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Joseph DiMartino

James R. Green
University of Windsor

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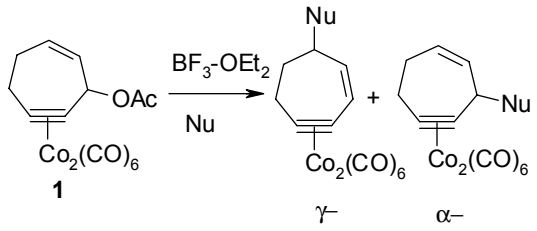
* Manuscript (including Graphical Abstract)

Lewis and Protic Acid Mediated Nicholas Reactions of 3-Acetoxycyclohept-1-en-4-ynedicobalt Hexacarbonyl: Site Selectivity of Nucleophile Incorporation

Joseph DiMartino and James R. Green*



Kinetic Product:
Predominantly γ-

Thermodynamic product:
Exclusively γ-

Lewis and Protic Acid Mediated Nicholas Reactions of 3-Acetoxycyclohept-1-en-4-ynedicobalt Hexacarbonyl: Site Selectivity of Nucleophile Incorporation

Joseph DiMartino and James R. Green*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada

Keywords: Nicholas reaction, cobalt-alkyne complexes, cycloheptyne, propargyl cations

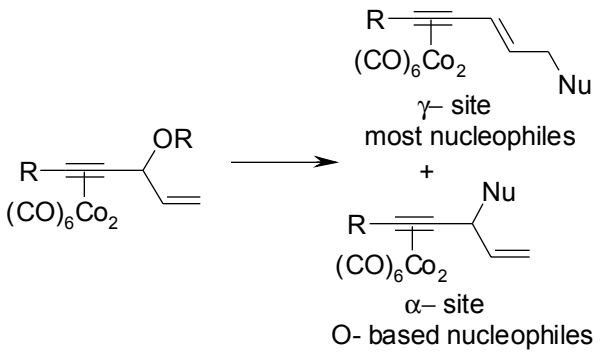
Abstract- Nicholas reactions on the cation derived from the cyclic allylic acetate alkynedicobalt complex **1** favour the γ- site kinetically for most nucleophiles, with increasing amounts of α-products in cases with greater nucleophilicity. Some regiocontrol in introduction of a specific nucleophilic fragment is possible by using different nucleophiles. Under conditions where reversibility is possible, the thermodynamically favoured site is exclusively γ-.

1. Introduction

Propargyl cation dicobalt hexacarbonyl complexes are one of the most widely employed transition metal stabilized reactive intermediates in organic synthesis; their chemistry is often referred to as the Nicholas reaction.[1] These cations, which may stem from alkynedicobalt complexes with propargylic leaving groups and a protic or Lewis acid, or from enyne-$Co_2(CO)_6$ complexes and an electrophile,[2] normally substitute exclusively at the propargylic site, unless the

* Corresponding Author. Tel.: 519-253-3000, Ext. 3545; fax: 519-973-7098; e-mail: jgreen@uwindsor.ca

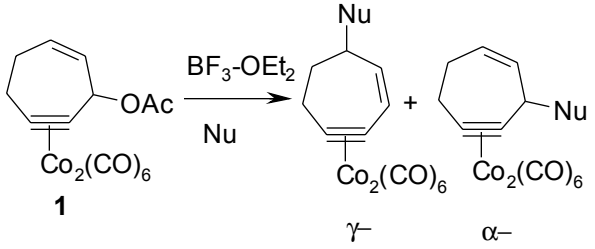
cation is also allylic. In these allylic/propargylic situations, substitution has been found to occur predominantly at the site remote to the alkyne-$Co_2(CO)_6$ unit (γ-site).[3] Exceptions exist however, particularly where intramolecular nucleophilic attack reactions are entropically driven towards the α- site;[4] in some cases with nucleophiles which are oxygen based, α- substitution is also observed (Scheme 1). [2a,5]



Scheme 1

While previous studies of Nicholas reactions of allylic substrates have been focussed on acyclic cations or cyclization reactions, the analogous question for cyclic cations has not been addressed to our knowledge. We have interest in this matter from several perspectives. Our group, and other groups, have been interested in the preparation and reactivity of cycloheptynedicobalt complexes.[6,7,8] We have been able to incorporate nucleophiles γ- with respect to the alkynedicobalt unit in tandem 4+3 cycloaddition / trapping reactions, but the list of participating nucleophiles in the process is quite restricted.[6a] Substitution at the remote (γ-) position in the cycloheptenyne-$Co_2(CO)_6$ complexes (Scheme 2) would open up the ability to employ the now nucleophilic alkene function in annulation reactions with any highly electrophilic groups contained within the γ- substituent, ultimately giving fused 7,5- and 7,6- ring systems. In addition, we have an interest in clean α- substitution reactions on these complexes for facilitation of cycloaddition reactions employing the alkynedicobalt function.[9] As a result, we

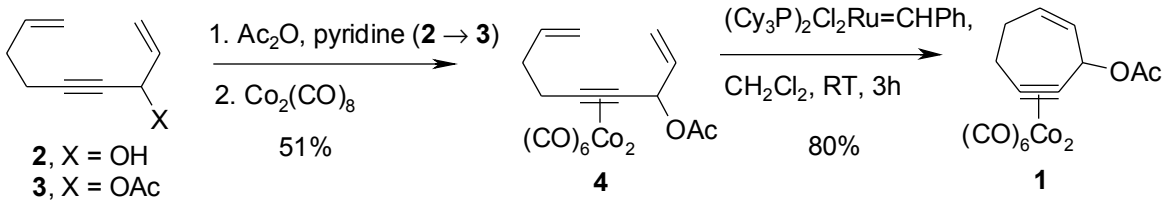
have deemed it of importance to study the Nicholas substitution reactions of cycloheptyne-allyl acetate complex **1**, with a range of nucleophiles.



Scheme 2

2. Results and Discussion

Cycloheptyne-allyl acetate complex **1** was prepared in straightforward fashion from the known allyl propargyl alcohol **2** (Scheme 3).[10] Standard acetylation of **2**, affording acetate **3**, followed by complexation with $Co_2(CO)_8$, gave **4** (51 % yield, two steps). Ring closing metathesis, employing 10 mol% of $(Cy_3P)_2Cl_2Ru$=CHPh (Grubbs' I catalyst), afforded **1** in 80% yield.[11]



Scheme 3

With the desired substrate in hand, we chose to investigate its reaction with 1,3,5-trimethoxybenzene in order to optimize the conditions of reaction. In CH_2Cl_2 solvent (0.05 M), and with excess BF_3-OEt_2 present (10 equiv), **1** underwent reaction with 1,3,5-trimethoxybenzene at temperatures as low as -30 ^oC to give mixtures of the γ- substitution (C-7 substitution) product **5a** and the α- substitution (C-3 substitution) product **5b** (Figure 1). Variation of reaction temperature revealed that the γ- substitution product predominated in all

cases, with optimal yields of condensation products realized at -10 °C (Table 1) with BF_3-OEt_2 as Lewis acid. Curiously, the amount of α- substitution *decreased* with increasing temperature, from 41% of the products -30 °C to 14% of the product composition at 23 °C. Changing the Lewis acid from BF_3-OEt_2 to $SnCl_4$ gave similar results at -10 °C, with a marginally inferior yield. Use of Bu_2BOTf as Lewis acid, however, caused extensive unproductive decomposition, even at -30 °C. As a result, the -10 °C, BF_3-OEt_2 combination was chosen as the standard set of conditions and applied in all other cases.

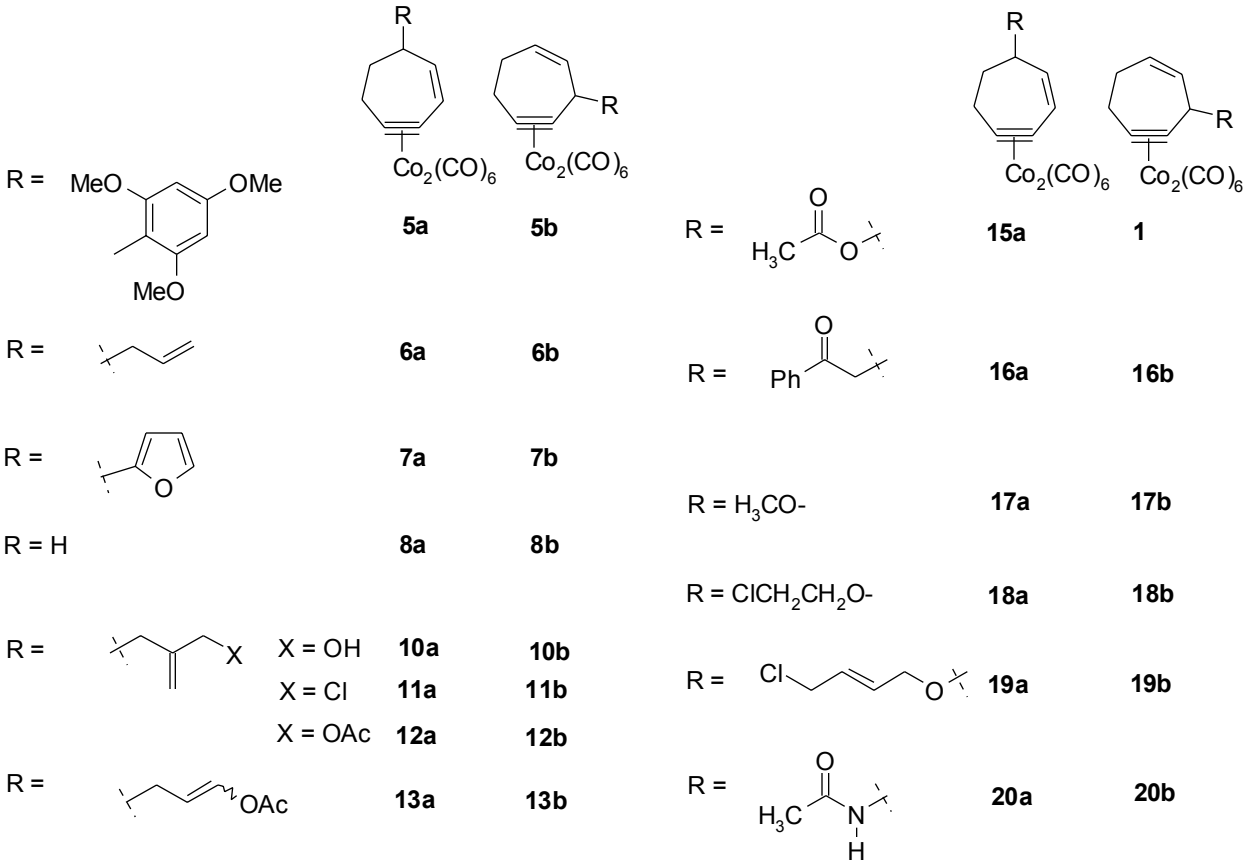


Figure 1. Nicholas reaction products of **1**

Table 1. Reaction of **1** with 1,3,5-trimethoxybenzene

Conditions	*Yield **5a/5b** (%)*	*γ-:α- ratio*
BF_3-OEt_2, -30 ^oC	70	59:41
BF_3-OEt_2, -10 ^oC	86	70:30
BF_3-OEt_2, 0 ^oC	73	81:19
BF_3-OEt_2, 23 ^oC	52	86:14
$SnCl_4$, -10 ^oC	77	76:24
Bu_2BOTf, -30 ^oC	0	-

The change in isomer ratio towards increased amounts of the major, γ-substitution product at higher reaction temperatures suggested the possibility that the results with 1,3,5-trimethoxybenzene were not the consequence of purely kinetic reactivity of the propargyl allyl cation. Past work in our group has shown evidence of reversibility in Nicholas reactions involving this nucleophile,[12] and these results would be consistent with that feature here. In fact, subjecting purified α-substitution product **5b** to the 0 ^oC conditions of reaction (without added 1,3,5-trimethoxybenzene) afforded a **5a**/**5b** mixture (23:77, 67% recovery) along with some decomposition. By contrast, subjecting **5a** to these conditions gave only recovered **5a**. Consequently, allyltrimethylsilane was also investigated as a nucleophile with **1** under varying reaction temperatures (Table 2), as reversibility in this reaction is far less likely. Under analogous concentration and stoichiometry conditions, allyltrimethylsilane afforded γ-substitution product **6a** and α- substitution product **6b.** Once again the yield reached a maximum at -10 ^oC, but in these cases the α- :γ- product ratios remained relatively consistent (81:19 – 84:16) over the temperature range investigated.

Table 2. Reaction of 1 with allyltrimethylsilane

Conditions	*Yield **6a/6b**(%)*	*γ-:α- ratio*
BF_3-OEt_2, -30 ^oC	68	82:18
BF_3-OEt_2, -10 ^oC	83	84:16
BF_3-OEt_2, 0 ^oC	77	81:19
BF_3-OEt_2, 23 ^oC	56	83:17

Several other carbon and hydride based nucleophiles were investigated (Table 3). Allyltributylstannane gave **6a** and **6b** in good yield (74%), but with minimal γ- :α- selectivity (**6a**:**6b** = 50:50). Conversely, furan gave condensation product **7a** through its C-2 site, with almost none of α- condensation product **7b** in evidence (62% yield, **7a**:**7b** = >96:<4)[13]. The overall reduction products **8a** and **8b** could be obtained in fair yield using triethylsilane (54%, **8a**:**8b** = 63:37) or triisopropylsilane (62% yield, **8a**:**8b** = 84:16). The 2-hydroxymethyl-, 2-chloromethyl-, and 2-acetoxymethyl- substituted allylsilanes (**9a**, **9b**, and **9c**, respectively) (Figure 2) afforded analogous products **10a/b**, **11a/b**, and **12a/b**, respectively, with somewhat lower γ-:α- ratios (59:41 – 72:28) relative to allyltrimethylsilane itself. Homoenolate equivalent 1-trimethylsilylallyl acetate gave the enol acetate products **13a** and **13b** (as Z-/E- isomeric mixtures) with relatively high γ- selectivity (65% yield, **13a**:**13b** = 89:11), along with small amounts of elimination product **14** (7%) and γ-acetoxy substitution product **15a** (7%). To our knowledge, this is the first example of a discrete homoenolate equivalent participating directly in a Nicholas reaction, although the cyclization-rearrangement processes of Tanino[14] and Magnus' cyclization-dyotropic rearrangements[15] may be considered specialized cases of homoenolate equivalent reactivity. In addition, complexes with analogous functional group connectivity have been made by radical reactions on enyne complexes.[16] Finally, two acetophenone enolate equivalents were introduced. The trimethylsilyl enol ether of acetophenone underwent reaction with **1** to give **16a** and **16b** in good yield (74%), but the α- condensation product actually predominated slightly with this nucleophile (**16a**:**16b** = 44:56). The enol acetate of acetophenone gave somewhat lower yields (61%, with 19% of **15a**), with the γ- product once again as the major regioisomer (**16a**:**16b** = 72:28).

Table 3. Reaction of **1** with carbon and hydrogen nucleophiles[a]

Nucleophile	*Product*	*Yield (%)*	*γ-:α- ratio*	***15a** (%)*	***14** (%)*
1,3,5-trimethoxybenzene	**5a/5b**	86	70:30		
Allyltrimethylsilane	**6a/6b**	83	84:16		
Allyltributylstannane	**6a/6b**	74	50:50		
Furan	**7a/7b**	62	>96:4		
Et_3SiH	**8a/8b**	54	72:28		
$^{i}Pr_3SiH$	**8a/8b**	62	84:16	3.5	
9a	**10a/10b**	76	59:41		
9b	**11a/11b**	70	72:28		
9c	**12a/12b**	76	64:36		
1-Trimethylsilylallyl acetate	**13a/13b**	65	89[b]:11[c]	7	7
$H_2C{=}C(OSiMe_3)Ph$	**16a/16b**	74	44:56		
$H_2C{=}C(OAc)Ph$	**16a/16b**	61	72:28	19	

[a] Reaction conditions: Nucleophile, 1.5 – 2.0 equiv; solvent, CH_2Cl_2 (0.05 M); temperature, -10 °C; Lewis acid, BF_3-OEt_2 (10 equiv); reaction time, 1h.
[b] **13a** (*E*-:*Z*-) = 38:62
[c] **13b** (*E*-:*Z*-) = 51:49

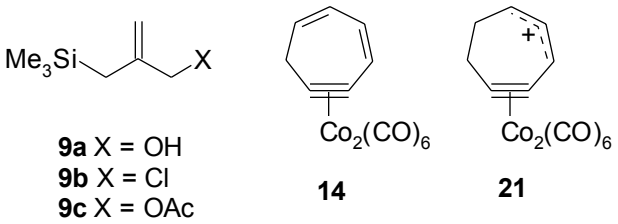


Figure 2

Investigation of heteroatom based nucleophiles was also warranted due to the likelihood of reversibility in the substitution process (Table 4). Under standard conditions, acetic acid could be incorporated with great facility to give **15a** in good yield (79%) exclusively as the γ-substitution product. In this case, abandonment of the standard conditions in favour of neat acetic acid and H_2SO_4 gave superior results (97% yield) for **15a**. Under the standard conditions, methanol, 2-chloroethanol, and 4-chloro-2-buten-1-ol gave **17a** (65%), **18a** (59%), and **19a** (68%), each exclusively as the γ- substitution products. The latter two cases also gave modest amounts of elimination product **14** and γ-acetoxy substitution product **15a.** Again, use of a large excess of nucleophile and H_2SO_4 gave yield improvement for each of the commercially available

alcohols (**17a**, 87%; **18a**, 76%). Attempts to incorporate a nitrogen based nucleophile, acetamide, met with little success under the standard reaction conditions. While a small amount of γ- substitution product **20a** could be obtained (12% yield), the major resulting product was γ-acetoxy substituted **15a** (83% yield); a small amount of elimination product **14** (5% yield) also could be isolated. Conversely, good yields of **20a** (85%) could be realized by resorting to the addition of H_2SO_4 to a solution of **1** in CH_3CN. In no cases have we observed even traces of the heteroatom based α- condensation products **1**, **17b** – **20b** as a result of these protic- or Lewis acid mediated reactions.

Table 4. Reaction of **1** with heteroatom nucleophiles[a]

Nucleophile	*Product*	*Yield (%)*	***15a** (%)*	***14** (%)*
CH_3CO_2H	**15a**	79		
CH_3CO_2H	**15a**	97[b]		
CH_3OH	**17a**	65		
CH_3OH	**17a**	87[b]		
2-chloroethanol	**18a**	59	15	15
2-chloroethanol	**18a**	76[b]		
4-chloro-2-buten-1-ol	**19a**	68	13	4
$CH_3C(O)NH_2$	**20a**	12	83	5
CH_3CN	**20a**	85[b]		

[a] Reaction conditions, unless otherwise stated: Nucleophile, 1.5 – 2.0 equiv; solvent, CH_2Cl_2 (0.05 M); temperature, -10 °C; Lewis acid, BF_3-OEt_2 (10 equiv); reaction time, 1h.
[b] Using H_2SO_4 in place of BF_3-OEt_2 and excess nucleophile.

With the ready availability of γ-acetoxy substitution product **15a**, and the belief that the same cation could be generated from this compound as from **1**, we briefly explored its BF_3-OEt_2 induced Nicholas reactions. Under the otherwise standard conditions, allyltrimethylsilane reacted with **15a** to give **6a** and **6b** (81% yield) in the same ratio as from **1** (**6a**:**6b** = 84:16), strongly suggesting an identical reactive intermediate from the two allyl acetate complexes. Compound **15a** also reacted with 1,3,5-trimethoxybenzene, affording **5a** and **5b** in 80% yield (**5a**:**5b** = 76:24).

The distinction of γ- from α-adducts was readily apparent from the ^{1}H NMR spectra. Noteworthy in this respect were the resonances attributable to the vinyl proton adjacent to the alkyne-$Co_2(CO)_6$ unit in the γ-regioisomer, which appeared as a doublet (J ≈ 10 Hz) at 6.5-6.7 ppm, deshielded by ≥ 0.5 ppm relative to the other alkene protons. The most distinctive features of the analogous spectra of the α- isomers were the allylic and propargylic methine protons (or methylene in **8b**), which resonated at 3.7-4.0 ppm (excepting **5b**). The ^{1}H NMR spectrum of **5b** was also noteworthy in that the resonances for two of the methoxy CH_3's appeared as a broadened signal, which sharpened upon warming and decoalesced to two singlets at -20 ^{o}C. Variable temperature ^{1}H NMR studies established a coalescence T_c of 25 ^{o}C for these methyl group resonances, and a barrier at coalescence of ΔG_c = 15.2 kcal/mol. This process was attributed to restricted rotation about the C_α- aryl C bond, which interchanged the two aryl *ortho* methoxy functions.

Our analysis of the reactivity patterns in this system is as follows. The allyl propargyldicobalt cation **21** generated from either **1** or **15a** reacts in a kinetic fashion with nucleophiles predominantly, but not exclusively, at the site γ- with respect to the alkynedicobalt unit (C-7). We find it particularly instructive that a comparison the γ-: α- selectivities with Mayr's published N (nucleophilicity) values[17] reveals that greater nucleophilicity results in greater amounts of α- attack (Table 5). While the exact correlation between N and γ-: α- ratios probably involves some coincidence and other factors likely contribute,[18] a comparison between similar nucleophiles particularly supports this trend. For example, the less nucleophilic allyltrimethylsilane (N = 1.79, γ-:α- = 84:16) has a much greater preference for the γ- site than allyltributylstannane (N = 5.46, γ-:α- = 50:50). In addition, the less nucleophilic acetophenone enol acetate[19] reacts with greater γ- selectivity (γ-:α- = 72:28) than the more nucleophilic

trimethylsilyl enol ether (N = 6.22, γ-:α- = 44:56). This is consistent with earlier work of Nicholas and Isobe on acyclic systems; low temperature reactions with alcohols and (to a small extent) enol acetates give α- attack kinetically, and these are the most reactive nucleophiles examined by these authors. The comparison of Et_3SiH and $^{i}Pr_3SiH$ suggests that increased γ-selectivity is encouraged by larger nucleophiles, likely as a consequence of the significant steric size of the alkyne-$Co_2(CO)_6$ unit.

Table 5. Nucleophile N values versus γ-:α- ratios

Nucleophile[a]	*N value*	*γ-:α- Ratio*
$H_2C=C(OSiMe_3)Ph$	6.22	44:56
Allyltributylstannane	5.46	50:50
Et_3SiH	3.64	72:28
Allyltrimethylsilane	1.79	84:16
Furan	1.36	>96:4

[a] 1,3,5-Trimethoxybenzene (N = 3.40) is excluded as it is likely not reacting at the kinetic limit

Conversely, the product of thermodynamic reaction, as with the heteroatom based nucleophiles, is clearly exclusively γ-. This is supported by the results of reaction of **5b** and BF_3-OEt_2, and also by the fact that methyl ether **17a** underwent reaction with nucleophile **9a** (66%, 59:41 **10a**:**10b**) under the standard conditions. The conjugation between the alkene function and the complexed alkyne unit in the γ- products, and the assertion that the γ- products are more stable than the α-adducts, are also reflected by a shortened C-3/C-4 single bond length (1.450 Å) in **17a** and a 6.7 kcal/mol (28.0 kJ/mol) energy difference between **17a** and **17b** in DFT calculations (DFT B88-PW91, CAChe®).[20] The reaction of **1** with 1,3,5-trimethoxybenzene itself is neither at the kinetic nor thermodynamic limit.

In summary, the Nicholas reactions on the cation derived from the cyclic allylic acetate alkynedicobalt complex **1** kinetically favour the γ- site for most nucleophiles, with increasing amounts of α- products in cases with greater nucleophilicity. In the introduction of a

specific nucleophilic fragment, some regiocontrol is possible through variation of the nucleophile. The thermodynamically favoured site is exclusively γ-. Work on employing some of the γ- adducts for access to 7,5- and 7,6- ring systems containing the alkynedicobalt unit, by way of cyclization reactions using the alkene function, is in progress and will be reported in due course.

3. Experimental Section

3.1. General Methods

All reaction solvents were used after passage through a solvent purification system from Innovative Technologies. Commercial BF_3-OEt_2 was distilled and stored under nitrogen. All reactions were conducted under a nitrogen atmosphere unless otherwise noted. Flash chromatography was performed as described by Still using silica gel 60 (230-400 mesh).[21]

All new compounds are >95% purity as determined by ^1H and ^{13}C NMR spectroscopy. Reported regioisomeric ratios are on based on the ^1H NMR spectra of crude reaction products. NMR spectra were run at 500 MHz or 300 MHz for ^1H and 125 MHz or 75 MHz for ^{13}C in $CDCl_3$; chemical shifts are given in ppm and coupling constants (*J*) are given in Hz. High resolution mass spectra were run at the McMaster Regional Centre for Mass Spectrometry and the Ohio State Chemistry Mass Spectrometry Facility.

3.2. Hexacarbonyl[μ-η^4-(3-acetoxynona-1,8-dien-4-yne)]dicobalt (4)

To a mixture of alcohol **2** (0.3031 g, 2.23 mmol) and acetic anhydride (1 mL) at 0 ^oC was added pyridine (1 mL). The solution was stirred over a 6 h period and allowed to come to room temperature. The volatiles were removed under reduced pressure, and the resulting residue containing **3** was dissolved in Et_2O (15 mL). An excess amount of $Co_2(CO)_8$ was added and the

solution stirred 12 h at room temperature. The removal of volatiles under reduced pressure followed by flash chromatography (100% petroleum ether – 10:1 petroleum ether:Et_2O) gave acetate complex **4** (0.5239 g, 51% yield) as a red-brown oil; IR (neat, KBr, cm^{-1}): 3085, 2958, 2093, 2050, 2020, 1746; ^1H NMR δ: 6.48 (d, *J* = 6.5, 1H), 5.92 (m, 2H), 5.42 (d, *J* = 17.0, 1H), 5.28 (d, *J* = 10.3, 1H), 5.16 (d, *J* = 17.1, 1H), 5.09 (d, *J* = 10.3, 1H), 2.89 (m, 2H), 2.40 (m, 2H), 2.13 (s, 3H); ^{13}C NMR δ 199.5, 169.8, 137.0, 135.3, 117.3, 115.9, 97.8, 94.5, 74.7, 35.5, 33.0, 20.6. MS EI *m/e* 408 (M^+ - 2CO). HRMS *m/e* for $C_{17}H_{14}Co_2O_8$ calcd (M^+ - 2CO) 407.9454, found 407.9455.

3.3. Hexacarbonyl[μ-η^4-(3-acetoxycyclohept-1-en-4-yne)]dicobalt (1)

To a solution of **4** (0.0577 g, 0.124 mmol) in CH_2Cl_2 (5 mL) was added dichloro(phenylmethylene)bis(tricyclohexylphosphine)ruthenium (1st generation Grubbs' catalyst, 0.0102 g, 10.0 mol%) in CH_2Cl_2 (1 mL). The solution was stirred for 3 h, and subsequently concentrated under reduced pressure. Flash chromatography (20:1 petroleum ether:Et_2O) gave **1** (0.0436 g, 80%) as a red-brown oil; IR (neat, KBr, cm^{-1}) 3035, 2940, 2093, 2051, 2021, 1747; ^1H NMR δ 6.70 (br s, 1H), 5.94 (m, 1H), 5.78 (dt, *J* = 11.2, 2.2, 1H), 3.18 (dt, *J* = 17.1, 4.3, 1H), 3.00 (ddd, *J* = 3.7, 11.4, 17.1, 1H), 2.25 - 2.33 (m, 2H), 2.30 (s, 3H); ^{13}C NMR δ 199.3, 170.4, 134.3, 130.4, 98.0, 93.0, 73.9, 33.2, 27.2, 20.6. MS *m/e* 408 (M^+ -1CO), 380 (M^+ -2CO), 352 (M^+ -3CO), 324 (M^+ - 4CO), 296 (M^+ -5CO), 268 (M^+ -6CO); HRMS *m/e* for $C_{15}H_{10}Co_2O_8$ calcd (M^+ -1CO) 407.9090, found 407.9103.

3.3. General Procedure: Reactions of the Cycloheptenyne Dicobalt Complex with Carbon–and Heteroatom–Based Nucleophiles

To a solution of the nucleophile (1.5 -2.0 equiv) and cycloheptenyne **1** in CH_2Cl_2 (0.05 M) at -10^{o}C was added BF_3-OEt_2 (10 equiv) over 30 min as a solution in CH_2Cl_2 (1.0 M). The solution

was stirred for 1 h and followed by addition of aqueous sodium bicarbonate. A typical workup was performed. The crude product was purified by flash chromatography

3.3.1 Hexacarbonyl[μ–η^4–(7–(2,4,6-trimethoxyphenyl)cyclohept–1–en–3–yne)] dicobalt (5a) and Hexacarbonyl[μ–η^4–(3–(2,4,6-trimethoxyphenyl)cyclohept–1–en–4–yne)] dicobalt (5b)

A solution of cycloheptenyne **1** (0.0385 g, 0.0883 mmol) and 1,3,5–trimethoxybenzene (0.0297 g, 0.1766 mmol) in CH_2Cl_2 (2 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.11 mL, 0.88 mmol) via the **General Procedure**. The product was purified by flash chromatography (25:1 petroleum ether: Et_2O) gave **5a** and **5b** (0.0412 g, 86%, **5a:5b** = 70:30) as a red–brown oil. Careful repeated TLC afforded (in order of elution) **5b** followed by **5a**. **5a** IR (neat, KBr, cm^{-1}): 2925, 2851, 2087, 2017, 1609, 1385; ^1H NMR δ: 6.46 (d, *J* = 9.8, 1H), 6.14 (s, 2H), 5.97 (dd, *J* = 2.7, 9.9, 1H), 4.03 (m, 1H), 3.79 (s, 9H), 3.35 (m, 1H), 3.16 (m, 1H), 2.19 (m, 1H), 1.82 (m, 1H); ^{13}C δ: 200.0, 159.0, 143.1, 123.7, 116.0, 99.3, 91.5, 89.7, 55.8, 55.5, 38.0, 35.9, 31.4, 24.3; MS EI *m/e*: 544 (M^+), 516 (M^+ -1CO), 488 (M^+ -2CO), 460 (M^+ -3CO), 432 (M^+ –4CO), 404 (M^+-5CO), 376 (M^+-6CO). HRMS *m/e* for $C_{22}H_{18}Co_2O_9$ calcd (M^+) 543.9615, found 543.9609. **5b** IR (neat, KBr, cm^{-1}): 2926, 2085, 2043, 2014, 1733, 1609; ^1H NMR δ: 6.22 (m, 1H), 6.17 (s, 2H), 5.88 (m, 1H), 5.63 (s, 1H), 3.83 (s, 3H), 3.79 (br s, 6H), 3.24 (m, 1H), 3.03 (m, 1H), 2.41 (m, 2H); ^{13}C NMR δ: 200.3, 160.4, 137.4, 128.4, 111.0, 101.0, 100.2, 91.2, 90.2, 55.5, 54.3, 38.5, 34.5, 27.3. MS EI *m/e*: 544 (M^+), 516 (M^+ -1CO), 488 (M^+ -2CO), 460 (M^+ -3CO), 432 (M^+ –4CO), 404 (M^+-5CO), 376 (M^+-6CO). HRMS *m/e* for $C_{22}H_{18}Co_2O_9$ calcd (M^+-CO) 515.9666, found 515.9666.

Reaction of 5b with BF_3-OEt_2

To a 0 ^oC solution of **5b** (0.0281 g, 0.0517 mmol) in CH_2Cl_2 (4 mL) was added BF_3-OEt_2 (65 μL, 0.52 mmol). After stirring for 1 h at 0 ^oC, $NH_4Cl_{(aq)}$ was added and the reaction was

subjected to a conventional workup. Flash chromatography (20:1 petroleum ether : Et_2O) gave **5a** and **5b** (0.0189, 67% recovery, **5a:5b** = 23:77).

3.3.2 Hexacarbonyl[μ–η^4–(7–allylcyclohept–1–en–3–yne)]dicobalt (6a) and Hexacarbonyl[μ–η^4–(3– allylcyclohept–1–en–4–yne)]dicobalt (6b)

A solution if cycloheptenyne **1** (0.0817 g, 0.187 mmol) and allyltrimethylsilane (45 μL, 0.28 mmol) in CH_2Cl_2 (3.7 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.24 mL, 1.9 mmol) via the **General Procedure**. Flash chromatography (25:1 petroleum ether: Et_2O) resulted in the co–elution of **6a** and **6b** (0.0650 g, 83%, **6a**:**6b** = 84:16) as a red–brown oil. IR (neat, KBr, cm^{-1}): 3015, 2926, 2854, 2089, 2046, 2017, 1641, 1582; ^{1}H NMR **6a** δ: 6.52 (d, *J* = 9.9, 1H), 5.95 (dd, *J* = 4.3, 9.9, 1H), 5.78 (m, 1H), 5.08 (m, 2H), 3.25 (m, 1H), 3.10 (m, 1H), 2.46 (m, 1H), 2.26 (m, 2H), 2.21 (m, 1H), 1.88 (m, 1H); resonances for **6b** could be observed at δ 5.94 (m, 1H), 5.65 (m, 1H), 5.13 (m, 2H), 3.75 (m, 1H), 3.20 (m, 1H), 2.95 (m, 1H), 2.65 (m, 1H), 2.40 (m, 1H); ^{13}C NMR δ: 200.1, 139.7, 136.3, 126.4, 117.2, 98.1, 87.5, 41.0, 40.6, 33.4, 30.3; resonances for **6b** could be observed at 136.1, 131.5, 41.8, 34.3, 30.1, 27.1. MS EI *m/e*: 418 (M^+), 390 (M^+ -1CO), 362 (M^+ -2CO), 334 (M^+ -3CO), 306 (M^+-4CO), 278 (M^+ -5CO), 250 (M^+ -6CO). HRMS *m/e* for $C_{16}H_{12}Co_2O_6$ calcd (M^+) 417.9298, found 417.9287.

3.3.3 Hexacarbonyl[μ–η^4–(2–cyclohept–2–en–4–ynylfuran)]dicobalt (7a)

A solution of cycloheptenyne **1** (0.0540 g, 0.124 mmol) and furan (0.136 g, 0.186 mmol) in CH_2Cl_2 (2.5 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.16 mL, 1.2 mmol) via the **General Procedure**. The crude product was purified by flash chromatography (100 % petroleum ether) to yield **7a** (0.0341 g, 62%) as a red–brown oil. IR (neat, KBr, cm^{-1}): 2927, 2089, 2048, 2017, 1622, 1428; ^{1}H NMR δ: 7.35 (d, *J* = 1.8, 1H), 6.71 (d, *J* = 9.9, 1H), 6.28 (dd, *J* = 1.8, 3.1, 1H), 6.15 (dd, *J* = 3.1, 9.9, 1H), 6.03 (d, *J* = 3.2, 1H), 3.89 (m, 1H), 3.17 (m, 1H), 2.98 (m, 1H), 2.23

(m, 1H), 2.08 (m, 1H); ^{13}C NMR δ: 199.9, 155.8, 141.7, 133.7, 127.8, 110.1, 106.3, 98.1, 86.8, 41.1, 32.2, 30.1. MS EI *m/e*: 444 (M^+), 416 (M^+ -1CO), 388 (M^+ -2CO), 360 (M^+-3CO), 332 (M^+ -4CO), 304 (M^+ -5CO), 276 (M^+ -6CO). HRMS *m/e* for $C_{17}H_{10}Co_2O_7$ calcd (M^+) 443.9091, found 443.9082.

3.3.4 Hexacarbonyl[μ–η^4–(cyclohept–1–en–3–yne)]dicobalt (8a) and Hexacarbonyl[μ–η^4–(cyclohept–1–en–4–yne)]dicobalt (8b)

A solution of cycloheptenyne **1** (0.0500 g, 0.115 mmol) and triethylsilane (0.0200 g, 0.173 mmol) in CH_2Cl_2 (2.3 mL) at -10 ^{o}C was subjected to BF_3-OEt_2 (0.15 mL, 1.1 mmol) via the **General Procedure**. After flash chromatography (100% petroleum ether), an inseparable mixture of **8a** and **8b** (0.0235g, 54%, **8a**:**8b** = 72:28) was isolated. IR (neat, KBr, cm^{-1}): 2928, 2089, 2046, 2016, 1581, 1385; ^{1}H NMR δ: 6.54 (d, *J* = 9.7, 1H), 6.10 (m, 1H), 3.20 (t, *J* = 5.6, 2H), 2.41 (m, 2H), 1.87 (m, 2H); peaks for **8b** could be observed at δ: 5.97 (m, 1H), 5.88 (m, 1H), 3.10 (m, 2H), 2.41 (m, 2H), 2.33 (m, 2H); ^{13}C δ: 199.5, 135.1, 127.1, 97.9, 89.4, 35.7, 30.9, 24.9; resonances for **8b** could be observed at δ: 199.5, 132.4, 130.2, 98.1, 89.6, 34.5, 33.6, 27.2. MS EI *m/e*: 378 (M^+), 350 (M^+ -1CO), 322 (M^+ -2CO), 294 (M^+ -3CO), 266 (M^+ -4CO), 238 (M^+ -5CO), 210 (M^+ -6CO). HRMS *m/e* for $C_{13}H_8Co_2O_6$ calcd (M^+ -CO) 349.9030, found 349.9008.

3.3.5 Hexacarbonyl[μ–η^4–(2–cyclohept–2–en–4–ynylmethyl–prop–2–en–1–ol)] dicobalt (10a) and Hexacarbonyl[μ–η^4–(2–cyclohept–2–ynyl–methyl–prop–2–en–1–ol)] dicobalt (10b)

A solution of cycloheptenyne **1** (0.0776 g, 0.178 mmol) and 2-(trimethylsilylmethyl)-2-propen-1-ol (**9a**) (0.0384 g, 0.266 mmol) in CH_2Cl_2 (3.6 mL) at -10 ^{o}C was subjected to BF_3-OEt_2 (0.23 mL, 1.8 mmol) via the **General Procedure**. Flash chromatography (3:1 petroleum

ether: Et_2O) resulted in the isolation of **10a** and **10b** (0.0607g, 76%, **10a**:**10b** = 59:41) as a red–brown oil. Careful repeated TLC afforded (in order of elution) **10b** followed by **10a. 10a:** IR (neat, KBr, cm^{-1}) 3354, 2923, 2086, 2047, 2021, 1608, 1435, 1384; ^1H NMR δ: 6.54 (d, *J* = 9.9, 1H), 5.96 (dd, *J* = 3.8, 9.9, 1H), 5.17 (s, 1H), 4.94 (s, 1H), 4.09 (s, 2H), 3.28 (m, 1H), 3.12 (m, 1H), 2.61 (m, 1H), 2.28 (m, 2H), 1.91 (m, 1H), 1.75 (m, 1H), 1.51 (br s, 1H); ^{13}C NMR δ: 200.0, 146.1, 139.2, 126.3, 112.3, 98.0, 87.5, 65.6, 39.5, 38.7, 33.3, 30.3 . MS EI *m/e*: 448 (M^+), 420(M^+ -1CO), 392 (M^+ -2CO), 364 (M^+ -3CO), 336 (M^+ -4CO), 308 (M^+ -5CO), 280 (M^+ -6CO). HRMS *m/e* for $C_{17}H_{14}Co_2O_7$ calcd (M^+-2CO) 391.9500, found 391.9513. **10b:** IR (neat, KBr, cm^{-1}) 3385, 2925, 2088, 2046, 2016, 1608, 1506, 1093; ^1H NMR for the δ: 5.95 (m, 1H), 5.67 (m, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 4.18 (s, 2H), 3.92 (m, 1H), 3.24 (m, 1H), 3.01 (m, 1H), 2.35 (m, 4H), 1.59 (br s, 1H); ^{13}C NMR δ: 199.9, 146.1, 135.9, 131.4, 112.2, 100.9, 99.9, 65.9, 40.4, 39.3, 34.2, 26.9; MS EI *m/e*: 448 (M^+), 420(M^+ -1CO), 392 (M^+ -2CO), 364 (M^+ -3CO), 336 (M^+ -4CO), 308 (M^+ -5CO), 280 (M^+ -6CO). HRMS *m/e* for $C_{17}H_{14}Co_2O_7$ calcd (M^+) 447.9403, found 447.9376.

3.3.6 Hexacarbonyl[μ–η^4–(7-(2–chloromethylallyl)cyclohept-1-en-3-yne)]dicobalt (11a) and Hexacarbonyl[μ–η^4–(3-(2–chloromethylallyl)cyclohept-1-en-4-yne)]dicobalt (11b)

A solution of cycloheptenyne **1** (0.0477 g, 0.109 mmol) and 2-chloromethyl-3-trimethylsilyl-1-propene (**9b**) (0.030 mL, 0.17 mmol) in CH_2Cl_2 (2.5mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.14 mL, 1.1 mmol) via the **General Procedure**. Flash chromatography (25:1 petroleum ether: Et_2O) resulted in the co–elution of **11a** and **11b** (0.0358 g, 70%, **11a**:**11b** = 72:28) as a red–brown oil. IR (neat, KBr, cm^{-1}): 2927, 2090, 2047, 2016, 2017, 1506, 1430; ^1H NMR δ: 6.55 (dd, *J* = 1.6, 9.9, 1H), 5.97 (dd, *J* = 4.1, 9.9, 1H), 5.27 (s, 1H), 5.02 (s, 1H), 4.05 (s,

2H), 3.28 (m, 1H), 3.18 (m, 1H), 2.68 (m, 1H), 2.37 (m, 2H), 1.89 (m, 1H), 1.87 (m, 1H); resonances for **11b** could be observed at δ: 5.97 (m, 1H), 5.68 (dd, *J* = 3.3, 10.5, 1H), 5.31 (s, 1H), 5.14 (s, 1H), 4.13 (s, 2H), 3.26 (m, 2H), 3.14 (m, 1H), 2.45 (m, 1H), 2.33 (m, 2H), 1.71 (m, 1H); ^{13}C NMR δ: 199.9, 142.5, 138.8, 126.7, 117.1, 96.3, 86.2, 47.8, 39.6, 38.5, 33.3, 30.3; resonances for **11b** could be observed at δ: 135.7, 133.0, 116.9, 96.3, 86.2, 48.0, 40.1, 39.1, 34.1, 27.2. MS EI *m/e*: 466 (M^+), 438 (M^+ -1CO), 410 (M^+ -2CO), 382 (M^+ -3CO), 354 (M^+-4CO), 326 (M^+ -5CO), 298 (M^+ -6CO). HRMS *m/e* for $C_{17}H_{13}ClCo_2O_6$ calcd (M^+) 465.9065, found 465.9038.

3.3.7. Hexacarbonyl[μ–η^4–(acetic acid 2-cyclohept-2-en-4-ynylmethylallyl ester)] dicobalt (12a) and Hexacarbonyl[μ–η^4–(acetic acid 2-cyclohept-2-en-6-ynylmethylallyl ester)] dicobalt (12b)

A solution of cycloheptenyne **1** (0.0706 g, 0.162 mmol) and 2-(acetoxymethyl)allyltrimethylsilane (**9c**) (0.0509 g, 0.274 mmol) in CH_2Cl_2 (3.5 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.205 mL, 1.62 mmol) via the **General Procedure**. Flash chromatography (25:1 petroleum ether: Et_2O) resulted in the co-elution of **12a** and **12b** (0.0606 g, 76%, **12a**:**12b** = 64:36) as a red–brown oil. **12a** IR (neat, KBr, cm^{-1}): 2927, 2089, 2048, 2018, 1747, 1053; ^{1}H NMR δ: 6.54 (dd, *J* = 1.9, 9.8, 1H), 5.94 (dd, *J* = 4.3, 9.8, 1H), 5.18 (s, 1H), 5.01 (s, 1H), 4.55 (1/2 ABq, *J* = 13.5, 1H), 4.51 (1/2 ABq, *J* = 13.5, 1H), 3.28 (m, 1H), 3.13 (m, 1H), 2.61 (m, 1H), 2.27 (m, 2H), 2.22 (s, 3H), 2.09 (m, 1H), 2.06 (m, 1H); resonances for **12b** could be observed at ^{1}H NMR δ: 5.94 (m, 1H), 5.65 (br d, *J* = 10.5, 1H), 5.23 (s, 1H), 5.12 (s, 1H), 4.68 (1/2 ABq, *J* = 13.2, 1H), 4.59 (1/2 ABq, *J* = 13.2, 1H), 3.87 (m, 1H), 3.22 (m, 1H), 2.98 (m, 1H), 2.71 (dd, *J* = 4.1, 14.9, 1H), 2.33 (m, 2H), 2.28 (m, 1H), 2.11 (s, 3H); ^{13}C NMR δ: 199.9,

170.7, 156.1, 141.2, 138.9, 126.5, 115.35, 97.9, 87.4, 66.6, 39.7, 38.6, 33.2, 30.1; resonances for **12b** could be observed at δ: 170.7, 141.2, 135.40, 131.5, 115.4, 100.8, 99.8, 66.6, 40.1, 39.1, 34.1, 30.3, 27.0, 20.8. MS EI *m/e*: 434 (M^+ -2CO), 406 (M^+ -3CO), 378 (M^+ -4CO), 350 (M^+ -5CO), 322 (M^+ -6CO). HRMS *m/e* for $C_{19}H_{16}Co_2O_8$ calcd (M^+-2CO) 433.9605, found 433.9636.

3.3.8. Hexacarbonyl[μ–η^4–(7–(3-acetoxypropen-2-yl)cyclohept-1-en-3-yne)] dicobalt (13a) and Hexacarbonyl[μ–η^4–(3–(3-acetoxypropen-2-yl)cyclohept-1-en-4-yne)]dicobalt (13b)

A solution of cycloheptenyne **1** (0.0524 g, 0.120 mmol) and 1-trimethylsilylallyl acetate (0.0384 g, 0.223 mmol) in CH_2Cl_2 (2.4 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.15 mL, 1.2 mmol) via the **General Procedure**. The crude product was purified by flash chromatography (25:1 petroleum ether: Et_2O) to yield of **13a** and **13b** (0.0369g, 65%) as Z/E- isomeric mixtures as a red–brown oil. IR (neat, KBr, cm^{-1}): 2926, 2089, 2047, 2016, 1760, 1673, 1217; **13a** ^1H NMR δ: 7.13 (d, *J* = 6.8, 1H, *Z*-isomer) and 7.14 (d, *J* = 12.3, 1H, *E*-isomer), 6.55 (d, *J* = 9.9, 1H), 5.97 (dd, *J* = 4.4, 10.0, 1H, Z-isomer) and 5.95 (dd, *J* = 4.1, 9.9, 1H, *E*-isomer), 4.89 (apparent q, *J* = 6.8, 1H, *Z*-isomer) and 5,41 (dt, *J* = 12.3, 7.8, 1H, *E*-isomer), 3.28 (m, 1H), 3.12 (m, 1H), 2.40-2.50 (m, 1H), 2.34 (m, 1H), 2.19 (m, 1H), 2.15 (s, 3H, *Z*-isomer) and 2.13 (s, 3H, *E*-isomer), 1.86 (m, 1H), 1.73 (m, 1H); absorptions for **13b** could be observed at 5.67 (m, 1H), 5.56 (dt, *J* = 12.5, 7.5, 1H, *E*-isomer) and 5.08 (apparent q, *J* = 7.0, 1H, *Z*-isomer), 3.22 (m, 1H), 3.00 (m, 1H); ^{13}C NMR δ: 200.1, 168.4, 168.2, 139.3, 139.1, 137.2, 135.8, 126.9, 126.7, 112.3, 111.4, 98.3, 87.0, 41.3, 41.2, 34.1, 33.2, 30.9, 30.3, 30.1, 29.9, 20.9. MS EI *m/e*: 476 (M^+), 448 (M^+ -1CO), 420 (M^+ -2CO), 392 (M^+ -3CO), 364 (M^+ -4CO), 336 (M^+ -5CO), 308 (M^+ -6CO). HRMS *m/e* for $C_{18}H_{14}Co_2O_8$ calcd (M^+-2CO) 419.9449, found 419.9455.

3.3.9. Hexacarbonyl[μ-η^4-(2-cyclohep-2-en-4-ynyl-1-phenylethanone)]dicobalt (16a) and **Hexacarbonyl[μ-η^4-(2-cyclohept-2-en-6-ynyl-1-phenylethanone)]dicobalt (16b)**

A solution of cycloheptenyne **1** (0.0592 g, 0.135 mmol) and 1-phenyl-1-(trimethylsiloxy)ethane (0.0519 g, 0.270 mmol) in CH_2Cl_2 (6 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.17 mL, 1.3 mmol) via the **General Procedure**. The crude product was purified by flash chromatography (25:1 petroleum ether: Et_2O) to yield **16a** + **16b** (0.0496 g, 74%, 44:56 ratio) as a red–brown oil. Repeated TLC (10:1 petroleum ether: Et_2O) allowed sequential isolation of α-**16b** and γ-**16a**. **16a:** IR (neat, KBr, cm^{-1}): 3018, 2927, 2089, 2047, 2017, 1683; ^1H NMR δ: 8.03 (d, *J* = 7.8, 2H), 7.40-7.60 (m, 3H), 6.57 (dd, *J* = 9.8, 1.4, 1H), 6.02 (dd, *J* = 9.8, 4.5, 1H), 3.10-3.30 (m, 5H), 1.80-1.96 (m, 2H) ^{13}C NMR 199.8, 198.3, 138.7, 136.9, 133.3, 128.7, 128.0, 126.7, 97.8, 87.2, 44.0, 36.7, 32.9, 30.3. MS EI *m/e*: 468 (M^+ -1CO), 440 (M^+ -2CO), 412 (M^+ -3CO), 384 (M^+ -4CO), 356 (M^+ -5CO), 328 (M^+ -6CO). HRMS *m/e* for calcd (M^+-CO) 467.9454, found 467.9445. **16b:** IR (neat, KBr, cm^{-1}): 3022, 2930, 2089, 2046, 2014, 1688; ^1H NMR δ: 7.96 (d, *J* = 7.8, 2H), 7.40 – 7.60 (m, 3H), 5.94 (m, 1H), 5.65 (dd, *J* = 3.6, 9.8, 1H), 4.46 (m, 1H), 3.56 (dd, *J* = 5.4, 17.3, 1H), 3.32 (dd, *J* = 8.4, 17.3, 1H), 3.21 (m, 1H), 3.03 (m, 1H), 2.35-2.50 (m, 2H). ^{13}C NMR 199.9, 197.9, 136.7, 135.8, 133.3, 131.5, 128.7, 128.1, 100.3, 100.1, 45.7, 37.8, 34.0, 27.0. MS EI *m/e*: 496 (M^+), 468 (M^+ -1CO), 440 (M^+ -2CO), 412 (M^+ -3CO), 384 (M^+ -4CO), 356 (M^+ -5CO), 328 (M^+ -6CO). HRMS *m/e* for $C_{21}H_{14}Co_2O_7$ calcd (M^+) 495.9403, found 495.9401.

3.3.10. Hexacarbonyl[μ–η^4–(7–acetoxycyclohept–1–en–3–yne)] dicobalt (15a)

A solution of cycloheptenyne **1** (0.0540 g, 0.124 mmol) and glacial acetic acid (0.0149 g, 0.248 mmol) in CH_2Cl_2 (2.5 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.16 mL, 1.3 mmol) via

the **General Procedure**. The crude product was purified by flash chromatography (10:1 petroleum ether: Et_2O) to yield the **15a** (0.0427 g, 79%) as a red–brown oil: IR (neat, KBr, cm^{-1}): 2923, 2850, 2092, 2051, 2021, 1740, 1238; ^1H NMR δ: 6.68 (d, *J* = 10.0, 1H), 6.06 (dd, *J* = 4.6, 10.0, 1H), 5.48 (m, 1H), 3.30 (m, 1H), 3.22 (m, 1H), 2.12 (m, 1H), 2.09 (s, 3H), 2.00 (m, 1H); ^{13}C NMR δ: 199.4, 170.0, 133.2, 128.6, 96.6, 85.0, 72.4, 30.3, 30.1, 21.0. MS EI *m/e*: 436 (M^+), 408 (M^+ -1CO), 380 (M^+ -2CO), 352 (M^+ -3CO), 324 (M^+ -4CO), 296 (M^+ -5CO), 268 (M^+ -6CO). HRMS *m/e* for $C_{15}H_{10}Co_2O_8$ calcd (M^+) 435.9040, found 435.9012.

H_2SO_4 conditions: To a solution of cycloheptyne **1** (0.1681 g, 0.386 mmol) in acetic acid (5 mL) was added H_2SO_4 (5 drops). The solution was stirred 1h, at which point $NH_4Cl_{(aq)}$ was added and the mixture subjected to a conventional extractive workup. Flash chromatography as described above afforded **15a** (0.1631 g, 97%).

3.3.11. Hexacarbonyl[μ–η^4–(7–methoxy–cyclohept–1–en–3–yne)] dicobalt (Co–Co) (17a)

A solution of cycloheptenyne **1** (0.0623 g, 0.143 mmol) and methanol (7.0 μL, 0.17 mmol) in CH_2Cl_2 (2.9 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.18 mL, 1.4 mmol) via the **General Procedure**. The crude product was purified by flash chromatography (10:1 petroleum ether: Et_2O) to yield the **17a** (0.0379 g, 65%) as a red–brown oil. IR (neat, KBr, cm^{-1}): 2923, 2090, 2048, 2017, 1615, 1430; ^1H NMR δ: 6.61 (d, *J* = 10.0, 1H), 6.17 (dd, *J* = 3.9, 10.0, 1H), 3.95 (m, 1H), 3.37 (s, 3H), 3.34 (m, 1H), 3.12 (m, 1H), 2.04 (m, 2H); ^{13}C NMR δ: 199.5, 136.6, 127.3, 97.2, 86.1, 79.8, 56.3, 30.8, 30.1. MS EI *m/e*: 408 (M^+), 380 (M^+ -1CO), 352 (M^+ -2CO), 324 (M^+ -3CO), 296 (M^+ -4CO), 268 (M^+ -5CO), 240 (M^+ -6CO). HRMS *m/e* for $C_{14}H_{10}Co_2O_7$ calcd (M^+) 407.9091, found 407.9080.

H_2SO_4 conditions: To a solution of cycloheptyne **1** (0.0540, 0.124 mmol) in MeOH (2 mL) and CH_2Cl_2 (2 mL) at 0 ^oC was added H_2SO_4 (2 drops). The ice bath was removed and the

reaction stirred for 1h. $NH_4Cl_{(aq)}$ was added and the reaction was subjected to a conventional workup. Flash chromatography as described above afforded **17a** (0.0442 g, 87%).

3.3.12. Hexacarbonyl[μ–η^4–(7–(2–chloroethoxy)–cyclohept–1–en–3–yne)]dicobalt (18a)

A solution of cycloheptenyne **1** (0.0510 g, 0.117 mmol) and 2-chloroethanol (10.0 μL, 0.150 mmol) in CH_2Cl_2 (2.3 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.15 mL, 1.2 mmol) via the **General Procedure**. The crude product was purified by flash chromatography (20:1 petroleum ether: Et_2O) to yield the **18a** (0.0315g, 59%) as a red–brown oil. IR (neat, KBr, cm^{-1}): 2927, 2856, 2091, 2050, 2021, 1612; ^1H NMR δ: 6.63 (d, *J* = 9.9, 1H), 6.16 (dd, *J* = 4.0, 10.0, 1H), 4.13 (m, 1H), 3.78 (m, 2H), 3.62 (t, *J* = 5.9, 2H), 3.36 (m, 1H), 3.14 (m, 1H), 2.06 (m, 2H); ^{13}C NMR δ: 199.6, 136.0, 127.8, 97.1, 85.8, 78.8, 68.9, 43.0, 30.6, 30.4. MS EI *m/e*: 456 (M^+), 400 (M^+ -2CO), 372 (M^+ -3CO), 344 (M^+ -4CO), 316 (M^+ -5CO), 288 (M^+ -6CO). HRMS *m/e* for $C_{15}H_{11}ClCo_2O_7$ calcd (M^+) 455.8857, found 455.8841.

H_2SO_4 conditions: To a solution of cycloheptyne **1** (0.0858 g, 0.197 mmol) and 2-chloroethanol (1 mL) in CH_2Cl_2 (5 mL) at 0 ^oC was added H_2SO_4 (3 drops). The solution was stirred for 1 h, at which point $NH_4Cl_{(aq)}$ was added and a standard workup performed. Flash chromatography as above afforded **18a** (0.0679 g, 76%).

3.3.13. Hexacarbonyl[μ–η^4–(7-(4-chlorobut-2-enyloxy)-cyclohept–1–en–3–yne)]dicobalt (19a)

A solution of cycloheptenyne **1** (0.0589 g, 0.135 mmol) and 4-chloro-2-buten-1-ol (0.022 g, 0.21 mmol) in CH_2Cl_2 (2.7 mL) at -10 ^oC was subjected to BF_3-OEt_2 (0.17 mL, 1.3 mmol) via the **General Procedure**. The crude product was purified by flash chromatography (25:1 petroleum ether: Et_2O) to yield the **19a** (0.0440 g, 68%) as a red–brown oil. IR (neat, KBr, cm^{-1}):

2925, 2091, 2051, 2021, 1457, 1054; ^{1}H NMR δ: 6.65 (d, *J* = 10.0, 1H), 6.15 (dd, *J* = 4.0, 10.0, 1H), 5.76 (m, 2H), 4.18 (d, *J* = 5.7, 2H), 4.12 (d, *J* = 7.4, 2H), 4.10 (m, 1H), 3.34 (m, 1H), 3.12 (m, 1H), 2.04 (m, 2H); ^{13}C NMR δ: 199.7, 136.1, 131.0, 128.1, 127.9, 97.1, 85.9, 63.7, 48.6, 39.1, 30.6, 30.4. MS EI *m/e*: 482 (M^+), 454 (M^+ -1CO), 426 (M^+ -2CO), 398 (M^+ -3CO), 370 (M^+ -4CO), 342 (M^+ -5CO), 314(M^+ -6CO). HRMS *m/e* for $C_{17}H_{13}ClCo_2O_7$ calcd (M^+) 481.9014, found 481.9001.

3.3.14. Hexacarbonyl[μ–η^4–(cyclohept–2–en–4–ynylacetamide)]dicobalt (20a)

H_2SO_4 conditions: Concentrated sulfuric acid was added dropwise (3 drops) to a solution of cycloheptenyne **1** (0.0645 g, 0.148 mmol) in acetonitrile (5 mL). After ten minutes the aqueous sodium bicarbonate was added and a typical workup proceeded. The crude reaction product was purified by flash chromatography (1:2 petroleum ether: ethyl acetate) to yield the **20a** (0.0546 g, 85%) as a red–brown oil. IR (neat, KBr, cm^{-1}) 2927, 2091, 2048, 2021, 1651, 1548, 1431; ^{1}H NMR δ: 6.66 (dd, *J* = 1.6, 9.9, 1H), 6.17 (dd, *J* = 4.7, 9.9, 1H), 5.48 (br d, J = 7.2, 1H), 4.75 (m, 1H) 3.15-3.25 (m, 2H), 2.05 (m, 1H), 1.99 (s, 3H), 1.96 (m, 1H); ^{13}C NMR δ: 199.4, 168.9, 135.1, 128.1, 97.1, 85.5, 50.6, 31.1, 23.2. MS EI *m/e*: 435 (M^+), 407 (M^+ -1CO), 379 (M^+ -2CO), 351 (M^+ -3CO), 323 (M^+ -4CO), 295 (M^+ -5CO), 267 (M^+ -6CO). HRMS *m/e* for $C_{15}H_{11}Co_2NO_7$ calcd (M^+-CO) 406.9250, found 406.9242.

Acknowledgments

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18. In particular, the kinetic γ-: α- ratio for 1,3,5,-trimethoxybenzene (N = 3.40) can be no *greater* than 70:30, so that it likely does not fit the exact trend of the other entries of Table 5.

19. The N value of acetophenone enol acetate is unpublished but is possibly comparable to α-methylstyrene (N = 2.35); Noyce, D. S.; Pollack, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 7158.

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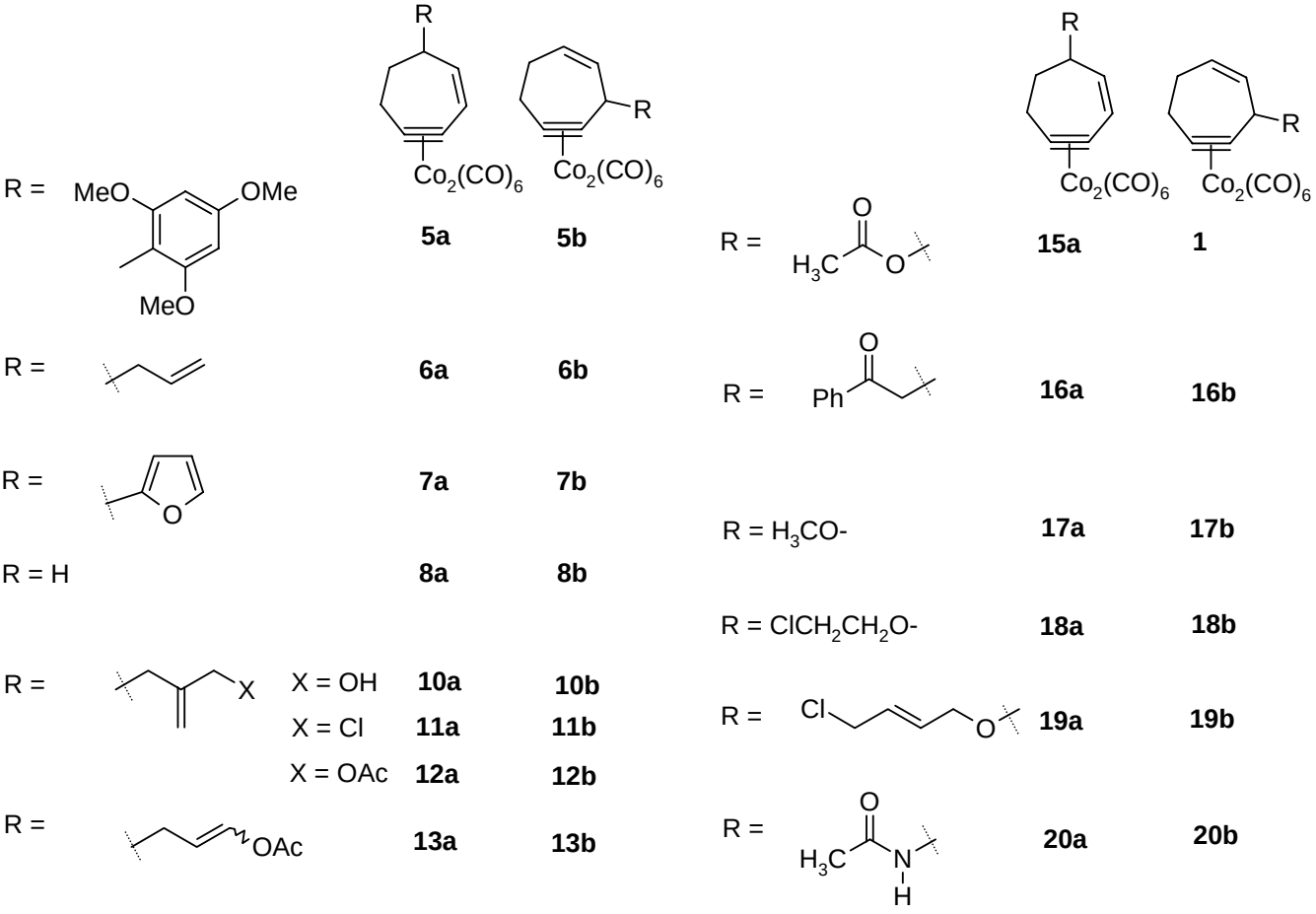

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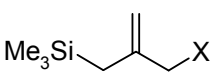
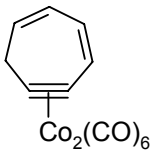
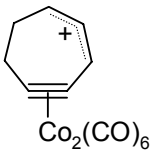


9a X = OH
9b X = Cl
9c X = OAc



14



21

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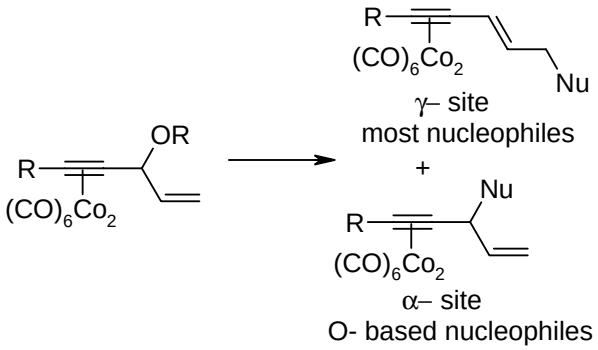

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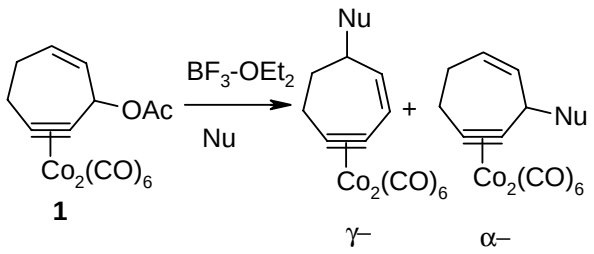
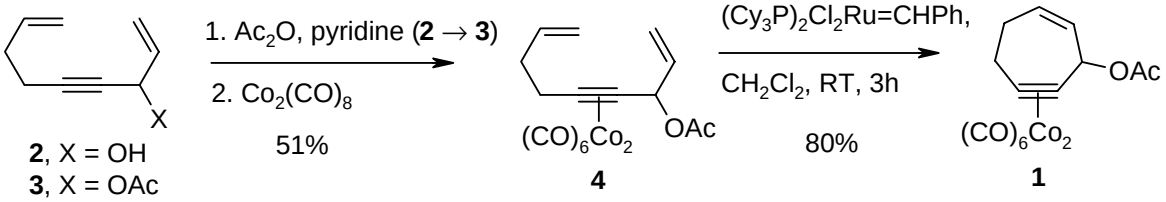


1

γ– α–

Figure(s) (use if uploading high quality figure files)



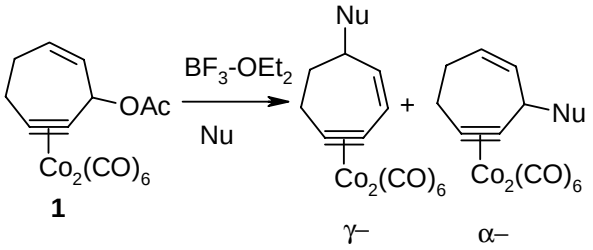
2, X = OH
3, X = OAc

4

1

Lewis and Protic Acid Mediated Nicholas Reactions of 3-Acetoxycyclohept-1-en-4-ynedicobalt Hexacarbonyl: Site Selectivity of Nucleophile Incorporation

Joseph DiMartino and James R. Green*



Kinetic Product:
Predominantly γ-

Thermodynamic product:
Exclusively γ-