Lewis and protic acid mediated Nicholas reactions of 3-acetoxycyclohept-1-en-4-ynedicobalt hexacarbonyl: site selectivity of nucleophile incorporation

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Keywords: Nicholas reaction, cobalt-alkyne complexes, cycloheptene, 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. These cations, which may stem from alkynedicobalt complexes with propargylic leaving groups and a protic or Lewis acid, or from enyne-Co₂(CO)₆ complexes and an electrophile, normally substitute exclusively at the propargylic site, unless the
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 ($\gamma$-site).$^3$ Exceptions exist however, particularly where intramolecular nucleophilic attack reactions are entropically driven towards the $\alpha$- site;$^4$ in some cases with nucleophiles which are oxygen based, $\alpha$- substitution is also observed (Scheme 1).$^{2a,5}$

![Scheme 1](image)

**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 $\gamma$- 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 ($\gamma$-) 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 $\gamma$- substituent, ultimately giving fused 7,5- and 7,6- ring systems. In addition, we have an interest in clean $\alpha$- 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). Standard acetylation of 2, affording acetate 3, followed by complexation with Co₂(CO)₈, gave 4 (51% yield, two steps). Ring closing metathesis, employing 10 mol% of (Cy₃P)₂Cl₂Ru=CHPh (Grubbs’ I catalyst), afforded 1 in 80% yield.

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 CH₂Cl₂ solvent (0.05 M), and with excess BF₃-OEt₂ present (10 equiv), 1 underwent reaction with 1,3,5-trimethoxybenzene at temperatures as low as -30 °C 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 at -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$_2$BOTf 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
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, and these results would be consistent with that feature here. In fact, subjecting purified α-substitution product 5b to the 0 °C 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 °C, but in these cases the α- : γ- product ratios remained relatively consistent (81:19 – 84:16) over the temperature range investigated.

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

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Yield 5a/5b (%)</th>
<th>γ-:α- ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF3-OEt2, -30 °C</td>
<td>70</td>
<td>59:41</td>
</tr>
<tr>
<td>BF3-OEt2, -10 °C</td>
<td>86</td>
<td>70:30</td>
</tr>
<tr>
<td>BF3-OEt2, 0 °C</td>
<td>73</td>
<td>81:19</td>
</tr>
<tr>
<td>BF3-OEt2, 23 °C</td>
<td>52</td>
<td>86:14</td>
</tr>
<tr>
<td>SnCl4, -10 °C</td>
<td>77</td>
<td>76:24</td>
</tr>
<tr>
<td>Bu2BOTf, -30 °C</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Reaction of 1 with allyltrimethylsilane

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Yield 6a/6b (%)</th>
<th>γ-:α- ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF3-OEt2, -30 °C</td>
<td>68</td>
<td>82:18</td>
</tr>
<tr>
<td>BF3-OEt2, -10 °C</td>
<td>83</td>
<td>84:16</td>
</tr>
<tr>
<td>BF3-OEt2, 0 °C</td>
<td>77</td>
<td>81:19</td>
</tr>
<tr>
<td>BF3-OEt2, 23 °C</td>
<td>56</td>
<td>83:17</td>
</tr>
</tbody>
</table>
Several other carbon and hydride based nucleophiles were investigated (Table 3). Allyltributylstannane gave 6a and 6b in good yield (74%), but with minimal $\gamma$-: $\alpha$- selectivity ($6a:6b = 50:50$). Conversely, furan gave condensation product 7a through its C-2 site, with almost none of $\alpha$- condensation product 7b in evidence (62% yield, $7a:7b = >96:<4$). 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 $\gamma$-$\alpha$- 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 $\gamma$- selectivity (65% yield, $13a:13b = 89:11$), along with small amounts of elimination product 14 (7%) and $\gamma$-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 $\alpha$- 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 $\gamma$- product once again as the major regioisomer ($16a:16b = 72:28$).
Table 3. Reaction of 1 with carbon and hydrogen nucleophiles

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Product</th>
<th>Yield (%)</th>
<th>γ-:α- ratio</th>
<th>15a (%)</th>
<th>14 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3,5-trimethoxybenzene</td>
<td>5a/5b</td>
<td>86</td>
<td>70:30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allyltrimethylsilane</td>
<td>6a/6b</td>
<td>83</td>
<td>84:16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allyltributylstannane</td>
<td>6a/6b</td>
<td>74</td>
<td>50:50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furan</td>
<td>7a/7b</td>
<td>62</td>
<td>&gt;96:4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et$_3$SiH</td>
<td>8a/8b</td>
<td>54</td>
<td>72:28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iPr$_3$SiH</td>
<td>8a/8b</td>
<td>62</td>
<td>84:16</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>10a/10b</td>
<td>76</td>
<td>59:41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td>11a/11b</td>
<td>70</td>
<td>72:28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9c</td>
<td>12a/12b</td>
<td>76</td>
<td>64:36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Trimethylsilylallyl acetate</td>
<td>13a/13b</td>
<td>65</td>
<td>89$^b$:11$^c$</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>H$_2$C=C(OSiMe$_3$)Ph</td>
<td>15a/15b</td>
<td>74</td>
<td>44:56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$C=C(OAc)Ph</td>
<td>15a/15b</td>
<td>61</td>
<td>72:28</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

*a Reaction conditions: Nucleophile, 1.5 – 2.0 equiv; solvent, CH$_2$Cl$_2$ (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$_2$SO$_4$ 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$_2$SO$_4$ 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 $\gamma$-substitution product 20a could be obtained (12% yield), the major resulting product was $\gamma$-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$_2$SO$_4$ to a solution of 1 in CH$_3$CN. In no cases have we observed even traces of the heteroatom based $\alpha$-condensation products 1, 17b – 20b as a result of these protic- or Lewis acid mediated reactions.

Table 4. Reaction of 1 with heteroatom nucleophiles$^a$

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Product</th>
<th>Yield (%)</th>
<th>15a (%)</th>
<th>14 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>15a</td>
<td>79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>15a</td>
<td>97$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>17a</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>17a</td>
<td>87$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-chloroethanol</td>
<td>18a</td>
<td>59</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>2-chloroethanol</td>
<td>18a</td>
<td>76$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-chloro-2-buten-1-ol</td>
<td>19a</td>
<td>68</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>CH$_3$C(O)NH$_2$</td>
<td>20a</td>
<td>12</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>20a</td>
<td>85$^b$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions, unless otherwise stated: Nucleophile, 1.5 – 2.0 equiv; solvent, CH$_2$Cl$_2$ (0.05 M); temperature, -10 $^\circ$C; Lewis acid, BF$_3$-OEt$_2$ (10 equiv); reaction time, 1h.

$^b$ Using H$_2$SO$_4$ in place of BF$_3$-OEt$_2$ and excess nucleophile.

With the ready availability of $\gamma$-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 \((J \approx 10 \text{ Hz})\) 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 °C. Variable temperature \(^1\)H NMR studies established a coalescence \(T_c\) of 25 °C for these methyl group resonances, and a barrier at coalescence of \(\Delta G_c = 15.2 \text{ kcal/mol}\). This process was attributed to restricted rotation about the C\(_{\alpha}\)-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\(^1^7\) 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,\(^1^8\) a comparison between similar nucleophiles particularly supports this trend. For example, the less nucleophilic allyltrimethylsilane \((N = 1.79, \gamma-:\alpha- = 84:16)\) has a much greater preference for the γ- site than allyltributylstannane \((N = 5.46, \gamma-:\alpha- = 50:50)\). In addition, the less nucleophilic acetophenone enol acetate\(^1^9\) reacts with greater γ- selectivity \((\gamma-:\alpha- = 72:28)\) 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 Et₃SiH and iPr₃SiH suggests that increased γ-selectivity is encouraged by larger nucleophiles, likely as a consequence of the significant steric size of the alkyne-Co₂(CO)₆ unit.

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

<table>
<thead>
<tr>
<th>Nucleophilea</th>
<th>N value</th>
<th>γ-:α- Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C=C(OSiMe₃)Ph</td>
<td>6.22</td>
<td>44:56</td>
</tr>
<tr>
<td>Allyltributylstannane</td>
<td>5.46</td>
<td>50:50</td>
</tr>
<tr>
<td>Et₃SiH</td>
<td>3.64</td>
<td>72:28</td>
</tr>
<tr>
<td>Allyltrimethylsilane</td>
<td>1.79</td>
<td>84:16</td>
</tr>
<tr>
<td>Furan</td>
<td>1.36</td>
<td>&gt;96:4</td>
</tr>
</tbody>
</table>

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 BF₃-OEt₂, 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 $^1$H and $^{13}$C NMR spectroscopy. Reported regioisomeric ratios are on based on the $^1$H NMR spectra of crude reaction products. NMR spectra were run at 500 MHz or 300 MHz for $^1$H 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[$\mu$-$\eta^4$-(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 °C 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$_2$O (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:Et₂O) 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); ¹³C 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 C₁₇H₁₄Co₂O₈ calcd (M⁺ - 2CO) 407.9454, found 407.9455.

3.3. Hexacarbonyl[µ-η₄-(3-acetoxycyclohept-1-en-4-yne)]dicobalt (1)

To a solution of 4 (0.0577 g, 0.124 mmol) in CH₂Cl₂ (5 mL) was added dichloro(phenylmethylene)bis(tricyclohexylphosphine)ruthenium (1st generation Grubbs’ catalyst, 0.0102 g, 10.0 mol%) in CH₂Cl₂ (1 mL). The solution was stirred for 3 h, and subsequently concentrated under reduced pressure. Flash chromatography (20:1 petroleum ether:Et₂O) gave 1 (0.0436 g, 80%) as a red-brown oil; IR (neat, KBr, cm⁻¹) 3035, 2940, 2093, 2051, 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); ¹³C 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 C₁₅H₁₀Co₂O₈ 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 CH₂Cl₂ (0.05 M) at -10°C was added BF₃-OEt₂ (10 equiv) over 30 min as a solution in CH₂Cl₂ (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–η⁴–(7–(2,4,6-trimethoxyphenyl)cyclohept–1–en–3–yne)] dicobalt (5a) and Hexacarbonyl[µ–η⁴–(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 CH₂Cl₂ (2 mL) at -10 °C was subjected to BF₃-OEt₂ (0.11 mL, 0.88 mmol) via the General Procedure. The product was purified by flash chromatography (25:1 petroleum ether: Et₂O) 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, 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); ¹³C 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 C₂₂H₁₈Co₂O₉ calcd (M⁺) 543.9615, found 543.9609.

5b IR (neat, KBr, cm⁻¹): 2926, 2805, 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), 2.61 (m, 2H); ¹³C 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 C₂₂H₁₈Co₂O₉ calcd (M⁺-CO) 515.9666, found 515.9666.

**Reaction of 5b with BF₃-OEt₂**

To a 0 °C solution of 5b (0.0281 g, 0.0517 mmol) in CH₂Cl₂ (4 mL) was added BF₃-OEt₂ (65 µL, 0.52 mmol). After stirring for 1 h at 0 °C, NH₄Cl(aq) was added and the reaction was...
subjected to a conventional workup. Flash chromatography (20:1 petroleum ether : Et₂O) gave 5a and 5b (0.0189, 67% recovery, 5a:5b = 23:77).

3.3.2 Hexacarbonyl[µ–η⁴–(7–allylcyclohept–1–en–3–yne)]dicobalt (6a) and Hexacarbonyl[µ–η⁴–(3–allylcyclohept–1–en–4–yne)]dicobalt (6b)

A solution if cycloheptyne 1 (0.0817 g, 0.187 mmol) and allyltrimethylsilane (45 µL, 0.28 mmol) in CH₂Cl₂ (3.7 mL) at -10 °C was subjected to BF₃-OEt₂ (0.24 mL, 1.9 mmol) via the General Procedure. Flash chromatography (25:1 petroleum ether: Et₂O) 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; ¹H 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); ¹³C 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 C₁₆H₁₂Co₂O₆ calcd (M⁺) 417.9298, found 417.9287.

3.3.3 Hexacarbonyl[µ–η⁴–(2–cyclohept–2–en–4–ynylfuran)]dicobalt (7a)

A solution of cycloheptyne 1 (0.0540 g, 0.124 mmol) and furan (0.136 g, 0.186 mmol) in CH₂Cl₂ (2.5 mL) at -10 °C was subjected to BF₃-OEt₂ (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; ¹H 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 $\delta$: 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$_2$O$_7$ 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$_2$Cl$_2$ (2.3 mL) at -10 °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 $\delta$: 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 $\delta$: 5.97 (m, 1H), 5.88 (m, 1H), 3.10 (m, 2H), 2.41 (m, 2H), 2.33 (m, 2H); $^{13}$C $\delta$: 199.5, 135.1, 127.1, 97.9, 89.4, 35.7, 30.9, 24.9; resonances for 8b could be observed at $\delta$: 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$_8$Co$_2$O$_6$ 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$_2$Cl$_2$ (3.6 mL) at -10 °C was subjected to BF$_3$-OEt$_2$ (0.23 mL, 1.8 mmol) via the General Procedure. Flash chromatography (3:1 petroleum
ether: Et₂O) resulted in the isolation of 10a and 10b (0.0607 g, 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); ¹³C 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 C₁₇H₁₄Co₂O₇ 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), 5.05 (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); ¹³C 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 C₁₇H₁₄Co₂O₇ calcd (M⁺) 447.9403, found 447.9376.

3.3.6 Hexacarbonyl[μ–η⁴–(7-(2–chloromethylallyl)cyclohept-1-en-3-yne)]dicobalt (11a) and Hexacarbonyl[μ–η⁴–(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 CH₂Cl₂ (2.5 mL) at -10 °C was subjected
to BF₃-OEt₂ (0.14 mL, 1.1 mmol) via the General Procedure. Flash chromatography (25:1 petroluem ether: Et₂O) 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); 13C 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 El 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 C₁₇H₁₁ClCo₂O₆ calcd (M⁺) 465.9065, found 465.9038.

3.3.7. Hexacarbonyl[μ–η⁴–(acetic acid 2-cyclohept-2-en-4-ynylmethylallyl ester)] dicobalt (12a) and Hexacarbonyl[μ–η⁴–(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)allytrimethylsilane (9c) (0.0509 g, 0.274 mmol) in CH₂Cl₂ (3.5 mL) at -10 °C was subjected to BF₃-OEt₂ (0.205 mL, 1.62 mmol) via the General Procedure. Flash chromatography (25:1 petroleum ether: Et₂O) 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; ¹H 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 ¹H 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); 13C NMR δ: 199.9,
170.7, 156.1, 141.2, 138.9, 126.5, 115.3, 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 C19H16Co2O8 calcd (M+-2CO) 433.9605, found 433.9636.

3.3.8. Hexacarbonyl[µ–η⁴–(7–(3-acetoxypropen-2-yl)cyclohept-1-en-3-yne)] dicobalt (13a) and Hexacarbonyl[µ–η⁴–(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 CH2Cl2 (2.4 mL) at -10 °C was subjected to BF3-OEt2 (0.15 mL, 1.2 mmol) via the General Procedure. The crude product was purified by flash chromatography (25:1 petroleum ether: Et2O) 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); ¹³C 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 C18H14Co2O8 calcd (M⁺-2CO) 419.9449, found 419.9455.
3.3.9. Hexacarbonyl[µ-η⁴-(2-cyclohep-2-en-4-ynyl-1-phenylethanone)]dicobalt (16a) and Hexacarbonyl[µ-η⁴-(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 CH₂Cl₂ (6 mL) at -10 °C was subjected to BF₃-OEt₂ (0.17 mL, 1.3 mmol) via the General Procedure. The crude product was purified by flash chromatography (25:1 petroleum ether: Et₂O) to yield 16a + 16b (0.0496 g, 74%, 44:56 ratio) as a red–brown oil. Repeated TLC (10:1 petroleum ether: Et₂O) 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) ¹³C 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, 2047, 2017, 1683; 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). ¹³C 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 C₂₁H₁₄Co₂O₇ calcd (M⁺) 495.9403, found 495.9401.

3.3.10. Hexacarbonyl[µ-η⁴-(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 CH₂Cl₂ (2.5 mL) at -10 °C was subjected to BF₃-OEt₂ (0.16 mL, 1.3 mmol) via
the General Procedure. The crude product was purified by flash chromatography (10:1 petroleum ether: Et$_2$O) to yield the **15a** (0.0427 g, 79%) as a red–brown oil: IR (neat, KBr, cm$^{-1}$): 2923, 2850, 2092, 2051, 1740, 1238; $^1$H NMR $\delta$: 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 $\delta$: 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$_2$O$_8$ calcd (M$^+$) 435.9040, found 435.9012.

**H$_2$SO$_4$ conditions:** To a solution of cycloheptyne **1** (0.1681 g, 0.386 mmol) in acetic acid (5 mL) was added H$_2$SO$_4$ (5 drops). The solution was stirred 1h, at which point NH$_4$Cl(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$_2$Cl$_2$ (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$_2$O) to yield the **17a** (0.0379 g, 65%) as a red–brown oil. IR (neat, KBr, cm$^{-1}$): 2923, 2090, 2048, 2017, 1615, 1430; $^1$H NMR $\delta$: 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 $\delta$: 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$_2$O$_7$ calcd (M$^+$) 407.9091, found 407.9080.

**H$_2$SO$_4$ conditions:** To a solution of cycloheptyne **1** (0.0540, 0.124 mmol) in MeOH (2 mL) and CH$_2$Cl$_2$ (2 mL) at 0 ºC was added H$_2$SO$_4$ (2 drops). The ice bath was removed and the
reaction stirred for 1 h. NH₄Cl(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-η⁴–(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 CH₂Cl₂ (2.3 mL) at -10 °C was subjected to BF₃·OEt₂ (0.15 mL, 1.2 mmol) via the General Procedure. The crude product was purified by flash chromatography (20:1 petroleum ether: Et₂O) to yield the 18a (0.0315 g, 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); ¹³C 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 C₁₅H₁₁ClCo₂O₇ calcd (M⁺) 455.8857, found 455.8841.

H₂SO₄ conditions: To a solution of cycloheptyne 1 (0.0858 g, 0.197 mmol) and 2-chloroethanol (1 mL) in CH₂Cl₂ (5 mL) at 0 °C was added H₂SO₄ (3 drops). The solution was stirred for 1 h, at which point NH₄Cl(aq) was added and a standard workup performed. Flash chromatography as above afforded 18a (0.0679 g, 76%).

3.3.13. Hexacarbonyl[µ-η⁴–(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 CH₂Cl₂ (2.7 mL) at -10 °C was subjected to BF₃·OEt₂ (0.17 mL, 1.3 mmol) via the General Procedure. The crude product was purified by flash chromatography (25:1 petroleum ether: Et₂O) to yield the 19a (0.0440 g, 68%) as a red–brown oil. IR (neat, KBr, cm⁻¹):
2925, 2091, 2051, 2021, 1457, 1054; \( ^1H \) NMR \( \delta \): 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 \( \delta \): 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\(_2\)O\(_7\) calcd (M\(^+\)) 481.9014, found 481.9001.

3.3.14. Hexacarbonyl[\( \mu-\eta^4-\)cyclohept–2–en–4–ynylacetamide]dicobalt (20a)

**H\(_2\)SO\(_4\) 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; \( ^1H \) NMR \( \delta \): 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 \( \delta \): 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\(_2\)NO\(_7\) calcd (M\(^+\)-CO) 406.9250, found 406.9242.

**Acknowledgments**

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**References and notes**


13. Reaction with furan at -30 °C gave no additional α-product 7b, suggesting that the -10 °C conditions give kinetic products.


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.

20. Attempts to isolate cation 21 for study of possible kinetic reactions with heteroatom nucleophiles resulted only in elimination product 14.

$\text{Me}_3\text{Si} \underset{\text{X}}{\text{CH}} \text{Co}_2(\text{CO})_6$ $\text{Co}_2(\text{CO})_6$

9a $\text{X} = \text{OH}$

9b $\text{X} = \text{Cl}$

9c $\text{X} = \text{OAc}$

$\text{Me}_3\text{Si} \underset{\text{X}}{\text{CH}}$

$\text{Co}_2(\text{CO})_6$

$\text{Co}_2(\text{CO})_6$

9a $\text{X} = \text{OH}$

9b $\text{X} = \text{Cl}$

9c $\text{X} = \text{OAc}$

14

21
Figure(s) (use if uploading high quality figure files)
\[
\begin{align*}
\text{OAc} & \quad \text{Co}_2(\text{CO})_6 \\
& \quad \text{BF}_3\text{-OEt}_2 \\
\gamma^- & \quad \alpha^-
\end{align*}
\]
2, X = OH
3, X = OAc

1. Ac₂O, pyridine (2 → 3)
2. Co₂(CO)₈

(51%)

4

(CO)₆Co₂

OAc

CH₂Cl₂, RT, 3h

(80%)

(CO)₆Co₂

1
Lewis and Proton Acid Mediated Nicholas Reactions of 3-Acetoxycyclohept-1-en-4-yne-dicobalt Hexacarbonyl: Site Selectivity of Nucleophile Incorporation
Joseph DiMartino and James R. Green*

**Kinetic Product:**
Predominantly γ-

**Thermodynamic product:**
Exclusively γ-