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Investigation of the Scope of a Co-Mediated O → C Ring-Contraction

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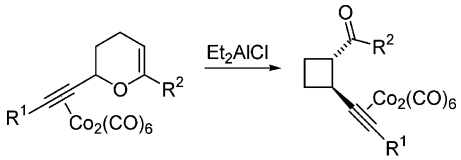

A series of dihydropyrans bearing a dicobalthexacarbonyl moiety have been found to undergo an efficient Al-promoted O → C ring-contraction process. This rearrangement reaction operates successfully for a broad range of substrates. Moreover, the potential of this approach for generating cyclopropanes from the corresponding dihydrofurans has been demonstrated.

Introduction

The cyclobutane motif is not ubiquitous throughout nature, yet this strained (26.3 kcal/mol),[1] uncommon nucleus is found in a variety of architecturally diverse natural products, which display a broad range of biological activities. Such examples include: (1) caryophyllene (**1**)[2] and various derivatives thereof, which protect plants against insects; (2) (+)-grandisol (**2**),[3] a sex pheromone of the cotton boll weevil, a destructive pest that destroys food crops; (3) punctatin A (**3**),[4] a powerful antibiotic; (4) pestalotiopin A (**4**),[5] an isolate from the Pacific Yew, which displays immunosuppressive and cytotoxic activity; and (5) uncommon cis-fused cyclobutanes hebelophyllene D (**5**) and F (**6**).[6]

The evolution of convergent strategies to heavily functionalized cyclobutane cores has led to numerous methods for their formation.[7] The overriding difficulty in their synthesis is caused by the unfavorable activation enthalpies (and entropies) for ring closure. As a result, a number of methods have been used to construct cyclobutanes via ring-contractions; these reactions generally involve Wolff rearrangements, Favorskii rearrangements, photoinduced decarbonylation, and Wagner−Meerwein rearrangements of cyclopentanes containing a leaving group.[8]

The tactic of generating cyclobutanols via the ring-contraction of 2-alkoxy-3,4-dihydro-2*H*-pyrans has been known for more than 25 years,[9] yet it has rarely been utilized in organic synthesis.

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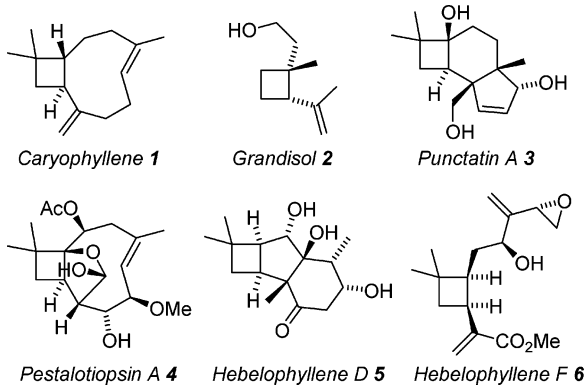
CHART 1

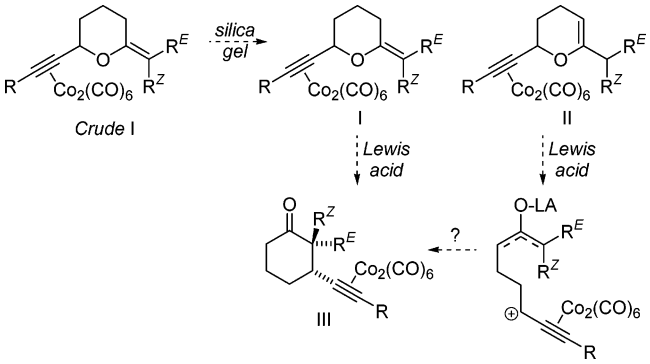


Nonetheless, such processes deliver the four-membered ring products with high levels of diastereocontrol but with modest levels of enantiocontrol. More recently, a similar strategy has been extended to the diastereoselective synthesis of highly functionalized cyclobutanols by the ring-contraction of 4-vinylfuranosides mediated by zirconium[10] or samarium iodide.[11] This process affords highly functionalized carbocycles in a single operation, often with good yield and with predictably high diastereoselectivity, and has been exploited by Paquette and coworkers in the synthesis of enantiomerically pure cyclooctene polyols and carbasugars.[10d−g] Importantly, however, neither of the aforementioned approaches provides stereoselective access to their deoxygenated analogues. Accordingly, a similar stereoselective ring-contraction strategy to yield cyclobutanes not bearing hydroxyl or ether functionality, such as compounds **1** and **2** displayed in Chart 1, has yet to be developed.

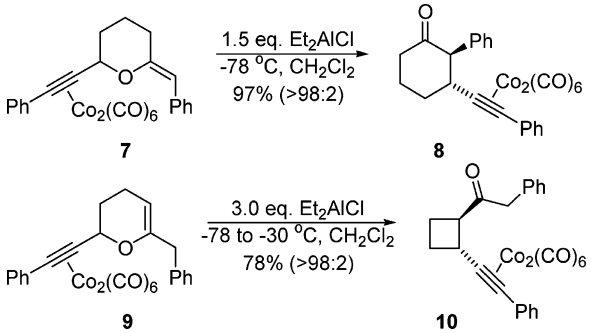
Results and Discussion

Studies in our laboratory over the past several years have focused on developing a stereoselective O → C rearrangement[12] for the diastereoselective synthesis of 3-alkynyl cyclohexanones.[13] During these investigations, we found that chromatographic purification of the substrate exocyclic enol ethers (**I**) often resulted in the formation of small amounts of the corresponding $Co_2(CO)_6$-complexed 3,4-dihydro-2*H*-pyrans (**II**) (Scheme 1), which is the consequence of a Brønsted acid catalyzed isomerization to the thermodynamically more stable vinyl ether.[14] Although the dihydropyran complexes were considered to be unwanted byproducts, it was postulated that under the correct conditions, an in situ enolate isomerization and cyclization could be effected that would lead to the desired cyclohexanones (**III**). Such a recycling strategy would circumvent the need for careful chromatography, and the use of a mixture of isomers in the rearrangement would result in an increase in the overall yield of the sequence.

SCHEME 1



SCHEME 2



To test this hypothesis, we isolated pure samples of complex **7** and isomeric dihydropyran **9** and studied their participation in the Lewis acid promoted rearrangement reaction. While **7** underwent smooth rearrangement to furnish the expected cyclohexanone complex **8**, the isomeric complex **9** underwent a direct ring closure to furnish the *trans*-cyclobutane **10** in good yield and diastereoselectivity (Scheme 2, determined by analysis of the unpurified reaction mixture by a 250 MHz ^{1}H NMR). We were intrigued by the generality of this unusual ring-contraction process and set about investigating the scope of this O → C reaction.[15]

To explore the novel Co-mediated cyclobutane forming reaction, synthesis of the requisite dihydropyran rearrangement precursors was examined. On the basis of our observations that exo to endo enol ether isomerization occurs, albeit in low yield, during silica gel chromatography, it was expected that the synthesis of the required pyran substrates could be achieved through isomerization of the parent exocyclic enol ethers by the application of an appropriate Brønsted acid. A potential problem that was anticipated in this strategy was that once the pyran was activated by $Co_2(CO)_6$, under mild acidic conditions, the compound may have a greater propensity toward C−O cleavage (to generate a Co-stabilized cation[16]) rather than isomerization to the desired dihydropyran. However, as outlined in Table 1, we were pleased to find that the known phosphonium salts **11**−**14**[13d] could be smoothly converted in a three-step sequence to the desired dihydropyrans with acceptable overall yields.

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(12) For an overview of O → C rearrangements see Meek, S. J.; Harrity, J. P. A. *Tetrahedron* **2007**, *63*, 3081.

(13) (a) Carbery, D. R.; Reignier, S.; Myatt, J. W.; Miller, N. D.; Harrity, J. P. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2584. (b) Carbery, D. R.; Miller, N. D.; Harrity, J. P. A. *Chem. Commun.* **2002**, 1546. (c) Carbery, D. R.; Reignier, S.; Miller, N. D.; Adams, H.; Harrity, J. P. A. *J. Org. Chem.* **2003**, *68*, 4392. (d) Meek, S. J.; Pradaux, F.; Carbery, D. R.; Demont, E. H.; Harrity, J. P. A. *J. Org. Chem.* **2005**, *70*, 10046.

(14) Taskinen, E. *Tetrahedron* **1978**, *34*, 433.

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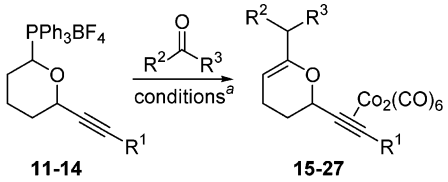
TABLE 1. Synthesis of Dihydropyran Complexes



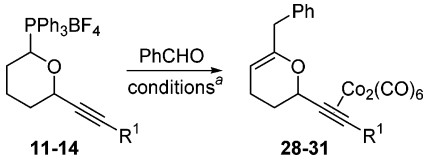
11-14 **15-27**

entry	R^1	aldehyde/ ketone	yield[b]
1	Ph; **11**	*t*-BuCHO	**15;** 33%
2	Me_3Si; **12**	*t*-BuCHO	**16;** 56%
3	$CH_2OTBDPS$; **13**	*t*-BuCHO	**17;** 52%
4	Ph; **11**	*i*-PrCHO	**18;** 40%
5	Me_3Si; **12**	*i*-PrCHO	**19;** 45%
6	*n*-Bu; **14**	*i*-PrCHO	**20;** 59%
7	$TBDPSOCH_2$; **13**	*i*-PrCHO	**21;** 34%
8	Ph; **11**		**22;** 31%
9	Me_3Si; **12**		**23;** 29%
10	$TBDPSOCH_2$; **13**		**24;** 47%
11	Ph; **11**	MeCHO	**25;** 37%
12	$TBDPSOCH_2$; **13**	MeCHO	**26;** 33%
13	Me_3Si; **12**	*n*-BuCHO	**27;** 33%
14	Ph; **11**	PhCHO	**9;** 0%

[a] Conditions: (a) *n*-BuLi, THF, −78 °C; $R_2C{=}O$. (b) $Co_2(CO)_8$, CH_2Cl_2, rt. (c) 5 mol % PPTS, CH_2Cl_2, rt. [b] Isolated yield over three steps.

Wittig olefination between pyranyl phosphonium salts **11**−**14** and the corresponding aldehyde/ketone in the presence of *n*-butyllithium (THF, −78 °C) afforded the resultant exocyclic enol ether adducts. The unpurified intermediates were complexed with $Co_2(CO)_8$ (0.1 M in CH_2Cl_2) and then subjected to PPTS (0.05 equiv, 0.1 M in CH_2Cl_2) to afford the corresponding dihydropyrans in good yield over the three steps. Isomerization of the alkyl substituted exocyclic enol ethers with freshly dried PPTS proceeded smoothly to furnish the thermodynamically more stable 3,4-dihydro-2*H*-pyran in 1−3 h in all cases. However, benzaldehyde derived O → C substrate **9** (entry 14, Table 1) proved to be more robust to the mild isomerization protocol. Isomerization with 5 mol % of PPTS led only to undesired acyclic products, which is most likely due to the extra inherent stability of the conjugated aryl enol ether, wherein the solution to the problem presented itself. Activation of the exocyclic enol ether system by $Co_2(CO)_6$ was only tolerated for alkyl substrates because isomerization occurred rapidly. In the case of the aryl counterparts, slow isomerization required longer reaction times, which ultimately led to competitive ring cleavage and to a complex mixture of products (as judged by the formation of more polar compounds by the TLC analysis). To address this problem, isomerization was carried out prior to activation of the ring by $Co_2(CO)_8$ complexation. Accordingly, simply reversing the isomerization and complexation steps in the former sequence and changing the isomerization conditions to 5 mol % of PPTS in benzene (0.1 M, 80 °C, 16 h) yielded the benzyl-substituted 3,4-dihydro-2*H*-pyrans in moderate yield from the parent phosphonium salts (Table 2).

TABLE 2. Synthesis of Bn-Substituted Dihydropyran Complexes

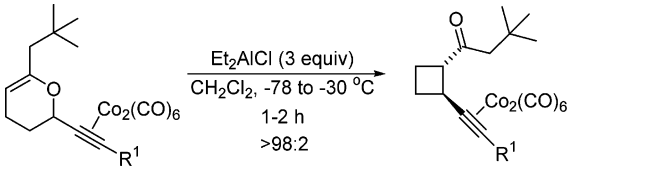


11-14 **28-31**

entry	R^1	yield[b]
1	Ph; **11**	**9;** 42%
2	*n*-Bu; **14**	**28;** 30%
3	Me_3Si; **12**	**29;** 22%
4	$CH_2OTBDPS$; **13**	**30;** 44%

[a] Conditions: (a) *n*-BuLi, THF, −78 °C; PhCHO. (b) 5 mol % PPTS, benzene, 80 °C. (c) $Co_2(CO)_8$, CH_2Cl_2, rt. [b] Isolated yield over three steps.

SCHEME 3



15; R^1 = Ph
16; R^1 = $SiMe_3$
17; R^1 = $CH_2OTBDPS$

31; R^1 = Ph; 89%
32; R^1 = $SiMe_3$; 84%
33; R^1 = $CH_2OTBDPS$; 78%

These initial results were encouraging. Examination of the scope of the Co-mediated ring-contraction thus commenced with the rearrangement of the *t*-Bu-substituted dihydropyran series in an attempt to ascertain any effect the nature of the alkyne-substituent imparted on the transformation. Accordingly, under the optimized conditions, rearrangement of complexes **15**−**17** proceeded to afford diastereomerically pure cyclobutanes **31**−**33** in high yield (Scheme 3). These results mirrored that which was observed for the rearrangement of compound **9** (cf. Scheme 2), and they suggested that the rearrangement would proceed in good yield and with high diastereoselectivity irrespective of the alkyne substituent.

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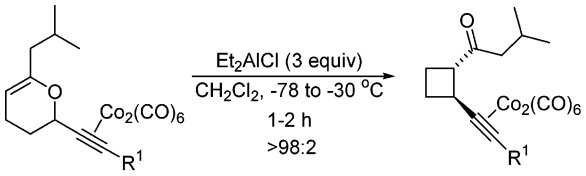
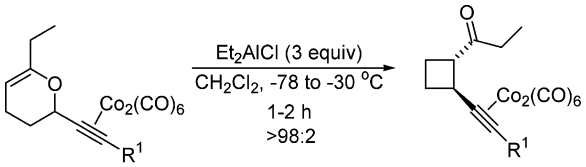
SCHEME 4



18; R^1 = Ph
19; R^1 = $SiMe_3$
20; R^1 = *n*-Bu
21; R^1 = $CH_2OTBDPS$

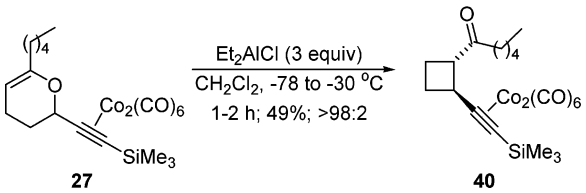
34; R^1 = Ph; 75%
35; R^1 = $SiMe_3$; 73%
36; R^1 = *n*-Bu; 86%
37; R^1 = $CH_2OTBDPS$; 68%

SCHEME 5



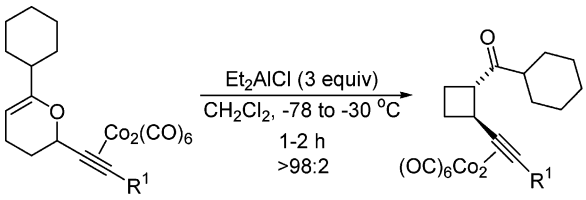
25; R^1 = Ph
26; R^1 = $CH_2OTBDPS$

38; R^1 = Ph; 50%
39; R^1 = $CH_2OTBDPS$; 49%



27 **40**

SCHEME 6



22; R^1 = Ph
23; R^1 = $SiMe_3$
24; R^1 = $CH_2OTBDPS$

41; R^1 = Ph; 53%
42; R^1 = $SiMe_3$; 75%
43; R^1 = $CH_2OTBDPS$; 68%

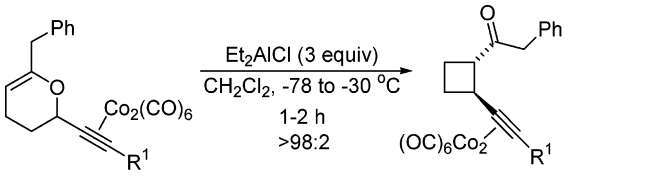
The question as to the behavior of the rearrangement with various six-substituted dihydropyrans began with the alkyl analogues. Under the Al-promoted system, decreasing the steric bulk in the β-position of the alkyl chain (*i*-Pr), again with different alkyne functionality, gave the products **34**−**37** diastereoselectively and in good isolated yield (Scheme 4).

A similar outcome was observed for the rearrangement of compounds **25**−**27** that bear primary alkyl chains of varying length. The Et_2AlCl-promoted ring-contraction provided the 1,2-disubstituted cyclobutanes diastereoselectively but in a lower yield than in the more substituted systems (Scheme 5).

The action of Et_2AlCl on cyclohexanone derivatives **22**, **23**, and **24**, which carry a more sterically demanding cyclohexyl group attached to the dihydropyran (cf. CH_2R vs CHR_2), cleanly delivered the corresponding products **41**−**43** as single isomers in respectable yield. Once again, we were unable to detect the cis-isomer by 250 MHz ^1H NMR analysis of the crude reaction mixture (Scheme 6).

Finally, the Al-promoted ring-contraction was performed on the benzyl substituted series **28**−**30**. This led to the diastereoselective collapse of the Al-enolate on to the Nicholas carbocation, which generated the resultant cyclobutyl products **44**−**46** once more in good yield (Scheme 7).

SCHEME 7



28; R^1 = *n*-Bu
29; R^1 = $SiMe_3$
30; R^1 = $CH_2OTBDPS$

44; R^1 = *n*-Bu; 63%
45; R^1 = $SiMe_3$; 82%
46; R^1 = $CH_2OTBDPS$; 71%

The above results in Schemes 3−7 demonstrate the efficiency of the Al−Lewis acid promoted rearrangement. In all of the examined cases, the transformation proceeded in good yield, with high diastereoselectivity, and independent of the size of the enol ether appendage and nature of the alkyne substituent. Of particular note are the transformations depicted for **17**, **21**, **24**, **26**, and **30**; these demonstrate that propargylic silyl ethers are tolerated under the reaction conditions and that Nicholas carbocation formation is regioselective in these systems. Furthermore, formation of cyclohexanone products as a result of enolate isomerization was not observed in any cases (cf. Scheme 1).

Although initial operations had focused on diethylaluminium chloride as an efficient Lewis acid to effect cyclobutane formation, it was questioned whether a Ti-promoter system would mediate the same ring-contraction and as efficiently. Indeed, $TiCl_4$ had previously been found to mediate cyclohexanone forming O → C rearrangements in high yield.[13a,c] Accordingly, dihydropyran **18**, which had been found to rearrange in good yield using Et_2AlCl (Scheme 4), was treated with 3.0 equiv of freshly distilled $TiCl_4$ (−78 to −30 °C). After 6 h, the presence of dihydropyran-ruptured intermediates was observed by TLC analysis; however, none had collapsed to form the expected cyclobutane. The ability of Et_2AlCl to promote cyclobutane formation while $TiCl_4$ does not is possibly associated with the strength of diethylaluminium chloride as a Lewis acid when employed in a stoichiometry of >1.0 equiv. It was proposed by Evans[17] that the addition of a second equivalent of Et_2AlCl resulted in a redistribution reaction that produced a dialkyl aluminum cation. This increased reactivity could facilitate cyclization and overcome the unfavorable activation enthalpies (and entropies) associated with four-membered ring closure.

The high trans-diastereoselectivity observed in the Al-promoted rearrangement of $Co_2(CO)_6$-dihydropyrans can be rationalized as proceeding through either puckered four-membered ring transition states **IV** or **V**, as depicted in Scheme 9.[18] Lewis acid mediated heterolytic C−O bond scission of the pyran selectively generates the aluminum *Z*-enolate; the pseudo-equatorial orientation of the Co-cluster and Al-enolate in **V** leads

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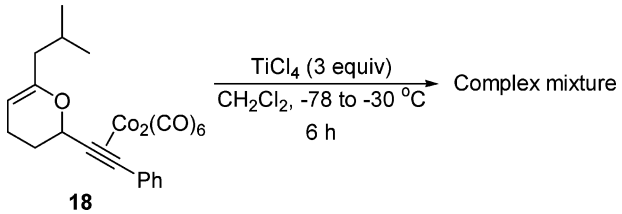
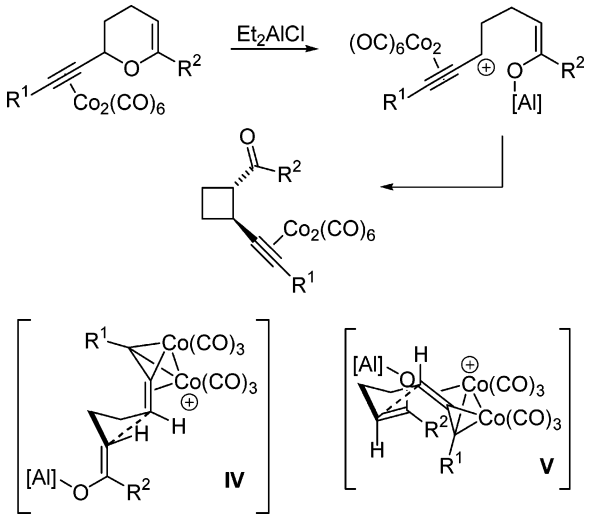
(18) A four-center transition-state-type mechanism has been proposed in the ring-contraction of simple dihydropyrans,[9b] but our proposed mechanism is based on NMR and theoretical studies of intermediate Co-stabilized propargylic cations: (a) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749. (b) Pfletschinger, A.; Koch, W.; Schmalz, H.-G. *Chem. Eur. J.* **2001**, *7*, 5325.

SCHEME 8



SCHEME 9

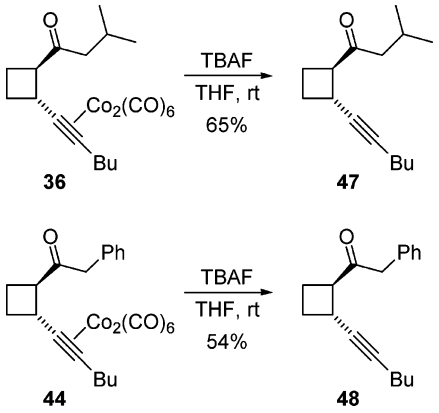


directly to the trans-product. Alternatively, the possibility of unfavorable steric compression engendered in a gauche interaction between the Co-cluster and *Z*-enolate in pseudo-diequatorial positions can be alleviated by a transition state such as **IV**. In this case, a pseudo-diaxial disposition of the Al-enolate and Co-cluster affords the diaxially trans-disubstituted cyclobutane that undergoes a ring-flip to the diequatorial product.

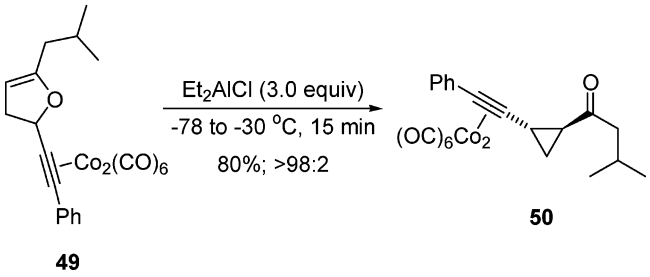
We wished to confirm that the metals could be removed from the cyclobutane products while avoiding epimerization or decomposition of the cyclobutane fragment. Pleasingly, decomplexation of the cobalt moiety was established for compounds **36** and **44** by the employment of TBAF in THF[19] to provide cyclobutanes **47** and **48** in a diastereomerically pure form.

The broad success achieved in the pyran → cyclobutane rearrangement prompted us to establish whether other ring-contractions were feasible. In particular, we were intrigued by the prospect of converting dihydrofurans to cyclopropanes. In an effort to establish the feasibility of the transformation we prepared dihydrofuran **49** by analogy to the chemistry outlined in Table 1. Pleasingly, this complex was found to rapidly rearrange (3.0 equiv of Et_2AlCl, −78 to −30 °C, 15 min), to the corresponding *trans*-cyclopropane **50** in good yield (Scheme 11).[20] The stereochemistry of the product was established through analysis of the ^1H NMR coupling constants of the cyclopropyl proton signals. All the observed ddd signals corresponding to the cyclopropyl unit in *trans*-**50** display only

SCHEME 10



SCHEME 11



one large cis-coupling ($^3J_H \sim 8.5$ Hz),[21] whereas the alternate cis-isomer of **50** would be expected to display three ddd's that contain two cis-couplings (N.B. vicinal trans-coupling in cyclopropanes, $^3J_H \sim 4.0$ Hz).

Conclusion

We have developed an efficient strategy to form trans-1,2-disubstituted cyclobutanes via a Co-mediated and Al-promoted O → C ring-contraction. This process operates successfully for a broad range of substrates. Finally, the potential of this approach for generating cyclopropanes has been demonstrated, the development of this reaction is underway and will be reported in due course.

Experimental Section

General Procedure for the Conversion of Wittig Salts into Dihydropyran Complexes: Method A. *n*-BuLi (1.05 equiv) was added in a dropwise fashion to a stirring solution of the phosphonium salt[22] (1.0 equiv) in THF (0.2 M) at −78 °C, which generated a deep red color. The red solution was allowed to stir for 5 min prior to the addition of the neat aldehyde or ketone (1.1 equiv). The reaction mixture was stirred for 2 h at −78 °C unless stated otherwise; the mixture was slowly warmed to room temperature, and the reaction was quenched by the addition of water. The mixture was poured into water and extracted three times with Et_2O. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, filtered through a pad of celite, and concentrated in vacuo.

The crude adduct was dissolved in 1 mL of CH_2Cl_2 and treated with 20 mL of petroleum ether before cooling to −78 °C; The

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(20) For the use of related Co-alkyne containing cyclopropanes in cycloaddition reactions see (a) Christie, S. D. R.; Davoile, R. J.; Elsegood, M. R. J.; Fryatt, R.; Jones, R. C. F.; Pritchard, G. J. *Chem. Commun.* **2004**, 2474. (b) Christie, S. D. R.; Davoile, R. J.; Jones, R. C. F. *Org. Biomol. Chem.* **2006**, *4*, 2683.

(21) (a) Hutton, H. M.; Schaefer, T. *Can. J. Chem.* **1962**, *40*, 875. (b) Wiberg, K. B.; Nist, B. J. *J. Am. Chem. Soc.* **1963**, *85*, 2788. (c) Wiberg, K. B.; Bareth, D. E.; Schertler, P. *J. Org. Chem.* **1973**, *38*, 378.

(22) The synthesis and characterization of phosphonium salts **11**−**14** has been previously reported.[13d]

organic extracts were decanted from the formed precipitates through a pad of celite, and the solvent was removed in vacuo. The crude enol ether in CH_2Cl_2 (0.2 M) was added via cannula to a 0.2 M solution of octacarbonyldicobalt (1 equiv, based on the starting phosphonium salt) in CH_2Cl_2 at room temperature. After the mixture was stirred for 1 h, it was filtered through a pad of celite, concentrated in vacuo, and flash chromatographed on silica gel that was eluted with petroleum ether/Et_2O/Et_3N (100:10:1) to afford an endo/exo mixture of pyran complexes.

To a 0.1 M solution of the endo/exo $Co_2(CO)_6$ complexes (1 equiv) in CH_2Cl_2 at room temperature, pyridinium para-toluene sulfonate (0.05 equiv) was added portionwise. After the mixture was stirred for 3 h, 1.0 equiv of Et_3N was added, and the reaction was concentrated. The resulting residue was taken up in petroleum ether (40−60) and was then filtered through a short pad of silica to yield the title compound.

Method B. *n*-BuLi (1.05 equiv) was added in a dropwise fashion to a stirring solution of the phosphonium salt (1.0 equiv) in THF (0. 2 M) at −78 °C, which generated a deep red color. The red solution was allowed to stir for 5 min, prior to the addition of the neat aldehyde or ketone (1.1 equiv). The mixture was stirred for 2 h at −78 °C unless stated otherwise and slowly warmed to room temperature; the reaction was quenched by the addition of water. The mixture was poured into water and was extracted three times with Et_2O. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, filtered through a pad of celite, and concentrated in vacuo.

To a 0.1 M solution of the crude enol ether (1 equiv) in benzene at room temperature, pyridinium *para*-toluene sulfonate (0.05 equiv) was added portionwise. The reaction mixture was heated under reflux for 16−24 h. The mixture was then diluted with petroleum ether (40−60), filtered through a short pad of silica, and the organics were evaporated.

The crude residue was dissolved in 1 mL of CH_2Cl_2 and treated with 20 mL of petroleum ether before cooling to −78 °C. The organic extracts were decanted from the formed precipitates through a pad of celite, and the solvent was removed in vacuo. The crude dihydropyran in CH_2Cl_2 (0.2 M) was added via cannula to a 0.2 M solution of octacarbonyldicobalt (1 equiv based on the starting phosphonium salt) in CH_2Cl_2 at room temperature. After being stirred for 1 h, the mixture was filtered through a pad of celite, concentrated in vacuo, and flash chromatographed on silica gel (eluted with a continuous gradient starting with 100:1:1 petroleum ether/Et_3N/Et_2O and ending with 100:10:1 petroleum ether/Et_3N/Et_2O) to afford the title compound.

Dicobalthexacarbonyl-6-benzyl-2-(2-phenylethynyl)-3,4-dihydro-2*H*-pyran (9). Phosphonium salt **11** (350 mg, 0.655 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method B) using benzaldehyde. The product was isolated as a dark red oil (155 mg, 42%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.75−1.96 (1H, m), 2.05−2.45 (3H, m), 3.38 (2H, s), 4.63−4.70 (1H, m), 5.01 (1H, dd, J = 11.0, 2.0 Hz), 7.17−7.37 (8H, m), 7.39−7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4 (br), 154.0, 138.7, 137.8, 129.8, 128.9, 128.8, 128.2, 127.8, 126.2, 96.9, 96.7, 90.3, 75.8, 40.6, 30.3, 21.4; FTIR (film, cm^{-1}): 3063 (w), 3030 (w), 2925 (w), 2850 (w), 2092 (s), 2053 (s), 2023 (s), 1678 (m), 1615 (w), 1495 (w), 1484 (w), 1454 (w), 1443 (w), 1362 (w), 1287 (w), 1232 (w), 1157 (w), 1055 (m), 1040 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{26}H_{19}O_7Co_2$ 560.9795, found 560.9813.

Dicobalthexacarbonyl-6-neopentyl-2-(2-phenylethynyl)-3,4-dihydro-2*H*-pyran (15). Phosphonium salt **11** (323 mg, 0.604 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using pivalaldehyde. The product was isolated as a dark red oil (106 mg, 33%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.93 (9H, s), 1.70−1.86 (1H, m), 1.90 (1H, d, J = 13.5 Hz), 1.98 (1H, d, J = 13.5 Hz), 2.04−2.24 (2H, m), 2.27−2.45 (1H, m), 4.52−4.58 (1H, m), 5.08 (1H, dd, J = 11.0, 2.0 Hz), 7.25−7.38 (3H, m), 7.49−7.58 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.3 (br), 153.8, 137.9, 129.7, 128.8, 127.8, 98.0, 97.3, 90.0, 75.5, 48.0, 31.0, 30.6, 29.8, 21.6; FTIR (film, cm^{-1}): 3058 (w), 2956 (m), 2854 (w), 2092 (s), 2053 (s), 2022 (s), 1673 (m), 1616 (w), 1476 (w), 1443 (w), 1364 (w), 1272 (w), 1235 (m), 1046 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{24}H_{23}O_7Co_2$ 541.0108, found 541.0120.

Dicobalthexacarbonyl-trimethyl(2-(6-neopentyl-3,4-dihydro-2*H*-pyran-2-yl)ethynyl)silane (16). Phosphonium salt **12** (251 mg, 0.473 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using pivalaldehyde. The product was isolated as a dark orange−red solid (142 mg, 56%). mp 29.0−29.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.30 (9H, s), 0.92 (9H, s), 1.63−2.15 (5H, m), 2.20 (1H, m), 4.46−4.54 (1H, m), 4.83 (1H, dd, J = 10.5, 2.0 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.2 (br), 153.6, 111.2, 97.8, 77.5, 75.5, 47.9, 31.6, 31.0, 29.8, 21.5, 0.8; FTIR (film, cm^{-1}): 2958 (s), 2906 (m), 2866 (w), 2090 (s), 2048 (s), 2022 (s), 1673 (m), 1580 (m), 1476 (w), 1364 (w), 1302 (w), 1250 (m), 1163 (w), 1048 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{21}H_{27}O_7SiCo_2$ 537.0190, found 537.0190.

Dicobalthexacarbonyl-*tert*-butyl(3-(6-neopentyl-3,4-dihydro-2*H*-pyran-2-yl)prop-2-ynyloxy)diphenylsilane (17). Phosphonium salt **13** (401 mg, 0.552 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using pivalaldehyde. The product was isolated as an orange−red oil (210 mg, 52%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (9H, s), 1.08 (9H, s), 1.56−1.75 (1H, m), 1.81 (1H, d, J = 13.5 Hz), 1.89 (1H, d, J = 13.5 Hz), 1.94−2.09 (2H, m), 2.12−2.30 (1H, m), 4.20−4.50 (1H, m), 4.78 (1H, dd, J = 10.5, 2.0 Hz), 4.79 (2H, s), 7.35−7.50 (6H, m), 7.67−7.76 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.7 (br), 153.7, 135.6, 133.0, 129.8, 127.8, 97.7, 96.2, 95.4, 75.3, 64.7, 48.0, 30.9, 30.5, 29.8, 26.6, 21.3, 19.2; FTIR (film, cm^{-1}): 3073 (w), 2955 (m), 2900 (m), 2860 (m), 2094 (s), 2053 (s), 2030 (s), 1673 (m), 1612 (w), 1590 (w), 1474 (w), 1429 (w), 1363 (w), 1235 (w) 1113 (m), 1054 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{35}H_{38}O_8NaSiCo_2$ 755.0898, found 755.0889.

Dicobalthexacarbonyl-6-isobutyl-2-(2-phenylethynyl)-3,4-dihydro-2*H*-pyran (18). Phosphonium salt **11** (178 mg, 0.333 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using isobutyraldehyde. The product was isolated as a dark red oil (70 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85−0.92 (6H, m), 1.70−1.99 (4H, m), 2.02−2.42 (3H, m), 4.52−4.60 (1H, m), 5.08 (1H, dd, J = 11.0, 2.0 Hz), 7.27−7.38 (3H, m), 7.52−7.60 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.5 (br), 154.1, 137.9, 129.8, 128.8, 127.8, 97.3, 96.1, 89.9, 75.7, 43.6, 30.6, 25.9, 22.4, 22.2, 21.4; FTIR (film, cm^{-1}): 2958 (w), 2929 (w), 2869 (w), 2092 (s), 2052 (s), 2023 (s), 1678 (w), 1615 (w), 1443 (w), 1368 (w), 1286 (w), 1233 (w), 1159 (w), 1061 (w), 1038 (w); HRMS (ES) m/z (M^+ + H) calcd for $C_{23}H_{21}O_7Co_2$ 526.9951, found 526.9952.

Dicobalthexacarbonyl-(2-(6-isobutyl-3,4-dihydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (19). Phosphonium salt **12** (388 mg, 0.731 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using isobutyraldehyde. The product was isolated as a dark red solid (172 mg, 45%). mp 32.5−33.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.30 (9H, s), 0.83−0.89 (6H, m), 1.62−1.98 (4H, m), 1.98−2.14 (2H, m), 2.17−2.37 (1H, m), 4.47−4.55 (1H, m), 4.84 (1H, dd, J = 11.0, 2.0 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.2 (br), 154.1, 111.3, 95.9, 77.7, 75.8, 43.6, 31.5, 25.8, 22.3, 22.2, 21.4, 0.7; FTIR (film, cm^{-1}): 2959 (s), 2930 (m), 2870 (w), 2851 (w), 2090 (s), 2048 (s), 2021 (s), 1678 (m), 1586 (m), 1465 (w), 1368 (w), 1295 (w), 1250 (m), 1233 (w), 1161 (w), 1041 (m), 840 (s); HRMS (ES) m/z (M^+ + H) calcd for $C_{20}H_{25}O_7SiCo_2$ 523. 0034, found 523.0020.

Dicobalthexacarbonyl-2-(hex-1-ynyl)-6-isobutyl-3,4-dihydro-2*H*-pyran (20). Phosphonium salt **14** (620 mg, 1.21 mmol) was converted to the title compound according to the general procedure

for dihydropyran complex formation (method A) using isobutyraldehyde. The product was isolated as a dark red oil (358 mg, 59%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.82−0.90 (6H, m), 0.96 (3H, t, J = 7.0 Hz), 1.38−1.96 (8H, m), 1.98−2.14 (2H, m), 2.16−2.35 (1H, m), 2.76−2.88 (2H, m), 4.46−4.54 (1H, m), 4.87 (1H, dd, J = 10.5, 2.0 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.1 (br), 154.0, 98.5, 97.4, 95.8, 75.5, 43.6, 34.0, 33.6, 30.5, 25.9, 22.7, 22.3, 22.2, 21.3, 13.9; FTIR (film, cm^{-1}): 2959 (m), 2931 (m), 2871 (w), 2091 (s), 2049 (s), 2024 (s), 1677 (m), 1618 (w), 1466 (w), 1368 (w), 1296 (w), 1286 (w), 1233 (w), 1162 (w), 1054 (m); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{21}H_{25}O_7Co_2$ 507.0264, found 507.0252.

Dicobalthexacarbonyl-*tert*-butyl(3-(6-isobutyl-3,4-dihydro-2*H*-pyran-2-yl)prop-2-ynyloxy)diphenylsilane (21). Phosphonium salt **13** (377 mg, 0.519 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using isobutyraldehyde. The product was isolated as an orange−red oil (128 mg, 34%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.82 (6H, d, J = 6.5 Hz), 1.07 (9H, s), 1.55−1.89 (4H, m), 1.91−2.08 (2H, m), 2.09−2.27 (1H, m), 4.43−4.51 (1H, m), 4.78 (1H, dd, J = 10.5, 2.0 Hz), 4.79 (2H, s), 7.35−7.50 (6H, m), 7.68−7.77 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.7 (br), 153.9, 135.6, 133.0, 129.8, 127.8, 96.4, 95.8, 94.8, 75.5, 64.6, 43.5, 30.5, 26.6, 25.9, 22.4, 22.2, 21.1, 19.2; FTIR (film, cm^{-1}): 3073 (w), 2957 (s), 2932 (s), 2860 (m), 2094 (s), 2053 (s), 2030 (s), 1677 (m), 1618 (w), 1464 (w), 1429 (m), 1363 (w), 1296 (w), 1234 (w), 1113 (s), 1054 (s); HRMS (ES) *m*/*z* (M^+ + Na) calcd for $C_{34}H_{36}O_8NaSiCo_2$ 741.0740, found 741.0763.

Dicobalthexacarbonyl-6-cyclohexyl-2-(2-phenylethynyl)-3,4-dihydro-2*H*-pyran (22). Phosphonium salt **11** (156 mg, 0.29 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using cyclohexanone. The product was isolated as a dark red oil (38 mg, 24%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.05−1.40 (5H, m), 1.55−2.40 (10H, m), 4.52−4.59 (1H, m), 5.06 (1H, dd, J = 11.0, 2.0 Hz), 7.28−7.39 (3H, m), 7.54−7.62 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.4 (br), 159.6, 137.9, 129.8, 128.8, 127.8, 97.4, 92.8, 89.8, 75.7, 42.9, 30.8, 30.7, 26.4, 26.2, 21.3; FTIR (film, cm^{-1}): 3077 (w), 2928 (m), 2853 (m), 2091 (s), 2051 (s), 2023 (s), 1673 (m), 1616 (w), 1484 (w), 1444 (w), 1280 (w), 1239 (w), 1063 (m); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{25}H_{23}O_7Co_2$ 553.0108, found 553.0095.

Synthesis of dicobalthexacarbonyl-(2-(6-cyclohexyl-3,4-dihydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (23). Phosphonium salt **12** (316 mg, 0.596 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using cyclohexanone. The product was isolated as a dark red solid (96 mg, 29%). mp 59.5−60.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.30 (9H, s), 1.09−1.37 (5H, m), 1.44−1.97 (7H, m), 1.98−2.14 (2H, m), 2.17−2.35 (1H, m), 4.45−4.53 (1H, m), 4.81 (1H, dd, J = 11.0, 2.0 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.3 (br), 159.6, 111.4, 92.6, 76.8, 75.8, 42.8, 31.8, 30.7, 30.6, 26.4, 26.3, 26.2, 21.4, 0.7; FTIR (film, cm^{-1}): 2929 (m), 2854 (m), 2090 (s), 2048 (s), 2023 (s), 1674 (m), 1582 (w), 1451 (w), 1280 (w), 1249 (m), 1056 (m). HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{22}H_{27}O_7SiCo_2$ 549.0190, found 549.0180.

Dicobalthexacarbonyl-*tert*-butyl(3-(6-cyclohexyl-3,4-dihydro-2*H*-pyran-2-yl)prop-2-ynyloxy)diphenylsilane (24). Phosphonium salt **13** (712 mg, 0.98 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using cyclohexanone. The product was isolated as a red oil (340 mg, 47%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.00−1.32 (5H, m), 1.07 (9H, s), 1.54−1.77 (6H, m), 1.79−2.06 (3H, m), 2.07−2.25 (1H, m), 4.40−4.48 (1H, m), 4.76 (1H, dd, J = 10.5, 2.0 Hz), 4.79 (2H, s), 7.33−7.49 (6H, m), 7.64−7.77 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.7 (br), 159.3, 135.6, 133.0, 129.9, 127.8, 96.6, 94.9, 92.5, 75.6, 64.7, 42.8, 30.8, 30.6, 26.6, 26.4, 26.3, 26.2, 21.0, 19.2; FTIR (film, cm^{-1}): 3073 (w), 2930 (s), 2856 (s), 2093 (s), 2052 (s), 2026 (s), 1673 (m), 1618 (w), 1450 (w), 1429 (w), 1362 (w), 1280 (w), 1239 (w), 1113 (m), 1058 (s); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{36}H_{39}O_8SiCo_2$ 745.1078, found 745.1042.

Dicobalthexacarbonyl-6-ethyl-2-(2-phenylethynyl)-3,4-dihydro-2*H*-pyran (25). Phosphonium salt **11** (222 mg, 0.415 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using acetaldehyde. The product was isolated as a red oil (76 mg, 37%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.06 (3H, t, J = 7.5 Hz), 1.72−1.92 (1H, m), 2.02−2.41 (5H, m), 4.53−4.61 (1H, m), 5.10 (1H, dd, J = 11.0, 2.0 Hz), 7.25−7.39 (3H, m), 7.53−7.61 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.5 (br), 156.5, 137.9, 129.8, 128.8, 127.8, 97.3, 93.6, 89.9, 75.7, 30.5, 27.1, 21.2, 11.6; FTIR (film, cm^{-1}): 3062 (w), 2969 (w), 2924 (w), 2850 (w), 2092 (s), 2052 (s), 2023 (s), 1678 (m), 1617 (w), 1484 (w), 1443 (w), 1297 (w), 1232 (w), 1160 (w), 1055 (m); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{21}H_{17}O_7Co_2$ 498.9638, found 498.9634.

Dicobalthexacarbonyl-*tert*-butyl(3-(6-ethyl-3,4-dihydro-2*H*-pyran-2-yl)prop-2-ynyloxy)diphenylsilane (26). Phosphonium salt **13** (253 mg, 0.348 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using acetaldehyde. The product was isolated as an orange−red oil (69 mg, 29%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (3H, t, J = 7.5 Hz), 1.07 (9H, s), 1.56−1.75 (1H, m), 1.88−2.26 (5H, m), 4.43−4.51 (1H, m), 4.79 (2H, s), 4.82 (1H, dd, J = 10.5, 2.0 Hz), 7.35−7.49 (6H, m), 7.67−7.76 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.7 (br), 156.2, 135.6, 133.0, 129.8, 127.8, 96.5, 94.7, 93.3, 75.5, 64.6, 30.4, 27.0, 26.6, 20.9, 19.2, 11.4; FTIR (film, cm^{-1}): 3073 (w), 2933 (m), 2895 (m), 2858 (m), 2094 (s), 2053 (s), 2030 (s), 1678 (m), 1618 (w), 1590 (w), 1473 (w), 1429 (w), 1362 (w), 1296 (w), 1232 (w), 1113 (m), 1056 (s); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{32}H_{33}O_8SiCo_2$ 691.0609, found 691.0588.

Dicobalthexacarbonyl-trimethyl(2-(6-pentyl-3,4-dihydro-2*H*-pyran-2-yl)ethynyl)silane (27). Phosphonium salt **12** (227 mg, 0.428 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method A) using *N*-pentanal. The product was isolated as a dark red oil (74 mg, 32%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.30 (9H, s), 0.86 (3H, t, J = 6.5 Hz), 1.18−2.35 (12H, m), 4.48−4.55 (1H, m), 4.85 (1H, dd, J = 11.0, 2.0 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.3 (br), 155.1, 111.3, 94.6, 77.7, 75.8, 34.1, 31.4, 31.3, 26.5, 22.5, 21.3, 14.0, 0.7; FTIR (film, cm^{-1}): 2958 (m), 2930 (m), 2853 (w), 2090 (s), 2049 (s), 2023 (s), 1678 (m), 1585 (w), 1459 (w), 1294 (w), 1250 (m), 1160 (w), 1044 (m); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{21}H_{27}O_7SiCo_2$ 537.0190, found 537.0186.

Dicobalthexacarbonyl-6-benzyl-2-(hex-1-ynyl)-3,4-dihydro-2*H*-pyran (28). Phosphonium salt **14** (225 mg, 0.437 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method B) using benzaldehyde. The product was isolated as a dark red oil (87 mg, 36%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.94 (3H, t, J = 7.0 Hz), 1.34−1.84 (5H, m), 1.99−2.15 (2H, m), 2.16−2.36 (1H, m), 2.70−2.83 (2H, m), 3.32 (2H, s), 4.51−4.60 (1H, m), 4.87 (1H, dd, J = 10.5, 2.0 Hz), 7.14−7.31 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4 (br), 154.4, 139.1, 129.3, 128.5, 126.5, 99.1, 97.3, 96.8, 76.2, 40.9, 34.3, 33.9, 30.6, 23.1, 21.5, 14.3; FTIR (film, cm^{-1}): 3065 (w), 3031 (w), 2960 (m), 2931 (m), 2852 (w), 2090 (s), 2048 (s), 2020 (s), 1678 (m), 1605 (w),1496 (w), 1455 (w), 1362 (w), 1285 (w), 1231 (w), 1160 (w), 1052 (m); HRMS (ES) *m*/*z* (M^+ + H) calcd for $C_{24}H_{23}O_7Co_2$ 541.0108, found 541.0113.

Dicobalthexacarbonyl-(2-(6-benzyl-3,4-dihydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (29). Phosphonium salt **12** (315 mg, 0.594 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method B) using benzaldehyde. The product was isolated as a dark red oil (73 mg, 22%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.24 (9H, s), 1.66−

1.84 (1H, m), 2.01−2.15 (2H, m), 2.19−2.37 (1H, m), 3.33 (2H, s), 4.52−4.59 (1H, m), 4.86 (1H, dd, J = 11.0, 2.0 Hz), 7.13−7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2 (br), 154.1, 138.6, 128.9, 128.2, 126.1, 110.8, 96.8, 78.0, 76.1, 40.5, 31.2, 21.4, 0.6; FTIR (film, cm^{-1}): 3065 (w), 3031 (w), 2957 (m), 2926 (m), 2850 (w), 2090 (s), 2049 (s), 2021 (s), 1678 (m), 1577 (m), 1496 (w), 1454 (w), 1362 (w), 1249 (m), 1231 (w), 1159 (w), 1070 (w), 1043 (m), 840 (s); HRMS (ES) m/z (M^+ + H) calcd for $C_{23}H_{23}O_7SiCo_2$ 556.9877, found 556.9883.

Dicobalthexacarbonyl-(3-(6-benzyl-3,4-dihydro-2*H*-pyran-2-yl)prop-2-ynyloxy)(*tert*-butyl)diphenylsilane (30). Phosphonium salt **13** (342 mg, 0.471 mmol) was converted to the title compound according to the general procedure for dihydropyran complex formation (method B) using benzaldehyde. The product was isolated as an orange−red oil (156 mg, 44%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.07 (9H, s), 1.59−1.77 (1H, m), 1.92−2.26 (3H, m), 3.27 (2H, s), 4.47−4.53 (1H, m), 4.75 (2H, s), 4.80 (1H, dd, J = 10.5, 2.0 Hz), 7.06−7.19 (5H, m), 7.35−7.50 (6H, m), 7.68−7.76 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.7 (br), 153.9, 138.5, 135.6, 133.0, 129.9, 128.9, 128.1, 127.8, 126.0, 96.4, 95.8, 95.2, 75.8, 64.6, 40.5, 30.2, 26.6, 21.0, 19.1; FTIR (film, cm^{-1}): 3072 (w), 3030 (w), 2955 (m), 2932 (m), 2896 (m), 2858 (m), 2093 (s), 2053 (s), 2029 (s), 1677 (m), 1604 (w), 1429 (m), 1362 (m), 1284 (w), 1232 (m), 1113 (s), 1053 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{37}H_{34}O_8SiCo_2Na$ 775.0585, found 775.0598.

General Procedure for Lewis Acid Mediated Ring-Contraction Reactions. The dicobalthexacarbonyl complex was dissolved in CH_2Cl_2 (0.1 M) and cooled to −78 °C. Et_2AlCl (3 equiv) was then added in a dropwise fashion; after the addition was complete, the reaction mixture was stirred for 1 min at −78 °C. The reaction vessel was then transferred to a −30 °C bath, and the mixture was stirred for the indicated amount of time. The −30 °C bath was removed, and the reaction mixture was warmed to 0 °C, followed by an addition of water. The reaction mixture was poured onto water and extracted three times with Et_2O. The ethereal layers were combined, washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by silica gel chromatography. In all cases, a single diastereomer was observed by ^{1}H NMR to give an estimated selectivity of >98:2.

Synthesis of Dicobalthexacarbonyl-2-phenyl-1-(2-(2-phenylethynyl)cyclobutyl)ethanone (10). Following the general procedure, complex **9** (26 mg, 0.046 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (20 mg, 78%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.81−2.16 (2H, m), 2.25−2.42 (1H, m), 2.25−2.42 (1H, m), 3.19−3.33 (1H, m), 3.60 (2H, s), 4.17−4.31 (1H, m), 7.02−7.10 (2H, m), 7.13−7.31 (6H, m), 7.35−7.43 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 207.1, 199.5 (br), 137.8, 133.6, 129.5 (x2C), 128.9, 128.7, 127.8, 127.0, 101.4, 90.9, 53.0, 48.3, 39.1, 27.3, 23.4; FTIR (film, cm^{-1}): 3064 (w), 3031 (w), 2947 (m), 2866 (w), 2088 (s), 2049 (s), 2016 (s), 1705 (s), 1605 (w), 1486 (w), 1483 (w), 1455 (w), 1442 (w), 1358 (w), 1235 (w), 1212 (w); HRMS (ES) m/z (M^+ + Na) calcd for $C_{26}H_{18}O_7NaCo_2$ 582.9614, found 582.9623.

Dicobalthexacarbonyl-3,3-dimethyl-1-(2-(2-phenylethynyl)cyclobutyl)butan-1-one (31). Following the general procedure, complex **15** (32 mg, 0.059 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red solid (28 mg, 89%). mp 50.1−50.4 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (9H, s), 1.90−2.15 (2H, m), 2.18−2.49 (4H, m), 3.18 (1H, app q, J = 8.5 Hz), 4.16−4.30 (1H, m), 7.27−7.39 (3H, m), 7.44−7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 199.6 (br), 137.8, 129.5, 128.9, 127.8, 101.8, 90.9, 54.9, 53.1, 39.4, 30.7, 29.6, 26.9, 22.2; FTIR (film, cm^{-1}): 3078 (w), 2955 (s), 2870 (m), 2089 (s), 2049 (s), 2016 (s), 1711 (s), 1614 (w), 1482 (m), 1443 (m), 1365 (m), 1232 (w); HRMS (ES) m/z (M^+ + H) calcd for $C_{24}H_{23}O_7Co_2$ 541.0108, found 541.0102.

Dicobalthexacarbonyl-3,3-dimethyl-1-(2-(2-(trimethylsilyl)-ethynyl)cyclobutyl)butan-1-one (32). Following the general procedure, complex **16** (30 mg, 0.056 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (25 mg, 83%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.29 (9H, s), 0.99 (9H, s), 1.74−2.05 (2H, m), 2.16−2.39 (4H, m), 3.03 (1H, app q, J = 9.0 Hz), 3.95−4.09 (1H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 208.9, 200.5 (br), 114.9, 78.4, 55.6, 53.0, 40.0, 30.7, 29.6, 27.7, 22.2, 0.7; FTIR (film, cm^{-1}): 2957 (m), 2907 (w), 2871 (w), 2087 (s), 2045 (s), 2016 (s), 1712 (m), 1584 (w), 1466 (w), 1365 (m), 1250 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{21}H_{27}O_7SiCo_2$ 537.0190, found 537.0188.

Dicobalthexacarbonyl-1-(2-(3-(*tert*-butyldiphenylsilyloxy)-prop-1-ynyl)cyclobutyl)-3,3-dimethylbutan-1-one (33). Following the general procedure, complex **17** (210 mg, 0.287 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as an orange−red oil (163 mg, 78%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.94 (9H, s), 1.08 (9H, s), 1.75−2.07 (2H, m), 2.09−2.29 (4H, m), 3.04 (1H, app q, J = 8.5 Hz), 3.88 (1H, app q, J = 8.5 Hz), 4.78 (2H, s), 7.36−7.50 (6H, m), 7.69−7.78 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 209.1, 199.8 (br), 135.6, 132.9, 129.9, 127.9, 100.1, 95.9, 64.6, 55.1, 52.7, 39.7, 30.7, 29.6, 27.0, 26.6, 21.9, 19.2; FTIR (film, cm^{-1}): 3074 (w), 3052 (w), 2955 (s), 2896 (s), 2862 (s), 2090 (s), 2049 (s), 2027 (s), 1711 (s), 1616 (w), 1590 (w), 1474 (m), 1428 (m), 1364 (s), 1113 (s), 1066 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{35}H_{38}O_8NaSiCo_2$ 755.0898, found 755.0875.

Dicobalthexacarbonyl-3-methyl-1-(2-(2-phenylethynyl)cyclobutyl)butan-1-one (34). Following the general procedure, complex **18** (70 mg, 0.133 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (53 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (3H, d, J = 6.5 Hz), 0.87 (3H, d, J = 6.5 Hz), 1.97−2.35 (6H, m), 2.35−2.46 (1H, m), 3.18−3.24 (1H, m), 4.23−4.30 (1H, m), 7.27−7.36 (3H, m), 7.47−7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 199.6 (br), 137.8, 129.5, 128.9, 127.8, 101.6, 90.9, 53.8, 49.8, 39.3, 27.1, 24.0, 22.5, 22.5, 22.4; FTIR (film, cm^{-1}): 3078 (w), 2959 (s), 2873 (m), 2089 (s), 2049 (s), 2016 (s), 1709 (s), 1614 (w), 1483 (m), 1468 (m), 1443 (m), 1368 (m), 1232 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{23}H_{21}O_7Co_2$ 526.9951, found 526.992.

Dicobalthexacarbonyl-3-methyl-1-(2-(2-(trimethylsilyl)ethynyl)cyclobutyl)butan-1-one (35). Following the general procedure, complex **19** (78 mg, 0.149 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (57 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.29 (9H, s), 0.89 (6H, d, J = 6.5 Hz), 1.82−1.91 (1H, m), 1.92−2.01 (1H, m), 2.09−2.34 (5H, m), 3.02−3.09 (1H, m), 4.03−4.10 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 200.4 (br), 114.7, 78.3, 54.5, 49.7, 39.8, 27.9, 24.0, 22.6, 22.6, 22.3, 0.8; FTIR (film, cm^{-1}): 2960 (s), 2874 (m), 2087 (s), 2044 (s), 2016 (s), 1711 (s), 1584 (m), 1469 (w), 1407 (w), 1368 (m), 1250 (s); HRMS (ES) m/z (M^+ + H) calcd for $C_{20}H_{25}O_7SiCo_2$ 523.0034, found 523.0010.

Dicobalthexacarbonyl-1-(2-(hex-1-ynyl)cyclobutyl)-3-methylbutan-1-one (36). Following the general procedure, complex **20** (355 mg, 0.701 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (304 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (6H, d, J = 6.5 Hz), 0.95 (3H, t, J = 7.0 Hz), 1.37−1.66 (4H, m), 1.79−2.35 (7H, m), 2.73−2.86 (2H, m), 3.06 (1H, app q, J = 9.0 Hz), 3.97 (1H, app q, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 200.2 (br), 101.4, 99.5, 53.9, 49.7, 39.2, 34.0, 33.8, 26.8, 24.0, 22.7, 22.6, 22.2, 13.9; FTIR (film, cm^{-1}): 2961 (s), 2935 (s), 2875 (m), 2087 (s), 2044 (s), 2015 (s), 1710 (s), 1617 (w), 1467 (m), 1368 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{21}H_{25}O_7Co_2$ 507.0264, found 507.0263.

Dicobalthexacarbonyl-1-(2-(3-(*tert*-butyldiphenylsilyloxy)-prop-1-ynyl)cyclobutyl)-3-methylbutan-1-one (37). Following the general procedure, complex **21** (74 mg, 0.103 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (50 mg, 68%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.83 (3H, d, J = 6.0 Hz), 0.83 (3H, d, J = 6.5 Hz), 1.07 (9H, s), 1.76−2.29 (7H, m), 3.00−3.13 (1H, m), 3.85−3.98 (1H, m), 4.78 (2H, s), 7.35−7.49 (6H, m), 7.68−7.76 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 199.8 (br), 135.5, 132.8, 129.9, 127.8, 99.9, 95.7, 64.5, 54.0, 49.5, 39.5, 27.1, 26.5, 23.9, 22.5 (x2), 22.0, 19.1; FTIR (film, cm^{-1}): 3074 (w), 3052 (w), 2958 (s), 2861 (m), 2090 (s), 2049 (s), 2026 (s), 1710 (s), 1618 (w), 1590 (w), 1472 (m), 1429 (m), 1365 (m), 1113 (s), 1066 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{34}H_{36}O_8NaSiCo_2$ 741.0741, found 741.0740.

Dicobalthexacarbonyl-1-(2-(2-phenylethynyl)cyclobutyl)propan-1-one (38). Following the general procedure, complex **25** (78 mg, 0.157 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (39 mg, 50%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.03 (3H, t, J = 7.5 Hz), 1.93−2.16 (2H, m), 2.22−2.53 (4H, m), 3.19−3.32 (1H, m), 4.22−4.34 (1H, m), 7.25−7.39 (3H, m), 7.45−7.52 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 210.3, 199.6 (br), 137.8, 129.5, 128.9, 127.8, 107.5, 90.9, 53.2, 39.6, 34.1, 27.2, 22.6, 7.6; FTIR (film, cm^{-1}): 3078 (w), 2981 (w), 2944 (w), 2089 (s), 2049 (s), 2018 (s), 1712 (m), 1614 (w), 1483 (w), 1460 (w), 1443 (w), 1363 (w), 1233 (w), 1124 (w); HRMS (ES) m/z (M^+ + H) calcd for $C_{21}H_{17}O_7Co_2$ 498.9638, found 498.9660.

Dicobalthexacarbonyl-1-(2-(3-(*tert*-butyldiphenylsilyloxy)-prop-1-ynyl)cyclobutyl)propan-1-one (39). Following the general procedure, complex **26** (68 mg, 0.098 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as an orange−red oil (31 mg, 46%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.99 (3H, t, J = 7.5 Hz), 1.07 (9H, s), 1.77−2.46 (6H, m), 3.05−3.18 (1H, m), 3.88−4.00 (1H, m), 4.78 (2H, s), 7.36−7.50 (6H, m), 7.68−7.76 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 199.8 (br), 135.5, 132.8, 129.9, 127.8, 99.8, 95.6, 64.5, 53.4, 39.6, 33.6, 27.3, 26.5, 22.3, 19.1, 7.5; FTIR (film, cm^{-1}): 3074 (w), 3052 (w), 2936 (s), 2895 (s), 2860 (s), 2090 (s), 2049 (s), 2024 (s), 1712 (s), 1621 (w), 1590 (w), 1473 (m), 1462 (m), 1429 (m), 1363 (m), 1113 (s), 1066 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{32}H_{32}O_8NaSiCo_2$ 713.0428, found 713.0432.

Dicobalthexacarbonyl-1-(2-(2-(trimethylsilyl)ethynyl)cyclobutyl)hexan-1-one (40). Following the general procedure, complex **27** (43 mg, 0.080 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (21 mg, 49%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.29 (9H, s), 0.86 (3H, t, J = 7.0 Hz), 1.18−1.35 (4H, m), 1.49−1.62 (2H, m), 1.77−2.06 (2H, m), 2.20−2.47 (4H, m), 3.02−3.15 (1H, m), 4.00−4.13 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 200.4 (br), 114.7, 78.3, 54.2, 40.7, 39.9, 31.4, 27.9, 23.2, 22.5, 22.4, 13.9, 0.8; FTIR (film, cm^{-1}): 2959 (m), 2864 (w), 2087 (s), 2045 (s), 2016 (s), 1711 (m), 1583 (w), 1459 (w), 1408 (w), 1370 (w), 1250 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{21}H_{27}O_7SiCo_2$ 537.0190, found 537.0187.

Dicobalthexacarbonyl-cyclohexyl(2-(2-phenylethynyl)cyclobutyl)methanone (41). Following the general procedure, complex **22** (18 mg, 0.033 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1.5 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (10 mg, 53%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.09−1.37 (5H, m), 1.59−1.83 (5H, m), 1.93−2.14 (2H, m), 2.24−2.47 (3H, m), 3.30−3.42 (1H, m), 4.23−4.36 (1H, m), 7.27−7.38 (3H, m), 7.45−7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 199.5 (br), 137.8, 129.5, 128.9, 127.8, 101.7, 90.8, 52.1, 49.1, 39.1, 28.3, 27.3, 25.7, 25.6, 23.1; FTIR (film, cm^{-1}): 3078 (w), 2934 (m), 2857 (m), 2088 (s), 2049 (s), 2018 (s), 1703 (m), 1615 (w), 1483 (w), 1444 (m), 1373 (w), 1238 (w); HRMS (ES) m/z (M^+ + H) calcd for $C_{25}H_{23}O_7Co_2$ 553.0108, found 553.0110.

Dicobalthexacarbonyl-cyclohexyl(2-(2-(trimethylsilyl)ethynyl)-cyclobutyl)methanone (42). Following the general procedure, complex **23** (51 mg, 0.093 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (38 mg, 75%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.29 (9H, s), 1.12−1.42 (5H, m), 1.58−2.04 (7H, m), 2.18−2.39 (3H, m), 3.14−3.27 (1H, m), 4.03−4.16 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 200.4 (br), 114.8, 78.3, 52.9, 48.9, 39.5, 28.4, 28.2, 28.0, 25.8, 25.7, 25.6, 23.1, 0.7; FTIR (film, cm^{-1}): 2935 (s), 2858 (m), 2086 (s), 2045 (s), 2016 (s), 1705 (s), 1585 (m), 1451 (m), 1249 (s); HRMS (ES) m/z (M^+ + H) calcd for $C_{22}H_{27}O_7SiCo_2$ 549.0190, found 549.0182.

Dicobalthexacarbonyl-(2-(3-(*tert*-butyldiphenylsilyloxy)prop-1-ynyl)cyclobutyl)(cyclohexyl)methanone (43). Following the general procedure, complex **24** (122 mg, 0.164 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as an orange−red oil (83 mg, 68%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.07 (9H, s), 1.01−1.33 (4H, m), 1.55−2.04 (8H, m), 2.09−2.33 (3H, m), 3.21 (1H, app q, J = 8.5 Hz), 3.95 (1H, app q, J = 8.5 Hz), 4.76 (2H, s), 7.36−7.49 (6H, m), 7.68−7.75 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 199.8 (br), 135.5, 132.8, 129.8, 127.8, 100.0, 95.7, 64.5, 52.3, 48.9, 39.2, 28.3, 28.3, 27.3, 26.5, 25.7, 25.6, 25.6, 22.8, 19.1; FTIR (film, cm^{-1}): 3073 (w), 2933 (s), 2858 (s), 2090 (s), 2048 (s), 2025 (s), 1703 (s), 1619 (w), 1590 (w), 1473 (m), 1450 (m), 1429 (m), 1363 (m), 1113 (s), 1066 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{36}H_{38}O_8NaSiCo_2$ 767.0898, found 767.0905.

Dicobalthexacarbonyl-1-(2-(hex-1-ynyl)cyclobutyl)-2-phenylethanone (44). Following the general procedure, complex **28** (54 mg, 0.10 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/

Et_2O) afforded the product as a dark red oil (34 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, t, J = 7.5 Hz), 1.38−1.49 (2H, m), 1.50−1.62, (2H, m), 1.78−2.00 (2H, m), 2.03−2.13 (1H, m), 2.20−2.29 (1H, m), 2.71−2.79 (2H, m), 3.14−3.22 (1H, m), 3.67 (2H, s), 3.98−4.06 (1H, m), 7.13−7.19 (2H, m), 7.22−7.34 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 200.1 (br), 133.6, 129.5, 128.7, 127.0, 101.0, 99.4, 53.1, 48.2, 38.9, 34.0, 33.7, 26.9, 23.2, 22.7, 13.9; FTIR (film, cm^{-1}): 3031 (w), 2960 (m), 2935 (m), 2875 (m), 2087 (s), 2044 (s), 2015 (s), 1706 (m), 1603 (w), 1496 (w), 1455 (w), 1357 (w), 1236 (w), 1211 (w), 1103 (w); HRMS (ES) m/z (M^+ + H) calcd for $C_{24}H_{23}O_7Co_2$ 541.0108, found 541.0083.

Dicobalthexacarbonyl-2-phenyl-1-(2-(2-(trimethylsilyl)ethynyl)cyclobutyl)ethanone (45). Following the general procedure, complex **29** (18 mg, 0.032 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (15 mg, 82%). ^1H NMR (250 MHz, $CDCl_3$) δ 0.25 (9H, s), 1.72−2.15 (3H, m), 2.20−2.33 (1H, m), 3.08−3.22 (1H, m), 3.66 (2H, s), 4.03−4.16 (1H, m), 7.12−7.19 (2H, m), 7.20−7.35 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 200.3 (br), 133.6, 129.5, 128.7, 127.1, 114.4, 78.3, 53.7, 48.3, 39.5, 28.0, 23.3, 0.7; FTIR (film, cm^{-1}): 3031 (w), 2956 (m), 2086 (s), 2045 (s), 2016 (s), 1706 (m), 1585 (m), 1585 (m), 1496 (w), 1249 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{23}H_{23}O_7SiCo_2$ 556.9877, found 556.9870.

Dicobalthexacarbonyl-1-(2-(3-(*tert*-butyldiphenylsilyloxy)-prop-1-ynyl)cyclobutyl)-2-phenylethanone (46). Following the general procedure, complex **30** (155 mg, 0.206 mmol) in CH_2Cl_2 was treated with 3 equiv of Et_2AlCl, and the mixture was stirred for 1 h. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as an orange/red oil (110 mg, 71%). ^1H NMR (250 MHz, $CDCl_3$) δ 1.00 (9H, s), 1.65−2.04 (3H, m), 2.06−2.23 (1H, m), 3.10 (1H, app q, J = 9.0 Hz), 3.53 (2H, s), 3.91 (1H, app q, J = 8.5 Hz), 4.68 (2H, s), 6.98−7.06 (2H, m), 7.12−7.23 (3H, m), 7.29−7.43 (6H, m), 7.61−7.69 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 206.8, 199.7 (br), 135.5, 133.6, 132.9, 129.9, 129.4, 128.6, 127.8, 127.0, 99.7, 95.7, 64.5, 53.3, 48.0, 39.2, 27.3, 26.6, 23.1, 19.1; FTIR (film, cm^{-1}): 3072 (m), 3031 (m), 2934 (s), 2894 (s), 2860 (s), 2090 (s), 2048 (s), 2026 (s), 1706 (s), 1604 (w), 1590 (w), 1496 (w), 1473 (m), 1455 (w), 1429 (s), 1362 (m), 1113 (s), 1067 (s); HRMS (ES) m/z (M^+ + Na) calcd for $C_{37}H_{34}O_8NaSiCo_2$ 775.0585, found 775.0564.

Synthesis of 1-((1*S*,2*S*)-2-(hex-1-ynyl)cyclobutyl)-3-methylbutan-1-one (47). TBAF (0.29 mL, 0.29 mmol, 1 M in THF, 1.5 equiv) was added dropwise to a stirring solution of complex **36** (98 mg, 0.194 mmol, 1 equiv) in THF (1.9 mL) at room temperature. The resulting mixture was stirred for 1 h then diluted with diethyl ether (4 mL) and filtered through a short plug of silica. The silica plug was washed with diethyl ether (3 mL, twice), and the combined ethereal layers were condensed in vacuo. The resulting residue was purified by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 50:1 petroleum ether/Et_2O) to afforded the product ketone as a clear oil (28 mg, 65%). ^1H NMR (250 MHz, $CDCl_3$) δ 0.86−0.93 (9H, m), 1.31−1.53 (4H, m), 1.85−2.21 (7H, m), 2.24−2.30 (2H, m), 2.93−3.08 (1H, m), 3.12−3.24 (1H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 209.8, 82.4, 82.2, 52.9, 49.8, 31.0, 28.1, 25.7, 24.3, 22.7, 22.6, 21.9, 20.6, 18.5, 13.6; FTIR (film, cm^{-1}): 2957 (s), 2934 (s), 2872 (s), 1710 (s), 1467 (m), 1368 (m), 1333 (w), 1234 (w), 1170 (w), 1146 (w); HRMS (ES) m/z (M^+ + H) calcd for $C_{15}H_{25}O$ 221.1905, found 221.1901.

Synthesis of 1-(2-(hex-1-ynyl)cyclobutyl)-2-phenylethanone (48). TBAF (0.32 mL, 0.32 mmol, 1 M in THF, 5.0 equiv) was added dropwise to a stirring solution of the dark red complex **44** (35 mg, 0.065 mmol, 1 equiv) in THF (1.0 mL) at 0 °C, and the resulting mixture immediately turned green−brown. The reaction mixture was stirred for 1 h, diluted with Et_2O (3 mL), and filtered through a short plug of silica. The silica plug was washed with Et_2O (3 mL, twice), and the combined ethereal layers were condensed in vacuo. The resulting residue was purified by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/EtOAc) to afforded the product ketone as a clear oil (9 mg, 54%). ^1H NMR (250 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 7.0 Hz), 1.26−1.49 (4H, m), 1.72−2.09 (4H, m), 2.13 (2H, td, J = 7.0, 2.0 Hz), 2.94−3.09 (1H, m), 3.18−3.33 (1H, m), 3.64 (2H, s), 7.11−7.30 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 207.2, 134.0, 129.6, 128.7, 127.0, 82.8, 82.1, 52.1, 47.9, 31.1, 28.3, 25.8, 22.0, 20.9, 18.6, 13.7; FTIR (film, cm^{-1}): 3030 (w), 2956 (s), 2932 (s), 2872 (m), 1708 (s), 1603 (w), 1495 (m), 1454 (m), 1362 (m), 1332 (m), 1234 (w); HRMS (ES) m/z (M^+ + Na) calcd for $C_{18}H_{22}ONa$ 277.1568, found 277.1570.

Dicobalthexacarbonyl-5-isobutyl-2-(2-phenylethynyl)-2,3-dihydrofuran Complex (49). Isobutyraldehyde (19 μL, 0.214 mmol, 1.1 equiv) was added to a solution of triphenyl(5-(-2-phenylethynyl)tetrahydrofuran-2-yl)phosphonium tetrafluoroborate[13(d)] (101 mg, 0.194 mmol, 1 equiv) that was dissolved in THF (1 mL). The mixture was cooled to −90 °C, and then a solution of KO^{t}Bu (24 mg, 0.214 mmol, 1.1 equiv) in THF (0.9 mL) added dropwise via cannula. The reaction was stirred at −90 °C for 3 h, slowly warmed to room temperature over 2 h, and then stirred for an additional 3 h. The reaction was quenched by the addition of water, and the mixture was extracted three times with Et_2O. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, filtered through a pad of celite, and concentrated in vacuo.

The crude adduct was dissolved in 1 mL of CH_2Cl_2, and the mixture was treated with 20 mL of petroleum ether before cooling to −78 °C. The organic extracts were decanted from the formed precipitates through a pad of celite, and the solvent was removed in vacuo. The crude enol ether in CH_2Cl_2 (1 mL) was added via cannula to a solution of octacarbonyldicobalt (66 mg, 0.194 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) at room temperature. After the mixture was stirred for 1 h, it was filtered through a pad of celite, concentrated in vacuo, and flash chromatographed on silica gel eluted with petroleum ether/Et_2O/Et-$_3$N (100:10:1) to afford an endo/exo mixture of pyran complexes.

Pyridinium para-toluene sulfonate (2 mg, 0.0097 mmol, 0.05 equiv) was added portionwise to a solution of the endo/exo $Co_2(CO)_6$ complexes (1 equiv) in CH_2Cl_2 (1.25 mL) at room temperature. After the mixture was stirred for 3 h, 1.0 equiv of Et_3N was added, and the reaction was concentrated. The resulting residue was taken up in petroleum ether (40−60) then filtered through a short pad of silica to afford the product (19 mg, 19%) as a dark red oil. (Because of its instability and propensity to ring-open, complex **49** was tentatively characterized by ^1H NMR before subjection to the rearrangement reaction). ^1H NMR (250 MHz, $CDCl_3$) δ 0.93 (3H, d, J = 6.5 Hz), 0.94 (3H, d, J = 6.5 Hz), 1.80−2.05 (3H, m), 2.57−2.69 (1H, m), 3.12−3.26 (1H, m), 4.58−4.62 (1H, m), 5.86 (1H, dd, J = 10.5, 7.0 Hz), 7.28−7.39 (3H, m), 7.52−7.60 (2H, m).

Dicobalthexacarbonyl-3-methyl-1-(2-(2-phenylethynyl)cyclopropyl)butan-1-one (50). Following the general procedure for cyclobutane formation, a solution of complex **49** (19 mg, 0.037 mmol) in CH_2Cl_2 was treated with 1.5 equiv of Et_2AlCl, and the mixture was stirred for 15 min. Purification by column chromatography on silica gel (eluted with a continuous gradient starting with petroleum ether and ending with 10:1 petroleum ether/Et_2O) afforded the product as a dark red oil (15 mg, 80%). ^1H NMR (250 MHz, $CDCl_3$) δ 0.93 (3H, d, J = 6.5 Hz), 0.94 (3H, d, J = 6.5 Hz), 1.30 (1H, ddd, J = 8.0, 6.0, 4.0 Hz), 1.92 (1H, ddd, J = 8.5, 5.5, 4.0 Hz), 2.12−2.33 (2H, m), 2.44 (1H, dd, J = 15.5, 6.5 Hz),

2.52 (1H, dd, J = 15.5, 7.0 Hz), 2.86 (1H, ddd, J = 8.5, 6.0, 4.0 Hz), 7.30−7.40 (3H, m), 7.44−7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 199.1 (br), 137.6, 129.1, 129.0, 128.0, 99.4, 91.4, 53.2, 34.2, 28.4, 24.9, 22.6, 22.5; FTIR (film, cm^{-1}): 3079 (w), 2961 (s), 2874 (m), 2090 (s), 2050 (s), 2019 (s), 1699 (s), 1613 (w), 1484 (w), 1467 (w), 1443 (w), 1384 (m), 1306 (w), 1070 (m), 1040 (m); HRMS (ES) m/z (M^+ + H) calcd for $C_{22}H_{19}O_7Co_2$ 512.9795, found 512.9799.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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