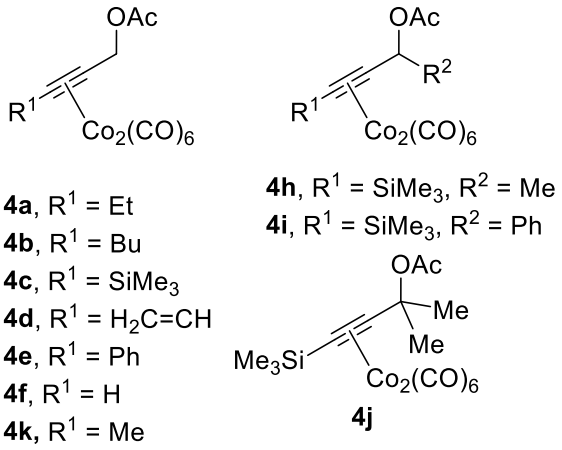
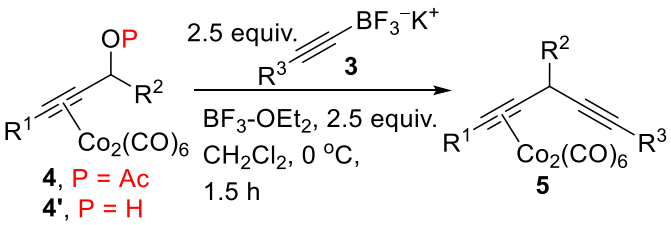


Figure 2. Nicholas reaction precursors employed

Table 1. Nicholas reactions of alkynyltrifluoroborates.



entry	3	4	5	R^1	R^2	R^3	Yield[a]
1	**3a**	**4a**	**5aa**	Et	H	Ph	91
2	**3b**	**4a**	**5ba**	Et	H	Bu	73
3	**3c**	**4a**	**5ca**	Et	H	H	67(77)
4	**3a**	**4b**	**5ab**	Bu	H	Ph	74
5	**3a**	**4c**	**5ac**	$SiMe_3$	H	Ph	65
6	**3a**	**4c'**	**5ac**	$SiMe_3$	H	Ph	34[b]
7	**3b**	**4c**	**5bc**	$SiMe_3$	H	Bu	77
9	**3d**	**4f**	**5df**	H	H	$(CH_2)_4Cl$	66(75)
10	**3b**	**4d**	**5bd**	H_2C=CH	H	Bu	65(72)
11	**3b**	**4e**	**5be**	Ph	H	Bu	60(67)
12	**3b**	**4f**	**5bf**	H	H	Bu	70(81)
13	**3a**	**4g**	**5ag**	CO_2Me	H	Ph	65[c]
14	**3a**	**4h**	**5ah**	$SiMe_3$	Me	Ph	90
15	**3d**	**4c**	**5dh**	$SiMe_3$	Me	$(CH_2)_4Cl$	67(77)
16	**3a**	**4i**	**5ai**	$SiMe_3$	Ph	Ph	97
17	**3a**	**4j**	**5aj**	$SiMe_3$	Me, Me	Ph	0[d]

[a] Yields in parentheses based on recovered starting material, **4** (brsm).

[b] Reaction of alcohol **4c'** using HBF_4-OEt_2

[c] Reaction employs 2.5 equiv. of Bu_2BOTf as the Lewis acid

[d] Elimination product **6** was isolated in 54% yield

Reactions between additional examples of alkynyltrifluoborates **3** and propargyl acetate-$Co_2(CO)_6$ complexes **4** were attempted. Yields of Nicholas reaction products **5** were, in general, satisfactory to good. In a few cases, particularly with vinyl- and phenyl-substituted complexes **4d** and **4e**, and unsubstituted **4f**, the reactions did not proceed to completion (Table 1, entries 3, 10-12, 15); nevertheless, the yields of the desired 1,4-diyne-$Co_2(CO)_6$ complexes were still acceptable.

There are a few examples that deviate from the reactivity pattern. In the case with a remote electron withdrawing group on the starting complex, we have found greater success in most Nicholas reactions upon changing the Lewis acid to Bu_2BOTf;[15] this allowed the successful combination of **4g** with **3a** is give **5ag** (65% yield, entry 13). Attempts to use BF_3-OEt_2 as a Lewis acid in this case failed. We attempted to use the propargyl alcohol complex (**4c'**), instead of the acetate (**4c**), for the transformation with HBF_4 as a Brønsted acid; reaction with **3a** gave some **5ac**, but in inferior yield (entry 6, 34%) compared to using the acetate/BF_3-OEt_2 protocol (entry 5, 65%). Finally, monosubstitution at the propargylic site of **4** (**4h**, **4i**) was very well tolerated in the reaction (entries 14, 15), but disubstitution at the propargylic site (**4j**, entry 17) resulted only in the formation of elimination product **6** during an attempted Nicholas reaction with **3a** (entry 17).

To investigate the reactivity of alkenyltrifluoroborates in Nicholas reactions, we chose six representative nucleophiles, including the potassium salts of (*E*)- and (*Z*)-propen-1-yltrifluoroborate **7a**, (*E*)- and (*Z*)-styryltrifluoroborate **7b**, isopropenyltrifluoroborate **7c**, and vinyltrifluoroborate **7d** (Figure 3).

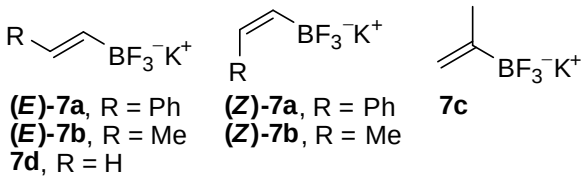
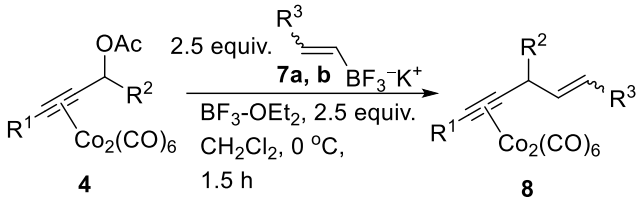


Figure 3. Potassium alkenyltrifluoroborates employed

The reactions of the styrenyltrifluoroborates and propen-1-yltrifluoroborates were the most straightforward. Under our standard conditions derived from the alkynyltrifluoroborates, (*E*)-styrenyltrifluoroborate ((**(*E*)-7a**) reacted with complex **4b** to afford **(*E*)-8ab** in 68% yield (Table 2, entry 1), and with complex **4c**, to provide **8ac** in 71% yield. In all cases the products completely retained the (*E*)- stereochemistry within the limits of detection of ^{1}H NMR spectroscopy. Conversely, the (*Z*)-styrenyltrifluoroborate ((**(*Z*)-7a**) reacted with **4b** to give **(*Z*)-8ab**; however in this case, we did observe the loss of some stereochemical integrity (87:13 Z:E).

The corresponding reactions of 1-propen-1-yltrifluoroborate behaved analogously, although standard reaction conditions tended to give less than complete conversion. For instance, treatment of **4a** with (***E***)-**7b**, gave (***E***)-**8ba** in 51% yield (58% brsm), whereas the same alkene with **4c** gave (***E***)-**8bc** in 35% yield (69% brsm). Increasing the amount of BF_3-OEt_2 and **4c** to 7.5 equiv. and 10 equiv., respectively, gave (***E***)-**8bc** in 53% yield (94% brsm). (***Z***)-**7b** reacted with **4b** to form (***Z***)-**8bb** in 65% yield, with almost complete retention of alkene stereochemistry (97:3 Z:E).

Table 2. Reactions of C-2 substituted potassium alkenyltrifluoroborates.



Entry	7	4	R^1	R^2	R^3	8	Yield[a]
1	(***E***)-**7a**	**4b**	Bu	H	Ph	(**E**)-**8ab**	68
2	(***E***)-**7a**	**4b**	$SiMe_3$	H	Ph	(**E**)-**8ac**	71
3	(***Z***)-**7a**	**4b**	Bu	H	Ph	(**Z**)-**8ab**	65(74)[b]
4	(***E***)-**7b**	**4a**	Et	H	Me	(**E**)-**8ba**	51(58)
5	(***E***)-**7b**	**4c**	$SiMe_3$	H	Me	(**E**)-**8bc**	35(69)
6	(***E***)-**7b**	**4c**	$SiMe_3$	H	Me	(**E**)-**8bc**	53(94)[c]
7	(***Z***)-**7b**	**4b**	Bu	H	Me	(**Z**)-**8bb**	65[d]

[a] Yields in parentheses based on recovered **4** (brsm)

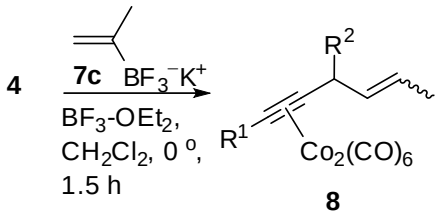
[b] (**Z**)-**8ab**:(**E**)-**8ab** = 87:13

[c] 10 equiv **7b**, 7.5 equiv BF_3-OEt_2

[d] (**Z**)-**8bb**:(**E**)-**8bb** = 97:3

Isopropenyltrifluoroborate **7c** proceeded through a distinct reaction pathway with propargyldicobalt cations (Table 3). Instead of direct replacement of the C-B bond of **7c** with a carbon-carbon bond, the products from condensation were those of analogous to those of propen-1-yltrifluoroborate in terms of product regiochemistry. Specifically, **4c** gave **8bc** in 77% yield as a 7.1:1 mixture of *Z*- and *E*- isomers, whereas **4h** gave **8bh** in 76% yield as a 2.9:1 *Z*:*E* mixture.

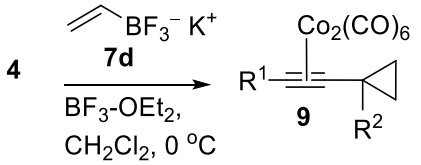
Table 3. Reactions of potassium isopropenyltrifluoroborate



Entry	4	R^1	R^2	8	Yield (*Z*-:*E*-)
1	**4c**	$SiMe_3$	H	**8bc**	77 (7.1:1)
2	**4h**	$SiMe_3$	Me	**8bh**	76 (2.9:1)

Vinyltrifluoroborate (**7d**) followed a further different mode of reactivity, giving cyclopropanated alkynes **9** as the dominant products, with very small amounts (normally <10%) of the desired alkenes **8** or **8'**. In these cases, the standard conditions (see Table 4, entry 1) gave modest to moderate yields of **9**, with incomplete conversion of **4**. Other Lewis acids gave multiple products ($SnCl_4$), minimal conversion to **9** (Et_2AlCl, 8% **9b**; Me_3SiOTf, <5% **9b**), or ethoxylation byproducts (HBF_4–OEt_2). After much experimentation, it was found that increasing the number of equivalents of **7d** and BF_3–OEt_2 to 10 equiv. and 7.5 equiv.; or 15 equiv. and 12.5 equiv. respectively, gave improved conversions to **9** (see Supporting Information Table S1). In the case of substrate **4i**, containing a propargyl phenyl group, treatment with **7d** and BF_3-OEt_2 gave only a low conversion to **9i.** In this case, the use of protic acid HBF_4–OEt_2 in place of the Lewis acid (entry 7) allowed formation of **9i** in moderate yield.

Table 4. Reactions of potassium vinyltrifluoroborate



Entry	4	R^1	R^2	9	Yield[a]
1	**4b**	Bu	H	**9b**	33(80)
2	**4b**	Bu	H	**9b**	74(78)[b,c]
3	**4c**	$SiMe_3$	H	**9c**	69(81)[b,d]
4	**4e**	Ph	H	**9e**	70(80)[e,f]
5	**4h**	$SiMe_3$	Me	**9h**	59(73)[e,g]
6	**4i**	$SiMe_3$	Ph	**9i**	43(53)[h]
7	**4k**	Me	H	**9k**	73(76)[b,i]

[a] Yields in parentheses based on recovered **4** (brsm)

[b] Employing 10 equiv. potassium vinyltrifluoroborate, 7.5 equiv. BF_3-OEt_2; [c] Contained 5% **8db**; [d] Contained 5% **8dc** [e] Employing 15 equiv. potassium vinyltrifluoroborate, 12.5 equiv. BF_3-OEt_2; [f] Contained 5% **8de**, 4% **8de'**; [g]

Contained 7% **8dh;** [h] Employing 3 equiv. potassium vinyltrifluoroborate, 6 equiv. HBF_4-OEt_2; [i] Contained 4% **8dk**

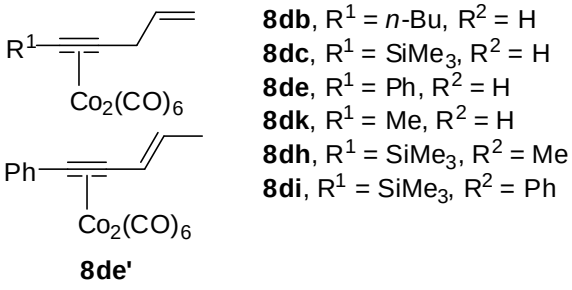
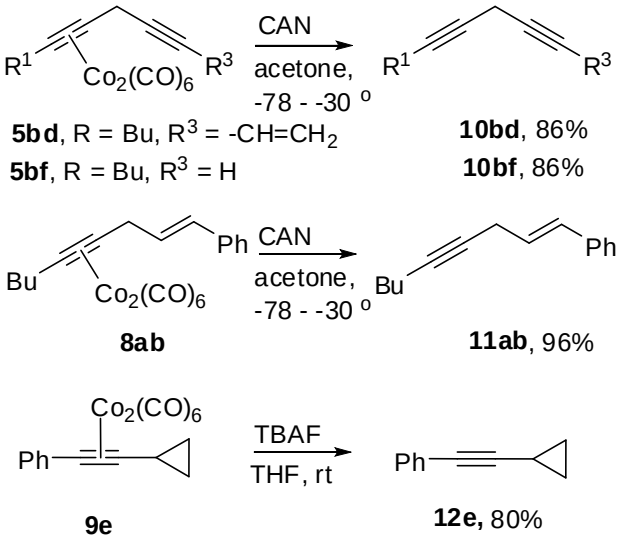


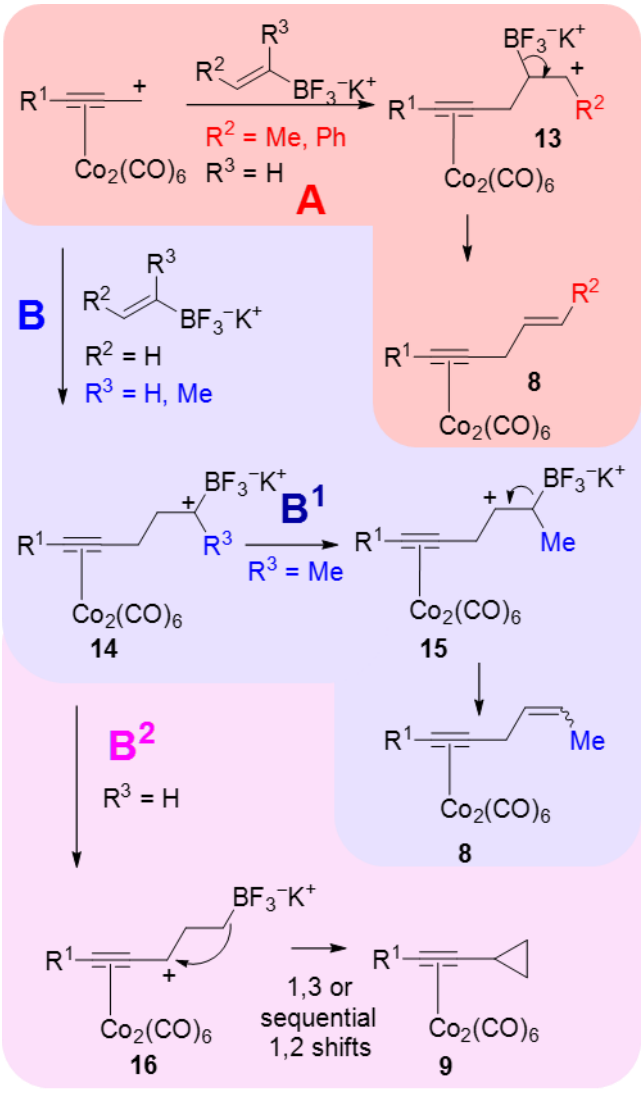
Figure 4. Enyne side products from reaction with **7d**

With the substitution products in hand from these various systems, we wished to demonstrate the facility of removing the $Co_2(CO)_6$ unit from the alkyne function to provide the target diynes and enynes (Scheme 2). Ceric ammonium nitrate (CAN) proved effective for this purpose, converting diyne complex **5bd** to **10bd** and **5bf** to **10bf**, each in 86% yield. Similarly, enyne complex **(*E*)-8ab** gave enyne **11ab** in 96% yield under analogous conditions. Cyclopropanated complex **9e** was a more sensitive compound, as attempted decomplexation with either CAN or Me_3NO resulted in gross decomposition. Fortunately, use of *n*-$Bu_4N^+F^-$ (TBAF) afforded **12e** in 80% yield. [16]



Scheme 2. Decomplexation of product alkynedicobalt complexes.

The Nicholas reactions with alkynyltrifluoroborates are reliable for alkynylations. The yields are fair to very good and tolerate both unsubstituted and monosubstituted propargyl cations well. Conversely, the reactions with alkenyltrifluoroborates gave distinctly different reaction pathways, depending upon the substitution pattern. The 2-substituted alkenyltrifluoroborates, **7a** and **7b**, reacted conventionally, with direct substitution of the BF_3^- unit through intermediate **13** and retention of configuration of the alkene (Scheme 3, **Path A**). As such, they serve as more nucleophilic analogs of vinylsilanes.[17] For 1-substituted alkenyltrifluoroborate **7c**, the products are consistent with an initial reaction at the unsubstituted end of the alkene, followed by the resulting cation **14** undergoing a 1,2-hydride migration to give β-boryl cation **15**, which in turn undergoes elimination to give alkenylation products **8** (Scheme 3, **Path B**[1]). For the unsubstituted vinyltrifluoroborate **7d**, an analogous attack to give **14** may be followed by either two successive 1,2-hydride migrations or a 1,3-hydride migration to give **16**, which in turn undergoes ring closure to afford cyclopropane **9** (Scheme 3, **Path B**[2]). These mechanisms all superficially appear feasible, and it is challenging to differentiate or support the argument for any of these pathways, especially as they involve fast intramolecular interactions. Isotope-labelled derivatives might be able to inform mechanism through kinetic isotope effects, but these are subtle differences and the unresolved transformations are not likely to be responsible for the rate limiting steps and might not be experimentally differentiable. Consequently, we have employed a computational study to assist us to differentiate the possibilities.



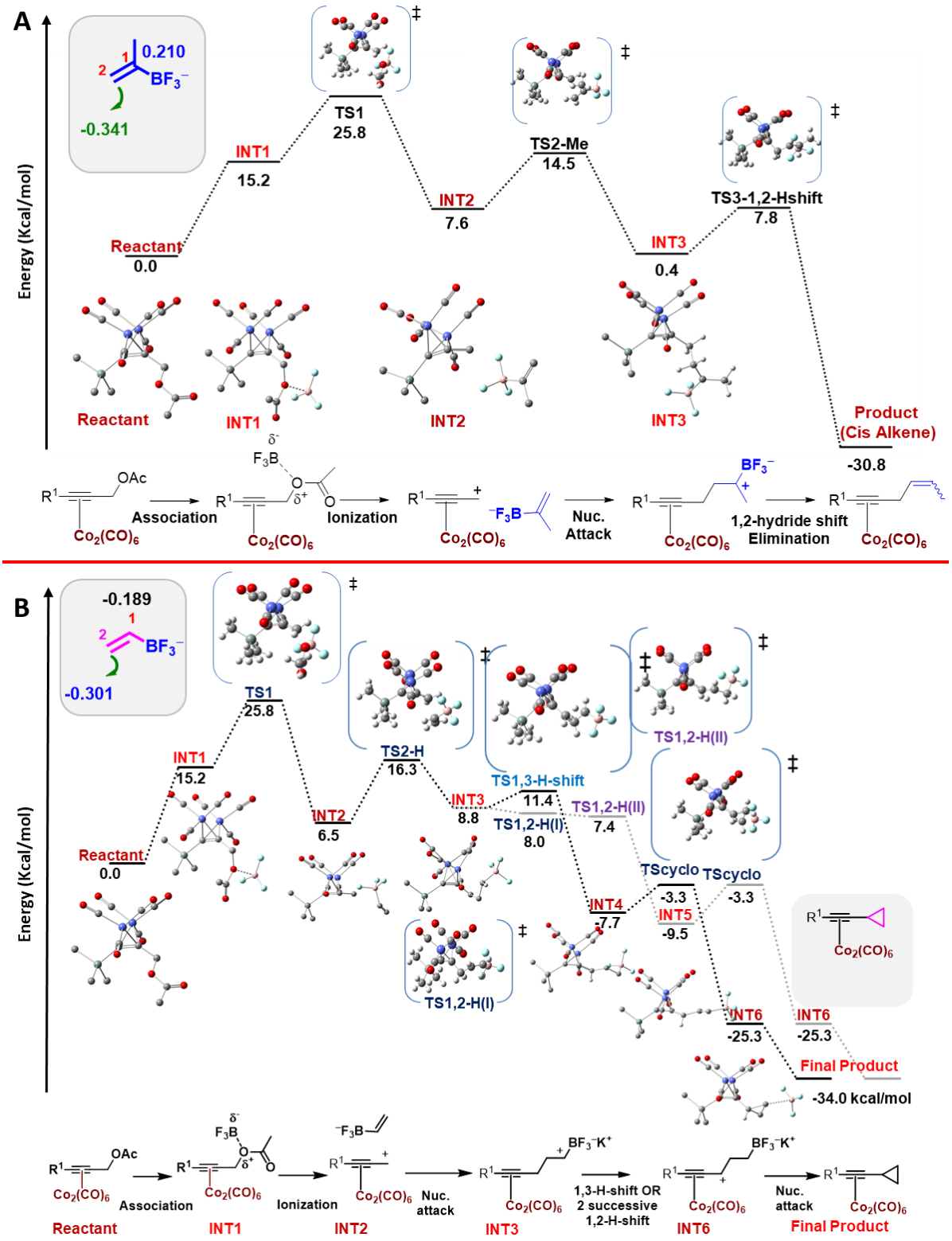
Scheme 3. Proposed mechanistic routes for the formation of **8** and **9**.

The geometry and electronic factors contributing to the configurational stability of the various Nicholas cation intermediates and the regio-determining transition states were computationally investigated using the B3LYP/Gen(6-31-G*/Def2TZVP functional (see Supporting Information). The potential energy surface (PES) of the competing pathways was plotted using the same level of theory. This allowed for an estimation of each kinetic barrier, and the relative energies of the key pre-complexes, intermediates and TS. Together, these values can assist in the rationalization of the observed regiochemical outcomes. The traditional mechanism, route A, requires no further investigation. The reaction proceeds as expected smoothly to the trans alkene from a reaction at the *ipso* carbon of the alkenyltrifluoroborate. It is the B routes, with the terminal alkene, all presumably beginning with distal attack providing intermediate **14**, that are unusual. Why do these not react conventionally? The energy diagram for these transformations is provided as Scheme 4. In all cases, the initial step involves substrate activation by BF_3 (**INT1**$_{Me}$), followed by the dissociation of the BF_3·OAc group.[18] In all studied cases, the generation of this Nicholas cation is our rate determining step. In the second step of the reaction, the incoming alkenyltrifluoroborates attack the Nicholas cation *via* transition state **TS2** (**TS2**$_{Me}$ = 14.5 kcal/mol; **TS2**$_{H}$ = 16.3 kcal/mol; see the Supporting Information for the predicted higher energy stereoisomeric transition states) to generate **INT3**$_{Me}$ (**14** $_{Me}$; in Scheme 3). The preferred site of the reaction of alkenyltrifluoroborate nucleophiles is further supported by our calculated Mulliken charge analysis that matches with the observed site of reactivity (Scheme 4, inset). For the unsubstituted vinyltrifluoroborate the greater calculated charge is proposed to be at C2 ((site of attack) = - 0.301 *e* vs. C1 = + 0.024 *e*), and for 1-substituted alkenyl trifluoroborate it is also predicted to be at C2 ((site of attack) = - 0.341 *e* vs. C1 = - 0.188 *e*). This charge distribution suggests why the reaction occurs at the unsubstituted end of the alkene, rather than from the carbon bearing the boron as is seen in normal Nicholas reactions with **7a** and **7b**.

INT3$_{Me}$ is shared by both substituted (R_3=Me) or unsubstituted (R_3=H), but this is where their reactivity diverges. We will follow the substituted version(**INT3**$_{Me}$) first, represented as path B^1 in Scheme 3 (Scheme 4A). This species, despite exhibiting charge separation and a formal carbocation, is only 0.4 kcal/mol endergonic of the reactants. This readily undergoes a facile 1,2-hydride migration *via* **TS3**$_{1,2\text{-Hshift}}$ that would technically form a *β*-boryl cation, **15**, which eliminates to generate the final alkene adduct (with the *cis* olefin being slightly favored). This, we believe, is critical for the difference in reactivity between the isopropenyltrifluoroborate and the vinyltrifluoroborate.

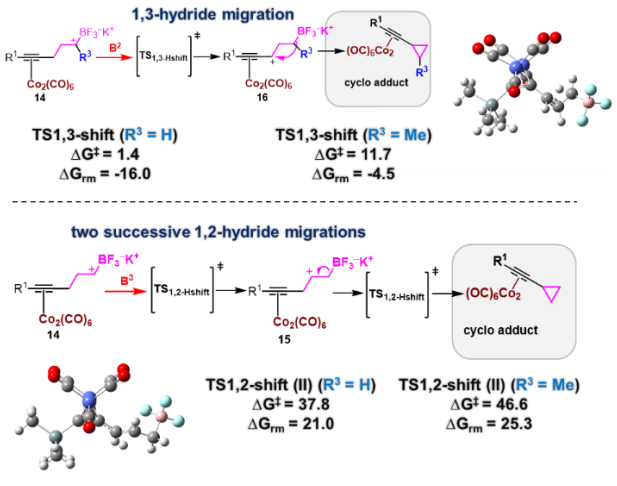
On the other hand, unsubstituted vinyltrifluoroborate **7d** diverges at **INT3**. The first few steps leading to this are analogous to the substituted version as the steps involve the same carbocation; the smaller nucleophile even forms a more stable precomplex (**INT2**$_{H}$) than the substituted derivative. Addition is slightly more challenging than for the substituted case, but the big difference is that the resulting γ-propargylic cation is 8.8 kcal/mol above the reactants (**INT3**$_{H}$). This is the key barrier that changes the mechanism. Experimentally we know these reactions proceed to the cyclopropane. This requires either two sequential 1,2- hydride shifts or a single 1,3- hydride shift. The computational analysis found each of these transition states and all are feasible. The transition state of the first 1,2- hydride shift, **TS3**$_{H1,2\text{-H(I)}}$, is

barrierless, lying 0.8 kcal/mol below **INT3$_H$**. The second one, **TS3$_{H1,2\text{-}H(II)}$**, would happen spontaneously and immediately as it is also barrierless and a further 0.6 kcal/mol downhill. This provides a very stable propargylic cation **INT5$_H$** that lies 9.5 kcal/mol below the reactants. Alternatively, the 1,3- shift proceeds through **TS3$_{H1,3\text{-}H}$**, 2.6 kcal/mol above, dropping to a less stable conformation of the carbocation, **INT4$_H$**. This can then relax to **INT5$_H$** through simple rotation. In the last step of the process, **INT4$_H$** or **INT5$_H$** then undergo ring closure via **TS4$_{H\ cyclo}$** to afford cyclopropane **9,** -25.3 kcal/mol below the reactants. (Scheme 3, Scheme 4B). The kinetic barrier for the cyclization step is 4.4 kcal/mol above **INT4$_H$** or 6.2 kcal/mol from **INT5$_H$**. Examining this PES, the sequential 1,2-shifts are favoured. Were the reactions in equilibrium, then the greater barrier for cyclization might be meaningful, but the barrierless shifts suggest that **INT3$_H$** will spontaneously decay to **INT5$_H$** immediately upon formation, and the barrier going back to the γ-cation is effectively insurmountable. In contrast, there is a barrier, if not large, complicating the 1,3-transfer so this will be slower. Depending on the precise conditions of the reaction, both are feasible, but the sequential 1,2- shifts are favored.



Scheme 4. A) Potential energy surface of the reactions leading to **8** (A) and to **9** (B)**.** All optimized structures of the intermediates are shown, as are the transition states. For the cyclopropane both the sequential 1,2- hydride shift pathway (in gray), and the 1,3- hydride shift pathway are plotted. All energies are represented in kcal relative to the reactant complex.

To further support the observed reactivity and the product trends, we also optimized the key competing transition states originated from Nicholas cationic **INT3**, for the Me-substituted structures (**Scheme 5**). Why does the Me-substituted one undergo the 1,2-shift followed immediately by elimination, while the H-substituted system proceed through an additional 1,2- shift? Initially we had considered that the H-substituted system reacted through the 1,3-shift and never generated the homopropargylic cation at all. That would be convenient, obviating the need for a detailed comparison. Unfortunately, that does not look to be the case; the reaction does seem to proceed through sequential 1,2-shifts. This leads to a need to understand why reactivity proceeds differently from the homopropargylic cation. First, we looked to see if a (1,3)-H-shift was possible for both systems. We've already noted that for the unsubstituted system, the 1,3- shift is disfavored compared to the sequential 1,2- shifts. The 1,3- shift is also greatly disfavored for the C-1 methylated system. The 1,2- required for elimination is preferred. Once generated, the second 1,2- in this system, which is barrierless in the unsubstituted system, is extremely uphill (25.3 kcal/mol; Figure 4). The second 1,2- shift is disallowed, and the elimination proceeds without a barrier.



Scheme 5. The calculated competing critical transition states (TS1,3-shift and TS1,2-shift (II)) for Me-substituted systems.

Together, these calculations explain the observed reactivity. The methyl-substituted nucleophile is forced to proceed through a 1,2-shift followed by elimination as both the 1,3- shift and the second 1,2- shift are energetically exacting. The unsubstituted version undergoes sequential 1,2-shifts setting up the cyclopropanation because the 1,3 shift is energetically costly whereas the two 1,2-shifts are both barrierless. The unusual reactivity of these systems is a direct result of the demands of the underlying physical chemistry.

Conclusions: We have disclosed a consistent set of experimental results in the Nicholas reactions of alkynyl- and alkenyltrifluoroborates. The alkynyl- and C-2 substituted alkenyltrifluoroborates react via direct substitution of the BF_3^- function, with predominant retention of stereochemistry in the latter case. C-1 substituted and unsubstituted alkenyltrifluoroborates react initially through the C-2 site, with isopropenyltrifluoroborate giving alkenylation products and vinyltrifluoroborate giving cyclopropanes. The diverse reactivities of the alkenyltrifluoroborate results are explained through the DFT calculations comparing the various possible pathways. The lack of C-2 substituents on the alkene leads to the unorthodox regiochemistry of addition, and the specifics of the substitution, or lack thereof, on the carbon bearing the boron determine whether it leads to a cis-alkene, or, in the case of fully unsubstituted ethenyltrifluoroborate, two sequential 1,2- hydride shifts and a cyclopropane. This provides an interesting new route to the synthesis of alkynyl cyclopropanes and explains this unusual new mode of Nicholas reactivity.

Associated Content

Supporting Information

The Supporting Information is available free of charge at

Table of optimization in reactions with **7d**. Copies of ^{1}H and ^{13}C NMR spectra of new compounds (PDF). Full computational details and the coordinates are also provided.

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Notes

The authors declare no competing financial interest.

Computational Methods

All structures were calculated using the Gaussian 09 suite of programs[19] at the B3LYP functional[20] using the Gen basis set (the small 6-31G* basis set for all atoms and the much larger def2-TZVP set for Co) and employing the conductor-like polarizable continuum solvation model (CPCM) [21] to account for solvent effects (default solvent parameters for dichloro-methane) were used). The success of the B3LYP/Gen(6-31G*/def2-TZVP) method combined with a polarizable continuum model (PCM) for CH_2Cl_2 as solvent for the similar systems has been reported.[18] All minima were confirmed by real vibrational frequencies, and transition states were confirmed with one imaginary frequency. Thermochemical quantities were evaluated at 273 K. The IRC methodology was applied to further verify all the transition states along the favorable pathways which obtain the minima on either side of transition states. Mulliken charge analysis of the organotrifluoroborates was performed applying Scigress. For simplicity, the counterion of the trifluoroborate was omitted from these initial calculations. Structure analysis, such as visualization of imaginary transition state frequencies was performed by GaussView v5.0.8.4.

Experimental

General Information: Reagents were obtained from commercial sources unless otherwise stated. Reactions were conducted under inert atmosphere (N_2) using glassware dried in an oven (110 °C, > 1h). The solvent for each reaction was acquired from a solvent purification system (Innovative Technologies). BF_3-OEt_2 was distilled prior to use and stored under an inert atmosphere (N_2). Reactions were subject to a ''conventional workup'' by partitioning the reaction mixture between an aqueous phase and a diethyl ether or dichloromethane phase, combining the organic phases, followed by drying ($MgSO_4$), filtration, and concentration of the organic phase. Flash chromatography was performed according to the method of Still.[22] High- Resolution Mass Spectrometry (HRMS) results were obtained via a Direct Insertion Probe-Electron Ionization method (70 eV), on a GCT Time of Flight (Tof) Mass Spectrometer at the McMaster Regional Centre for Mass Spectrometry, or on a GCT Time of Flight (Tof) Mass Spectrometer at Queen's University, and in the University of Windsor Mass Spectrometry lab with a Tof mass spectrometer using the Atmospheric Solids Analysis Probe (ASAP) and a corona discharge to facilitate ionization. ^{1}H NMR spectra were obtained on 300 or 500 MHz spectrometers (Bruker). Chemical shifts (δ are reported in parts per million (ppm), relative to the 7.27 ppm resonance for the residual $CHCl_3$ in $CDCl_3$, unless otherwise indicated. Coupling constants are reported in Hertz (Hz). ^{13}C NMR data were obtained at either 75 or 125 MHz. Infrared spectra (IR) were recorded on a FT-IR spectrophotometer using an ATR attachment. Compounds **4a**,[23], **4c**,[24] **4e**,[19], **4f**,[25] **4k**[26], **3a-d**[27] and **(*Z*)-6a**[28] were prepared according to literature methods.

Hexacarbonyl[μ-η^4-(1-acetoxyhept-2-yne)]dicobalt (4b)

To a solution of 1-acetoxyhept-2-yne (0.7080 g, 4.59 mmol) in Et_2O (25 mL), excess dicobalt octacarbonyl was added. The

reaction was monitored by TLC, and after 2 h was judged as complete. Volatiles were removed under reduced pressure, and the residue subjected to flash chromatography (30:1 petroleum ether: Et_2O), affording **4b** (1.5509 g, 82% yield) as a red-brown oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.31 (s, 2H) 2.85 (apparent t, J =7.6 Hz, 2H) 2.13 (s,3H) 1.61, (m, 2H), 1.47 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) 199.5, 170.7, 98.7, 90.5, 64.6, 33.8, 33.6, 22.6, 20.4, 13.8; IR ν_{max} 2962, 2933, 2876, 2090,1992,1744; HRMS m/e for $C_{15}H_{14}Co_2O_8$ calcd (M^+ -2CO) 383.9454, found 383.9449.

Hexacarbonyl[μ-η⁴-(1-acetoxy-pent-4-en-2-yne)]dicobalt (4d)

To a solution containing 1-acetoxy-pent-4-en-2-yne (0.3945 g, 3.18 mmol) in Et_2O (25 mL), excess dicobalt octacarbonyl was added. The reaction was monitored by TLC, and after 2 h was judged as complete. Volatiles were removed under reduced pressure, and the residue subjected to flash chromatography (20:1 petroleum ether: Et_2O), affording **4d** (0.9780 g, 75% yield) as a red-brown oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 (dd, J = 16.6, 10.1 Hz, 1H), 5.58 (dd, J = 16.6, 1.1 Hz, 1H), 5.52 (dd, J = 10.1, 1.1 Hz, 1H), 5.34 (s, 2H), 2.14 (s, 2H),; ^{13}C NMR (75 MHz, $CDCl_3$) 198.8, 170.7, 133.2, 120.4, 91.1, 89.5, 64.7, 20.5; IR ν_{max} 3006, 2928, 2093, 1996, 1744, 1631; HRMS m/e for $C_{13}H_8Co_2O_8$ calcd (M^+-CO) 410.8961, found 410.8956.

Hexacarbonyl[μ-η⁴-(1-phenyl-1-acetoxy-3-(trimethylsilyl)prop-2-yne)]dicobalt (4i)

To a solution containing 1-phenyl-1-acetoxy-3-(trimethylsilyl)prop-2-yne (0.3520 g, 1.43 mmol) in Et_2O (20 mL), excess dicobalt octacarbonyl was added. The reaction was monitored by TLC and after 12 h was judged as complete. The solvent was removed under reduced pressure, and the residue subjected to flash chromatography (15:1 petroleum ether : Et_2O) to give **4i** (0.6925 g, 91% yield) as a dark red solid, mp 65 – 67 °C: ^1H NMR (500 MHz, $CDCl_3$) δ7.31-7.39 (m, 5H) 7.01 (s, 1H) 2.19 (s, 3H) 0.21 (s, 9H); ^{13}C (125 MHz, $CDCl_3$) 199.6, 169.6, 140.7, 128.6, 126.2, 111.2, 78.9, 75.8, 20.8, 0.5; IR ν_{max}: 2966, 2923, 2088, 2044, 2010, 1739, 1578, 1492, 1450, 1248; HRMS m/e for $C_{20}H_{18}Co_2O_8Si$ calcd (M-CO) 503.9485 found 503.9494.

General Procedure: To a (0.03 M) CH_2Cl_2 solution of alkynedicobalt complex **4** and organotrifluoroborate **3** or **7** (2.5 equiv) at 0° C was added BF_3•OEt_2 (2.5 equiv). After 1.5 h, saturated NH_4Cl(aq) was added and the mixture subjected to conventional workup (CH_2Cl_2). Flash chromatography afforded the reaction products.

Hexacarbonyl[μ-[(3,4-η:3,4-η)(7-phenylhepta-3,6-diyne)]dicobalt (5aa)

The general procedure was followed, employing **4a** (89.7 mg, 0.218 mmol), potassium trifluoro(phenylethynyl)borate **3a** (0.113 g, 0.544 mmol) and BF_3•OEt_2 (67 μL, 0.54 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5aa** as a red solid (90.3 mg, 91% yield). **5aa:** mp 43-44 °C; ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C (75 MHz, $CDCl_3$) 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_{max}: 2971, 2088, 2043, 1989, 1600, 1490 cm^{-1}; HRMS m/e for $C_{19}H_{12}Co_2O_6$ calcd (M^+-CO+H) 454.9376 found 454.9367.

Hexacarbonyl[μ-[(3,4-η:3,4-η)(undeca-3,6-diyne)]dicobalt (5ba)

The general procedure was followed, employing **4a** (82.8 mg, 0.201 mmol), potassium trifluoro(hex-1-yn-1-yl)borate **3b** (0.0945 g, 0.502 mmol) and BF_3•OEt_2 (62 μL, 0.50 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5ba** as a red oil (63.8 mg, 73% yield). **(5ba):** ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C (75 MHz, $CDCl_3$) 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_{max}: 2964, 2874, 2087, 2043, 1990, 1457; HRMS m/e for $C_{17}H_{16}Co_2O_6$ calcd (M^+-CO+H) 406.9740 found 406.9733.

Hexacarbonyl[μ-[(3,4-η:3,4-η)(hepta-3,6-diyne)]dicobalt (5ca)

The general procedure was followed, employing **4a** (79.5 mg, 0.193 mmol), potassium ethynyl trifluoroborate (**3c**) (0.0636 g, 0.482 mmol) and BF_3•OEt_2 (59 μL, 0.48 mmol). Flash chromatography (40:1 petroleum ether: Et_2O) afforded **5ac** as a dark red oil (48.7 mg, 67% yield). Recovered **4a** (10.4 mg, 13% recovery) subsequently eluted. **(5ca):** ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C (75 MHz, $CDCl_3$) 200.2, 128.7, 128.0, 101.3, 98.9, 37.0, 27.1, 17.5, 15.6. IR ν_{max} 3314, 2972, 2877,2089, 2044, 1994 cm^{-1}; HRMS m/e for $C_{13}H_8Co_2O_6$ calcd (M^++ H) 378.9063, found 378.9063.

Hexacarbonyl[μ-[(5,6-η:5,6-η)(9-phenylnona-5,8-diyne)]dicobalt (5ab)

The general procedure was followed, employing **4b** (91.4 mg, 0.208 mmol), potassium trifluoro(phenylethynyl)borate **3a**

(0.108 g, 0.519 mmol) and BF_3•OEt_2 (64 μL, 0.52 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5ab** as a red solid (73.7 mg, 74% yield,). (**5ab**): mp 225 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.27-7.33 (m, 3H), 4.00 (s, 2H), 2.90 (t, J = 7.8 Hz, 2H), 1.70 (m, 2H), 1.50 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 199.9, 131.5, 128.2, 128.0, 123.3, 99.7, 93.9, 86.2, 86.5; IR ν_{max}:3079, 3056, 2960, 2874, 2087, 2043, 1990, 1490 cm^{-1}; HRMS m/e for $C_{21}H_{16}Co_2O_6$ calcd (M^+-CO+H) 454.9740 found 454.9725.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(5-phenyl-1-(trimethylsilyl)penta-1,4-diyne)]dicobalt (5ac)

The general procedure was followed, employing **5c** (86.9 mg, 0.190 mmol), potassium trifluoro(phenylethynyl)borate **3a** (0.0991 g, 0.476 mmol) and BF_3•OEt_2 (59 μL, 0.48 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5ac** as a red solid (61.7 mg, 65% yield). (**5ac**)**:** mp 105 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.28-7.33 (m, 3H), 4.01 (s, 2H), 0.35 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 200.0, 131.5, 128.3, 128.2, 123.2, 107.5, 86.9, 82.2, 79.5; IR ν_{max}: 3086, 3064, 3037, 3023, 2960, 2087, 2044, 1995, 1574, 1490 cm^{-1}; HRMS m/e for $C_{21}H_{16}Co_2O_6Si$ calcd (M^+-CO+H) 470.9509 found 470.9501.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1-(trimethylsilyl)-1,4-nonadiyne)]dicobalt (5bc)

The general procedure was followed, employing **4c** (80.1 mg, 0.176 mmol), potassium trifluoro(hex-1-yn-1-yl)borate **3b** (0.0825 g, 0.439 mmol) and BF_3•OEt_2 (54 μL, 0.44 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5bc** as a red oil (64.8 mg, 77% yield). (**5bc**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (t, J = 2.3 Hz, 2H) 2.13 – 2.12 (m, 2H), 1.36 – 1.52 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H), 0.32 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 200.5, 109.4, 82.9, 79.5,77.5, 30.8, 25.6, 22.3, 18.6, 13.81, 0.7; IR ν_{max}: 2959, 2875, 2086, 2043, 1994 cm^{-1}; HRMS m/e for $C_{18}H_{15}Co_2O_6Si$ calcd (M^+-CO+H) 450.9822 found 450.9809.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(8-chloro-1-(trimethylsilyl)octa-1,4-diyne)]dicobalt (5df)

The general procedure was followed, employing **4f** (120.7 mg, 0.314 mmol), alkynyltrifluoroborate **3d** (0.1748 g, 0.786 mmol) and BF_3•OEt_2 (100 μL, 0.79 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5df** as a red oil (92.0 mg, 66% yield). Recovered **4f** (14.4 mg, 12% recovery) subsequently eluted. (**5df**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (s, 1H), 3.71 (m, 2H), 3.56 (t, J = 6.7 Hz, 2H); 2.23 (m, 2H), 1.89 (m, 2H), 1.64 (m, 2H); ^{13}C (75 MHz) 199.6, 94.0, 81.5, 77.9, 72.7, 44.5, 31.6, 25.6, 24.5, 17.9; IR (neat) ν_{max}: 2952, 2873, 2093, 2048, 2001 cm^{-1}; HRMS m/e for $C_{15}H_{11}ClCo_2O_6$ calcd (M^++H) 440.8986 found 440.8970.

Hexacarbonyl[μ-[(3,4-η:3,4-η)(undec-1-ene-3,6-diyne)]dicobalt (5bd)

The general procedure was followed, employing **4d** (81.0 mg, 0.198 mmol), potassium trifluoro(hex-1-yn-1-yl)borate **3b** (0.0929 g, 0.482 mmol) and BF_3•OEt_2 (60 μL, 0.48 mmol). Flash chromatography (50:1 petroleum ether : Et_2O) afforded **5bd** as a red oil (55.1 mg, 65% yield). Starting **4d** (8.1 mg, 10% recovery) subsequently eluted. (**5bd**)**:** ^{1}H NMR: (300 MHz, $CDCl_3$) δ 6.85 (dd, J = 16.6, 10.1 Hz, 1H), 5.61 – 5.63 (dd, J = 19.9, 1.5 Hz, 1H), 5.49 (dd, J = 10.1, 1.5 Hz, 2H), 3.76 (t, J = 2.3 Hz, 2H), 2.18 (tt, J = 6.9, 2.3 Hz, 2H), 1.33 – 1.53 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 199.6, 133.5, 119.8, 96.7, 90.4, 82.8, 76.9, 30.6, 24.6, 22.0, 18.3, 13.6; IR ν_{max}: 3092, 2960, 2874, 2090, 2047, 1995, 1630; HRMS m/e for $C_{17}H_{14}Co_2O_6$ calcd (M^+-CO+H) 404.9583 found 404.9573.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1-phenyl-1,4-nonadiyne)]dicobalt (5be)

The general procedure was followed, employing **4e** (101.1 mg, 0.220 mmol), potassium trifluoro(hex-1-yn-1-yl)borate **3b** (103.2 mg, 0.549 mmol) and BF_3•OEt_2 (68 μL, 0.55 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5be** as a red oil (63.8 mg, 60% yield). Starting material **4e** (10.2 mg, 10% recovery) subsequently eluted. (**5be**)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.31-7.39 (m, 3H), 3.94 (t, J = 2.3 Hz, 2H), 2.18 (tt, J = 7.0, 2.3 Hz, 2H), 1.38 – 1.52 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 199.4, 137.9, 129.6, 128.8, 127.9, 95.6, 90.6, 83.0, 76.9, 30.6, 25.0, 22.0, 18.4, 13.6; IR ν_{max}: 3078, 3056, 3026, 3014, 2959, 2872, 2089, 2049, 2016, 1590 cm^{-1}; HRMS m/e for $C_{21}H_{16}Co_2O_6$ calcd (M^+-CO+H) 454.9739 found 454.9738.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1,4-nonadiyne)]dicobalt (5bf)

The general procedure was followed, employing **4f** (102.8 mg, 0.268 mmol), potassium trifluoro(hex-1-yn-1-yl)borate **3b** (125.8 mg, 0.669 mmol) and BF_3•OEt_2 (83 μL, 0.67 mmol). Flash chromatography (100% petroleum ether - 50:1 petroleum ether : Et_2O) afforded **5bf** as a red oil (75.8 mg, 70% yield). Recovered **4f** (16.7 mg, 16% recovery) subsequently eluted. (**5bf**)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (t, J = 0.9 Hz, 1H) 3.70 – 3.72 (dt, J = 0.9, 2.3 Hz, 2H), 2.17 (m, 2H) 1.37 – 1.51 (m, 4H), 0.91 (t, J = 7.1

Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 199.8, 94.3, 82.5, 77.4, 72.7, 30.6, 24.5, 22.0, 18.3, 13.6; IR ν_{max}: 2960, 2875, 2093, 2048, 1995 cm^{-1}; HRMS m/e for $C_{15}H_{12}Co_2O_6$ calcd (M^+-CO+H) 378.9426 found 378.9427.

Hexacarbonyl[μ-[(2,3-η:2,3-η)(methyl 6-phenylhexa-2,5-diynoate)]dicobalt (5ag)

The general procedure was followed, employing **4g** (73.7 mg, 0.178 mmol), potassium trifluoro(phenylethynyl)borate **3a** (92.6 mg, 0.445 mmol) and dibutylboron triflate (Bu_2BOTf, 1M in CH_2Cl_2, 0.45 mL). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5ag** as a red oil (56.1 mg, 65% yield). **(4ag):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.27-7.30 (m, 3H), 3.99 (s, 2H), 3.85 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) 197.8, 170.3, 131.5, 128.2, 128.1, 123.0, 95.3, 86.0, 82.5, 77.2, 53.1, 24.9; IR ν_{max}: 3084, 3055, 2957, 2098, 2050, 2009, 1707, 1595, 1502 cm^{-1}; HRMS m/e for $C_{19}H_{10}Co_2O_8$ calcd (M^+-2CO+H) 428.9219 found 428.9218.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(3-methyl-5-phenyl-1-(trimethylsilyl)penta-1,4-diyne)]dicobalt (5ah)

The general procedure was followed, employing **4h** (89.2 mg, 0.190 mmol), potassium trifluoro(phenylethynyl)borate **3a** (98.7 mg, 0.474 mmol) and BF_3•OEt_2 (59 μL, 0.47 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5ah** as a brown solid (87.7 mg, 90% yield). **(5ah):** mp 85 °C (decomp.) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.27-7.31 (m, 3H), 4.18 (q, J = 6.9 Hz, 1H), 1.65 (d, J = 6.9 Hz, 3H), 0.34 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 200.4, 131.5, 128.3, 128.0, 123.3, 115.6, 92.1, 82.0, 79.3, 31.9, 24.3, 0.70; IR ν_{max}: 3063, 2981, 2086, 2044, 1992, 1562 cm^{-1}; HRMS m/e for $C_{21}H_{18}Co_2O_6Si$ calcd (M^+-CO+H) 484.9666 found 484.9679.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(9-chloro-3-methyl-1-(trimethylsilyl)nona-1,4-diyne)]dicobalt (5dh)

The general procedure was followed, employing **4h** (102.1 mg, 0.217 mmol), alkynyltrifluoroborate **3d** (0.1207 g, 0.543 mmol) and BF_3•OEt_2 (69 μL, 0.54 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5dh** as a red oil (76.9 mg, 67% yield). Recovered **4h** (13.2 mg, 13% recovery) subsequently eluted. **(5dh):** mp 90 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (qt, J = 6.9, 2.1 Hz, 1H), 3.55 (t, J = 6.6 Hz, 2H), 2.21 (td, J = 7.1, 2.1 Hz, 2H), 1.87 (m, 2H), 1.63 (m, 2H), 1.51 (d, J = 6.9 Hz, 3H), 0.32 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 200.3, 116.8, 83.4, 81.3, 79.1, 44.5, 31.7, 31.4, 25.7, 24.5, 18.0, 0.6; IR (neat) ν_{max}: 2957, 2086, 2043, 1998 cm^{-1}; HRMS m/e for $C_{21}H_{18}Co_2O_6Si$ calcd (M^++H) 526.9538 found 526.9517.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(3,5-diphenyl-1-(trimethylsilyl)penta-1,4-diyne)]dicobalt (5ai)

The general procedure was followed, employing **4i** (95.0 mg, 0.178 mmol), potassium trifluoro(phenylethynyl)borate **3a** (92.8 mg, 0.446 mmol) and BF_3•OEt_2 (55 μL, 0.45 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **5ah** as a red brown solid (99.4 mg, 97% yield,). **(5ah):** mp 85 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.57 (m, 10H), 5.32 (s, 2H), 0.31 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 199.9, 141.5, 131.6, 128.8, 128.3, 128.2, 127.9, 123.1, 116.3, 89.9, 84.1, 79.7, 43.5, 0.70; IR ν_{max}: 3063, 3031, 2958, 2086, 2045, 2010, 1597, 1556 cm^{-1}; HRMS m/e for $C_{26}H_{20}Co_2O_6Si$ calcd (M^+-CO+H) 546.9822 found 546.9833.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(3-methyl-1-(trimethylsilyl)but-3-en-1-yne)]dicobalt (6)

The general procedure was followed, employing **4j** (82.9 mg, 0.171 mmol), potassium trifluoro(phenylethynyl)borate **2a** (89.0 mg, 0.428 mmol) and BF_3•OEt_2 (53 μL, 0.43 mmol). Flash chromatography as a red brown solid (40:1 petroleum ether : Et_2O) afforded **6** (39.2 mg, 54% yield). **(6):** mp 82 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.39 (m, 1H), 5.26 (m, 1H), 2.11 (dd, J = 1.2, 0.6 Hz, 3H), 0.34 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 200.2, 141.7, 117.4, 107.8, 80.3, 24.6, 0.8; IR ν_{max} : 2958, 2922, 2086, 2044, 1992, 1641, 1623 cm^{-1}; HRMS m/e for $C_{14}H_{14}Co_2O_6Si$ calcd (M^+-CO+H) 396.9352 found 396.9356.

(E)-Hexacarbonyl[μ-[(5,6-η:5,6-η)(9-phenylnon-8-en-5-yne)]dicobalt ((*E*)- 8ab)

The general procedure was followed, employing **4b** (89.5 mg, 0.203 mmol), potassium trifluoro(styryl)borate **(*E*)- 6a** (106.7 mg, 0.508 mmol) and BF_3•OEt_2 (63 μL, 0.51 mmol). Flash chromatography (20:1 petroleum ether : Et_2O) afforded **(*E*)- 8ab** as a red oil (67.0 mg, 68% yield). **((*E*)- 8ab)** (300 MHz, $CDCl_3$) ^{1}H NMR: δ 7.29 – 7.44 (m, 5H), 6.61 (d, J = 15.7 Hz, 1H), 6.36 (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); ^{13}C (75 MHz, $CDCl_3$) 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_{max}: 3084, 3062, 3028, 2960, 2874, 2085, 2040, 1994, 1495 cm^{-1}; HRMS m/e for $C_{21}H_{18}Co_2O_6$ calcd (M^+-CO+H) 456.9896 found 456.9907.

(Z)-Hexacarbonyl[μ-[(5,6-η:5,6-η)(9-phenylnon-8-en-5-yne)]dicobalt ((*Z*)- 8ab)

The general procedure was followed, employing **4b** (54.6 mg, 0.124 mmol), potassium trifluoro(*cis*-styryl)borate **(*Z*)- 6a** (69.0 mg, 0.328 mmol) and BF_3•OEt_2 (39 μL, 0.31 mmol). Flash chromatography (100% petroleum ether – 15:1 petroleum ether : Et_2O) afforded **8ab** (38.9 mg, 65% yield) as a 87:13 Z-:E- isomerix mixture, followed by recovered **4b** (6.8 mg, 12% recovery). Repeated preparative TLC gave an isomerically pure sample of **(*Z*)- 8ab** as a red-brown oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.40 (m, 2H), 7.30-7.32 (m, 2H), 7.28 (m, 1H), 6.63 (d, J = 11.5 Hz, 1H), 5.85 (dt, J = 11.5, 7.4 Hz, 1H), 3.87 (dd, J = 7.4, 1.5 Hz, 2H), 2.83 (t, J = 8.0 Hz, 2H), 1.61 (m, 2H), 1.46 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) 200.1, 136.8, 130.7, 129.1, 128.6, 128.0, 127.0, 99.7, 97.2, 33.8, 32.4, 22.7, 13.8; ; IR (neat) ν_{max} 3023, 2960, 2921, 2086, 2041, 1995, 1620, 1577, 1494 $cm^{-1;}$ HRMS m/e for $C_{21}H_{18}Co_2O_6$ calcd 483.9767 found 483.9781.

(E)-Hexacarbonyl[μ-[(1,2-η:1,2-η)(5-phenyl-1-(trimethylsilyl)pent-4-en-1-yne)]dicobalt ((*E*)- 8ac)

The general procedure was followed, employing **4c** (92.0 mg, 0.202 mmol), potassium trifluoro(styryl)borate **(*E*)-7a** (105.9 mg, 0.504 mmol) as the nucleophile and BF_3•OEt_2 (62 μL, 0.50 mmol). Flash chromatography (20:1 petroleum ether : Et_2O) afforded **(*E*)- 8ac** as a red oil.(71.9 mg, 71% yield). **((*E*)- 8ac):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.43 (m, 5H), 6.60 (d, J = 15.7 Hz, 1H), 6.29 – 6.39 (dt, J = 15.7, 7.2 Hz, 1H), 3.86 (dd, J = 7.2, 1.1 Hz, 2H), 0.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.4, 136.8, 132.3, 128.7, 127.8, 127.6, 126.2, 110.1, 78.9, 38.6, 0.7; IR ν_{max} 3084, 3062, 3028, 2958, 2085, 2041, 1994, 1577; HRMS m/e for $C_{20}H_{18}Co_2O_6Si$ calcd (M^+-CO+H) 472.9665 found 472.9648.

(E)-Hexacarbonyl[μ-[(3,4-η:3,4-η)((*E*)-oct-6-en-3-yne)]dicobalt ((*E*)-8ba)

The general procedure was followed, employing **4a** (42.8 mg, 0.104 mmol), potassium trifluoro(1-propenyl)borate **(*E*)-7b** (38.4 mg, 0.260 mmol) and BF_3•OEt_2 (32 μL, 0.26 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **(*E*)-8ba** (20.7 mg, 51%) followed by recovered **4a** (5.2 mg, 12% recovery). **((*E*)-8ba):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50-5.70 (m, 2H), 3.49 (d, J = 5.7 Hz, 2H), 2.86 (q, J = 7.4 Hz, 2H), 1.70 (d, J = 4.8 Hz, 3H), 1.29 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.2, 128.7, 128.0, 101.3, 98.9, 37.0, 27.1, 17.5, 15.6; IR ν_{max}3024, 2971, 2868, 2086, 2041, 2005, 1455 cm^{-1}; HRMS m/e for $C_{14}H_{12}Co_2O_6$ calcd (M^+-1CO+H) 366.9427, found 366.9420.

Hexacarbonyl[μ-[(1,2-η:1,2-η)((*E*)-1-(trimethylsilyl)hex-4-en-1-yne)]dicobalt ((E)-8bc)

The general procedure was followed, employing **4c** (79.0 mg, 0.173 mmol), potassium trifluoro(1-propenyl)borate **(*E*)-7b** (64.1 mg, 0.433 mmol) and BF_3•OEt_2 (53 μL, 0.43 mmol). Flash chromatography 40:1 petroleum ether : Et_2O afforded **(E)-8bc** (26.2 mg, 35% yield) as a viscous red oil, followed by recovered **4c** (38.7 mg, 49% recovery).

A modified version of the general procedure was followed, employing **4c** (33.4 mg, 0.0732 mmol), potassium trifluoro(1-propenyl)borate **(*E*)-7b** (0.1080 g, 0723 mmol), and BF_3•OEt_2 (70 μL, 0.57 mmol). Flash chromatography (100% petroleum ether – 40:1 petroleum ether : Et_2O) afforded **(E)-8bc** (16.9 mg, 53% yield) as a viscous red oil, followed by recovered **4c** (15.3 mg, 46% recovery). **((E)-8bc)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 – 5.70 (m, 2H), 3.56 (dd, J = 6.0, 0.9 Hz, 2H), 1.70 (d, J = 5.1 Hz, 3H), 0.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.5, 129.3, 128.0, 112.4, 78.7, 38.2, 17.5, 0.6; IR ν_{max}: 3025, 2959, 2857, 2084, 2041, 1993, 1578 cm^{-1}; HRMS m/e for $C_{15}H_{16}Co_2O_6Si$ calcd (M^+-CO) 409.9430 found 409.9421.

Hexacarbonyl[μ-[(3,4-η:3,4-η)((*Z*)-dec-2-en-5-yne)]dicobalt ((*Z*)-8bb)

The reaction scheme follows the general procedure employing **4b** (98.8 mg, 0.222 mmol), potassium trifluoro(1-propenyl)borate **(*Z*)- 7c** (82.0 mg, 0.555 mmol) as the nucleophile and BF_3•OEt_2 (69 μL, 0.56 mmol). Flash chromatography (40:1 petroleum ether : Et_2O) afforded **(*Z*)- 8cb** as a red oil (61.1 mg, 65% yield, red oil) and as a 97:3 ratio of Z-:E- isomers, ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43-5.67 (m, 2H), 3.60 (d, J = 6.8 Hz, 2H), 2.84 (t, J = 7.9 Hz, 2H), 1.72 (d, , J = 6.0 Hz, 3H), 1.64 (m, 2H), 1.49 (m, 2H), 0.99 (t, J = 7.3, 3H); irradiation of the 1.72 ppm resonance caused partial simplification of the 5.43 – 5.67 ppm pattern to δ 5.63 (m, 1H), 5.58 (1/2 AB, J = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 200.2, 127.4, 126.0, 99.6, 98.0, 33.8, 31.1, 22.7, 13.9, 12.8;; IR (neat) ν_{max}: 3025, 2961, 2931, 2086, 2042, 2008, 1652 cm^{-1}; HRMS m/e for $C_{16}H_{16}Co_2O_6$ calcd (M^+-CO) found .

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1-(trimethylsilyl)hex-4-en-1-yne)]dicobalt ((*Z*+*E*)-8bc)

The general procedure was followed, employing **4c** (97.4 mg, 0.213 mmol), potassium isopropenyltrifluoroborate **7c** (79.0 mg, 0.534 mmol) and BF_3•OEt_2 (66 μL, 0.53 mmol). Flash chromatography (40:1 petroleum ether: Et_2O) afforded **8bc** (71.8

mg, 77% yield, brown solid) as 7.1:1 (*Z*:*E*) mixture. **((*Z*)-8bc)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 – 5.67 (m, 2H), 3.68 (d, J = 6.7 Hz, 2H), 1.72 (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), 1.70 (d, obscured, 3H), 0.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer only): 200.4, 128.0, 125.9, 111.2, 78.7, 32.3, 12.9, 0.6; IR ν_{max}: 3025, 2959, 2984, 2085, 2041, 2000, 1581; HRMS m/e for $C_{15}H_{16}Co_2O_6Si$ calcd (M^+-CO+H) 410.9509 found 410.9501.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1-(trimethylsilyl)-3-methylhex-4-en-1-yne)]dicobalt ((Z+*E*)-8bh)

The general procedure was followed, employing **4h** (76.4 mg, 0.162 mmol), potassium isopropenyltrifluoroborate **7c** (60.1 mg, 0.406 mmol) and BF_3•OEt_2 (50 μL, 0.41 mmol). Flash chromatography (40:1 petroleum ether: Et_2O) afforded **8bh** (55.8 mg, 76% yield, brown solid) as 2.7:1 (*Z*:*E*) mixture. **((*Z*)-8bh):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 (dq, J = 10.4, 6.9 Hz, 1H), 5.37 (m, 1H), 3.99 (m, 2H), 1.72 (dd, J = 6.9, 1.6 Hz, 3H), 1.33 (d, J = 6.7 Hz, 3H), 0.31 (s, 9H); resonances from the minor isomer were observed at 5.57 (dq, J = 15.9, 6.3 Hz, 1H), 3.56 (m, 2H), 1.68 (dd, J = 6.3, 1.1 Hz, 3H), 1.36 (d, J = 6.8 Hz, 3H), 0.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.6, 135.2, 123.3, 118.3, 78.4, 36.5, 24.2, 13.3, 0.8; resonances from the minor isomer could be observed at 136.1, 125.1, 42.1, 23.3, 17.5, 1.1; IR ν_{max}: 3017, 2965, 2084, 2040, 1991, 1564; HRMS m/e for $C_{16}H_{18}Co_2O_6Si$ calcd (M^+-CO+H) 424.9666 found 424.9672.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(hexyn-1-ylcyclopropane)]dicobalt (9b)

A modified version of the general procedure was followed, employing **4b** (37.9 mg, 0.0861 mmol), potassium vinyltrifluoroborate **7d** (0.1196 g, 0.893 mmol) and BF_3•OEt_2 (82 μL, 0.66 mmol). Flash chromatography (100% petroleum ether - 40:1 petroleum ether : Et_2O) afforded **9b** as a red oil (26.1 mg, 74% yield). Recovered complex **4b** (1.9 mg, 5% recovery) subsequently eluted. **(9b):** ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C (75 MHz, $CDCl_3$) 200.1, 103.8, 98.4, 33.9, 33.6, 22.7, 15.2, 13.8, 12.5; IR ν_{max}: 2962, 2876, 2086, 2040, 2005, 1450 cm^{-1}; HRMS m/e for $C_{16}H_{14}Co_2O_6$ calcd (M^+-CO+H) 380.9583, found 380.9589.

Hexacarbonyl[μ-[(1,2-η:1,2-η)((trimethylsilylethynylcyclopropane)]dicobalt (9c)

A modified version of the general procedure was followed, employing **4c** (35.2 mg, 0.0772 mmol), potassium vinyltrifluoroborate **7d** (0.1051 g, 0.785 mmol) as the nucleophile, and BF_3•OEt_2 (74 μL, 0.60 mmol). Flash chromatography (100% petroleum ether - 40:1 petroleum ether : Et_2O) afforded **9c** as a brown solid (22.7 mg, 69% yield). Recovered **4c** (5.2 mg, 15% recovery) subsequently eluted. **(9c):** mp 80 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22 – 2.30 (tt, J = 7.0, 4.0 Hz, 1H), 1.17 (ddd, J = 7.4, 6.6, 4.3 Hz, 2H), 0.74 (ddd, J = 6.6, 4.3, 4.0 Hz, 2H), 0.33 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 201.0, 117.6, 75.7, 15.5, 14.1, 0.8; IR ν_{max}: 2959, 2920, 2851, 2084, 2040, 2000, 1450 cm^{-1}; HRMS m/e for $C_{14}H_{14}Co_2O_6Si$ calcd (M^+-CO+H) 396.9352 found 396.9357.

Synthesis of Hexacarbonyl[μ-[(1,2-η:1,2-η)(phenylethynylcyclopropane)]dicobalt (9e)

A modified version of the general procedure was followed, employing **4e** (74.7 mg, 0.162 mmol), potassium vinyltrifluoroborate **7d** (0.3346 g, 2.50 mmol) as the nucleophile, and BF_3•OEt_2 (0.25 mL, 2.0 mmol). Flash chromatography (100% petroleum ether - 40:1 petroleum ether : Et_2O) afforded **9e** as a red-brown solid (48.8 mg, 70% yield). Recovered **4e** (9.2 mg, 12% recovery) subsequently eluted. **(9e):** mp 35-36 °C; ^{1}H (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.2 Hz, 2H), 7.37 (apparent t, J = 7.3 Hz, 2H), 7.30 (m, 1H), 2.34 (m, 1H), 1.24 (m, 2H), 0.84 (m, 2H); resonances from the minor isomer **8de** were observed at 6.07 (m, 1H), 5.31 (dd, J = 16.9, 1.4 Hz, 1H), 5.22 (dd, J = 10.0, 1.1 Hz, 1H), 3.82 (d, J = 7.1 Hz, 2H); resonances from the minor isomer **8de'** were observed at 6.77 (dq, J = 14.8, 1.7 Hz, 1H), 6.29 (dq, J = 14.8, 6.8 Hz, 1H), 1.92 (dd, J = 6.8, 1.7 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) 199.7, 138.3, 129.2, 128.8, 127.6, 104.7, 91.1, 15.2, 12.5; IR ν_{max} 3082, 3010, 2920, 2085, 2056, 2001 cm^{-1}; HRMS m/e for $C_{17}H_{10}Co_2O_6$ calcd (M^+) 427.9141 found 427.9138.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1-methyl-1-(trimethylsilylethynyl)(cyclopropane))]dicobalt (9h)

A modified version of the general procedure was followed, employing **4h** (46.7 mg, 0.0993 mmol), potassium vinyltrifluoroborate **7d** (0.2082 g, 1.55 mmol) as the nucleophile, and BF_3•OEt_2 (0.15 mL, 1.2 mmol). Flash chromatography (100% petroleum ether - 40:1 petroleum ether : Et_2O) afforded **9h** as a brown solid (25.7 mg, 59% yield). Recovered **4k** (8.7 mg, 19% recovery) subsequently eluted. **9h**: mp 90 °C (dec.); ^{1}H (500 MHz, $CDCl_3$) δ 1.50 (s, 3H), 1.05 (m, 2H), 0.95 (m, 2H), 0.30 (s, 9H); resonances from the minor isomer **8dh** were observed at 5.87 (m, 1H), 5.16 (d, J = 15.0 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H); ^{13}C (125 MHz, $CDCl_3$) 200.8, 123.7, 76.1, 25.6, 22.8, 20.1, 1.1; IR ν_{max}

3084, 2964, 2926, 2084, 2039, 1999 cm^{-1}; HRMS m/e for $C_{15}H_{16}Co_2O_6Si$ calcd (M^+) 437.9380 found 437.9389.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(1-phenyl-1-(trimethylsilylethynyl)(cyclopropane))]dicobalt (9i)

To a mixture of **4i** (40.8 mg, 0.0766 mmol) and potassium vinyltrifluoroborate **7d** (30.0 mg, 0.224 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added HBF_4•OEt_2 (52 μL, 0.38 mmol). After 1.25 h, additional HBF_4 HBF_4•OEt_2 (25 μL, 0.18 mmol) was added. After and addition 45 min, NH_4Cl (aq) was added and the mixture subjected to a conventional workup (CH_2Cl_2). Flash chromatography (100% petroleum ether - 40:1 petroleum ether : Et_2O) (100% petroleum ether - 40:1 petroleum ether : Et_2O) afforded at mixture of **9i** and **8i** (23.0 mg, 43% **9i**, 18% **8i**), followed by recovered **4i** (8.2 mg, 20% recovery). Subsequent preparative TLC (100% hexanes) afforded pure sample of **9i** as a dark brown sold, **(9i)**: mp 66-71 °C.; ^1H (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2 Hz, 2H), 7.36 (apparent t, J = 7.2 Hz, 2H), 7.29 (m, 1H), 1.56 (br, 2H), 1.32 (br, 2H), 0.29 (s, 9H); ^{13}C (125 MHz, $CDCl_3$) 200.2, 144.4, 130.7, 128.3, 127.4, 124.5, 77.7, 30.3, 21.8, 1.1; IR (neat) υ_{max} 3030, 2061, 2084, 2019, 2004, 1970, 1572 cm^{-1}; HRMS m/e for $C_{20}H_{18}Co_2O_6Si$ calcd (M^+) 499.9537 found 499.9522.

Hexacarbonyl[μ-[(1,2-η:1,2-η)(propyn-1-ylcyclopropane)]-dicobalt (9k)

A modified version of the general procedure was followed, employing **4k** (42.8 mg, 0.108 mmol), potassium vinyltrifluoroborate **7d** (0.1440 g, 1.08 mmol) as the nucleophile, and BF_3•OEt_2 (0.105 mL, 0.85 mmol). Flash chromatography (100% petroleum ether - 40:1 petroleum ether : Et_2O) afforded **9k** as a brown oil (28.8 mg, 73% yield). Recovered **4k** (1.6 mg, 4% recovery) subsequently eluted. ^1H (500 MHz, $CDCl_3$) δ 2.62 (s, 3H), 2.14 (m, 1H), 1.15 (m, 2H), 0.77 (m, 2H); resonances from the minor isomer **8dk** were observed at 5.95 (m, 1H), 5.22 (dd, J = 16.9, 1.3 Hz, 1H), 5.16 (d, J = 9.9 Hz, 1H), 3.58 (d, J = 7.2 Hz, 2H); ^{13}C (125 MHz, $CDCl_3$) 200.2, 103.9, 92.0, 20.4, 15.3, 12.8; IR (neat) ν_{max} 3090, 3-12, 2960, 2086, 2039, 1994 cm^{-1}; HRMS m/e for $C_{12}H_8Co_2O_6$ calcd (M^+) 365.8985 found 365.8978.

Undec-1-en-3,6-diyne (10bd)

Complex **5bd** (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 workup (Et_2O). The product was filtered through a silica plug using Et_2O and concentrated under reduced pressure to give **10bd** (13.9 mg, 86%) as a faint tan oil. **(10bd):** ^1H NMR (300 MHz, $CDCl_3$) δ 5.73 – 5.84 (dt, J = 15.5, 2.1 Hz, 1H), 5.53 (dd, J = 15.2, 10.9, 2.2, Hz 1H), 3.27 (d, J = 2.3 Hz, 2H), 2.17 (tt, J = 7.0, 2.3 Hz, 2H), 1.33 – 1.52 (m , 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 126.7, 117.1, 85.0, 81.1, 79.1, 73.4, 30.8, 22.0, 18.4, 13.7, 10.4; IR ν_{max} 3011, 2957, 2856, 1630, 1610 cm^{-1}; HRMS m/e for $C_{11}H_{14}$ calcd (M^+-H) 145.1017, found 145.1014.

Nona-1,4-diyne (10bf)

Complex **5bf** (65.5 mg, 0.161 mmol) was dissolved in acetone (8 mL), and the solution cooled to -78°C. Ceric ammonium nitrate (0.442 g, 0.806 mmol, 5 equiv) was added and 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 workup (Et_2O). The product was filtered through a silica plug using Et_2O and concentrated under reduced pressure to give **10bf** (16.9 mg, 86%) as a faint tan oil. The product was spectroscopically identical to the literature report.[29] **(10bf):** ^1H NMR NMR (500 MHz, $CDCl_3$) δ 3.19 (q, J = 7.5, 2.5 Hz, 2H), 2.21(tt, J = 7.0, 2.4 Hz, 2H), 2.1 (t, J = 2.7 Hz, 1H), 1.39 – 1.55 (m, 4H), 0.95 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 81.3, 79.0, 73.0, 69.4 30.8, 22.0, 18.3, 13.6, 9.6; IR ν_{max}: 3312, 2957, 2926, 2218 cm^{-1}.

9-Phenylnon-8-en-5-yne ((E)-11ab

Complex **(*E*)-8ab** (57.8 mg) was added into a round bottom flask. 8 mL of acetone was added and cooled to -78°C. Once the temperature has reached -78°C, 5 equivalence of ceric ammonium nitrate was added and allowed to warm up to -30°C (2 h), with monitoring by TLC. A saturated sodium chloride solution was added and the mixture subjected to a conventional workup (Et_2O). The product was filtered through a silica plug using Et_2O and concentrated under reduced pressure to give **(*E*)-11ab** (22.8 mg, 86%) as a faint tan oil. The product was spectroscopically identical to the literature report.[30] **((*E*)-11ab):** ^1H NMR NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.43 (m, 5H) 6.69 (apparent doublet, J = 15.7 Hz, 1H), 6.19 – 6.28 (dt, J = 15.7, 5.6 Hz, 1H), 3.14 – 3.18 (m, 2H), 2.25 – 2.32 (m , 2H), 1.46 – 1.63 (m, 4H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.3, 130.8, 128.5, 127.2, 126.3, 125.3, 83.0, 76.7, 31.1, 22.5, 22.0, 18.6, 13.7; IR ν_{max} : 3081, 3059, 3027, 2956, 2871, 1597 cm^{-1}.

Phenylethynylcyclopropane (12e)

To a solution of **9e** (41.5 mg, 0.0969 mmol) in THF (4 mL) was added tetrabutylammonum fluoride (1.0 M, 0.19 mL, 0.19 mmol). After stirring for 105 min, the solution was filtered through a plug of silica gel and concentrated under educed pressure. Preparative TLC (100% hexanes) afforded **12e** (11.0 mg, 80% yield) as a faint tan oil, which was consistent with literature spectral data.[31]

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