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Development of the Scope of a Co-Mediated O→C Rearrangement Reaction

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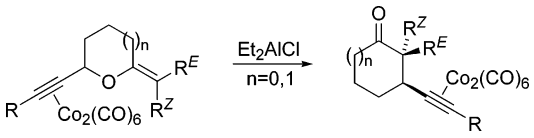

In this paper we describe an Al-promoted, Co-mediated O→C rearrangement reaction of cyclic enol ethers. This process delivers functionalized cyclohexanones with good to excellent levels of diastereocontrol, whereby the product stereochemistry is dependent on the *E*/*Z*-stereochemistry of the starting enol ether. The rearrangement process also permits access to highly substituted α-spirocyclic cyclohexanones as well as cyclopentanones. The latter rearrangement appears to proceed via an unusual 5-(enolendo)-exo-trig cyclization process.

Introduction

The stabilization of a cationic charge at a propargylic center by a cobalt carbonyl cluster is now well-established and allows efficient carbon−carbon bond formation to take place, especially when π-nucleophiles are employed.[1] We have recently exploited this chemistry in a Co-mediated O→C rearrangement reaction that allowed the stereoselective synthesis of functionalized cyclohexanones to take place in good to excellent yields.[2,3] Nonetheless, these preliminary studies highlighted some limitations associated with this methodology: (1) The substrate enol ethers were prepared by a lengthy and linear procedure. (2) The stereoselectivity of the rearrangement reaction was critically dependent on the nature and quality of Lewis acid employed; while *freshly distilled* $TiCl_4$ allowed access to cis- and trans-stereoisomers, Bu_2BOTf promoted isomerization to the trans-product in all cases studied. More recently, we have been endeavoring to simplify the reaction protocol by reducing the number of steps to the enol ethers and by uncovering a more general Lewis acid for the O→C rearrangement reaction; we report our results herein.

Our previously reported route to the requisite enol ether substrates is summarized in Scheme 1. Addition of the appropriate alkyne was carried out in the first step, and the pyranylphosphonium salt was ultimately delivered after a series of functional group interconversions. While this route required a number of synthetic steps, it allowed significant quantitites of phosphonium salt to be made available.

A significant drawback to our established route to the phosphonium salts was that the alkyne unit is incorporated in step 1. Accordingly, the preparation of substrates bearing various alkyne units by this procedure was prohibitively time-consuming, and our studies were limited to phenylacetylene- and 1-hexyne-based systems. Accordingly, we opted to develop a more efficient route to phosphonium salts that would allow a range of alkynes to be prepared in a more convenient manner.

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(1) (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Caffyn, A. J. M.; Nicholas, K. M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Hegedus, L. S., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 685. (c) Green, J. R. *Curr. Org. Chem.* **2001**, *5*, 809. (d) Teobald, B. J. *Tetrahedron* **2002**, *58*, 4133.

(2) (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.

(3) For other recent examples of O→C rearrangements, see: (a) Smith, A. B., III; Verhoest, P. R.; Minbiole, K. P.; Lim, J. J. *Org. Lett.* **1999**, *1*, 909. (b) Smith, A. B., III; Minbiole, K. P.; Verhoest, P. R.; Beauchamp, T. J. *Org. Lett.* **1999**, *1*, 913. (c) Sollogoub, M.; Mallet, J.-M.; Sinay, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 362. (d) Buffet, M. F.; Dixon, D. J.; Edwards, G. L.; Ley, S. V.; Tate, E. W. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1815. (e) Zhang, Y.; Reynolds, N. T.; Manju, K.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 9720.

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SCHEME 1

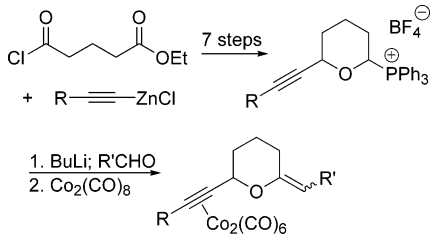
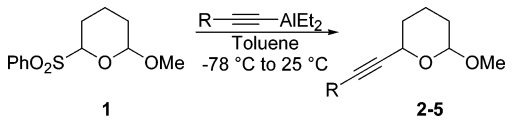


TABLE 1. Alkyne Incorporation via Sulfone Displacement



1 **2-5**

entry	R	product, % yield[a]
1	Ph	**2**, 89 (1:3.8)
2	*n*-Bu	**3**, 93 (1:3.2)
3	Me_3Si	**4**, 87 (1:12.3)
4	$TBDPSOCH_2$	**5**, 94 (1:6.4)

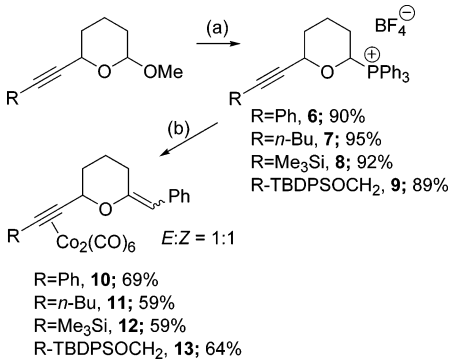
[a] Values in parentheses refer to cis:trans ratios.

Results and Discussion

We decided to use sulfone **1** as a convenient starting material, as it can be prepared in multigram quantities in a single step from commercial reagents.[4] Literature precedent suggested that alkynylmetal reagents could substitute the sulfone group, and we therefore began our investigations at this step. Our first attempts to displace the sulfone with alkynylzinc reagents met with mixed success. While phenylethynyl zinc chloride underwent smooth substitution to generate the product in 64% yield the procedure could not be reproduced with other alkyne substrates.[2c] We were intrigued by a report from Ley and co-workers in which an alkynylaluminum reagent successfully displaced an activated sulfone in a key fragment coupling toward the synthesis of okadaic acid.[5] As outlined in Table 1, we were pleased to find that addition of the alkynyl diethyl aluminum reagent to **1** resulted in a smooth and general protocol for sulfone displacement that provided an effective means for installing various alkyne substituents.

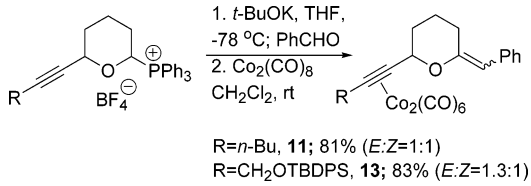
The conversion of the pyranyl ethers to the appropriate rearrangement precursors was carried out under established conditions, and the results are outlined in Scheme 2.[6] Heating the acetals in the presence of $Ph_3P{\cdot}HBF_4$ and molecular sieves provided the phosphonium salts in high yield as hygroscopic, colorless powders that were converted to Ph-substituted enol ethers after a Wittig reaction. All complexes were isolated as 1:1 mixtures of *E*:*Z* isomers, although isomers of complexes **10** and **12** were separable by column chromatography.[7]

SCHEME 2[a]



[a] Reagents and conditions: (a) $PPh_3{\cdot}HBF_4$, 4 Å molecular sieves, MeCN, reflux, 48 h. (b) (i) BuLi, THF, −78 °C; PhCHO. (ii) $Co_2(CO)_8$, CH_2Cl_2, rt, 1 h.

SCHEME 3



While enol ether formation took place in acceptable overall yield, we briefly investigated alternative conditions for the Wittig reaction. Indeed, as outlined in Scheme 3, we found that using *t*-BuOK in place of BuLi in the formation of the ylide resulted in higher overall yield in the two instanced examined.

With the enol ether complexes **10**−**13** in hand, we turned our attention to the rearrangement reaction. While previous work had shown that B- and Ti-based Lewis acids successfully mediated the cyclohexanone forming reaction, the quality of Lewis acid was critical for efficient rearrangement, and careful experimentation was required to achieve reproducibly high yields. In an effort to develop a more robust and simpler set of reaction conditions, we explored the use of alternative Lewis acid promoters. Indeed, we found commercial diethylaluminum chloride to be a convenient reagent for the efficient and reproducible conversion of enol ethers to the corresponding cyclohexanone products; our results are outlined in Table 2.[8] As we were able to isolate configurationally pure *E*/*Z*-isomers of enol ethers **10** and **12**, we were in a position to study their rearrangement reactions individually. We were pleased to find that these reactions proceeded smoothly such that the *Z*-enol ethers were transformed to the corresponding trans-disubstituted ketones, whereas *E*-enol ethers furnished the cis-isomers (entries 1−4). A similar trend was noted in cases where *E*/*Z*-mixtures of starting complexes were employed (en-

(4) Brown, D. S.; Bruno, M.; Davenport, R. J.; Ley, S. V. *Tetrahedron* **1989**, *45*, 4293.

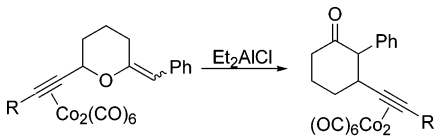
(5) Ley, S. V.; Humphries, A. C.; Eick, H.; Downham, R.; Ross, A. R.; Boyce, R. J.; Pavey, J. B. J.; Pietruszka, J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3907.

(6) Ley, S. V.; Lygo, B.; Organ, H. M.; Wonnacott, A. *Tetrahedron* **1985**, *41*, 3825.

(7) The assignment of *E*- and *Z*-stereochemistry in complexes **10** and **11** has been described;[2c] in both cases, the olefinic CH signal for the *Z*-isomer appears upfield in the ^1H NMR spectrum. The stereochemical assignments of complexes **12** and **13** were made by analogy.

(8) The addition of Lewis acid to noncomplexed enol ether substrates did not result in rearrangement to the corresponding ketones. A mixture of recovered starting material and alkene isomerization products were obtained instead. Additionally, significant substrate conversions were only observed when >1.0 equiv of diethylaluminium chloride was employed. Indeed, the Lewis acid character of dialkylaluminium chlorides has been found to be highly dependent on reaction stoichiometry: (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (b) Evans, D. A.; Allison, B. D.; Yang, M. G. *Tetrahedron Lett.* **1999**, *40*, 4457. (c) Castellino, S.; Dwight, W. J. *J. Am. Chem. Soc.* **1993**, *115*, 2986.

TABLE 2. Al-Mediated Stereoselective Rearrangement Reaction

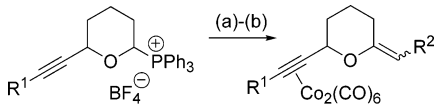


10-13 **14-17**

entry[a]	R, starting material	*E*/*Z*	product, % yield (*cis*/*trans*)
1	Ph, **10**	Z	**14**, 97 (0:100)
2	Ph, **10**	E	**14**, 63 (100:0)
3	Me_3Si, **12**	Z	**15**, 66 (0:100)
4	Me_3Si, **12**	E	**15**, 80 (100:0)
5	*n*-Bu, **11**	1:1.5	**16**, 83 (1:1.5)
6	$TBDPSOCH_2$, **13**	1:1	**17**, 89 (1:1)

[a] All reactions performed at −78 °C in CH_2Cl_2 with 1.5 equiv of Lewis acid.

TABLE 3. Enol Ether Synthesis[a]



6, 8 **18-21**

entry	R^1	R^2	conditions[b]	product, % yield (*E*/*Z*)
1	*n*-Bu	*E*-CH=CHPh	A	**18**, 61 (1.1:1)
2	Ph	*E*-CH=CHPh	A	**19**, 53 (1.3:1)
3	Ph	*i*-Pr	B	**20**, 76 (100:0)
4	Ph	*t*-Bu	B	**21**, 73 (100:0)

[a] Reagents and conditions: (a) (i) ylide formation (see footnote *b*), (ii) R^2CHO; (b) $Co_2(CO)_8$, pet. ether, rt. [b] Ylide formation: conditions A, BuLi, THF, −78 °C; conditions B, *t*-BuOK, THF, −78 °C.

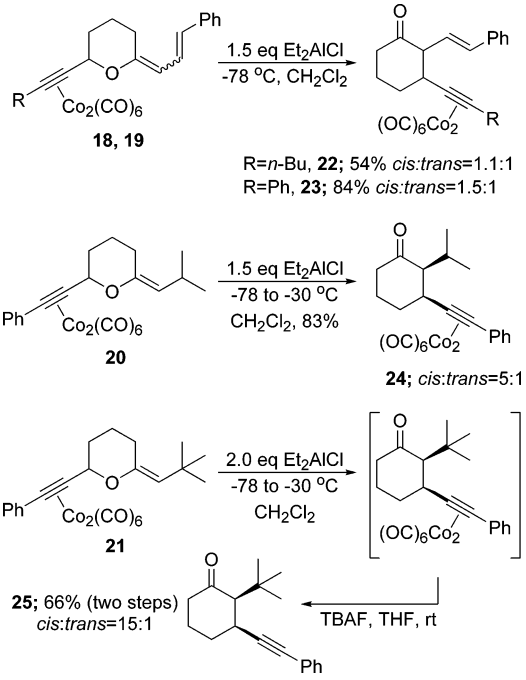
tries 5 and 6). Additionally, a propargylic silyl ether was tolerated in the rearrangement process (**13**→**17**), demonstrating the potential for regioselective Nicholas carbocation formation in these systems (entry 6).

We next decided to explore the efficiency and stereoselectivity of the rearrangement of substrates bearing alternative substituents at the enol ether moiety. In particular, our preliminary reports on the Ti-mediated rearrangement reaction of *E*-enol ethers bearing *i*-Pr and *t*-Bu-groups were all found to be highly trans-selective. Notably, this stereochemical trend is in contrast to that of enol ethers bearing sterically smaller substituents, whereby *E*-enol ethers provide cis-diastereomers with high levels of stereocontrol.[2c] Representative substrates were prepared from the corresponding phosphonium salts as before (Table 3).[9]

We first examined the rearrangement of complexes **18** and **19** in an effort to establish the regioselectivity of ring closure of the intermediate dienolates. In the event, treatment of these complexes with 1.5 equiv of the Al-Lewis acid resulted in selective formation of the cyclohexanone products **22** and **23** in moderate to excellent yield. We next turned our attention to the *i*-Pr-substituted enol ether **20**. The rearrangement of this substrate was relatively slow and required elevated temperatures and long reaction times to provide high yields of the corresponding product (−30 °C for 24 h). Nonetheless, these conditions provided ketone **24** in 84% yield as a

(9) The identity of the major isomers of **18** and **19** was not elucidated.

SCHEME 4



5:1 mixture of cis:trans isomers. Finally, the rearrangement of *t*-Bu enol ether substrate **21** under similar conditions gave a new complex that was found to readily undergo demetalation during chromatography. Accordingly, we employed a mild decomplexation reaction with TBAF[10] upon workup and were pleased to find that the *cis*-cyclohexanone **25** had been formed with high levels of stereoselectivity and in good yield.[11] Presumably, the unusual instability of this complex is due to the proximity of the bulky Co−alkyne cluster and *t*-Bu groups in this compound (Scheme 4).

Accordingly, as described in Table 2 and Scheme 4, the Et_2AlCl-mediated rearrangement reaction provides good to excellent levels of stereocontrol in the Co-mediated rearrangement reaction, whereby *cis*-cyclohexanones are generated from the corresponding *E*-enol ether substrates while the trans-diastereomers are formed from the *Z*-isomers (Figure 1). Furthermore, *and in direct contrast to our earlier studies involving Ti- and B-Lewis acids*, this trend is independent of the size of the enol ether substituent, although the levels of stereochemical control can be affected by the nature of the enol ether substituent.

(10) Jones, G. B.; Wright, J. M.; Rush, T. M.; Plourde, G. W., II; Kelton, T. F.; Mathews, J. E.; Huber, R. S.; Davidson, J. P. *J. Org. Chem.* **1997**, *62*, 9379.

(11) The relative stereochemistry was proved by demetalation of authentic Co-complexed trans-**25**[2c]: To a 0.1 M solution of *trans*-dicobalthexacarbonyl-2-*tert*-butyl-3-(2-phenylethynyl)cyclohexanone (28 mg, 0.052 mmol, 1.0 equiv) in THF at room temperature was added TBAF (1 M in THF, 78 μL, 1.5 equiv). The reaction was stirred for 1.5 h and filtered through a plug of alumina, and the plug was washed with Et_2O (2 × 10 mL) Et_2O. The resulting ethereal solution was shaken with water (10 mL), dried over $MgSO_4$, and filtered through a pad of Celite. Concentration in vacuo and purification by flash chromatography (10:1, pet. ether:ether) afforded *trans*-ketone **25** (13.3 mg, 100%) as a clear oil: ^1H NMR (250 MHz, $CDCl_3$) δ 1.07 (9H, s), 1.77−2.53 (7H, m), 3.25−3.33 (1H, m), 7.22−7.30 (3H, m), 7.30−7.39 (2H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 22.6, 28.7, 29.4, 31.0, 33.8, 41.8, 64.9, 82.6, 92.8, 123.5, 127.8, 128.2, 131.5, 212.5; FTIR (film, υ_{max} cm^{-1}) 3056, 2960, 2870, 1700, 1598, 1490, 1476, 1443, 1369, 1314 1216; HRMS (ES) *m*/*z* (M^++ Na) calcd for $C_{18}H_{22}ONa$ 277.1568, found 277.1556.

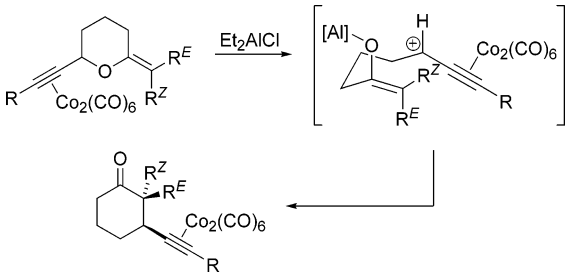
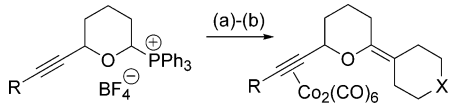


FIGURE 1. Stereochemical rationale of the rearrangement reaction.

TABLE 4. Enol Ether Synthesis[a]



6-9 **26-33**

entry	R	X	product, % yield
1	Ph	CH_2	**26**, 35
2	*n*-Bu	CH_2	**27**, 48
3	Me_3Si	CH_2	**28**, 46
4	$CH_2OTBDPS$	CH_2	**29**, 54
5	Ph	NTs	**30**, 31
6	Me_3Si	NTs	**31**, 25
7	$CH_2OTBDPS$	NTs	**32**, 47
8	$CH_2OTBDPS$	$C[(OCH_2)_2]$	**33**, 50

[a] Reagents and conditions: (a) BuLi, THF, −78 °C; ketone; (b) $Co_2(CO)_8$, CH_2Cl_2, rt.

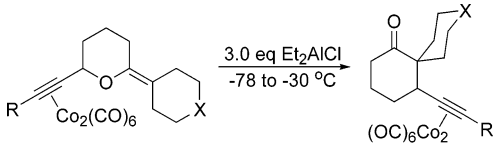
We next opted to exploit this technique for the synthesis of more heavily substituted cyclohexanones. Specifically, we were intrigued by the opportunity to prepare α-spirocyclic systems via the rearrangement of cycloalkylidene enol ethers. These substrates were once again accessed from the phosphonium salts by Wittig olefination procedures, as outlined in Table 4.[12]

Not surprisingly, the rearrangement reaction of these substrates was found to be rather sluggish, however, the employment of 3 equiv of the Lewis acid followed by warming the reaction mixture to −30 °C and strirring overnight provided the α-spirocyclic products in good to excellent yield. Remarkably, even in these hindered pyranyl enol ether substrates, we were pleased to find that the desired Nicholas carbocation could be generated in the presence of a propargyl ether (entries 4, 7, 8 in Table 5).

Having demonstrated the effectiveness of Et_2AlCl in the formation of cyclohexanone systems, we decided to establish the potential of this technique for the formation of cyclopentanones. Our earlier work with Ti- and B-based Lewis acids failed to provide cyclopentanone products by this approach. Our rationale for the failure of the five-membered ring systems to rearrange was based on the requirement for a 5-(enolendo)-exo-trig ring closure reaction on to the Nicholas cation, which is disfavored on stereoelectronic grounds (Scheme 5).[13] Nonetheless, related ring closures are known,[14] and we therefore decided to investigate whether the Al-based Lewis acid would provide the corresponding cyclopentanone products.

(12) Surprisingly, the Wittig reaction was only successful for cyclohexanone derivatives and failed to provide enol ether products when ketones of other ring sizes were employed.

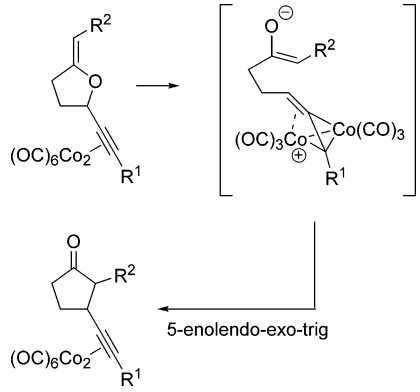
TABLE 5. Rearrangement toward Spirocyclic Ketones



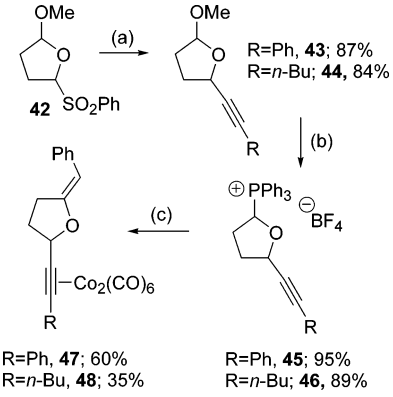
26-33 **34-41**

entry	R	X	product, % yield
1	Ph	CH_2	**34**, 91
2	*n*-Bu	CH_2	**35**, 82
3	Me_3Si	CH_2	**36**, 88
4	$CH_2OTBDPS$	CH_2	**37**, 97
5	Ph	NTs	**38**, 87
6	Me_3Si	NTs	**39**, 85
7	$CH_2OTBDPS$	NTs	**40**, 94
8	$CH_2OTBDPS$	$C[(OCH_2)_2]$	**41**, 70

SCHEME 5



SCHEME 6[a]

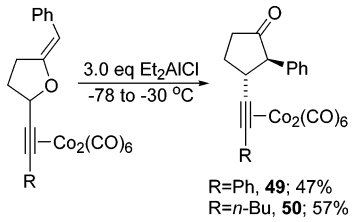


[a] Reagents and conditions: (a) $RCCAlEt_2$. (b) $PPh_3{\cdot}HBF_4$, 4 Å molecular sieves, MeCN, reflux, 48 h. (c) (i) *t*-BuOK, THF, −78 °C; PhCHO. (ii) $Co_2(CO)_8$, CH_2Cl_2, rt, 1 h.

To establish the feasibility of this transformation, we decided to prepare a furanyl-based enol ether, and we employed an analogous procedure to that described in Scheme 6. Treatment of sulfone **42**[15] with the alkynylaluminum reagent provided **43** and **44** in excellent yield. Conversion of **43** and **44** to the phosphonium salt and *t*-BuOK-mediated Wittig olefination proceeded smoothly to furnish **47** and **48** after complexation. The complexes

(13) Baldwin, J. E.; Lusch, M. J. *Tetrahedron* **1982**, *38*, 2939.
(14) (a) Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2485. (b) Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7559.
(15) Brown, D. S.; Bruno, M.; Davenport, R. J.; Ley, S. V. *Tetrahedron* **1989**, *45*, 4293.

were isolated as an inseparable 2:1 mixture of *E*:*Z* isomers[16] that were used directly in the rearrangement reaction. Pleasingly, utilizing 3 equiv of Et_2AlCl resulted in conversion of the *E*/*Z* mixture of enol ethers **47** and **48** into the corresponding *trans*-cyclopentanone complexes in 47% and 57% yield, respectively.



In conclusion, we have developed a modified protocol for the O→C rearrangement of Co-alkyne-containing cyclic enol ethers that uses Et_2AlCl. This reagent can be used as supplied without need for purification and mediates the rearrangement of a wide range of substrates in good yield. Additionally, this Lewis acid provides a consistent stereoselective reaction in the case of cyclohexanone formation such that *E*-enol ethers furnish cis-2,3-disubstituted ketones while *Z*-enol ethers provide the trans-products. Finally, our observations also suggest that cyclopentanones can be accessed by this strategy, albeit in modest yield, via a formally disfavored 5-(enolendo)-exo-trig cyclization.

Experimental Section

General Procedure for the 2-Substitution of Cyclic Ethers 1 and 42 with Alkynylaluminum Reagents for Synthesis of Compounds 2−5, 43, and 44. To a stirred 0.2 M solution of the alkyne (1.2 equiv) in toluene at −78 °C was added *n*-BuLi (1.2 equiv) in a dropwise fashion. After 10 min the reaction was warmed to 0 °C and stirred for a further 15 min. Et_2AlCl (1.2 equiv) was added to the reaction. After 30 min at 0 °C the reaction was cooled to −78 °C and the cyclic sulfone added dropwise via cannula as a solution in DCM (1.5 mL/g). The reaction was slowly warmed to room temperature, stirred for 16−20 h, and quenched at room temperature by addition of an equivalent volume of H_2O. The mixture was poured into water and extracted three times with EtOAc. The combined organic layers were washed with saturated K_2CO_3 and brine, dried ($MgSO_4$), and concentrated in vacuo. Chromatography with silica gel, eluting with an ethyl acetate/petroleum ether system of appropriate polarity, yielded the title compounds.

2-Methoxy-6-(2-phenylethynyl)tetrahydro-2*H*-pyran (2). Reaction of 2-(benzenesulfonyl)tetrahydro-6-methoxy-2*H*-pyran (5.0 g, 19.5 mmol) with the alkynylaluminum reagent prepared from phenyl acetylene gave compound **2** (3.77 g, 89%) isolated as a colorless oil containing an inseparable mixture of diastereomers (cis:trans 1:3.8) (chromatography, 10:1 petroleum ether/EtOAc). The physical and spectral data were identical to those previously reported for this compound.[2]

2-Hex-1-ynyl-6-methoxytetrahydro-2*H*-pyran (3). Reaction of 2-(benzenesulfonyl)tetrahydro-6-methoxy-2*H*-pyran (500 mg, 1.3 mmol) with the alkynylaluminum reagent prepared from 1-hexyne gave compound **3** (227 mg, 93%) isolated as a colorless oil containing an inseparable mixture of diastereomers (cis:trans 1:3.2) (chromatography, 10:1 petroleum ether/EtOAc). Trans-isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7 Hz), 1.29−1.90 (10H, m), 2.21 (2H, dt, J = 7, 2 Hz), 3.39 (3H, s), 4.50 (1H, dd, J = 9.5, 1.5 Hz), 4.70−4.77 (1H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 98.7, 85.0, 79.4, 60.4, 54.9, 32.2, 30.7, 29.4, 21.9, 18.4, 17.9, 13.5; FTIR (film, υ_{max} cm^{-1}) 2954 (s), 2871 (m), 1457 (m), 1440 (m), 1372 (m), 1196 (m), 1123 (s), 1022 (s); HRMS (EI) *m*/*z* (M^+) calcd for $C_{12}H_{20}O_2$ 196.146330, found 196.146622.

(2-(6-Methoxytetrahydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (4). Reaction of 2-(benzenesulfonyl)tetrahydro-6-methoxy-2*H*-pyran (5.0 g, 19.5 mmol) with the alkynylaluminum reagent prepared from trimethylsilylacetylene gave compound **4** (3.6 g, 87%) isolated as a colorless oil containing an inseparable mixture of diastereomers (cis:trans 1:12.3) (chromatography, 15:1 petroleum ether/EtOAc). Trans-isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.00 (9H, s), 1.34−1.72 (6H, m), 3.23 (3H, s), 4.36 (1H, dd, J = 10, 3 Hz), 4.56 (1H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 105.0, 98.8, 88.9, 60.6, 55.2, 31.9, 29.4, 17.9, 0.0; FTIR (film, υ_{max} cm^{-1}) 2955 (m), 1441 (w), 1371 (w), 1250 (m), 1196 (m), 1124 (m), 1082 (m), 1061 (m), 1023 (s); HRMS (ES) *m*/*z* (M^+ + Na) calcd for $C_{11}H_{20}O_2SiNa$ 235.1130, found 235.1123.

***tert*-Butyl(3-(6-methoxytetrahydro-2*H*-pyran-2-yl)prop-2-ynyloxy)diphenylsilane (5).** Reaction of 2-(benzenesulfonyl)tetrahydro-6-methoxy-2*H*-pyran (2.86 g, 11.0 mmol) with the alkynylaluminum reagent prepared from (1,1-dimethylethyl)diphenyl(2-propyn-1-yloxy)silane gave compound **5** (4.30 g, 94%) isolated as a colorless oil containing an inseparable mixture of diastereomers (cis:trans 1:5.6) (chromatography, 20:1 petroleum ether/EtOAc). Trans-isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.05 (9H, s), 1.42−1.91 (6H, m), 3.38 (3H, s), 4.36 (2H, d, J = 1.5 Hz), 4.53 (1H, d, J = 9 Hz), 4.69−4.74 (1H, m), 7.33−7.48 (6H, m), 7.66−7.75 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 135.7, 133.2, 129.8, 127.7, 98.7, 84.3, 82.9, 60.5, 55.1, 52.7, 31.4, 29.4, 26.7, 19.2, 17.9; FTIR (film, υ_{max} cm^{-1}) 3071 (w), 3049 (w), 2932 (s), 2895 (m), 2858 (s), 1961 (w), 1891 (w), 1825 (w), 1589 (w), 1473 (m), 1428 (m), 1372 (m), 1113 (s), 1079 (s), 1023 (s); HRMS (ES) *m*/*z* (M^+ + Na) calcd for $C_{25}H_{32}O_3SiNa$ 431.2018, found 431.2029.

General Procedure for the Formation of Phosphonium Wittig Salts 6−9, 45, and 46. To a round-bottom flask fitted with a water-jacketed reflux condenser and containing activated 4 Å molecular sieves was added $HPPh_3BF_4$ (2 equiv, 0.4 M in MeCN) followed by the cyclic acetal (1 equiv, 0.2 M in MeCN). The mixture was heated to reflux (82 °C) and stirred until complete consumption of the starting material was observed by TLC (16−18 h). The reaction was cooled to room temperature, diluted with DCM, and filtered through a Celite pad under reduced pressure. Concentration of the filtrate in vacuo afforded a crude residue, which was dissolved in DCM, refiltered over Celite, and concentrated. To the resulting residue taken up in DCM (2−5 mL) was added a 1:1 mixture diethyl ether/hexane (50−100 mL) and the mixture was subjected to a vigorous agitation for 10 min until the cloudy suspension became clear. The solvent was decanted to leave a gummy residue. The previous operation was repeated until the addition of diethyl ether/hexane no longer gave a cloudy suspension. The residue was then dissolved in DCM, filtered through a pad of Celite, and concentrated to yield the corresponding Wittig salt as a solid.

Triphenyl(6-(2-phenylethynyl)tetrahydro-2*H*-pyran-2-yl)phosphonium tetrafluoroborate (6) was prepared as described above using pyranyl ether **2** (3.77 g, 17.4 mmol) and isolated as a pale yellow solid containing an inseparable 1.1:1 mixture of diastereomers (8.40 g, 90%). The physical and spectral data were identical to those previously reported for this compound.[2]

(6-Hex-1-ynyltetrahydro-2*H*-pyran-2-yl)triphenylphosphonium tetrafluoroborate (7) was prepared as described above using cyclic acetal **3** (82 mg, 0.418 mmol) and isolated as a pale yellow solid containing an inseparable 1.3:1 mixture of diastereomers (205 mg, 95%). The physical and spectral data were identical to those previously reported for this compound.[2]

Triphenyl(6-(2-(trimethylsilyl)ethynyl)tetrahydro-2*H*-pyran-2-yl)phosphon ium tetrafluoroborate (8) was pre-

(16) The identity of the major isomer was not elucidated.

pared as described above using pyranyl ether **4** (3.6 g, 16.97 mmol) and isolated as a white powder containing an inseparable 1.4:1 mixture of diastereomers (8.24 g, 92%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.00 (9H, s), 0.13 (9H, s), 1.39−2.01 (12H, m), 4.53 (1H, d. J = 10 Hz), 4.79−4.85 (1H, m), 5.42−5.52 (1H, m), 5.64−5.75 (1H, m), 7.50−7.79 (30H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) see Supporting Information; FTIR (film, υ_{max} cm^{-1}) 3646 (w), 3559 (w), 3065 (w), 2958 (m), 2262 (w), 1823 (w), 1588 (w), 1485 (w), 1440 (s), 1251 (m), 1195 (m), 1111 (s), 1058 (s); HRMS (FAB) *m/z* ($M^+ - BF_4$) calcd for $C_{28}H_{32}OSiP$ 443.1960, found 443.1976.

(6-(3-*tert*-Butyldiphenylsilyloxy)prop-1-ynyl)tetrahydro-2*H*-pyran-2-yl)triphenylphosphonium tetrafluoroborate (9) was prepared as described above using pyranyl ether **5** (5.36 g, 13.13 mmol) and isolated as a pale yellow solid containing an inseparable 1:1 mixture of diastereomers (8.44 g, 88%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.00 (9H, s), 1.02 (9H, s), 1.44−2.13 (12H, m), 4.25−4.32 (2H, m), 4.50−5.56 (2H, m), 4.63 (1H, br d, J = 10.5 Hz), 4.87−4.95 (1H, m), 5.39−5.53 (1H, m), 5.73−5.87 (1H, m), 7.24−7.91 (50H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) see Supporting Information; FTIR (film, υ_{max} cm^{-1}) 3644 (w), 3552 (w), 3070 (m), 2957 (m), 2858 (m), 2263 (w), 1976 (w), 1903 (w), 1826 (w), 1588 (m), 1440 (s), 1112 (s) 1061 (s); HRMS (FAB) *m/z* ($M^+ - BF_4$) calcd for $C_{42}H_{44}O_2$-SiP 639.2848, found 639.2817.

General Procedure for the Conversion of Wittig Salts into Cyclic Enol Ether Complexes for Compounds 10−13, 18−21, 26−33, 47, and 48. Method A. The appropriate amount of *n*-BuLi (1.1 equiv) was added dropwise to a 0.1 M solution of the phosphonium salt (1 equiv) in THF at −78 °C. The deep red solution was stirred for a further 5 min prior to addition of the neat aldehyde or ketone (1.1 equiv). The reaction was stirred for 2 h at −78 °C, unless stated otherwise, warmed to room temperature, and quenched by 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 ($MgSO_4$), filtered through a pad of Celite, and concentrated in vacuo. The crude enol ether was dissolved in 1 mL of ether and treated with 20 mL of petroleum ether before cooling to −78 °C and decanting the organic extracts from the formed precipitates through a pad of Celite, and the solvent was removed in vacuo. The crude enol ether in DCM (0.2 M) was added via cannula to a 0.2 M solution of octacarbonyldicobalt (1.1 equiv) in DCM at room temperature. After stirring for 1 h the mixture was filtered through a pad of Celite, concentrated, and purified by silica gel chromatography.

Method B. To a 0.2 M solution of KO^{t}Bu (1.2 equiv) in THF at −78 °C was added via cannula the phosphonium salt (1 equiv, 0.2 M in THF). After 1 h the neat aldehyde (1.2 equiv) was added to the red mixture and the reaction slowly warmed to room temperature. The reaction was stirred for a further 16 h and quenched by the addition of water. The mixture was poured into water and the organics extracted three times with Et_2O. The combined organic layers were washed with water and brine, dried ($MgSO_4$), and filtered through a pad of Celite and concentrated. The crude mixture was taken up in 1 mL of Et_2O or DCM and treated with 20 mL of petroleum ether. The resulting solution was cooled to −78 °C, the organic extracts were decanted from the formed precipitates through a pad of Celite, and the solvent was removed in vacuo. To a solution of octacarbonyldicobalt (1.1 equiv) in either DCM or petroleum ether (0.2 M) at room temperature was added a 0.2 M solution of the crude enol ether in the same solvent. After stirring for 1 h the mixture was filtered through a pad of Celite, concentrated, and purified by silica gel chromatography.

***E*/*Z*-Dicobalthexacarbonyl-2-benzylidene-6-(phenylethynyl)tetrahydro-2*H*-pyran (10)** (Wittig method A) was isolated as a dark red oil (280 mg, 69% from **6**) containing a separable 1:1 mixture of stereoisomers (*E*)-**10** (122 mg, 30%) and (*Z*)-**10** (129 mg, 32%) as dark red oils (chromatography, 100:1 petroleum ether/Et_3N). The physical and spectral data were identical to those previously reported for this compound.[2]

***E*/*Z*-Dicobalthexacarbonyl-2-benzylidene-6-hex-1-ynyltetrahydro-2*H*-pyran (11)** (Wittig method A) was isolated as a dark red oil (125 mg, 59% from **7**) containing an inseparable 1:1 mixture of (*E*)- and (*Z*)-stereoisomers (chromatography, 100:1:1 petroleum ether/Et_3N/Et_2O). The physical and spectral data were identical to those previously reported for this compound.[2]

***E*/*Z*-Dicobalthexacarbonyl-((6-benzylidenetetrahydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (12)** (Wittig method A) was isolated as a dark red oil (162 mg, 59% from **8**) containing a separable 1:1 mixture of stereoisomers (*E*)-**12** (82 mg, 30%) and (*Z*)-**12** (80 mg, 32%) as dark red oils (chromatography, 100:1:1 petroleum ether/Et_3N/Et_2O). (*Z*)-**12**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.32 (9H, s), 1.65−2.17 (4H, m), 2.30−2.45 (2H, m), 4.93 (1H, br d, J = 10.5 Hz), 5.48 (1H, s), 7.07−7.33 (3H, m), 7.56−7.67 (2H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 200.1, 154.0, 135.8, 128.4, 127.9, 125.7, 110.4, 108.2, 107.5, 79.1, 78.3, 35.3, 30.9, 23.4, 0.9; FTIR (film, υ_{max} cm^{-1}) 3057 (w), 2955 (m), 2866 (w), 2090 (s), 2049 (s), 2022 (s), 1729 (w), 1657 (m), 1576 (w), 1446 (w), 1364 (w), 1250 (m), 1164 (w), 1132 (w), 1066 (w), 1036 (w); HRMS (ES) *m/z* (M^+ + H) calculated for $C_{23}H_{23}O_7SiCo_2$ 556.9877, found 556.9861. (*E*)-**12**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.33 (9H, s), 1.61−2.39 (5H, m), 2.86 (1H, br d, J = 13.5 Hz), 4.78 (1H, br d, J = 7.5 Hz), 6.12 (1H, s), 7.11−7.37 (5H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 200.5, 155.7, 136.8, 129.1, 128.5, 126.0, 111.3, 110.3, 80.0, 78.4, 34.4, 25.2, 23.0, 1.1; FTIR (film, υ_{max} cm^{-1}) 3025 (w), 2955 (m), 2090 (s), 2049 (s), 2023 (s), 1657 (m), 1574 (w), 1446 (w), 1365 (w), 1250 (m), 1164 (w), 1132 (w), 1066 (w), 1136 (w); HRMS (ES) *m/z* (M^+ + H) calculated for $C_{23}H_{23}O_7SiCo_2$ 556.9877, found 556.9874.

***E*/*Z*-Dicobalthexacarbonyl-[3-(6-benzylidenetetrahydro-2*H*-pyran-2-yl)prop-2-ynyloxy]*tert*-butyldiphenylsilane (13)** (Wittig method A) was isolated as a dark orange oil (132 mg, 64% from **9**) containing a separable 1:1 mixture of stereoisomers (*E*)-**13** (66 mg, 32%) and (*Z*)-**13** (66 mg, 32%) as orange oils (chromatography, 100:1:1 petroleum ether/Et_3N/Et_2O). (*Z*)-**13**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.09 (9H, s), 1.64−2.14 (4H, m), 2.28−2.37 (2H, m), 4.80 (1H, dd, J = 10.5, 2.5 Hz), 4.83 (1H, d, J = 14 Hz), 4.92 (1H, d, J = 14 Hz), 5.42 (1H, s), 6.89−7.02 (3H, m), 7.35−7.52 (8H, m), 7.69−7.79 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.5 (br), 154.2, 135.8, 135.6, 132.9, 129.9, 128.1, 127.9 (×2), 125.6, 107.9, 96.4, 95.0, 78.6, 64.7, 33.4, 30.5, 26.6, 23.0, 19.2; FTIR (film, υ_{max} cm^{-1}) 3073 (w), 2934 (m), 2860 (m), 2094 (s), 2053 (s), 2030 (s), 1659 (w), 1600 (w), 1429 (w), 1352 (w), 1301 (w), 1166 (w), 1113 (m), 1062 (m), 1030 m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{37}H_{35}O_8SiCo_2$ 753.0765, found 753.0740. (*E*)-**13**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (9H, s), 1.55−1.90 (3H, m), 1.96−2.08 (1H, m), 2.19−2.37 (1H, m), 2.78 (1H, dt, J = 14.5, 3.5 Hz), 4.76 (1H, dd, J = 10, 2.5 Hz), 4.83 (2H, s), 6.07 (1H, s), 7.10−7.20 (3H, m), 7.22−7.33 (2H, m), 7.35−7.51 (6H, m), 7.68−7.78 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6 (br), 155.1, 136.4, 135.6, 132.9, 129.8, 128.7, 128.1, 127.8, 125.6, 110.0, 95.8, 95.2, 79.3, 64.6, 33.0, 26.6, 24.8, 22.2, 19.1; FTIR (film, υ_{max} cm^{-1}) 3073 (w), 2934 (m), 2860 (m), 2094 (s), 2053 (s), 2030 (s), 1656 (w), 1600 (w), 1473 (w), 1429 (w), 1232 (w), 1113 (m), 1065 (m), 1039 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{37}H_{35}O_8$-$SiCo_2$ 753.0765, found 753.0754.

General Procedure for Et_2AlCl-Promoted Rearrangement of Cyclic Enol Ethers 10−13 and 18−20 to Cyclohexanones. To a solution of the complex (1 equiv) in DCM (0.02 M) at −78 °C was added diethylaluminum chloride (1.5 equiv, 1 M in hexanes). The reaction was stirred for the

indicated amount of time at the stated temperature, quenched by addition of water, and then warmed to ambient temperature. The mixture was poured into water and extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude reaction mixture was then chromatographed on silica gel, eluting with petroleum ether/Et_2O (10:1).

***cis*-Dicobalthexacarbonyl-2-phenyl-3-(2-phenylethynyl)-cyclohexanone (*cis*-14)** was isolated from (*E*)-**10** (25 mg, 0.046 mmol) following the general procedure with a reaction time of 2 h at −78 °C, as a single diastereomer and as a dark red oil (16 mg, 63%). The physical and spectral data were identical to those previously reported for this compound.[2]

***trans*-Dicobalthexacarbonyl-2-phenyl-3-(2-phenylethynyl)cyclohexanone (*trans*-14)** was isolated from (*Z*)-**10** (13 mg, 0.024 mmol) following the general procedure with a reaction time of 2 h at −78 °C, as a single diastereomer and as a dark red solid (12 mg, 97%). The physical and spectral data were identical to those previously reported for this compound.[2]

***cis*-Dicobalthexacarbonyl-2-phenyl-3-(2-(trimethylsilyl)ethynyl)cyclohexanone (*cis*-15)** was isolated from (*E*)-**12** (52 mg, 0.093 mmol) following the general procedure with a reaction time of 1.1 h at −78 °C, as a single diastereomer and as a brown-red oil (41 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (9H, s), 1.85−2.01 (1H, m), 2.14−2.40 (3H, m), 2.64 (1H, td, J = 13.5, 4.0 Hz), 2.79 (1H, td, J = 14.5, 6.5 Hz), 3.64 (1H, app dt, J = 13.0, 5.0 Hz), 4.00 (1H, d, J = 5.5 Hz), 7.17−7.37 (3H, m), 7.46−7.58 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 200.4, (br), 135.6, 130.4, 129.0, 127.8, 110.7, 80.1, 63.7, 48.5, 36.4, 31.3, 25.2, 0.9; FTIR (film, υ_{max} cm^{-1}) 3062 (w), 3031 (w), 2958 (m), 2085 (s), 2045 (s), 2015 (s), 1714 (s), 1602 (w), 1496 (w), 1452 (w), 1249 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{23}H_{23}O_7SiCo_2$ 556.9877, found 556.9884.

***trans*-Dicobalthexacarbonyl-2-phenyl-3-(2-(trimethylsilyl)ethynyl)cyclohexanone (*trans*-15)** was isolated from (*Z*)-**12** (60 mg, 0.11 mmol) following the general procedure with a reaction time of 4.5 h at −78 °C, as a single diastereomer and as a brown-red solid (40 mg, 66%): mp 101−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (9H, s), 1.85−2.04 (2H, m), 2.13−2.22 (1H, m), 2.36−2.52 (2H, m), 2.57−2.66 (1H, m), 3.56 (1H, d, J = 9.5 Hz), 3.81 (1H, td, J = 9.5, 4.0 Hz), 7.17−7.22 (2H, m), 7.25−7.38 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 200.3 (br), 136.5, 129.2, 128.8, 127.6, 114.8, 80.8, 63.9, 46.0, 40.3, 35.4, 23.7, 1.0; FTIR (film, υ_{max} cm^{-1}) 3033 (w), 2957 (w), 2086 (s), 2046 (s), 2015 (s), 1716 (m), 1576 (w), 1538 (w), 1498 (w), 1449 (w), 1249 (m); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{23}H_{22}O_7SiCo_2Na$ 578.9696, found 578.9703.

***cis/trans*-Dicobalthexacarbonyl-3-hex-1-ynyl-2-phenylcyclohexanone (16)** was isolated from (*E*/*Z*)-**11** (36 mg, 0.066 mmol, *E*/*Z* 1:1.5) following the general procedure with a reaction time of 15 min at −78 °C, as a dark red oil containing an inseparable 1.5:1 (cis:trans) mixture of diastereomers (30 mg, 83%). The physical and spectral data were identical to those previously reported for this compound.[2]

***cis/trans*-Dicobalthexacarbonyl-3-(3-(*tert*-butyldiphenylsilyloxy)prop-1-ynyl)-2-phenylcyclohexanone (17)** was isolated from (*E*/*Z*)-**13** (292 mg, 0.39 mmol, *E*/*Z* 1:1) following the general procedure with a reaction time of 15 min at −78 °C, as a dark red oil containing a 1:1 (cis:trans) mixture of diastereomers (261 mg, 89%). *cis*-**17**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.00 (9H, s), 1.81−2.04 (1H, m), 2.10−2.55 (4H, m), 2.66−2.84 (1H, m), 3.50−3.70 (2H, m), 3.89 (1H, app d, J = 5.5 Hz), 4.08 (1H, d, J = 14.0 Hz), 6.78−6.98 (3H, m), 7.25−7.68 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 199.7 (br), 135.9, 135.6, 135.5, 132.9, 132.7, 129.7, 128.9, 127.7, 97.9, 95.8, 63.8, 62.7, 48.3, 36.7, 31.5, 26.5, 25.0, 19.0; FTIR (film, υ_{max} cm^{-1}) 3071 (w), 2933 (m), 2859 (m), 2089 (s), 2047 (s), 2025 (s), 1713 (m), 1590 (w), 1428 (m), 1362 (m), 1111 (m), 1059 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{37}H_{35}O_8SiCo_2$ 753.0765, found 753.0760. *trans*-**17**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (9H, s), 1.85−2.07 (2H, m), 2.20−2.39 (1H, m), 2.42−2.63 (3H, m), 2.89 (1H, d, J = 15.0 Hz), 3.31−3.48 (2H, m), 3.53 (1H, d, J = 15.0 Hz), 6.52−6.62 (1H, m), 6.72−6.88 (4H, m), 7.45−7.63 (10H,m); ^{1}H NMR (250 MHz, benzene-d_6) δ 1.12 (9H, s), 1.28−1.44 (1H, m), 1.46−1.60 (1H, m), 1.67−2.06 (2H, m), 2.13−2.28 (2H, m), 3.09 (1H, d, J = 15.0 Hz), 3.12 (1H, d, J = 12.0 Hz), 3.19 (1H, ddd, J = 22.5, 12.0, 3.5 Hz), 3.69 (1H, d, J = 15.0 Hz), 6.44−6.52 (1H, m), 6.64−6.80 (4H, m), 7.21−7.30 (6H, m), 7.61−7.69 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 199.9 (br), 136.1, 135.6, 135.5, 132.8, 129.6, 129.5, 129.0, 128.5, 127.6, 127.5, 100.0, 99.4, 64.0, 62.9, 47.4, 41.5, 34.9, 26.5, 24.9, 18.9; FTIR (film, υ_{max} cm^{-1}) 3071 (w), 2933 (m), 2859 (m), 2089 (s), 2049 (s), 2029 (s), 1719 (m), 1605 (w), 1428 (m), 1354 (w), 1112 (m), 1057 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{37}H_{35}O_8SiCo_2$ 753.0765, found 753.0771.

***(E/Z)*-Dicobalthexacarbonyl-2-hex-1-ynyl-6-((*E*)-3-phenylallylidene)tetrahydro-2*H*-pyran (18)** (Wittig method A) was isolated as a dark red oil (258 mg, 61% from **7**) containing an inseparable 1.1:1 mixture of (*E*)-**18** and (*Z*)-**18** stereoisomers (chromatography, 100:1:1 petroleum ether/Et_3N/Et_2O). (*E*/*Z*)-**18**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (6H, t, J = 7.0 Hz), 1.44−2.44 (19H, m), 2.75−2.91 (5H, m), 4.76−4.86 (2H, m), 5.41 (1H, d, J = 11.0 Hz), 5.86 (1H, br d, J = 12.5 Hz), 6.37 (1H, d, J = 16.0 Hz), 6.42 (1H, d, J = 15.5), 6.86 (1H, dd, J = 15.0, 11.0 Hz), 7.15−7.20 (1H, m), 7.23−7.38 (10H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.0 (br), 156.4, 154.7, 138.3, 138.2, 128.5 (×2), 128.4 (×2), 127.8, 126.7, 126.6, 125.9 (×2), 125.8 (×2), 123.9, 122.9, 110.3, 109.2, 98.7, 96.6, 79.4, 79.0, 34.1, 34.0, 33.5, 33.2, 33.1, 29.3, 24.4, 22.8, 22.7, 22.6, 22.1, 13.9 (×2); FTIR (film, υ_{max} cm^{-1}) 2934 (m), 2837 (m), 2090 (s), 2048 (s), 1647 (m), 1595 (m), 1448 (w), 1298 (m), 1031 (m); HRMS (ES) *m/z* (M^+) calcd for $C_{26}H_{24}O_7Co_2$ 566.01860, found 566.01908.

***(E/Z)*-Dicobalthexacarbonyl-2-((*E*)-3-phenylallylidene)-6-(2-phenylethynyl)tetrahydro-2H-pyran (19)** (Wittig method A) was isolated as a dark red oil (134 mg, 53% from **6**) containing an inseparable 1.3:1 mixture of (*E*)-**19** and (*Z*)-**19** stereoisomers (chromatography, 100:1:1 petroleum ether/Et_3N/Et_2O). *(E/Z)*-**19**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.79−2.06 (6H, m), 2.18−2.42 (4H, m), 2.82−2.92 (1H, m), 4.99 (1H, dd, J = 10.5, 2.5 Hz), 5.09 (1H, dd, J = 10.5, 2.5 Hz), 5.45 (1H, app d, J = 10.5 Hz), 5.95 (1H, dd, J = 11.5, 1.5 Hz), 6.38 (1H, d, J = 16.0 Hz), 6.45 (1H, d, J = 16.5 Hz), 6.85 (1H, dd, J = 15.5, 11.0 Hz), 7.15−7.40 (17H, m), 7.58−7.63 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.3 (br), 156.4, 154.6, 138.2, 137.7, 129.8 (×2), 129.6, 128.9, 128.8 (×2), 128.7, 128.5, 128.4 (×2), 128.0, 127.9, 127.8, 126.7, 126.6, 126.0, 125.8 (×2), 123.8, 122.8, 110.4, 109.3, 96.5, 90.0, 79.5, 78.9, 33.3, 33.2, 29.3, 24.4, 22.7, 22.3; FTIR (film, υ_{max} cm^{-1}) 3029 (m), 2949 (m), 2868 (m), 2091 (s), 2053 (s), 1645 (m), 1595 (m), 1484 (m), 1442 (m), 1264 (m), 1200 (m), 1164 (m), 1128 (m), 1030 (m); HRMS (ES) *m/z* (M^+) calcd for $C_{28}H_{20}O_7Co_2$ 585.98730, found 585.98501.

***(E)*-Dicobalthexacarbonyl-2-isobutylene-6-(phenylethynyl)tetrahydro-2*H*-pyran (20)** (Wittig method B) was isolated following complexation in petroleum ether (40−60) as a dark red oil (301 mg, 76% from **6**) and as a single stereoisomer (chromatography, 100:1:10 petroleum ether/Et_3N/Et_2O). The physical and spectral data were identical to those previously reported for this compound.[2]

***(E)*-Dicobalthexacarbonyl-2-(2,2-dimethylpropylidene)-6-(phenylethynyl)tetrahydro-2*H*-pyran (21)** (Wittig method B) was isolated following complexation in petroleum ether (40−60), as a dark red oil (178 mg, 73% from **6**) and as a single stereoisomer (chromatography, 100:1:10 petroleum ether/Et_3N/Et_2O). The physical and spectral data were identical to those previously reported for this compound.[2]

***cis/trans*-Dicobalthexacarbonyl-3-hex-1-ynyl-2-((*E*)-styryl)cyclohexanone (22)** was isolated from *E*/*Z*-**18** (59 mg, 0.10 mmol, *E*/*Z* 1.1:1) according to the general procedure with a reaction time of 1 h at −78 °C, as a dark red oil containing a 1.1:1 (cis:trans) mixture of diastereomers (32 mg, 54%) (chromatography, 10:1 petroleum ether/Et_2O). For the purposes of characterization, the diastereomers were partially

separated by careful chromatography. *cis*-**22**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 7.0 Hz), 1.21−1.36 (2H, m), 1.40−1.70 (3H, m), 1.80−1.92 (1H, m), 2.08−2.27 (2H, m), 2.34−2.39 (1H, m), 2.58 (1H, dd, J = 14.0, 6.0 Hz), 2.74−2.76 (2H, m), 3.29−3.41 (1H, m), 3.53−3.61 (1H, m), 6.40 (1H, dd, J = 16.0, 8.5 Hz), 6.58 (1H, d, J = 16.0 Hz), 7.21−7.38 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.6, 200.1 (br), 136.3, 135.6, 128.6, 128.1, 126.3, 121.9, 100.7, 97.8, 61.2, 47.8, 38.5, 34.0 (×2), 30.1, 25.4, 22.6, 13.7; FTIR (film, υ_{max} cm^{-1}) 3028 (w), 2959 (m), 2933 (m), 2873 (m), 2086 (s), 2016 (s), 1716 (s), 1600 (w), 1450 (w); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{26}H_{24}O_7NaCo_2$ 589.0084, found 589.0110. *trans*-**22**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.74 (3H, t, J = 7.0 Hz), 0.89−1.09 (3H, m), 1.22−1.53 (2H, m), 1.83−1.96 (2H, m), 2.17−2.36 (2H, m), 2.46−2.61 (3H, m), 3.03−3.23 (2H, m), 6.19 (1H, dd, J = 16.0, 8.5 Hz), 6.50 (1H, d, J = 16.0 Hz), 7.23−7.40 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.2, 200.2 (br), 136.6, 134.8, 128.6, 127.8, 126.3 (×2), 101.9, 101.5, 61.9, 48.1, 41.4, 34.8, 34.0, 33.9, 24.9, 22.4, 13.7; FTIR (film, υ_{max} cm^{-1}) 3028 (w), 2933 (m), 2872 (m), 2006 (s), 2016 (s), 1715 (s), 1601 (w), 1449 (w), 1248 (w), 1165 (w), 1030 (w); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{26}H_{24}O_7NaCo_2$ 589.0084, found 589.0110.

***cis/trans*-Dicobalthexacarbonyl-3-(phenylethynyl)-2-((*E*)-styryl)cyclohexanone (23)** was isolated from *E/Z*-**19** (38 mg, 0.065 mmol, *E/Z* 1.3:1) according to the general procedure with a reaction time of 1 h at −78 °C, as a dark red oil containing a 1.5:1 (cis:trans) mixture of diastereomers (32 mg, 84%) (chromatography, 10:1 petroleum ether/Et_2O). For the purposes of characterization, the diastereomers were partially separated by careful chromatography. *cis*-**23**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82−1.94 (1H, m), 2.20−2.40 (4H, m), 2.60 (1H, td, J = 14.0, 6.0 Hz), 3.55 (1H, dt, J = 12.0, 4.0 Hz), 3.58−3.62 (1H, m), 6.21 (1H, dd, J = 16.0, 8.0 Hz), 6.35 (1H, d, J = 16.0 Hz), 6.89−6.94 (2H, m), 7.10−7.20 (3H, m), 7.30−7.35 (3H, m), 7.40−7.44 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 199.4 (br), 138.2, 136.2, 135.7, 129.2, 129.0, 128.3, 127.7, 127.5, 126.3, 121.8, 99.1, 93.1, 60.8, 47.4, 38.4, 30.1, 25.5; (film, υ_{max} cm^{-1}) 2928 (w), 2088 (s), 2049 (s), 2019 (s), 1714 (m), 1442 (w), 1177 (w); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{28}H_{20}O_7Co_2Na$ 608.9771, found 608.9761. *trans*-**23**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91−2.08 (2H, m), 2.20−2.32 (1H, m), 2.38−2.42 (1H, m), 2.43−2.52 (1H, m), 2.54−2.61 (1H, m), 3.13 (1H, app t, J = 9.0 Hz), 3.50 (1H, td, J = 11.0, 4.0 Hz), 5.91 (1H, dd, J = 16.0, 9.0 Hz), 6.15 (1H, d, J = 16.0 Hz), 6.82−6.84 (2H, m), 7.05−7.12 (3H, m), 7.13−7.21 (3H, m), 7.22−7.33 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.1, 199.6 (br), 138.2, 136.3, 135.3, 128.8, 128.7, 128.0, 127.2, 127.1, 126.2, 125.7, 102.2, 94.1, 62.1, 53.4, 41.3, 34.3, 25.0; FTIR (film, υ_{max} cm^{-1}) 2948 (w), 2088 (s), 2048 (s), 2019 (s), 1714 (s), 1442 (m); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{28}H_{20}O_7Co_2Na$ 608.9771, found 608.9793.

***cis trans*-Dicobalthexacarbonyl-2-isopropyl-3-(2-phenylethynyl)cyclohexanone (24)** was isolated from (*E*)-**20** (300 mg, 0.57 mmol) according to the general procedure with a reaction time of 16 h at −30 °C, as a dark brown-red oil containing a 5:1 (cis:trans) mixture of diastereomers (250 mg, 83%) (chromatography, 10:1 petroleum ether/Et_2O). For the purposes of characterization, the diastereomers were partially separated by careful chromatography. The physical and spectral data for *trans*-**24** were identical to those previously reported for this compound.[2] *cis*-**24**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (3H, d, J = 7.0 Hz), 0.93 (3H, d, J = 7.0 Hz), 1.88−2.05 (2H, m), 2.11−2.28 (3H, m), 2.34−2.53 (2H, m), 2.64 (1H, app t, J = 6.5 Hz), 3.79−3.88 (1H, m), 7.25−7.40 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 199.4 (br), 138.8, 129.0, 128.6, 127.4, 98.3, 96.1, 61.6, 45.0, 42.5, 33.1, 25.5, 24.0, 21.8, 21.7; FTIR (film, υ_{max} cm^{-1}) 3078 (w), 2961 (m), 2872 (w), 2089 (s), 2049 (s), 2020 (s), 1715 (s), 1597 (w), 1480 (w), 1442 (w), 1371 (w), 1312 (w), 1217 (w); HRMS (ES) *m*/z (M^+) calcd for $C_{23}H_{20}O_7Co_2$ 525.9873, found 525.9888.

***cis/trans*-2-*tert*-butyl-3-(2-phenylethynyl)cyclohexanone (25).** To a solution of (*E*)-**21** (85 mg, 0.157 mmol) in DCM (0.02 M) at −78 °C was slowly added Et_2AlCl (2 equiv). The reaction was stirred for 5 min at −78 °C, warmed to −30 °C, and stirred for 24 h. The reaction was quenched at −30 °C with H_2O, warmed to ambient temperature, and extracted twice with Et_2O. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo to yield the crude ketone. The crude residue was taken up in THF (0.1 M), treated with TBAF (1 M in THF, 157 μL, 0.157 mmol, 1.0 equiv), and stirred for 2 h at room temperature. The solution was filtered through a plug of alumina and the plug washed with Et_2O (2 × 10 mL). The resulting ethereal solution was washed with water (10 mL), dried over $MgSO_4$, filtered through a pad of Celite, and concentrated in vacuo. Purification by flash chromatography (10:1 petroleum ether/Et_2O) afforded ketone 25 (27 mg, 67%) as a clear oil and as an inseparable mixture of stereoisomers (cis/trans; 15:1). *cis*-**25**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.14 (9H, s), 1.85−2.43 (7H, m), 3.53−3.60 (1H, m), 7.22−7.29 (3H), 7.30−7.38 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 209.7, 131.4, 128.2, 127.8, 123.5, 89.9, 85.8, 63.0, 43.8, 33.0, 32.8, 32.7, 28.5, 24.0; FTIR (film, υ_{max} cm^{-1}) 3057 (w), 2954 (s), 2867 (m), 1715 (s), 1598 (w), 1490 (m), 1444 (w), 1362 (m), 1117 (m); HRMS (EI) *m/z* (M^+) calcd for $C_{18}H_{22}O$ 254.1671, found 254.1682.

Dicobalthexacarbonyl-2-cyclohexylidene-6-(phenylethynyl)tetrahydro-2*H*-pyran (26) (Wittig method A) was prepared using freshly distilled cyclohexanone and phosphonium salt **6** (2.034 g, 3.81 mmol). Following complexation in petroleum ether (40−60) and chromatography (100:1 petroleum ether/Et_3N), complex **26** (741 mg, 35% from **6**) was isolated as a deep red solid: mp 119−120 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.37−1.60 (6H, m), 1.62−1.84 (2H, m), 1.89−2.30 (6H, m), 2.32−2.45 (1H, m), 2.57−2.70 (1H, m), 4.76 (1H, dd, J = 10.5, 2.5 Hz), 7.27−7.38 (3H, m), 7.50−7.61 (2H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.6 (br), 144.0, 138.0, 129.7, 128.8, 127.7, 119.9, 97.9, 89.6, 79.6, 34.3, 29.0, 28.3, 27.7, 27.0, 26.6, 24.4 (×2); FTIR (film, υ_{max} cm^{-1}) 2926 (w), 2853 (w), 2091 (s), 2051 (s), 2022 (s), 1682 (w); HRMS (EI) *m/z* (M^+) calcd for $C_{25}H_{22}O_7Co_2$ 552.0029, found 552.0036.

Dicobalthexacarbonyl-2-cyclohexylidene-6-hex-1-yyltetrahydro-2*H*-pyran (27) (Wittig method A) was prepared using freshly distilled cyclohexanone and phosphonium salt **7** (681 mg, 1.32 mmol). Following complexation in DCM and chromatography (100:1 petroleum ether/Et_3N) complex **27** (335 mg, 48% from **7**) was isolated as a deep red oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (3H, t, J = 7.0 Hz), 1.38−1.56 (8H, m), 1.56−1.70 (4H, m), 1.86−2.01 (3H, m), 2.02−2.17 (2H, m), 2.18−2.40 (2H, m), 2.52−2.64 (1H, m), 2.77−2.87 (2H, m), 4.51 (1H, dd, J = 10.5, 2.5 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.1 (br), 144.0, 119.6, 98.5, 97.9, 79.4, 34.0 (×2), 33.6, 28.9, 28.2, 27.7, 26.9, 26.5, 24.3 (×2), 22.7, 13.9; FTIR (film, υ_{max} cm^{-1}) 2930 (s), 2855 (s), 2090 (s), 2047 (s), 2014 (s), 1681 (m), 1616 (m), 1450 (m), 1035 (s); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{23}H_{27}O_7Co_2$ 533.0421, found 533.0414.

Dicobalthexacarbonyl-((6-cyclohexylidenetetrahydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (28) (Wittig method A) was prepared using freshly distilled cyclohexanone and phosphonium salt **8** (332 mg, 0.626 mmol). Following complexation in DCM and chromatography (100:1 petroleum ether/Et_3N), complex **28** (159 mg, 46% from **8**) was isolated as a deep red solid: mp 54−55 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.24 (9H, s), 1.31−1.72 (8H, m), 1.78−2.08 (5H, m), 2.12−2.35 (2H, m), 2.48−2.59 (1H, m), 4.45 (1H, dd, J = 11 Hz, 2.5 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.4 (br), 144.0, 119.7, 111.9, 92.6, 79.6, 35.3, 29.0, 28.3, 27.7, 26.9, 26.6, 24.4, 24.4, 0.7; FTIR (film, υ_{max} cm^{-1}) 2927 (s), 2854 (s), 2089 (s), 2014 (s), 1681 (m), 1580 (m), 1449 (m), 1250 (s), 1033 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{22}H_{27}O_7SiCo_2$ 549.0190, found 549.0197.

Dicobalthexacarbonyl-*tert*-butyl-[3-(6-cyclohexylidenetetrahydro-2*H*-pyran-2-yl)prop-2-ynyloxy]diphenylsilane (29) (Wittig method A) was prepared using freshly distilled cyclohexanone and phosphonium salt **9** (470 mg, 0.648 mmol). Following complexation in DCM and chromatography

(100:1:1 petroleum ether/Et_3N/Et_2O), complex **29** (264 mg, 54% from **9**) was isolated as a red-orange oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10 (9H, s), 1.41−1.80 (8H, m), 1.82−1.98 (3H, m), 2.00−2.14 (2H, m), 2.15−2.33 (2H, m), 2.57 (1H, br d, J = 13 Hz), 4.46 (1H, dd, J = 10.5 Hz, 2.5 Hz), 4.82 (2H, s), 7.38−7.50 (6H, m), 7.71−7.77 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.8 (br), 143.9, 135.6, 133.0, 129.8, 127.8, 119.6, 96.8, 95.0, 79.4, 64.6, 34.1, 28.9, 28.2, 27.6, 26.9, 26.6, 26.5, 24.2 (×2), 19.2; FTIR (film, υ_{max} cm^{-1}) 3073 (w), 2931 (s), 2858 (s), 2093 (s), 2051 (s), 2028 (s), 1674 (m), 1614 (m), 1473 (m), 1448 (m), 1429 (m), 1113 (s), 1063 (s), 1036 (s); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{36}H_{38}O_8SiCo_2Na$ 767.0898, found 767.0892.

Dicobalthexacarbonyl-4-(6-(phenylethynyl)tetrahydropyran-2-ylidene)-1-tosylpiperidine (30) (Wittig method A) was prepared using *N*-tosylpiperidone and phosphonium salt **6** (200 mg, 0.374 mmol). The reaction was stirred for 5 h at −78 °C before warming to room temperature and quenching. Following complexation in DCM and chromatography (100:1:10 petroleum ether/Et_3N/Et_2O), complex **30** (81 mg, 31% from **6**) was isolated as a red metallic solid: mp >300 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.58 (2H, m), 1.87−2.11 (3H, m), 2.30 (2H, app t, J = 5.5 Hz), 2.36−2.57 (3H, m), 2.41 (3H, s), 2.81−3.14 (4H, m), 4.70 (1H, m), 7.26−7.34 (5H, m), 7.46−7.52 (2H, m), 7.59−7.65 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3 (br), 146.3, 143.3, 137.7, 133.4, 129.6, 129.5, 128.8, 127.9, 127.6, 112.9, 97.0, 89.8, 79.4, 47.3, 47.0, 33.8, 27.6, 25.3, 24.3, 23.6, 21.5; FTIR (film, υ_{max} cm^{-1}) 2927 (s), 2846 (s), 2091 (s), 2051 (s), 2025 (s), 1684 (m), 1598 (m), 1442 (m), 1339 (s), 1165 (s); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{31}H_{28}NO_9SCo_2$ 708.0149, found 708.0121.

Dicobalthexacarbonyl-1-tosyl-4-(6-trimethylsilylethynyl)tetrahydropyran-2-ylidene)piperidine (31) (Wittig method A) was prepared using *N*-tosylpiperidone and phosphonium salt **8** (341 mg, 0.643 mmol). The reaction was stirred for 5 h at −78 °C before warming to room temperature and quenching. Following complexation in DCM and chromatography (100:1:1 petroleum ether/Et_3N/Et_2O), complex **31** (111 mg, 25% from **8**) was isolated as a red-brown metallic solid: mp >300 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.29 (9H, s), 1.52−1.71 (2H, m), 1.85−2.01 (3H, m), 2.25−2.34 (2H, m), 2.38−2.54 (2H, m), 2.42 (3H, s), 2.54−2.63 (1H, m), 2.85−3.12 (4H, m), 4.51 (1H, dd, J = 10.5, 2.5 Hz), 7.27−7.36 (2H, m), 7.58−7.68 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2 (br), 146.3, 143.3, 133.5, 129.6, 127.6, 112.8, 111.1, 79.5, 77.5, 47.3, 47.0, 34.9, 27.6, 25.4, 24.3, 23.6, 21.5, 0.8; FTIR (film, υ_{max} cm^{-1}) 2951 (m), 2909 (m), 2847 (m), 2087 (s), 2027 (s), 1966 (m), 1683 (m), 1595 (m), 1339 (m), 1249 (m), 1164 (s); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{28}H_{31}NO_9SiSCo_2Na$ 726.0050, found 726.0026.

Dicobalthexacarbonyl-4-{6-[3-(*tert*-butyldiphenylsilyloxy)prop-1-ynyl]tetrahydropyran-2-ylidene}-1-tosylpiperidine (32) (Wittig method A) was prepared using *N*-tosylpiperidone and phosphonium salt **9** (200 mg, 0.276 mmol). The reaction was stirred for 5 h at −78 °C before warming to room temperature and quenching. Following complexation in DCM and chromatography (100:1:10 petroleum ether/Et_3N/Et_2O), complex **32** (117 mg, 47% from **9**) was isolated as a red metallic solid: mp >300 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.07 (9H, s), 1.47−1.61 (2H, m), 1.78−1.95 (3H, m), 2.26 (2H, t, J = 5.5 Hz), 2.39−2.63 (3H, m), 2.43 (3H, s), 2.76−3.12 (4H, m), 4.42 (1H, dd, J = 10.5, 2.0 Hz), 4.76 (2H, s,), 7.28−7.34 (2H, m), 7.37−7.48 (6H, m), 7.59−7.66 (2H, m), 7.67−7.76 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.5 (br), 146.0, 143.2, 135.4, 133.3, 132.7, 129.8, 129.5, 127.7, 127.5, 112.5, 95.8, 94.9, 79.2, 64.5, 47.2, 46.9, 33.5, 27.4, 26.4, 25.0, 24.0, 23.3, 21.4, 19.0; FTIR (film, υ_{max} cm^{-1}) 3073 (m), 2933 (s), 2860 (s), 2093 (s), 2051 (s), 1683 (m), 1599 (m), 1464 (m), 1429 (m), 1357 (m), 1340 (m), 1166 (s); HRMS (FAB) *m/z* (M^+ + Na) calcd for $C_{42}H_{43}NO_{10}SiSCo_2Na$ 922.0939, found 922.0953.

Dicobalthexacarbonyl-*tert*-butyl-{3-[6-(1,4-dioxaspiro[4.5]dec-8-ylidene)tetrahydropyran-2-yl]prop-2-ynyloxy}-diphenylsilane (33) (Wittig method A) was prepared using 1,4-cyclohexanedione monoethylene ketal and phosphonium salt **9** (308 mg, 0.42 mmol). The reaction was stirred for 5 h at −78 °C before warming to room temperature and quenching. Following complexation in DCM and chromatography (100:1:10 petroleum ether/Et_3N/Et_2O), complex **33** (170 mg, 50% from 9) was isolated as a orange-red oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (9H, s), 1.46−1.69 (6H, m), 1.78−2.01 (3H, m), 2.17−2.27 (2H, m), 2.32−2.44 (2H, m), 2.50−2.63 (1H, m), 3.96 (4H, s), 4.42−4.51 (1H, m), 4.80 (2H, s), 7.35−7.49 (6H, m), 7.67−7.75 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.7 (br), 144.8, 135.6, 133.0, 129.8, 127.8, 116.6, 109.1, 96.5, 94.9, 79.4, 64.6, 64.3, 36.0, 35.3, 33.9, 26.6, 25.5, 24.3, 24.0, 23.1, 19.2; FTIR (film, υ_{max} cm^{-1}) 3072 (w), 3051 (w), 2945 (m), 2888 (m), 2859 (m), 2093 (s), 2052 (s), 2030 (s), 1682 (w), 1615 (w), 1590 (w), 1473 (w), 1428 (m), 1364 (w), 1229 (w), 1138 (m), 1113 (m), 1094 (m), 1063 (m), 1034 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{38}H_{41}O_{10}SiCo_2$ 803.1133, found 803.1146.

General Procedure for Et_2AlCl-Promoted Rearrangement of Cyclic Enol Ethers to α-Spirocyclohexanones 34−41 and α-Alkylcyclopentanones 49 and 50. To a solution of the complex (1 equiv) in DCM (0.02 M) at −78 °C was added diethylaluminum chloride (3.0 equiv, 1 M in hexanes). The reaction was warmed to −30 °C and stirred for the indicated amount of time, quenched by addition of water, and then warmed to ambient temperature. The mixture was poured into water and extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude reaction mixture was then chromatographed on silica gel, eluting with a petroleum ether/Et_2O system of appropriate polarity.

Dicobalthexacarbonyl-5-(phenylethynyl)spiro[5.5]-undecan-1-one (34) was isolated from **26** (17 mg, 0.031 mmol) with a reaction time of 16 h as a dark red solid (16 mg, 93%) (chromatography, 20:1 petroleum ether/Et_2O): mp 118−120 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.73−1.07 (2H, m), 1.24−1.97 (8H, m), 2.02−2.35 (5H, m), 2.76 (1H, td, J = 12.5, 6.0 Hz), 3.19 (1H, dd, J = 11.0, 3.5 Hz), 7.23−7.42 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 199.9 (br), 138.8, 129.1, 128.7, 127.5, 99.3, 95.6, 55.8, 22.4, 53.0, 37.6, 32.0, 30.6, 29.0, 26.3, 25.3, 22.8; FTIR (film, υ_{max} cm^{-1}) 3077 (w), 2935 (w), 2858 (w), 2088 (s), 2049 (s), 2020 (s), 1707 (s), 1599 (w), 1442 (w); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{25}H_{23}O_7Co_2$ 553.0108, found 553.0110.

Dicobalthexacarbonyl-5-hex-1-ynylspiro[5.5]undecan-1-one (35) was isolated from **27** (106 mg, 0.20 mmol) with a reaction time of 15 h as a dark red oil (87 mg, 82%) (chromatography, 10:1 petroleum ether/Et_2O): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (3H, t, J = 7 Hz), 1.02−1.22 (2H, m), 1.35−1.85 (11H, m), 1.95−2.33 (6H, m), 2.71 (1H, td, J = 12.5, 6.5 Hz), 2.87 (1H, dd, J = 16.5, 6.5 Hz), 2.77−3.00 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 200.1 (br), 101.1, 98.4, 55.6, 53.5, 37.7, 35.0, 33.9, 32.1, 30.7, 26.2, 29.6, 22.8, 22.7, 22.6, 13.9; FTIR (film, υ_{max} cm^{-1}) 2948 (s), 2933 (s), 2859 (s), 2086 (s), 2044 (s), 2012 (s), 1965 (s), 1711 (s); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{23}H_{27}Co_2O_7$ 533.0421, found 533.0414.

Dicobalthexacarbonyl-5-(trimethylsilylethynyl)spiro[5.5]undecan-1-one (36) was isolated from **28** (46 mg, 0.084 mmol) with a reaction time of 15 h as a dark red solid (41 mg, 88%) (chromatography, 10:1 petroleum ether/Et_2O): mp 91−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (9H, s), 1.07−1.28 (2H, m), 1.54−1.81 (7H, m), 1.97 (1H, d, J = 9.0 Hz), 2.11−2.27 (4H, m), 2.31 (1H, dt, J =12.5, 4.5 Hz), 2.72 (1H, dt, J = 6.0, 2.5 Hz), 2.99 (1H, dd, J = 8.0, 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 200.5 (br), 110.7, 81.5, 54.6, 54.3, 37.6, 32.1, 31.2, 29.6, 26.1, 25.5, 22.7, 22.2, 1.5; FTIR (film, υ_{max} cm^{-1}) 2934 (s), 2859 (m), 2084 (s), 2043 (s), 2014 (s), 1709 (s), 1568 (m), 1450 (m), 1250 (s); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{22}H_{26}O_7Co_2SiNa$ 571.0009, found 571.0013.

Dicobalthexacarbonyl-5-[3-(*tert*-butyldiphenylsilyloxy)prop-1-ynyl]spiro[5.5]undecan-1-one (37) was isolated from **29** (64 mg, 0.086 mmol) with a reaction time of 19 h as a orange-red oil (62 mg, 97%) (chromatography, 10:1 petroleum

ether/Et_2O): ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (3H, m), 1.10 (9H, s), 1.27−1.81 (6H, m), 1.84−1.91 (1H, m), 1.93−2.21 (4H, m), 2.27 (1H, dt, J = 12.5, 4.5 Hz), 2.66 (1H, td, J = 12.5, 6.0 Hz), 2.93 (1H, dd, J = 10.5, 4.0 Hz), 4.79 (2H, s), 7.38−7.49 (6H, m), 7.70−7.75 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.7, 199.9 (br), 135.6, 132.7, 129.9, 127.8, 97.6, 97.0, 65.8, 55.0, 53.2, 37.6, 31.9, 31.0, 29.6, 26.6, 26.0, 25.6, 22.6, 22.4, 19.1; FTIR (film, υ_{max} cm^{-1}) 3072 (w), 2933 (s), 2859 (s), 2089 (s), 2048 (s), 2024 (s), 1707 (s), 1590 (w), 1448 (m), 1428 (s), 1106 (s), 1055 (s); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{36}H_{38}O_8SiCo_2Na$ 767.0898, found 767.0873.

Dicobalthexacarbonyl-11-(phenylethynyl)-3-tosyl-3-azaspiro[5.5]undecan-7-one (38) was isolated from **30** (168 mg, 0.237 mmol) with a reaction time of 24 h as a dark red-brown oil (146 mg, 87%) (chromatography, 3:1 petroleum ether/Et_2O): ^1H NMR (400 MHz, $CDCl_3$) δ 1.72−1.90 (2H, m), 1.96−2.44 (9H, m), 2.40 (3H, s), 2.53−2.63 (1H, m), 3.22−3.28 (1H, m), 3.42−3.49 (1H, m), 3.57−3.65 (1H, m), 7.23−7.28 (2H, m), 7.30−7.41 (5H, m), 7.47−7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4, 199.2 (br), 143.5, 138.0, 132.7, 129.6, 129.0, 128.7, 127.9, 127.5, 96.7, 95.5, 52.7, 51.4, 43.3, 43.0, 37.6, 31.2, 30.0, 28.3, 25.2, 21.5; FTIR (film, υ_{max} cm^{-1}) 3075 (w), 2956 (w), 2859 (w), 2090 (s), 2051 (s), 2023 (s), 1706 (m), 1598 (w), 1471 (w), 1342 (w), 1166 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{31}H_{28}NO_9SCo_2$ 708.0149, found 708.0148.

Dicobalthexacarbonyl-3-tosyl-11-(trimethylsilylethynyl)-3-azaspiro[5.5]undecan-7-one (39) was isolated from **31** (190 mg, 0.27 mmol) with a reaction time of 20 h as a dark red-brown solid (161 mg, 85%) (chromatography, 10:1 petroleum ether/Et_2O): mp dec 189−190 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.43 (9H, s), 1.68−1.82 (1H, m), 1.89−2.31 (9H, m), 2.42 (3H, s), 2.49−2.61 (2H, m), 3.09 (1H, dd, J = 10.5, 4.0 Hz), 3.67−3.76 (2H, m), 7.25−7.32 (2H, m), 7.55−7.61 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4, 200.2 (br), 143.6, 132.6, 129.7, 127.6, 109.5, 80.8, 54.2, 51.7, 43.3, 42.9, 37.8, 31.6, 30.7, 28.6, 25.6, 21.5, 1.6; FTIR (film, υ_{max} cm^{-1}) 2958 (w), 2871 (w), 2085 (s), 2045 (s), 2016 (s), 1706 (m), 1598 (w), 1560 (w), 1342 (w), 1250 (w), 1166 (m); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{28}H_{32}NO_9SiSCo_2$ 704.0231, found 704.0261.

Dicobalthexacarbonyl-11-[3-(*tert*-butyldiphenylsilyloxy)prop-1-ynyl]-3-tosyl-3-azaspiro[5.5]undecan-7-one (40) was isolated from **32** (92 mg, 0.102 mmol) with a reaction time of 24 h as a dark red oil (86 mg, 94%) (chromatography, 10:1 petroleum ether/Et_2O): ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (9H, s), 1.71−1.88 (3H, m), 1.90−2.01 (1H, m), 2.05−2.24 (5H, m), 2.24−2.33 (1H, m), 2.41 (3H, s), 2.37−2.50 (2H, m), 2.96 (1H, dd, J = 9.0, 3.5 Hz), 3.52−3.61 (2H, m), 4.79 (1H, d, J = 13.5 Hz), 4.84 (1H, d, J = 14.0 Hz), 7.26 (2H, d, J = 8.0 Hz), 7.41−7.50 (6H, m), 7.55 (2H, d, J = 8.0 Hz), 7.71−7.76 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.2, 199.5 (br), 143.5, 135.6, 132.6, 132.5, 132.4, 130.0, 129.7, 127.9, 127.6, 98.5, 94.6, 65.2, 52.1, 43.3, 43.1, 37.7, 31.8, 30.2, 29.0, 26.8, 25.0, 21.5, 19.2; FTIR (film, υ_{max} cm^{-1}) 3072 (w), 2933 (m), 2859 (m), 2090 (s), 2050 (s), 2025 (s), 1706 (s), 1598 (w), 1472 (m), 1429 (m), 1356 (m), 1343 (m), 1167 (s); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{42}H_{43}NO_{10}NaSiSCo_2$ 922.0939, found 922.0968.

Dicobalthexacarbonyl-13-[3-(*tert*-butyldiphenylsilyloxy)prop-1-ynyl]-1,4-dioxadispiro[4.2.5.2]pentadecan-9-one (41) was isolated from **33** (54 mg, 0.070 mmol) with a reaction time of 16 h as a dark orange-red oil (39 mg, 70%) (chromatography, 5:1 petroleum ether/Et_2O): ^1H NMR (250 MHz, $CDCl_3$) δ 1.08 (9H, s), 1.02−3.32 (13H, m), 2.69 (1H, td, J = 12.5, 5.5 Hz), 2.98 (1H, dd, J = 11.0, 3.5 Hz), 3.07−3.21 (2H, m), 3.65−3.74 (2H, m), 4.90 (1H, d, J = 14.5 Hz), 5.06 (1H, d, J = 14.0 Hz), 7.34−7.48 (6H, m), 7.68−7.79 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 214.1, 199.9 (br), 135.6, 135.6, 133.0, 129.7, 127.7, 97.7, 96.4, 65.5, 64.2, 63.4, 54.0, 53.2, 37.4, 32.0, 31.5, 31.1, 29.4, 27.0, 26.6, 26.2, 19.1; FTIR (film, υ_{max} cm^{-1}) 3073 (w), 2934 (m), 2860 (m), 2088 (s), 2047 (s), 2023 (s), 1706 (m), 1590 (w), 1473 (w), 1429 (w), 1111 (m), 1087 (m), 1049 (m); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{38}H_{40}O_{10}NaSiCo_2$ 825.0952, found 825.0912.

2-Methoxy-5-(2-phenylethynyl)tetrahydrofuran (43). Reaction of 2-methoxy-5-(phenylsulfonyl)tetrahydrofuran (4 g, 16.51 mmol) with the alkynlaluminum reagent prepared from phenyl acetylene gave compound **43** (2.91 g, 87%) isolated as a colorless oil containing an inseparable mixture of diastereomers (cis:trans 1:1, isomers not elucidated) (chromatography, 10:1 petroleum ether/EtOAc): ^1H NMR (250 MHz, $CDCl_3$) δ 1.88−2.46 (8H, m), 3.38 (3H, s), 3.43 (3H, s), 4.89−4.97 (2H, m), 5.08 (1H, dd, J = 5.0, 1.0 Hz), 5.15 (1H, dd, J = 5.0, 1.5 Hz), 7.26−7.35 (6H, m), 7.40−7.48 (4H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 131.7 (×2), 128.4, 128.2 (×3), 122.9, 122.6, 105.4, 105.3, 89.7, 88.1, 84.9, 84.1, 68.7, 67.6, 55.0, 54.6, 33.0, 32.2, 31.5, 31.3; FTIR (film, υ_{max} cm^{-1}) 3057 (w), 2989 (m), 2953 (m), 2829 (m), 1598 (w), 1490 (m), 1442 (m), 1356 (m), 1206 (m), 1100 (s), 1028 (s); HRMS (ES) *m/z* (M^+) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0992.

2-Hex-1-ynyl-5-methoxytetrahydrofuran (44). Reaction of 2-methoxy-5-(phenylsulfonyl)tetrahydrofuran (1.74 g, 7.2 mmol) with the alkynlaluminum reagent prepared from 1-hexyne gave compound **44** (1.10 g, 84%) isolated as a colorless oil containing an inseparable mixture of diastereomers (cis:trans 1:1, isomers not elucidated) (chromatography, 10:1 petroleum ether/EtOAc): ^1H NMR (250 MHz, $CDCl_3$) δ 0.90 (6H, t, J = 7.0 Hz), 1.34−1.55 (8H, m), 1.80−2.26 (12H, m), 3.34 (3H, s), 3.38 (3H, s), 4.68 (2H, m), 5.00 (1H, app d, J = 5.5 Hz), 5.06 (1H, app d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.1 (×2), 85.8, 84.9, 80.5, 79.0, 68.7, 67.4, 54.8, 54.5, 32.9, 32.2, 31.6, 31.4, 30.6 (×2), 21.9, 21.8, 18.4 (×2) 13.5 (×2); FTIR (film, υ_{max} cm^{-1}) 2932 (m), 2874 (s), 2830 (s), 1458 (m), 1356 (m), 1207 (s), 1161 (w), 1102 (s), 1033 (s); HRMS (ES) *m/z* (M^+) calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1302.

Triphenyl(5-(2-phenylethynyl)tetrahydrofuran-2-yl)-phosphonium tetrafluoroborate (45) was prepared according to the general procedure for Wittig salt formation as described above using acetal **43** (2.91 g, 14.38 mmol) and isolated as a pale yellow solid containing an inseparable 1.2:1 mixture of diastereomers (7.13 g, 95%): ^1H NMR (250 MHz, $CDCl_3$) δ 1.75−1.92 (2H, m), 1.98−2.12 (1H, m), 2.14−2.39 (2H, m), 2.48−2.64 (1H, m), 2.86−3.15 (2H, m), 4.57 (1H, app t, J = 6.5 Hz), 5.10 (1H, dd, J = 7.0, 5.0 Hz), 5.95−6.08 (2H, m), 7.19−7.88 (40H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) see Supporting Information; FTIR (film, υ_{max} cm^{-1}) 3650 (w), 3554 (w), 3063 (m), 2954 (m), 1976 (w), 1905 (w), 1826 (w), 1690 (w), 1588 (m), 1490 (m), 1440 (s); HRMS (ES) *m/z* ($M^+ - BF_4$) calcd for $C_{30}H_{26}OP$ 433.1721, found 433.1719.

(5-(Hex-1-ynyl)tetrahydrofuran-2-yl)triphenylphosphonium tetrafluoroborate (46) was prepared according to the general procedure for Wittig salt formation as described above using cyclic acetal **44** (1.10 g, 5.99 mmol) and isolated as a pale yellow solid containing an inseparable 1.2:1 mixture of diastereomers (2.65 g, 89%). ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 7.3 Hz), 1.25−1.39 (6H, m), 1.43−1.49 (2H, m), 1.60−1.66 (2H, m), 1.89−1.95 (1H, m), 2.01 (2H, tt, J = 7.0, 2.0 Hz), 2.07−2.25 (4H, m), 2.38−2.44 (1H, m), 2.83−3.01 (2H, m), 4.34 (1H, m), 4.83 (1H, m), 5.88−5.95 (2H, m), 7.65−7.83 (30H, m); ^{13}C NMR (125 MHz, $CDCl_3$) see Supporting Information; FTIR (film, υ_{max} cm^{-1}) 3064 (w), 2957 (m), 2872 (s), 1588 (s), 1440 (s), 1113 (s), 1057 (w); HRMS (ES) *m/z* ($M^+ - BF_4$) calcd for $C_{28}H_{30}OP$ 413.2034, found 413.2022.

(*E*/*Z*)-Dicobalthexacarbonyl-2-benzylidene-5-(2-phenylethynyl)tetrahydrofuran (47) (Wittig method B) was prepared using freshly distilled benzaldehyde and phosphonium salt **45** (200 mg, 0.38 mmol). Following complexation in DCM and chromatography (10:1 petroleum ether/Et_2O), complex **47** (128 mg, 60% from 45) was isolated as a dark red oil as an inseparable 2.3:1 mixture of isomers (*E*/*Z*-isomers not elucidated): ^1H NMR (250 MHz, $CDCl_3$) δ 1.88−2.10 (2H, m), 2.46−2.68 (2H, m), 2.84−3.10 (4H, m), 5.21−5.26 (1H, m), 5.61 (1H, app t, J = 7.0 Hz), 5.77 (1H, dd, J = 8.0, 6.0 Hz), 5.90−5.96 (1H, m), 6.95−7.60 (20H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.0 (br), 157.9, 156.0, 137.5, 137.4, 136.4, 129.8, 129.7 (×2),

128.9 (×2), 128.4 (×2), 128.0 (×2), 127.3, 127.1(×2), 124.8, 99.9, 97.9, 95.5, 94.5, 91.4, 91.2, 84.0, 80.6, 33.1, 32.4, 31.6, 28.9; FTIR (film, υ_{max} cm^{-1}) 3058 (w), 3024 (w), 2092 (s), 2054 (s), 2024 (s), 1668 (m), 1600 (w), 1484 (w), 1444 (w), 1224 (w), 1128 (m); HRMS (EI) *m/z* (M^+) calcd for $C_{25}H_{16}O_7Co_2$ 545.9560, found 545.9543.

(*E/Z*)-Dicobalthexacarbonyl-2-benzylidene-5-hex-1-ynyltetrahydrofuran (48) (Wittig method B) was prepared using freshly distilled benzaldehyde and phosphonium salt **46** (200 mg, 0.40 mmol). Following complexation in DCM and chromatography (100:1 petroleum ether/Et_2O), complex **48** (73 mg, 35% from 46) was isolated as a dark red oil as an inseparable 2:1 mixture of isomers (*E/Z*-isomers not elucidated). ^1H NMR (250 MHz, $CDCl_3$) δ 0.92 (3H, t, J = 7.2 Hz), 0.98 (3H, t, J = 7.3 Hz), 1.43−1.55 (5H, m), 1.63−1.75 (4H, m), 1.85−2.03 (2H, m), 2.24 (1H, m), 2.42−2.54 (2H, m), 2.83−3.04 (6H, m), 5.27 (1H, s), 5.48 (1H, t, J = 6.6 Hz), 5.63 (1H, app dd, J = 7.9, 6.4 Hz), 5.94 (1H, app s), 7.03−7.58 (10H, m); ^{13}C NMR (125 MHz, $CDCl_3$) (major isomer) δ 199.7 (br), 156.1, 136.5, 128.0 (×2), 127.3 (×2), 124.7, 97.7, 83.9, 34.0, 33.8, 32.2, 31.5, 22.8, 13.9; (minor isomer) δ 199.7 (br), 156.1, 136.5, 128.3 (×2), 128.2 (×2), 127.0, 99.7, 80.5, 32.9, 30.8, 30.5, 28.7, 18.5, 13.6; FTIR (film, υ_{max} cm^{-1}) 2960 (s), 2933 (s), 2874 (s), 2091 (s), 2858 (s), 2023 (s), 1674 (s), 1597 (w), 1493 (s), 1448 (m), 1364 (m), 1285 (m), 1132 (w), 1017 (w); HRMS (ES) *m/z* (M^+ + H) calcd for $C_{23}H_{21}O_7Co_2$ 526.9951, found 526.9937.

***trans*-Dicobalthexacarbonyl-2-phenyl-3-(2-phenylethynyl)cyclopentanone (*trans*-49).** According to the general procedure, with a reaction time of 3 h, the title compound was prepared from **47** (23 mg, 0.042 mmol) as a dark red oil (10 mg, 47%) (chromatography, 10:1 petroleum ether/Et_2O): ^1H NMR (250 MHz, $CDCl_3$) δ 1.82−2.04 (1H, m), 2.39−2.74 (3H, m), 3.23 (1H, d, J = 11.5 Hz), 4.04 (1H, td, J = 11.5, 6.0 Hz), 7.01−7.35 (10H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 215.5, 199.2 (br), 137.6, 136.7, 128.9 (×3), 128.6, 127.5 (×2), 99.7, 92.9, 64.2, 47.5, 38.4, 30.7; FTIR (film, υ_{max} cm^{-1}) 3062 (w), 3032 (w), 2970 (w), 2089 (s), 2049 (s), 2021 (s), 1748 (s), 1604 (w), 1498 (w), 1482 (w), 1454 (w), 1442 (w), 1129 (w); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{25}H_{16}O_7NaCo_2$ 568.9458, found 568.9480.

***trans*-Dicobalthexacarbonyl-3-hex-1-ynyl-2-phenylcyclopentanone (*trans*-50).** According to the general procedure, with a reaction time of 4 h, the title compound was prepared from **48** (31 mg, 0.058 mmol) as a dark red oil (16 mg, 57%) (chromatography, 50:1 petroleum ether/Et_2O): ^1H NMR (250 MHz, $CDCl_3$) δ 0.80 (3H, app t, J = 7.2 Hz), 1.16−1.25 (4H, m), 1.88−2.07 (1H, m), 2.26 (2H, m), 2.44−2.75 (3H, m), 3.16 (1H, app d, J = 11.3 Hz), 3.83 (1H, td, J = 11.6, 5.2 Hz), 7.15−7.40 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.1, 200.0 (br), 136.5, 128.9 (×2), 127.7, 101.1, 99.4, 64.4, 47.3, 37.9, 33.8, 33.7, 29.9, 22.6, 13.7; FTIR (film, υ_{max} cm^{-1}) 2961 (s), 2960 (s), 2875 (s), 2087 (s), 2044 (s), 2015 (w), 1749 (s), 1604 (m), 1498 (s), 1453 (m), 1261 (m), 1099 (w); HRMS (ES) *m/z* (M^+ + Na) calcd for $C_{23}H_{20}O_7NaCo_2$ 548.9771, found 548.9759.

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Supporting Information Available: ^1H 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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