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Cobalt-Mediated η^5-Pentadienyl/Alkyne [5 + 2] Cycloaddition Reactions: Substitution Effects, Bicyclic Synthesis, and Photochemical η^4-Cycloheptadiene Demetalation

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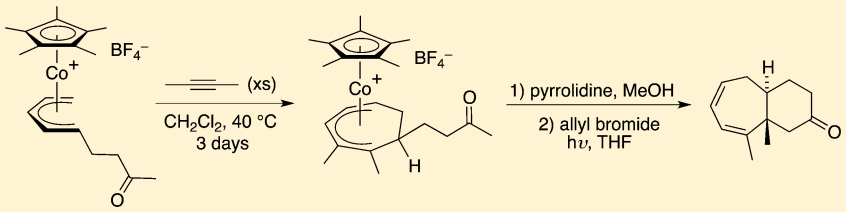
Supporting Information



ABSTRACT: The preparation of seven-membered carbocycles via traditional organic synthesis is difficult, yet essential, due to the prevalence of these moieties in bioactive compounds. As we report, the Co-mediated pentadienyl/alkyne [5 + 2] cycloaddition reaction generates kinetically stable η^2,η^3-cycloheptadienyl complexes in high yield at room temperature, which isomerize to the thermodynamically preferred η^5-cycloheptadienyl complexes upon heating at 60−70 °C. Here we describe an extended investigation of this reaction manifold, exploring substituent effects and extending the reaction to tandem cycloaddition/nucleophilic cyclizations, generating fused bicyclic compounds. We also describe a new high-yielding photolytic method for the decomplexation of organic cycloheptadienes from Co(I) complexes. Both C_5Me_5 (Cp*) and C_5H_5 (Cp) half-sandwich complexes are active in [5 + 2] cycloaddition with alkynes, with Cp* generally providing higher yields of cycloheptadienyl complexes. Cp cycloheptadienyl complexes, however, are resistant to thermal $\eta^2,\eta^3 \rightarrow \eta^5$ isomerization. The reaction remains limited to open pentadienyl complexes incorporating substituents in the terminal (1 and 5) positions, except for the unsubstituted CpCo(η^5-cycloheptadienyl)$^+$ complex, which is modestly reactive. Incorporation of tethered latent nucleophiles allows cyclization onto the intermediate cycloheptadienyl cations, producing bicyclo[5.3.0]decadiene and bicyclo[5.4.0]-undecadiene systems with complete diastereocontrol. A selection of intermediate complexes have been crystallographically characterized. Addition of tethered malonate nucleophiles occurs reversibly with equilibration to a thermodynamic elimination product, while enolate nucleophiles cyclize reliably under kinetic control. The resulting bicyclic products are decomplexed in high (>90%) yield by UV photolysis in the presence of allyl bromide to provide the organic bicyclic diene with complete retention of ring fusion geometry and without double-bond isomerization.

INTRODUCTION

Since the first report of the Diels−Alder reaction, cycloaddition methodology has become a key component of the synthetic organic chemist's toolbox. This utility is largely due to the formation of multiple carbon−carbon bonds in a single step, often with excellent control of regiochemistry and stereoselectivity. Thermal, photochemical, and metal-mediated cycloaddition reactions for the synthesis of small- and medium-sized carbocycles have been developed, with four-, five-, and six-membered rings receiving most of the attention (i.e., [2 + 2], [3 + 2], and [4 + 2] cycloaddition reactions). In contrast, the preparation of seven-membered rings by cycloaddition remains less developed,[1] despite the almost continuous discovery of bioactive natural products with seven-membered-ring structures in the core.[2] One important pathway to access the seven-membered ring is the formal [5 + 2] cycloaddition reaction, which has a rich and varied history.[3] Among unsolved problems in [5 + 2] cycloaddition is the cyclization of an alkyne with a pentadienyl fragment, a reaction that generally requires mediation by a transition metal.[4] The reaction has traditionally been hampered by poor control over the stoichiometry of alkyne incorporation, with most reactions leading to complex multicyclic systems. We have addressed this difficulty in our recent disclosure[5] of the [5 + 2] cycloaddition reaction of alkynes with Cp*Co(η^5-pentadienyl)$^+$ cations (Cp* = η^5-C_5Me_5),[6] which proceeds with complete control of alkyne stoichiometry and ring size, yielding cycloheptadienyl complexes (Scheme 1). Under kinetic control, thermally stable η^2,η^3-cycloheptadienyl complexes **2** are obtained for some substitution patterns, a previously unprecedented coordination mode for unbridged cycloheptadienyl systems.[7]

Our interest in the cycloaddition chemistry of η^5-pentadienyl cobalt complexes **1** was piqued by our observation of allyl/alkyne

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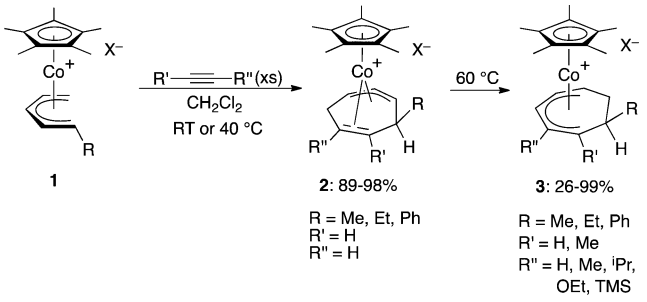
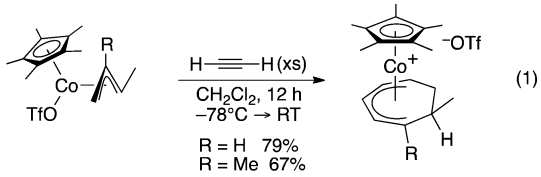
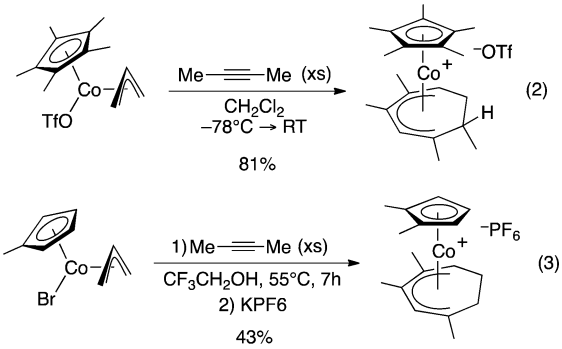
Scheme 1. Pentadienyl/Alkyne [5 + 2] Cycloaddition



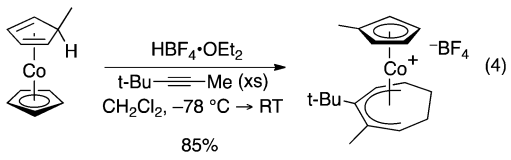
[3 + 2 + 2] cycloaddition reactions (eq 1) and anomalous [3 + 2 + 2] cyclo-rearrangements of Cp*Co(η^3-allyl)X



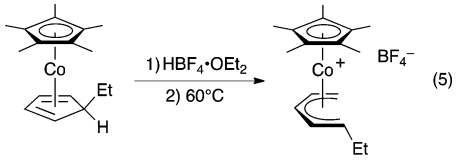
complexes upon treatment with alkynes (eqs 2 and 3).[8,9] The [3 + 2 + 2] reaction proceeds via a coordinatively unsaturated



η^3-allylmetal intermediate, which incorporates 2 equiv of terminal alkyne to produce cationic Cp*Co(η^5-cycloheptadienyl)$^+$ complexes in reasonable yield. Corresponding reactions of internal alkynes, however, afforded anomalous cycloaddition products, proceeding in a superficially similar fashion to the standard [3 + 2 + 2] reaction but producing unexpected substituent patterns in both the cycloheptadienyl ring (eq 2) and, oddly, the ancillary cyclopentadienyl ligand (eq 3). Isotopic (^{13}C, ^{2}H) labeling and synthetic studies established that these reactions proceed by a carbon−carbon bond activation of an intermediate η^3-cyclopentadienyl ring, an unexpected electrophilic cleavage of an unstrained ring system (eq 4).[10]



Two decades ago, Spencer et al., showed that upon protonation with HBF_4 Cp*Co(η^4-cyclopentadiene) and Cp*Co(η^5-cyclooctadiene) complexes undergo a suspiciously similar C−C bond cleavage reaction, yielding ring-opened cationic η^5-pentadienyl complexes (eq 5).[11] The possibility that such a bond activation could be embedded in the mechanism of

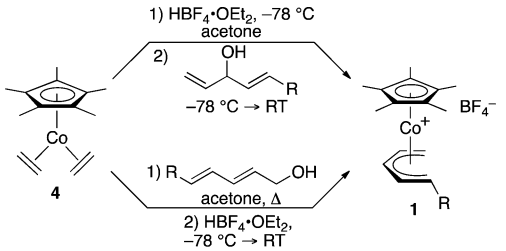


the anomalous [3 + 2 + 2] cycloaddition reaction prompted us to investigate directly the reactivity of alkynes with acyclic pentadienyl complexes of cobalt. While the [5 + 2] cycloaddition reactions indeed proceed,[5] the isolation of kinetically stable η^2,η^3-cycloheptadienyl complexes **2**, not observed during the anomalous [3 + 2 + 2] reaction, clearly demonstrates that the [5 + 2] cycloaddition is a mechanistically independent reaction manifold. Here we describe an extended investigation of (i) the effects of pentadienyl substitution and variation of the ancillary ligand on cycloaddition reactivity and product distribution and (ii) a proof-of-principle extension of the [5 + 2] reaction manifold to the synthesis of conjugated and nonconjugated bicyclo[5.3.0]- and bicyclo[5.4.0]-diene ring systems. We also report a novel photolytic method for the efficient decomplexation of cobalt η^4-cycloheptadiene complexes in high yield, addressing a longstanding problem in organocobalt chemistry.

RESULTS AND DISCUSSION

Cp*Co(η^5-pentadienyl)/alkyne [5 + 2] Cycloaddition. We began our investigations by preparing a series of mono-, di-, and trisubstituted pentadienyl complexes (Scheme 2).[5,6] Simple

Scheme 2. Preparation of η^5-Pentadienyl Complexes from 1,3- and 1,4-Pentadienols



1,3- and 1,4-pentadienols add to Cp*Co(C_2H_4)$_2$ in the presence of HBF_4·OEt_2 to yield Cp*Co(η^5-pentadienyl) cations **1** in reasonable to good yields. The yield decreases with an increasing number of pentadienyl substituents, presumably due to competing off-metal reactions. The air-stable complexes are readily isolated and purified by benchtop chromatography. In some cases, the purity was improved by an aqueous exchange of the BF_4^- counterion for PF_6^-.

Despite being coordinatively saturated, η^5-pentadienyl complexes **1a**,**c**−**e** react smoothly with excess ethyne at room temperature, providing the coordinatively saturated η^2,η^3-cycloheptadienyl complexes **2a**,**c**−**e** with excellent selectivity and complete diastereocontrol (Table 1, entries 1−4 and 7−11). The complexes **2a**,**c**,**d** could be quantitatively isomerized to more typical η^5-cycloheptadienyl complexes **3a**,**f**,**i** by heating to 70 °C in CH_2Cl_2 (entries 1, 6, and 9). It could be debated whether the isomerization is a thermal β-hydride elimination/reinsertion process or is mediated by an external basic agent from the solvent or glass. However, η^2,η^3-cycloheptadienyl complex **2e**, bearing two methyl groups proximal (syn) to the metal (entry 10), is completely inert at elevated temperature (see Figure 1 for the solid-state structure

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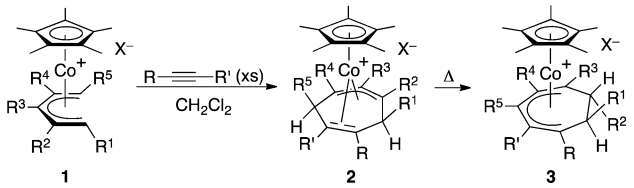
Table 1. Cp*Co(cycloheptadienyl)$^+$ Synthesis via [5 + 2] Cycloaddition[a]



entry	substrate	alkyne	2/yield (%)[b]	3/yield (%)[c]
1	**1a** (R^1 = Me; R^2, R^3, R^4, R^5 = H)	R, R′ = H	**2a**/98	**3a**/99
2	**1a**	R, R′ = Me		**3b**/99
3	**1a**	R = H, R′ = OEt		**3c**:**3c**′ (2:1)/82 **3c**: R = H, R′ = OEt **3c**′: R = OEt, R′ = H
4	**1a**	R = H, R′ = ^{n}Pr		**3d**:**3d**′ (2:1)/91 **3d**: R = H, R′ = ^{n}Pr **3d**′: R = ^{n}Pr, R′ = H
5[d]	**1b** (R^1, R^2 = Me; R^3, R^4, R^5 = H)	R, R′ = H	**2b**:**3e** (3.8:1)/68	
6	**1c** (R^1 = Ph; R^2, R^3, R^4, R^5 = H)	R, R′ = H	**2c**/89	**3f**/99
7	**1c**	R, R′ = Me		**3g**/96
8	**1c**	R = H, R′ = TMS		**3h**/26[e] R = H, R′ = TMS
9	**1d** (R^1 = Et; R^2, R^3, R^4, R^5 = H)	R, R′ = H	**2d**/91	**3i**/99
10	**1e** (R^1, R^5 = Me; R^2, R^3, R^4 = H)	R, R′ = H	**2e**/94	
11	**1e**	R, R′ = Me	**2f**/85	
12	**1f** (R^1, R^2, R^3, R^4, R^5 = H)	R, R′ = H		
13	**1g** (R^2 = Me; R^1, R^3, R^4, R^5 = H)	R, R′ = H		
14	**1h** (R^3 = Me; R^1, R^2, R^4, R^5 = H)	R, R′ = H		
15	**1i** (R^1, R^3 = Me; R^2, R^4, R^5 = H)	R, R′ = H		
16	**1j** (R^1, R^4 = Me; R^2, R^3, R^5 = H)	R, R′ = H		
17	**1k** (R^1, R^2, R^4 = Me; R^3, R^5 = H)	R, R′ = H		

[a]Detailed conditions are reported in the Supporting Information; yields of products after SiO_2 chromatography (3−4% MeOH in CH_2Cl_2) are given. [b]Conditions: ethyne (saturated solution in CH_2Cl_2), room temperature, 12−72 h (10 equiv of 2-butyne, room temperature, 72 h for **2f**). [c]As above, but 40−60 °C, 24−72 h (room temperature, 72 h for **3f**). [d]An additional minor byproduct, tentatively identified as a [3 + 2 + 2] cycloadduct, is detected in the ^{1}H NMR spectrum of this product. [e]Yield determined by ^{1}H NMR integration using 1,3,5-trimethoxybenzene as an internal standard.

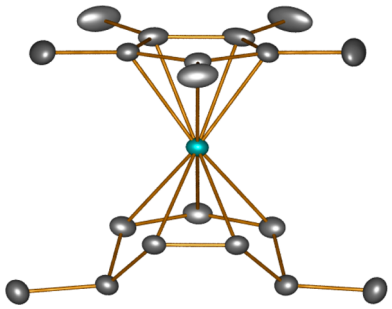
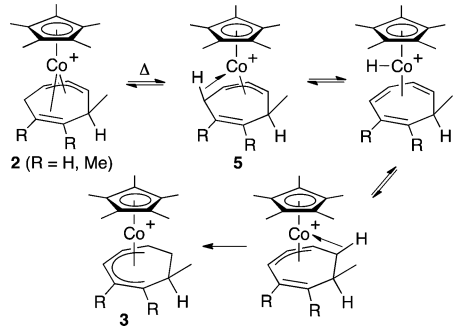


Figure 1. X-ray structure diagram for [Cp*Co(η^2,η^3-1,5-dimethylcycloheptadienyl)]$^+$$BF_4^-$ (**2e**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0312, wR2 = 0.0781.[13]

of complex **2e**). This result clearly demonstrates that a unimolecular β-hydride elimination mechanism is most likely at play during isomerization. This mechanistic proposal is supported by density functional theory (DFT) calculations, where the lowest energy mechanism entails reversible dissociation of the η^2-alkene moiety with concomitant formation of an agostic allyl hydride intermediate (Scheme 3).[12] This hydride undergoes β-hydride elimination and reinsertion to form a second agostic hydride, with subsequent dissociation of the C−H bond and association of the free olefin to form the final η^5-cycloheptadienyl complex.

Scheme 3. Mechanism of η^2,η^3 → η^5 Isomerization



2-Butyne is also an effective coupling partner; however, the cycloaddition reaction is considerably slower. To achieve reasonable reaction rates, the system is heated to 40 °C; under these conditions, formation of the intermediate η^2,η^3-cycloheptadienyl complex is not observed and the reaction proceeds directly to the η^5-dimethylcycloheptadienyl complexes **3**. The lower barrier to isomerization is attributed to weaker Co−alkene bonding arising from steric repulsion between the alkene methyl groups and the Cp* ancillary ligand, leading to facile alkene dissociation (**2** → **5** in Scheme 3).[12] Only cycloadduct **2e**, obtained from 1,5-dimethylpentadienyl complex **1e** (Table 1, entry 11), is kinetically stable under the reaction conditions—the η^2,η^3 → η^5 isomerization is again blocked by the *syn*-methyl substituents. The η^2,η^3-cycloheptadienyl

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complex **2e** decomposes without isomerization at elevated temperature, and the complex slowly decomposes in solution at room temperature. Interestingly, the cycloadditions of pentadienyl complexes **1c**,**e** with 2-butyne proceed at room temperature to yield the η^5-cycloheptadienyl complexes **3g** (entry 7), characterized by X-ray diffraction (Figure 2), and

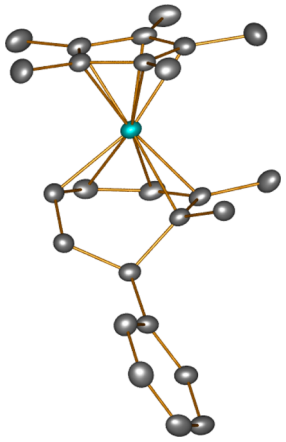


Figure 2. X-ray structure diagram for [Cp*Co(η^5-cycloheptadienyl)]$^+BF_4^-$ (**3g**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0479, wR2 = 0.1374.[13]

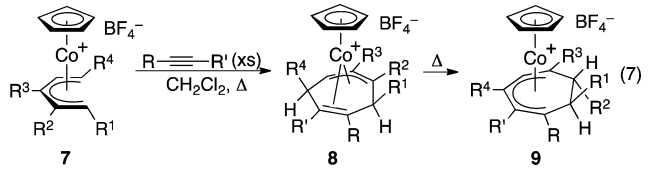
η^2,η^3-cycloheptadienyl complex **2f** (entry 11), respectively, suggesting a much higher degree of reactivity for terminally substituted pentadienyl systems.[12]

The reaction of 1-pentyne with pentadienyl complex **1a** requires heating at 40 °C, providing η^5-cycloheptadienyl complex **3d** in 91% yield as a 2:1 mixture of regioisomers (Table 1, entry 4). The reaction with isosteric but electronically biased ethoxyacetylene proceeds at a significantly accelerated rate (entry 3), albeit with no improvement in regioselectivity. The sterically differentiated terminal alkyne TMS-acetylene yields a single isolable product, η^5-cycloheptadienyl complex **3h**, but in poor yield (entry 8). While the product appears to be that arising from a sterically controlled regioselective insertion of the alkyne unit, the low yield suggests that the reaction is not truly regioselective. For the alternate regioisomer to form, a C−C bond must be formed between two secondary positions: steric effects between the TMS and Me substituents are expected to raise the TS energy for this process significantly, allowing unproductive (and thus far uncharacterized) side processes to become kinetically competitive. Trials with phenylacetylene led to similarly complex crude product mixtures and were not further investigated.

To our considerable consternation, pentadienyl complexes lacking 1-substituents or bearing additional internal methyl groups (i.e., 2- or 3-substituents) display considerably attenuated reactivity. This trend is most clearly illustrated by the reactions of ethyne with methylpentadienyl complexes **1a**,**g**,**h** and the unsubstituted complex **1f** (Table 1, entries 1, 12−14). Only the terminally substituted complex **1a** is reactive; neither unsubstituted complex **1f** nor the 2- or 3-substituted complexes **1h**,**g** show any conversion to tractable products. This trend immediately suggests that a 1-substituent is critical for dissociative reactivity. Necessary, but not sufficient, however: no reaction with ethyne is observed for the 1,3- or 1,4-dimethylated complexes **1i**,**j** (entries 15 and 16) or for the 1,2,4-trisubstituted complex **1k** (entry 17). Only the 1,2-disubstituted pentadienyl complex **1b** displays productive reactivity and gives a reasonable yield (entry 5).

A DFT investigation of the reaction mechanism[12] suggests that the rate-limiting step of the cycloaddition process is alkyne capture by dissociative interchange, forming cationic Cp*(η^3-pentadienyl)alkyne complex **6** (eq 6). The energy barrier for complex formation is related to the dihedral angle between the planes defined by the five carbon atoms of the open pentadienyl ligand and the five carbon atoms of the ancillary Cp*: the smaller the angle, the lower the TS energy barrier,

Table 2. CpCo(cycloheptadienyl)$^+BF_4^-$ Synthesis via [5 + 2] Cycloaddition[a]



7 **8** **9**

entry	substrate	alkyne	**8**/yield (%)[b]	**9**/yield (%)[c]
1	**7a** (R^1 = Me; R^2, R^3, R^4 = H)	R, R′ = H	**8a**/55	
2	**7a**	R, R′ = Me	**8b**/43	**9a**/99
3	**7b** (R^1 = TMS; R^2, R^3, R^4 = H)	R, R′ = H	**8c**/94	
4	**7b**	R, R′ = Me	**8d** + **9b**[d] (19:1)/68 **9b**: R^1, R^2, R^3, R^4 = H	
5	**7c** (R^1 = Ph; R^2, R^3, R^4 = H)	R, R′ = H	**8e**/12	
6	**7c**	R, R′ = Me	**8f** + **9c** (7:1)/63	
7	**7d** (R^1, R^2, R^3, R^4, R^5 = H)	R, R′ = H	**8g** + **9d** (1:1.8)/47	
8	**7d**	R, R′ = Me	**8h** (1:2)[e]	**9e** (1:3)/14[e]
9	**7e** (R^2 = Me; R^1, R^3, R^4 = H)	R, R′ = Me		
10	**7f** (R^3 = Me; R^1, R^2, R^4 = H)	R, R′ = Me		
11	**7g** (R^1, R^2 = Me; R^3, R^4 = H)	R, R′ = Me		
12	**7h** (R^1, R^4 = Me; R^2, R^3 = H)	R, R′ = Me		

[a]Detailed conditions are reported in the Supporting Information; yields of isolated products after SiO_2 chromatography (3−4% MeOH in CH_2Cl_2) are given. [b]Conditions: ethyne (saturated solution in CH_2Cl_2), 40 °C, 72 h or 2-butyne (10 equiv), 40 °C, 72 h. [c]As above, but 65−90 °C for 72 h. [d]The TMS group is cleaved under the conditions leading to η^2,η^3 → η^5 isomerization.[14] [e]Formed as a mixture favoring an unidentified coproduct.

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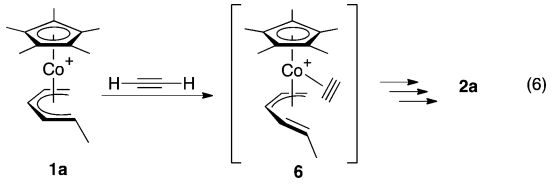


with angles of ca. 7.5° or less providing optimal reactivity. Only small deviations from coplanarity result from steric repulsions between the terminal (1 and 5) substituents and the ancillary ligand, but internal substituents serve to significantly raise the dihedral angle. Complexes with smaller dihedral angles are higher in energy and lie on the pathway for $\eta^5 \rightarrow \eta^3$ isomerization of the pentadienyl ligand leading to alkyne capture (eq 6).

CpCo(η^5-pentadienyl)/Alkyne [5 + 2] Cycloaddition. To explore the effects of the ancillary ligand on the [5 + 2] cycloaddition reaction (eq 7 in Table 2), we prepared a series of CpCo(η^5-pentadienyl)$^+$ complexes **7** (Table 2). Significantly reduced yields in comparison with the Cp* series were obtained in almost all cases; the primary exception to this trend is that of unsubstituted complex **7d** (Table 2, entries 7 and 8). The structure of 7-methyl-η^2,η^3-cycloheptadienyl complex **7a** was unambiguously confirmed by X-ray diffraction (Figure 3).

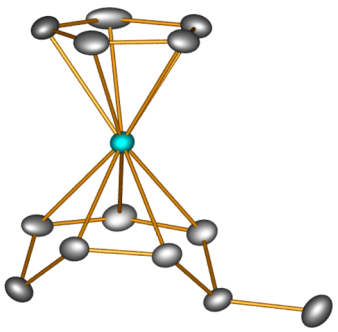


Figure 3. X-ray structure diagram for [CpCo(η^2,η^3-1-methylcycloheptadienyl)]$^+$BF$_4^-$ (**8a**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0336, wR2 = 0.0870.[13]

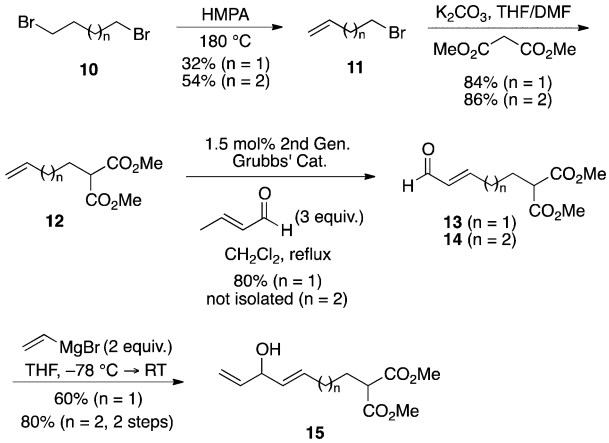
For cycloadditions with ethyne to proceed, the reaction mixture must be heated to 40 °C. Little to no reaction is observed at room temperature; in contrast, the Cp* analogues are reactive at room temperature and the reactions proceed to give excellent yields. In several cases, the cycloaddition reactions do not proceed to completion after 3 days at 40 °C, even for pentadienyl ligands known to be highly reactive such as Cp* analogues. Despite the generally reduced reactivity of the CpCo(η^5-pentadienyl)$^+$ complexes, unsubstituted complex **7d** is unexpectedly more reactive, giving a moderate yield of the inseparable η^2,η^3- and η^5-cycloheptadienyl complexes **8d** (17%) and **9b**, respectively (30%, entry 7). This result is particularly surprising in comparison to the complete lack of reactivity observed for the unsubstituted Cp* analogue **1f** (Table 1, entry 12). Complex **7d** is also reactive toward 2-butyne, providing the η^2,η^3-cycloheptadienyl adduct **8h** as a minor product in combination with an unidentified major product (entry 8). The nonconjugated η^2,η^3-cycloheptadienyl complexes cleanly isomerize to the η^5 isomers upon heating at 65 °C.

It is striking that the CpCo(η^2,η^3-cycloheptadienyl)$^+$ isomers display a higher degree of thermal stability than the Cp* analogues, resisting η^2,$\eta^3 \rightarrow \eta^5$ isomerization during [5 + 2] cycloaddition reactions with 2-butyne. When TMS-substituted **7b** is exposed to 2-butyne under the standard reaction conditions, the major isolated product (19:1) is the η^2,η^3-cycloheptadienyl isomer, despite the reaction being conducted at 40 °C (Table 2, entry 4). For Ph-substituted **7c**, the ratio of η^2,η^3 to η^5 isomers is 7:1 (entry 6); in contrast, the Cp* analogue **2c** shows significant isomerization even at room temperature in CH_2Cl_2.[15] DFT studies have suggested the lower barrier to isomerization in the Cp* case is the result of increased steric repulsion between the alkene substituents and the methyl groups of the Cp* ancillary ligand, leading to facile dissociation of the alkene prior to β-hydride elimination (**2** → **5** in Scheme 3).[12]

The reduced cycloaddition reactivity of the Cp vs the Cp* pentadienyl system is likely a result of differing steric effects. Computations have indicated that steric repulsion between the Cp* ancillary ligand and terminal pentadienyl substituents, manifested as a decrease in the dihedral angle between the pentadienyl planes, activates the system for cycloaddition (vide supra).[12] In the Cp system, the steric effects of the ancillary ligand are significantly reduced, likely leading to a larger dihedral angle and attenuated reactivity.

Preparation of Bicyclic Systems via Intramolecular Cyclization. *Preparation of Pentadienyl Complexes.* Nucleophilic addition to cationic metal species bearing unsaturated ligands is well-known.[16] We reasoned that an intramolecular nucleophilic addition of a tethered latent nucleophile could be used to prepare bicyclo[5.3.0] and bicyclo[5.4.0] systems from the cationic η^2,η^3- and η^5-cycloheptadienylcobalt complexes prepared via [5 + 2] cycloaddition. To this end, we synthesized the malonate-bearing pentadienol substrates **15** from the corresponding dibrominated alkanes **10** (Scheme 4). The α,ω-bromoalkenes

Scheme 4. Preparation of Malonyl 1,3-Pentadienol Substrates (15)



11 were prepared by "flash pyrolysis" in HMPA in acceptable yields (32 and 54%, n = 1, 2, respectively).[17] The malonate nucleophile was installed by using dimethyl malonate in THF/DMF (84 and 85%).[18] Cross metathesis of diester **12** with crotonaldehyde using Grubbs' second-generation catalyst yields aldehydes **13** and **14**.[19] The use of 3 equiv of crotonaldehyde is required to drive the reaction to completion; in the absence of excess crotonaldehyde, significant amounts of pseudodimerized **12** are observed after 16 h. Use of acrolein in place of crotonaldehyde gave reduced yields due to catalyst poisoning, indicated by a significant amount of undimerized **12**

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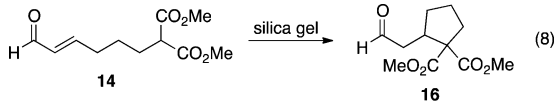
in the ^{1}H NMR spectrum of the crude reaction product. Whether this poisoning is due to the acrolein itself or an impurity was not investigated. Finally, addition of 2 equiv of vinylmagnesium bromide yields the nonconjugated 1,4-pentadienols **15** in reasonable to good yields (60 and 80%). Attempted purification of aldehyde **14** by silica gel chromatography leads instead to an intramolecular Michael addition (eq 8) generating cyclic aldehyde **16**, an undesired reaction that

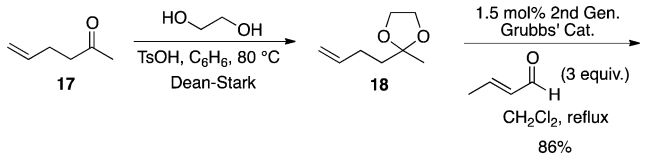


14 16 (8)

also occurs slowly under the metathesis reaction conditions. As a consequence, enal **14** was carried forward to dienol **15** without purification.

The tethered pronucleophile was varied by introduction of a masked ketone functionality (**20**) (Scheme 5). Acid-catalyzed

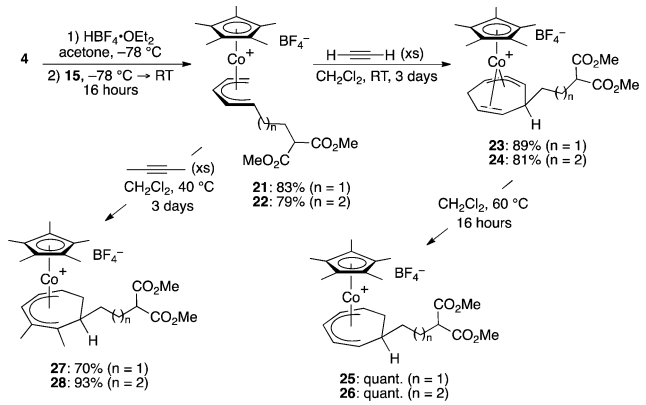
Scheme 5. Preparation of Masked Ketone Containing 1,3-Pentadienol 20



acetal formation under Dean–Stark conditions converts 1-hexen-5-one (**17**) into the protected alkene **18**.[20] Ruthenium-catalyzed cross metathesis and vinylmagnesium bromide addition, as described, complete the synthesis. We did not attempt unmasking of the ketone due to the possibility of a competing Nazarov cyclization,[21] opting instead to load acetal **20** directly onto the metal.

Both malonyl pentadienols **15** convert to cobalt pentadienyl complexes in good yields under the standard reaction conditions (Scheme 6). Pentadienylcobalt complex **21** was readily

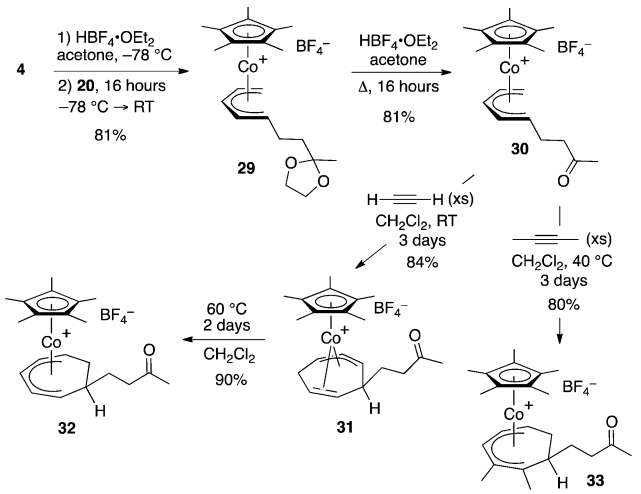
Scheme 6. Preparation and [5 + 2] Cycloaddition Reactions of Substituted Pentadienyls 21 and 22



purified and characterized. The homologous complex **22**, however, could not be rigorously purified, with the ^{1}H NMR spectrum of chromatography-purified material exhibiting paramagnetic impurities. Complex **22** also decomposes slowly in solution during crystallization and in the solid state at low temperature in air. Such sensitivity was not observed for any other Co(III) η^5-pentadienyl complex we have prepared. We tentatively ascribe this sensitivity to spontaneous intramolecular cyclization, analogous to that observed for noncomplexed enal **14**. An attempt to deliberately prepare such a cyclization product via deprotonation with Hünig's base under argon resulted in a complex mixture and was not further explored.

Acetal-protected pentadienol **20** was loaded onto the metal under the same low-temperature protonolysis conditions described previously (Scheme 7). With this method, the

Scheme 7. Preparation and [5 + 2] Cycloaddition Reactions of Ketone Substituted Pentadienyl Complex 30



protected pentadienyl complex **29** is obtained exclusively; the acetal functionality is stable under the reaction conditions and to silica gel chromatography but does hydrolyze slowly during slow crystallization from (presumably wet) CH_2Cl_2/Et_2O. The protecting group can be removed without competitive cyclization using catalytic $HBF_4{\cdot}OEt_2$ in wet acetone at reflux to yield ketone-substituted pentadienyl complex **30** in 81% yield. The structure was confirmed by X-ray diffraction (Figure 4).

Tethered Substrates: [5 + 2] Cycloaddition. Malonyl-tethered pentadienyl complexes **21** and **22** both undergo clean cycloaddition in the presence of excess ethyne to yield η^2,η^3-cycloheptadienyl complexes **23** and **24** in 89 and 81% yields, respectively (Scheme 6). Complex **24**, bearing the three-carbon tether, was unambiguously characterized by X-ray crystallography (Figure 5); no decomposition of this material is observed, suggesting that the intramolecular nucleophilic cyclization is not competitive with the cycloaddition, in contrast to the case for the open pentadienyl complex **22** and organic enal **14**. Isomerizations of **23** and **24** to the thermodynamically favored η^5-cycloheptadienyl complexes **25** and **26** also proceed smoothly at 60 °C.[22] The cycloaddition reactions with 2-butyne also proceed in good to excellent yields, providing η^5-1,2-dimethylcycloheptadienyl complexes **27** (70%) and **28** (93%), respectively.

The cycloaddition of η^5-pentadienyl ketone complex **30** (Scheme 7) with ethyne leads cleanly to η^2,η^3-cycloheptadienyl complex **31**, with subsequent thermal isomerization to η^5-cycloheptadienyl complex **32** also proceeding cleanly in

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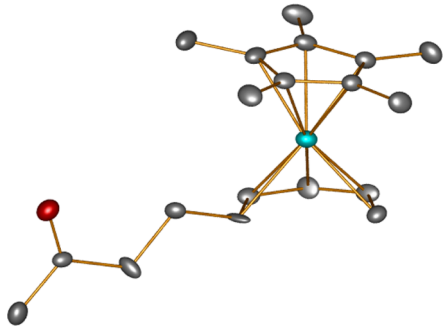


Figure 4. X-ray structure diagram for [Cp*Co(η^5-1-(2-butanoyl)-pentadienyl)]$^+BF_4^-$ (**30**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0363, wR2 = 0.0953.[13]

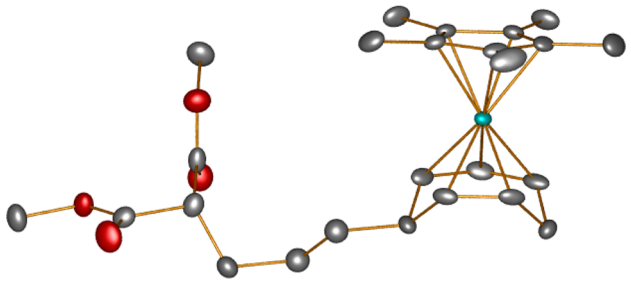


Figure 5. X-ray structure diagram for [Cp*Co(η^2,η^3-cycloheptadienyl)]$^+BF_4^-$ (**24**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0549, wR2 = 0.1584.[13]

excellent yield. Cycloheptadienyl complexes **31** and **32** were both crystallographically characterized, as illustrated in Figures 6 and 7. The X-ray structure of η^5-pentadienyl ketone

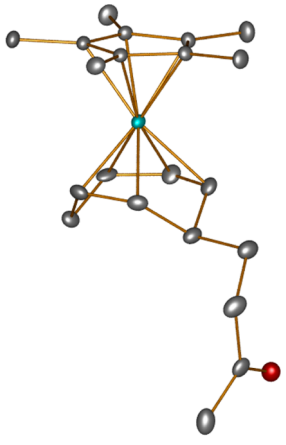


Figure 6. X-ray structure diagram for [Cp*Co(η^2,η^3-cycloheptadienyl)]$^+BF_4^-$ (**31**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0613, wR2 = 0.1641.[13]

complex **30** displays a dihedral angle of 7.40°, which supports our structure/reactivity model.[12] The corresponding cycloaddition with 2-butyne, however, does not consistently return spectroscopically homogeneous η^5-cycloheptadienyl ketone complex **33**. The byproduct is tentatively assigned as a cobaltocenium complex believed to arise via competitive [3 + 2] cycloaddition of the η^3-pentadienyl intermediate, on the basis of the characteristically small geminal coupling constants observed in the ^{1}H NMR spectra of cyclopentadienyl derivatives. In most

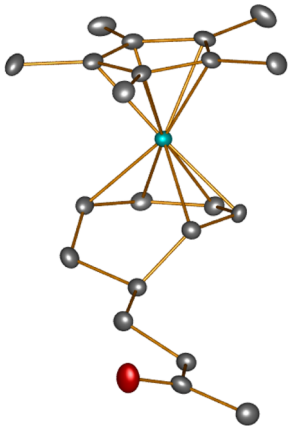
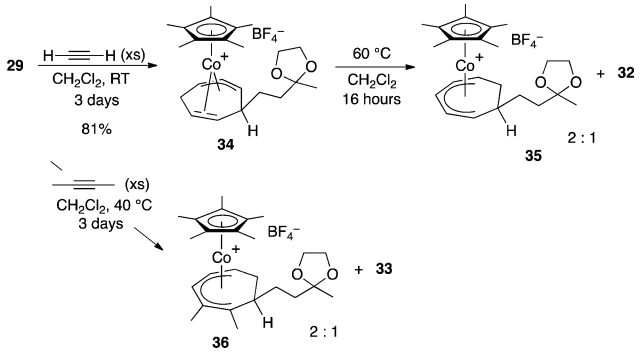


Figure 7. X-ray structure diagram for [Cp*Co(η^5-cycloheptadienyl)]$^+BF_4^-$ (**32**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0361, wR2 = 0.0961.[13]

experiments, this material was obtained in approximately 10% yield. Qualitative observations made over a series of experiments suggest that higher concentrations of 2-butyne minimize or eliminate the formation of this byproduct, although no rationale can be offered for this effect.

The η^5-pentadienyl acetal **29** also yields the expected η^2,η^3-cycloheptadienyl complex **34** upon reaction with ethyne (Scheme 8), as characterized by X-ray crystallography (Figure 8).

Scheme 8. [5 + 2] Cycloaddition Reactions of Acetal-Protected Pentadienyl Complex 29



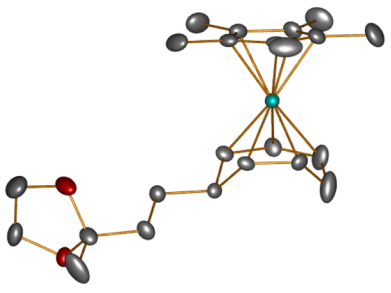


Figure 8. X-ray structure diagram for [Cp*Co(η^2,η^3-cycloheptadienyl)]$^+BF_4^-$ (**34**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0582, wR2 = 0.1601.[13]

However, the thermal η^2,η^3 → η^5 isomerization to produce complex **35**, also unambiguously characterized by X-ray diffraction (Figure 9), is accompanied by partial acetal hydrolysis,

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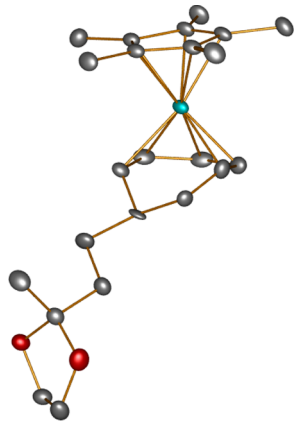
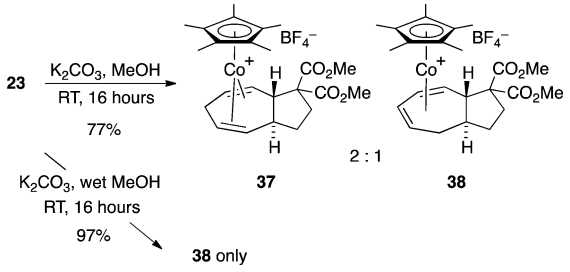


Figure 9. X-ray structure diagram for [Cp*Co(η^5-cycloheptadienyl)]$^+BF_4^-$ (**35**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0436, wR2 = 0.1189.[13]

which also occurs slowly during crystallization at room temperature. A similar competitive deprotection occurs during the cycloaddition of 2-butyne at 40 °C. Cyclic acetals are generally stable under neutral conditions, but it is possible that the Co(III) complex itself functions as a Lewis or Brønsted acid, resulting in competitive acetal hydrolysis by adventitious water at elevated temperature. Acid-catalyzed hydrolysis of both the η^2,η^3- and η^5-cycloheptadienyl acetal complexes **34** and **35** leads to η^5-cycloheptadienyl complex **32**, identical with that obtained via direct treatment of η^5-pentadienyl ketone complex **30** with ethyne followed by isomerization. Since acetal cleavage and $\eta^2,\eta^3 \rightarrow \eta^5$ isomerization can be achieved in one pot, the transformation of acetal complex **29** to ketone cycloheptadienyl complex **32** can be conducted conveniently as a one-step procedure.

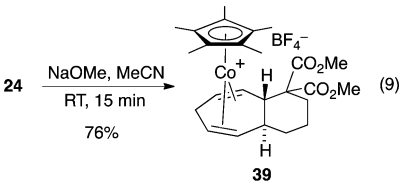
Intramolecular Cyclization. With cyclopheptadienyl complexes **23**, **24**, **27**, **28**, and **31**−**33** in hand, we turned our attention to the formation of bicyclic adducts via intramolecular nucleophilic addition. Initial attempts to deprotonate η^2,η^3-cycloheptadienyl complexes **23** and **24** were performed using NaOMe in MeCN at room temperature. The ^{1}H NMR spectra of the crude bicyclic reaction product contained significant impurities. The use of Hünig's base in THF at −78 °C reduced these side reactions, but the process unfortunately also proved to be irreproducible. Ultimately, we settled on the use of K_2CO_3 suspended in MeOH at room temperature as optimal (Scheme 9), returning a 77% yield of cyclization products, but

Scheme 9. Cyclization of Cycloheptadienyl Complex 23



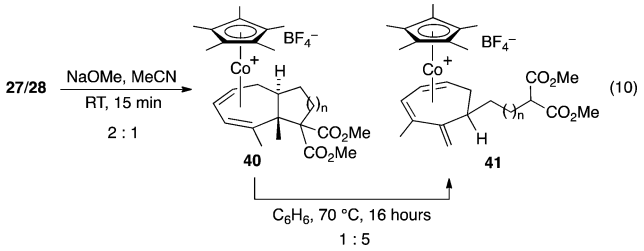
as an unselective 2:1 mixture of the anticipated 1,4-cycloheptadiene complex **37** and the isomerized 1,3-cycloheptadiene complex **38**. Using K_2CO_3 in wet MeOH, however, the conjugated product **38** is obtained exclusively in high yield. Importantly, the cyclization proceeds with complete diastereoselectivity, leading to the trans-fused bicyclic system exclusively.

Surprisingly, cyclization of the three-carbon-tethered complex **24** proceeds smoothly upon treatment with NaOMe in MeCN, providing only the 1,4-cycloheptadiene complex **39** in 76% yield, with no isomerization to the conjugated diene system (eq 9). Hünig's base was ineffective in inducing



cyclization. The thermal stability of bicyclic complexes **37** and **39** differs significantly—bicyclo[5.4.0] complex **39** is indefinitely stable in the solid state at −35 °C under a nitrogen atmosphere, while the bicyclo[5.3.0] system **37** slowly decomposes under identical conditions. ^{1}H NMR spectroscopy of the decomposition products suggests that reopening of the five-membered ring is relatively facile in solution, presumably by reionization of the tether. This process can be avoided by prompt demetalation (vide infra) and has not been investigated further.

The 2-butyne cycloadducts **27** and **28** were constructed with the goal of introducing quaternary centers into the bicyclic system upon nucleophilic cyclization. Using the NaOMe/MeCN cyclization conditions, both **27** and **28** returned mixtures of two products in a 2:1 ratio, as revealed by ^{1}H NMR spectroscopy of the isolated crude products. The major product is the desired bicyclic complex **40**, accompanied by a species tentatively assigned as cycloheptatriene complex **41**, arising from competitive deprotonation of the terminal methyl group (eq 10).



Upon heating in benzene-d_6 at 70 °C for 16 h, the crude product mixture equilibrates to a 1:5 ratio, now favoring the undesired exocyclic cycloheptatriene **41**. A reasonable equilibration mechanism invokes a reversible kinetic cyclization/reionization to the bicyclic complex **40** proceeding more slowly than deprotonation to give the thermodynamically favored triene **41**.

Equilibration of the kinetic cyclization product should be less favorable in the ketone enolate systems generated by deprotonation of complexes **31**−**33**. The use of the standard kinetic base LDA led to complex product mixtures, likely due to competing deprotonation of the allylic ring protons or a single-electron-transfer cascade. These difficulties were circumvented classically, by generating enamine intermediates[23] using pyrrolidine.[24] Treatment of η^5-ketone complex **32** with a stoichiometric amount of pyrrolidine in wet methanol leads to bicyclic 1,3-cycloheptadiene complex **42** in moderate yield,

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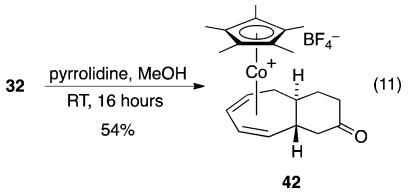


isolated as a spectroscopically pure compound after filtration through Celite under nitrogen (eq 11). Hydrolysis of the putative iminium intermediate occurs in situ; when rigorously dried MeOH is used as the reaction solvent, no cyclization products are obtained. The trans ring fusion was unambiguously determined through single-crystal X-ray diffraction (Figure 10).

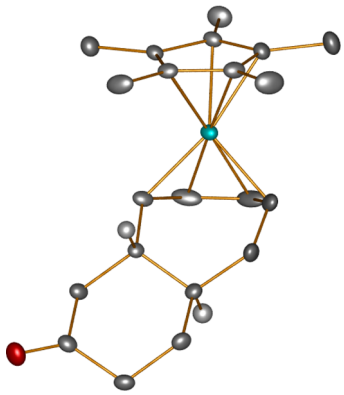
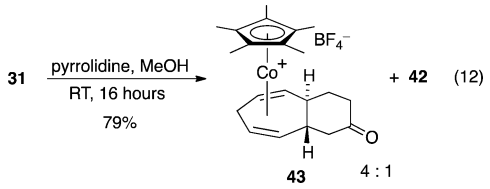


Figure 10. X-ray structure diagram for [Cp*Co(η^4-[5.4.0]-bicycloundecadienone)]$^+BF_4^-$ (**42**), with non-hydrogen atoms represented by thermal ellipsoids at the 20% probability level. Final residuals: R1 = 0.0294, wR2 = 0.0778.[13]

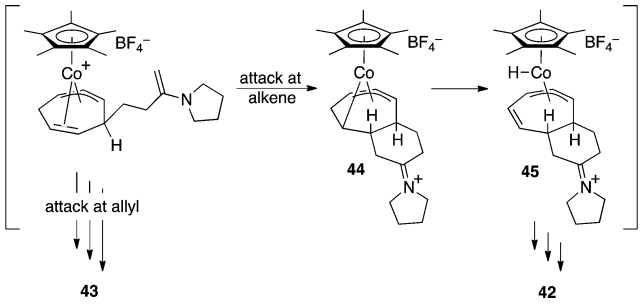
Exposure of η^2,η^3-cycloheptadienyl complex **31** to the same pyrrolidine-mediated conditions produces a 4:1 mixture of the desired 1,4-cycloheptadiene complex **43** accompanied by minor amounts of the conjugated 1,3-diene complex **42** (eq 12). The

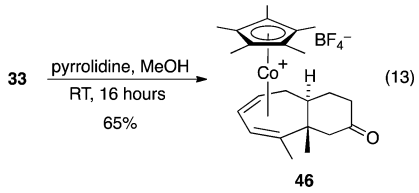


absence of strong base in this reaction suggests that competitive deprotonation/reprotonation is not likely to induce diene isomerization. We suggest, however, that the cyclization reaction proceeds via competitive *kinetic* alkylation at two electrophilic sites: the η^3-allyl moiety, leading directly to the nonconjugated product **43**, and the η^2-olefin, in accordance with the Davies–Green–Mingos selectivity rules (Scheme 10).[25] The latter gives rise to the η^1:η^3 intermediate **44**, which can undergo β-hydride elimination/reinsertion, resulting in the conjugated product **42**. It is conceivable that such a pathway is also at play in the formation of malonyl adducts **37** and **38** (Scheme 9). Such mechanistic ambiguities remain under investigation.

Upon exposure of 2-butyne cycloadduct **33** to pyrrolidine, the expected bicyclic complex **46** is obtained in a reasonable 65% yield (eq 13). The angular methyl substituent at the quaternary stereocenter is produced as a single diastereoisomer, and the ring fusion is tentatively assigned as trans and is

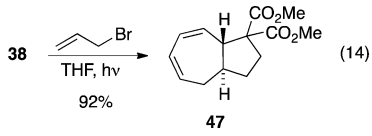
Scheme 10. Alternate Cyclization Mechanisms Leading to Bicyclic Isomers 42 and 43





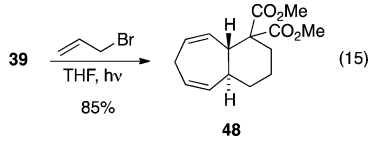
spectroscopically analogous to that of the crystallographically characterized complex **42**.

Decomplexation of Co(I) Cycloheptadiene Cycloadducts. The stereoselective synthesis of bicyclic cycloheptadiene compounds is completed by decomplexation to give the metal-free organic product. Standard methods, such as one- or two-electron oxidation using ferrocenium salts in biphasic pentane/MeCN,[8b] are productive but low-yielding. To improve the decomplexation yield and enable recyclability of the metal, we report a novel allylative demetalation procedure, potentially applicable to other demetalation-resistant cobalt diene systems. In the presence of allyl bromide under UV photochemical irradiation,[26] Cp*Co(cycloheptadiene) complexes are cleanly converted to Cp*Co(η^3-allyl)Br[27] with near-quantitative liberation of the intact cycloheptadiene ligand. The reaction is successful for both conjugated and nonconjugated diene complexes. Photolysis of the conjugated [5.3.0] complex **38** in the presence of excess allyl bromide, for example, provides an excellent yield of *trans*-hexahydroazulene **47** with complete retention of the ring fusion and diene position (eq 14). In



addition to the liberated organic, Cp*Co(η^3-allyl)Br is isolated as a red solid in moderate yield via silica gel chromatography, opening up the possibility for recycling of the metal reagent.

Under the same conditions, decomplexation of the nonconjugated diene complex **39** returns an 85% yield of bicyclo[5.4.0]undecadiene **48**, again with complete retention of geometric and structural features (eq 15). Unfortunately,



photochemical decomplexation of the mixture of complexes **37** and **38** results in a mixture of two organic products; the minor

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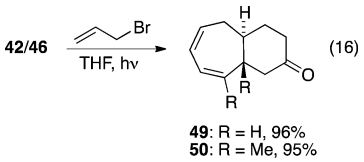
component is tentatively assigned as the desired nonconjugated bicycle, while the major component in the mixture could not be identified. The ^{1}H NMR spectrum of the crude product mixture displays signals reminiscent of the monocyclic organometallic precursor **23**, suggesting that this product derives from an oxidatively induced ring-opening process. The use of alternate decomplexation conditions, including ferrocenium oxidation or iodinolysis, resulted in similar complex product mixtures.

Photolytic decomplexations of the ketone-containing bicyclic complexes **42** and **46** proceed quantitatively; bicyclic ketones **49** and **50** were isolated as pure materials in 96% and 95% yields, respectively (eq 16). No loss of stereochemical or compositional integrity was detected in either system.



49: R = H, 96%
50: R = Me, 95%

CONCLUSION

While still an underexplored reaction, the metal-mediated [5 + 2] cycloaddition manifold is becoming increasingly utilized by the synthetic community.[3] Here we have established the synthetic scope of the cobalt-mediated pentadienyl/alkyne [5 + 2] cycloaddition reaction. Both Cp*- and CpCo(pentadienyl)$^+$ complexes undergo selective single insertion/cyclization upon reaction with alkynes. In comparison to the more general Cp* system, the CpCo(η^2,η^3-cycloheptadienyl)$^+$ complexes are obtained in reduced yields but show a higher barrier to η^2,η^3 → η^5 isomerization of the seven-membered ring. While the substituent scope remains modest, limited to substituents at the 1- and 5-positions of the pentadienyl fragment, metal-directed intramolecular cyclization of tethered nucleophiles postcycloaddition leads to an efficient synthesis of bicyclic organic products of reasonable structural complexity, with complete diastereocontrol. The process can be used to introduce quaternary stereocenters in high selectivity. From a more general perspective, the novel photolytic oxidative decomplexation addresses a longstanding problem in synthetic organocobalt chemistry, offering improved prospects for applications of Co(III)-mediated cycloaddition reactions to complex molecule synthesis.

EXPERIMENTAL SECTION

General Experimental Procedures. All manipulations of air-sensitive compounds were performed under an argon or nitrogen atmosphere using standard Schlenk techniques or in an MBraun LABmaster sp drybox. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl under nitrogen. Pentane was distilled from potassium/benzophenone ketyl under nitrogen. Dichloromethane and acetonitrile were distilled from calcium hydride and degassed. Acetone was dried over boric oxide, degassed via three freeze−pump−thaw cycles, vacuum-transferred, and stored under nitrogen. All other reagents were used without further purification. Flash column chromatography was performed with Silicycle silica gel (40−63 μm), neutralized with 1 mL of triethylamine for acid-sensitive compounds. Alumina filtrations were performed with Sigma-Aldrich neutral aluminum oxide, Brockman I, standard grade, 150 mesh, 58 Å, deactivated to Activity IV with 10 wt % water. Photolysis reactions were performed with a Hanovia 450 W high-pressure mercury lamp filtered through Pyrex or a Rayonette UV reaction carousel. The terms "reaction bomb" and "bomb" refer to a thick-walled glass vessel with a Teflon stopcock capable of withstanding moderately elevated internal pressure.

IR spectra were recorded on either a Nicolet Magna 750 FTIR spectrometer or a Nic-Plan FTIR microscope. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity-Inova 300 (^{1}H, 300 MHz), Varian Unity-Inova 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Varian Mercury 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Varian Unity-Inova 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz), Varian DirectDrive 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz), or Varian Unity-Inova 600 (^{1}H, 600 MHz) spectrometer. High-resolution mass spectra, performed by the University of Alberta Mass Spectrometry Facility, were obtained on an Applied Biosystems Mariner Biospectrometry Workstation (electrospray ionization) or a Kratos Analytical MS-50G workstation (electron impact ionization) with an ionization energy of 70 eV. Elemental analyses were performed by the University of Alberta Microanalysis Laboratories, using a Carlos Erba Instruments CHSN-O EA1108 Elemental Analyzer. X-ray diffraction data were recorded on a Bruker Platform diffractometer with a SMART 1000 CCD area detector at −80 °C. Data collection, structure solution, and refinements were performed by Drs. Robert McDonald and Michael J. Ferguson of the University of Alberta X-ray Crystallography Laboratory. Crystals suitable for X-ray crystallography were often grown with a technique herein referred to as "two-chambered liquid diffusion". In this method, a small quantity of material was dissolved in a single solvent and placed in a small glass crystallization tube, which was then topped up with additional solvent if needed. The tube was sealed with an NMR-tube cap that was perforated once with a narrow-gauge needle. This tube was placed in a large sample vial and immersed in a second solvent in which the complex has minimal solubility. Due to the very slow diffusion rate via the pinhole, several weeks may be required to achieve complete crystallization. ^{1}H NMR chemical shifts are reported relative to residual protiated solvent. ^{13}C NMR chemical shifts are reported relative to the deuterated solvent. All spectra were recorded at 27 °C. Values of the coupling constants were obtained directly from the spectrum. GCOSY denotes the standard COSY experiment, acquired using field gradients. Data for the ^{1}H−^{1}H COSY or GCOSY are presented such that correlations are listed only once.

Materials. Compounds prepared by published procedures are as follows: pentadienyl complexes **1a**−**k** and **7a**−**h**,[6] Cp*Co(CH$_2$CH$_2$)$_2$ (**4**),[28] 1-bromo-3-butene and 1-bromo-4-pentene (**11**),[17] methyl pent-1-ene-5-methylcarboxyloate and methyl hex-1-ene-6-methylcarboxyloate (**12**),[18] enal **13**,[22] 5-hexen-2-one cyclic 1,2-ethandiyl acetal (**18**).[20]

Cp*Co(η^2,η^3-4-methylcycloheptadienyl)$^+$PF$_6^-$ (2a). A test tube was charged with a solution of pentadienyl **1a** (39.5 mg, 0.0940 mmol) in freshly distilled dichloromethane (10 mL). The tube was fitted with a septum, and acetylene was streamed through the solution for ∼15 min, to ensure saturation. The solution was maintained at room temperature for 19 h, before the removal of solvent by rotary evaporation. The orange-red residue was chromatographed on silica gel with a 4% methanol in dichloromethane mixture, affording **2a** as a red solid (41.3 mg, 0.0925 mmol, 98%). A small amount of **2a** suitable for X-ray diffraction analysis was obtained by crystallization by pinhole diffusion from a 50:50 mixture of diethyl ether and dichloromethane. IR (microscope, cm^{-1}): 2974 (w), 2920 (w), 2876 (m), 1711 (s), 1575 (s), 1502 (w), 1470 (w), 1434 (w), 1381 (w), 1337 (s), 1303 (m), 1285 (m), 1262 (m), 1184 (s), 1161 (s), 1141 (s), 1113 (s), 1075 (m), 1027 (w), 987 (m), 967 (m), 912 (m), 845 (w), 796 (w), 740 (m). ^{1}H NMR (500 MHz, dichloromethane-d_2): δ 3.85 (app td, 1H, J_{1-2} = 7.6 Hz, J_{1-7eq} = 8.5 Hz, J_{1-7ax} = 4.2 Hz, H$_1$), 3.55 (dd, 1H, J_{2-3} = 7.6 Hz, J_{3-4} = 3.7 Hz, H$_3$), 3.22 (t, 1H, J_{1-2} = J_{2-3} = 7.6 Hz, H$_2$), 3.06 (ddd, 1H, $J_{7ax-7eq}$ = 14.2 Hz, J_{1-7eq} = 8.5 Hz, J_{6-7eq} = 8.3 Hz, H$_{7eq}$), 2.77 (ddd, 1H, J_{5-6} = 6.6 Hz, J_{6-7eq} = 8.3 Hz, J_{6-7ax} = 4.7 Hz, H$_6$), 2.40 (m, 1H, H$_4$), 2.35 (dd, 1H, J_{5-6} = 6.6 Hz, J_{4-5} = 5.0 Hz, H$_5$), 2.17 (dt, 1H, $J_{7ax-7eq}$ = 14.2 Hz, J_{6-7ax} = 4.7 Hz, J_{1-7ax} = 4.2 Hz, H$_{7ax}$), 1.82 (s, 15H, CpMe$_5$), 1.47 (d, 3H, J_{4-CH_3} = 6.9 Hz, H$_4$−CH$_3$). ^{13}C NMR (125 MHz, dichloromethane-d_2): δ 98.1 (C_5Me$_5$), 92.5 (C$_2$), 55.9 (C$_5$), 52.4 (C$_3$), 46.0 (C$_6$), 44.4 (C$_1$), 27.3 (C$_4$), 22.1 (C$_7$), 19.7 (C$_4$−CH$_3$),

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9.9 (C_5Me_5). HMQC (500 MHz, dichloromethane-d_2): δ 92.5 ↔ δ 3.22; δ 55.9 ↔ δ 2.35; δ 52.4 ↔ δ 3.55; δ 46.0 ↔ δ 2.77; δ 44.4 ↔ δ 3.85; δ 27.3 ↔ δ 2.40; δ 22.1 ↔ δ 3.06, δ 2.17; δ 19.7 ↔ δ 1.47; δ 9.9 ↔ δ 1.82. HMBC (500 MHz, dichloromethane-d_2): δ 92.5 ↔ δ 3.06; δ 55.9 ↔ δ 3.06, δ 1.47; δ 52.4 ↔ δ 1.47; δ 46.0 ↔ δ 3.06, δ 2.35, δ 2.17; δ 44.4 ↔ δ 3.55, δ 3.22, δ 3.06, δ 2.17; δ 27.3 ↔ δ 3.22, δ 2.77, δ 1.47; δ 22.1 ↔ δ 3.22, δ 2.77, δ 2.35; δ 19.7 ↔ δ 2.35. Anal. Calcd for $C_{18}H_{26}CoPF_6$: C, 48.44; H, 5.87. Found: C, 48.18; H, 5.91.

[Cp*Co(η^2,η^3-1-phenylcycloheptadienyl)]$^+$BF$_4^-$ (2c). [Cp*Co(η^5-1-phenylpentadienyl)]$^+$ BF$_4^-$ (16 mg, 0.038 mmol) was dissolved in CH_2Cl_2 (3 mL) and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature overnight. During this time, the color was seen to change gradually from dark red to orange-red. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 15 mg (89%) of product as a thick, red oil. The ^{1}H NMR spectrum showed that there was a small quantity (ca. 10%) of the fully conjugated isomer present. Since the product slowly isomerizes at room temperature, only spectroscopic characterization was obtained. IR (neat, cm^{-1}): 3639 (w), 3552 (w), 3061 (s), 3032 (s), 2964 (s), 2916 (s), 2861 (s), 2262 (s), 1817 (w), 1603 (s), 1552 (w), 1494 (s), 1453 (s), 1430 (s), 1384 (s), 1286 (s), 1184 (w), 1097 (s), 916 (s), 830 (w), 794 (w), 761 (s), 734 (s), 702 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.34 (m, 5H, Ph, overlaps solvent signal), 4.10 (dd, J_{1-2} = 7.3 Hz, J_{1-7} = 4.0 Hz, 1H, H_1), 4.06 (td, $J_{3-4endo}$ = J_{3-2} = 8.2 Hz, J_{3-4exo} = 4.1 Hz, 1H, H_3), 3.51 (t, J_{2-1} = J_{2-3} = 7.7 Hz, 1H, H_2), 3.40 (t, J_{7-1} = J_{7-6} = 4.2 Hz, 1H, H_7), 3.30 (dt, $J_{4endo-4exo}$ = 14.1 Hz, $J_{4endo-3}$ = $J_{4endo-5}$ = 8.6 Hz, 1H, H_{4endo}), 3.02 (td, $J_{5-4endo}$ = J_{5-6} = 7.5 Hz, J_{5-4exo} = 4.8 Hz, 1H, H_5), 2.75 (td, J_{6-5} = J_{6-7} = 6.0 Hz, J_{6-4exo} = 0.3 Hz, 1H, H_6), 2.31 (br app dt, $J_{4exo-4endo}$ = 13.9 Hz, J_{4exo-3} = J_{4exo-5} = 4.4 Hz, 1H, H_{4exo}), 1.84 (s, 15H, C_5Me_5). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 4.10 (H_1) ↔ δ 3.51 (H_2), 3.40 (H_7); δ 4.06 (H_3) ↔ δ 3.51 (H_2), 3.30 (H_{4endo}), 2.31 (H_{4exo}); δ 3.51 (H_2) ↔ δ 3.30 (H_{4endo}), 2.31 (H_{4exo}); δ 3.40 (H_7) ↔ δ 2.75 (H_6), 2.31 (H_{4exo}); δ 3.30 (H_{4endo}) ↔ δ 3.02 (H_5), 2.75 (H_6), 2.31 (H_{4exo}); δ 3.02 (H_5) ↔ δ 2.75 (H_6), 2.31 (H_{4exo}); δ 2.75 (H_6) ↔ δ 2.31 (H_{4exo}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.4, 129.4, 128.9, 128.0, 126.5, 98.0, 91.7, 48.7, 45.7, 45.5, 36.2, 21.7, 9.7. Electrospray MS: m/z calculated for $C_{23}H_{28}Co$ (M^+ − BF_4) 363.15175, found 363.15182 (100%).

Cp*Co(η^2,η^3-4-ethylcycloheptadienyl)$^+$PF$_6^-$ (2d). A test tube was charged with a solution of **1d** (47.9 mg, 0.127 mmol) in freshly distilled dichloromethane (5 mL). The tube was fitted with a septum, and acetylene was streamed through the solution for ∼15 min, to ensure saturation. The solution was maintained at room temperature for 18 h, before the removal of solvent by rotary evaporation. The orange-red residue was chromatographed on silica gel with a 4% methanol in dichloromethane mixture, affording a red gum (46.6 mg, 0.116 mmol, 91%) which was comprised primarily of **2d** as the BF$_4^-$ salt but contained traces (less than 5% each by ^{1}H NMR integration) of minor impurities. The salt was completely dissolved in water (∼3 mL) and treated with saturated aqueous KPF_6 (5 mL). The red precipitate was collected by filtration and chromatographed on silica gel with a 4% methanol in dichloromethane mixture to furnish **2d** as a red powder (41.3 mg, 0.0897 mmol, 77% from BF$_4^-$ salt). Crystals of analytical purity suitable for an X-ray diffraction study were grown from a 50:50 mixture of diethyl ether and dichloromethane at −80 °C. IR (microscope, cm^{-1}): 3003 (w), 2968 (m), 2928 (m), 2879 (w), 1470 (m), 1460 (m), 1388 (m), 1379 (m), 1308 (w), 1290 (w), 1236 (w), 1073 (w), 1028 (w), 991 (w), 940 (w), 907 (w), 891 (w), 877 (m), 843 (s), 806 (m), 777 (w). ^{1}H NMR (400 MHz, dichloromethane-d_2): δ 3.84 (dtm, 1H, J_{1-2} = 7.6 Hz, J_{1-7eq} = 8.4 Hz, J_{1-7ax} = 4.2 Hz, H_1), 3.61 (dd, 1H, J_{2-3} = 7.6 Hz, J_{3-4} = 3.6 Hz, H_3), 3.23 (tm, 1H, J_{1-H} = J_{2-3} = 7.6 Hz, H_2), 3.07 (dtm, 1H, $J_{7ax-7eq}$ = 14.2 Hz, J_{1-7eq} = 8.4 Hz, J_{6-7eq} = 8.4 Hz, H_{7eq}), 2.79 (dt_{app}, 1H, J_{5-6} = 6.6 Hz, J_{6-7eq} = 8.4 Hz, J_{6-7ax} = 4.7 Hz, H_6), 2.39 (dd, 1H, J_{5-6} = 6.6 Hz, J_{4-5} = 4.6 Hz, H_5), 2.19 (app dt, 1H, $J_{H1-H7ax}$ = 4.2 Hz, $J_{H7ax-H7eq}$ = 14.2 Hz, $J_{H6-H7ax}$ = 4.7 Hz, H_{7ax}), 2.16 (m, 1H, H_4), 1.85 (m, 2H, -CH_2CH$_3$), 1.81 (s, 15H, CpMe$_5$), 1.04 (t, 3H, $J_{CH_2-CH_3}$ = 7.4 Hz, −CH$_2$$CH_3$). ^{1}H−^{1}H GCOSY (500 MHz, dichloromethane-d_2) δ 3.84 ↔ δ 3.23, δ 3.07, δ 2.19; δ 3.61 ↔ δ 3.23, δ 2.16; δ 3.23 ↔ δ 2.19; δ 3.07 ↔ δ 2.79, δ 2.39, δ 2.19; δ 2.79 ↔ δ 2.39, δ 2.19; δ 2.39 ↔ δ 2.16; δ 2.16 ↔ δ 1.85; δ 1.85 ↔ δ 1.04; ^{13}C NMR (100 MHz, dichloromethane-d_2): δ 98.1 (C_5Me_5), 92.5 (C_2), 54.7 (C_5), 50.9 (C_3), 46.2 (C_6), 44.5 (C_1), 34.1 (C_4), 27.5 (-CH_2CH$_3$), 22.1 (C_7), 10.9 (−CH_2CH$_3$), 9.9 (C_5Me_5). HMQC (400 MHz, dichloromethane-d_2): δ 92.5 ↔ δ 3.23; δ 54.7 ↔ δ 2.39; δ 50.9 ↔ δ 3.61; δ 46.2 ↔ δ 2.79; δ 44.5 ↔ δ 3.84; δ 27.5 ↔ δ 1.85; δ 22.1 ↔ δ 3.07, δ 2.19; δ 10.9 ↔ δ 1.04; δ 9.9 ↔ δ 1.81. HMBC (500 MHz, dichloromethane-d_2): δ 98.1 ↔ δ 1.81; δ 92.5 ↔ δ 3.07; δ 54.7 ↔ δ 3.07, δ 2.79, δ 1.85; δ 50.9 ↔ δ 3.84, δ 3.23, δ 1.85; δ 46.2 ↔ δ 3.07, δ 2.39, δ 2.19; δ 44.5 ↔ δ 3.61, δ 3.23, δ 3.07; δ 27.5 ↔ δ 3.61, δ 2.39, δ 1.04; δ 22.1 ↔ δ 3.23, δ 2.79, δ 2.39; δ 10.9 ↔ δ 1.85. Anal. Calcd for $C_{19}H_{28}CoPF_6$: C, 49.58; H, 6.13. Found: C, 49.47; H, 5.98.

[Cp*Co(η^2,η^3-1,5-dimethylcycloheptadienyl)]$^+$BF$_4^-$ (2e). [Cp*Co(η^5-1,5-dimethylpentadienyl)]$^+$BF$_4^-$ (11 mg, 0.029 mmol) was dissolved in CH_2Cl_2 (3 mL) and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature for 3 days. The solvent was removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 11 mg (94%) of product as a thick, red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion and X-ray analysis. IR (neat, cm^{-1}): 2978 (w), 2930 (w), 2878 (w), 1460 (w), 1429 (w), 1383 (m), 1313 (w), 1283 (w), 1263 (w), 1050 (s), 1036 (s), 988 (w), 900 (w), 864 (w), 803 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59 (dd, J_{2-1} = 7.6 Hz, J_{2-3} = 3.8 Hz, 2H, H_2), 3.42 (tt, J_{1-2} = 7.7 Hz, J_{1-3} = 0.7 Hz, 1H, H_1), 2.38 (d, J_{4-3} = 3.2 Hz, 2H, H_4), 2.34 (m, 2H, H_3), 1.87 (s, 15H, C_5Me_5), 1.47 (d, J_{Me-3} = 6.8 Hz, 6H, Me). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 3.59 (H_2) ↔ δ 3.42 (H_1), 2.34 (H_3); δ 3.42 (H_1) ↔ δ 2.34 (H_3); δ 2.38 (H_4) ↔ δ 2.34 (H_3); δ 2.34 (H_3) ↔ δ 1.47 (Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 98.1, 91.7, 54.2, 52.9, 27.8, 19.9, 10.2. Electrospray MS: m/z calculated for $C_{19}H_{28}Co$ (M^+ − BF_4) 315.15175, found 315.15156 (100%). Anal. Calcd for $C_{19}H_{28}CoBF_4$: C, 56.74; H, 7.02. Found: C, 56.36, H, 7.33.

[Cp*Co(η^2,η^3-1,2,3,4-tetramethylcycloheptadienyl)]$^+$BF$_4^-$ (2f). [Cp*Co(η^5-1,5-dimethylpentadienyl]$^+$BF$_4^-$ (80 mg, 0.213 mmol) was dissolved in CH_2Cl_2 (15 mL) in a reaction bomb and degassed with argon for 5 min. To this was added 2-butyne (80 μL, 1.02 mmol) via syringe. The bomb was sealed and heated at 40 °C for 3 days in an oil bath. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 78 mg (85%) of product as a thick, red oil. Crystallization attempts would lead only to decomposition; thus, spectroscopic characterization alone was obtained. IR (neat, cm^{-1}): 3032 (w), 2966 (m), 2905 (m), 1473 (m), 1390 (m), 1329 (w), 1282 (w), 1259 (s), 1181 (w), 1044 (s), 901 (w), 861 (w), 799 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (dd, J_{2-1} = 7.4 Hz, J_{2-3} = 4.5 Hz, 2H, H_2), 3.12 (t, J_{1-2} = 7.4 Hz, 1H, H_1), 2.69 (qd, J_{3-Me} = 6.7 Hz, J_{3-2} = 4.4 Hz, 2H, H_3), 1.73 (s, 15H, C_5Me_5), 1.72 (s, 6H, Me), 1.46 (d, J_{Me-3} = 7.1 Hz, 6H, Me). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 3.67 (H_2) ↔ δ 3.12 (H_1), 2.69 (H_3); δ 3.12 (H_1) ↔ δ 2.69 (H_3); δ 2.69 (H_3) ↔ δ 1.72 (Me), 1.46 (Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 96.6, 89.6, 63.3, 52.1, 32.0, 18.5, 14.2, 9.5. Electrospray MS: m/z calculated for $C_{21}H_{32}Co$ (M^+ − BF_4): 343.18305, found 343.18302 (100%).

Cp*Co(7-methylcycloheptadienyl)$^+$PF$_6^-$ (3a). An NMR tube was charged with a solution of **2a** (10.7 mg, 0.161 mmol, >95% pure) in dichloromethane-d_2 (∼750 μL). The tube was tightly sealed and stored at room temperature for 4 days, at which point ^{1}H NMR analysis revealed a 12% conversion of **2a** to η^5-cycloheptadienyl complex **3a**. The NMR tube was then heated at 60 °C for 17 h, at which point

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the conversion was determined by ^{1}H NMR to be >98% complete. Upon removal of solvent in vacuo, **3a** (10.7 mg, 0.161 mmol, 100%, >95% pure) was recovered as an orange-red solid. As complex **3a** had been previously prepared and characterized, no further purification or characterization was undertaken.[29]

Cp*Co(η^5-1,2,7-trimethylcycloheptadienyl)$^+$PF$_6^-$ (3b). A glass bomb was charged with a solution of **1a** (67.8 mg, 0.161 mmol) in dichloromethane (~4 mL). Argon was streamed through the solution for several minutes, prior to the injection via syringe of 2-butyne (75 μL, ~0.96 mmol). The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent and subsequent drying under high vacuum, analytically pure **3b** (75.6 mg, 0.159 mmol, 99%) was obtained. IR (microscope, cm^{-1}): 2971 (s), 2912 (s), 2826 (s), 1675 (w), 1576 (w), 1436 (s), 1381 (s), 1325 (m), 1298 (m), 1230 (w), 1206 (w), 1195 (m), 1160 (w), 1118 (w), 1074 (m), 1029 (s), 961 (m), 933 (w), 904 (m), 874 (m), 843 (m), 776 (m), 740 (m), 677 (m). ^{1}H NMR (400 MHz, chloroform-d_3): δ 6.46 (d, 1H, J_{3-4} = 7.4 Hz, H$_3$), 4.58 (ddd, 1H, J_{3-4} = 7.4 Hz, J_{4-5} = 9.0 Hz, J_{4-6eq} = 1.2 Hz, H$_4$), 4.29 (ddd, 1H, J_{4-5} = 9.0 Hz, J_{5-6ax} = 3.0 Hz, J_{5-6eq} = 4.4 Hz, H$_5$), 2.49 (ddd, 1H, J_{5-6ax} = 3.0 Hz, $J_{6ax-6eq}$ = 16.8 Hz, J_{6ax-7} = 11.6 Hz, H$_{6ax}$), 2.20 (s, 3H, C$_2$−CH$_3$), 2.17 (ddt, 1H, J_{4-6eq} = 1.2 Hz, J_{5-6eq} = 4.4 Hz, $J_{6ax-6eq}$ = 16.8 Hz, J_{6eq-7} = 4.4 Hz, H$_{6eq}$), 1.74 (s, 15H, CpMe$_5$), 1.28 (s, 3H, C$_1$−CH$_3$), 0.86 (d, 3H, J_{7-CH_3} = 6.8 Hz, C$_7$−CH$_3$), 0.27 (m, 1H, J_{7-CH_3} = 6.8 Hz, H$_7$). ^{1}H−^{1}H GCOSY (400 MHz, chloroform-d_3): δ 6.46 ↔ δ 4.58, δ 2.20; δ 4.58 ↔ δ 4.29, δ 2.17; δ 4.29 ↔ δ 2.49, δ 2.17; δ 2.49 ↔ δ 2.17, δ 0.27; δ 2.17 ↔ δ 0.27; δ 0.86 ↔ δ 0.27. ^{13}C NMR (100 MHz, chloroform-d_3): δ 108.4 (C$_2$), 102.2 (C$_1$), 98.8(C$_3$), 97.5 (C$_5$Me$_5$), 96.4 (C$_4$), 87.1 (C$_5$), 50.3 (C$_6$), 36.6 (C$_7$), 19.5 (C$_1$−CH$_3$), 17.3 (C$_2$−CH$_3$), 16.0 (C$_7$−CH$_3$), 9.0 (C$_5$*Me*$_5$). HMQC (400 MHz, chloroform-d_3): δ 98.8 ↔ δ 6.46; δ 96.4 ↔ δ 4.58; δ 87.1 ↔ δ 4.29; δ 50.3 ↔ δ 2.49, δ 2.17; δ 19.4 ↔ δ 1.28; δ 17.3 ↔ δ 2.20; δ 16.0 ↔ δ 0.86; δ 9.0 ↔ δ 1.74. HMBC (400 MHz, chloroform-d_3): δ 108.4 ↔ δ 6.46, δ 4.58, δ 2.20, δ 1.28; δ 102.2 ↔ δ 6.46, δ 2.20, δ 1.28, δ 0.86; δ 98.8 ↔ δ 4.29, δ 2.20; δ 97.5 ↔ δ1.74; δ 96.4 ↔ δ 6.46, δ 2.49; δ 87.1 ↔ δ 6.46, δ 4.58, δ 2.49, δ 0.86; δ 50.3 ↔ δ 4.58, δ 0.86; δ 36.6 ↔ δ 4.29, δ 2.49, δ 1.28, δ 0.86; δ 17.3 ↔ δ 6.46; δ 16.0 ↔ δ 1.28. Electrospray high-resolution mass spectrometry: mass calculated for C$_{20}$H$_{30}$Co 329.16740, found 329.16741. Anal. Calcd for C$_{20}$H$_{30}$CoPF$_6$: C, 50.64; H, 6.37. Found: C, 50.53; H, 6.53.

Cp*Co^{III} 7-Methyl-2-ethoxycycloheptadienyl Hexafluorophosphate (3c) and Cp*Co^{III} 7-Methyl-1-ethoxy-cycloheptadienyl Hexafluorophosphate (3c′). A glass bomb was charged with a solution of **1a** (29.2 mg, 0.0695 mmol) in freshly distilled dichloromethane (~1 mL). Ethoxyacetylene (50 μL, 40% solution in hexanes, ~0.29 mmol) was added via syringe, the bomb was sealed, and the solution was maintained at 42 °C for 18 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent and subsequent drying under high vacuum, a 64:36 mixture (as determined by ^{1}H NMR integration) of **3c** and **3c**′ (27.9 mg, 0.0569 mmol, 82%) was obtained. The product was characterized as a mixture, although the NMR data for **3c** and **3c**′ are presented individually. IR (microscope, cm^{-1}): 2979 (m), 2927 (m), 1471 (m), 1381 (m), 1326 (w), 1296 (w), 1234 (w), 1199 (m), 1176 (m), 1152 (w), 1103 (w), 1077 (w), 1026 (m), 875 (m), 838 (s), 739 (w). ^{1}H NMR (400 MHz, chloroform-*d*): major isomer **3c**, δ 6.24 (dd, 1H, J_{3-4} = 7.2 Hz, J_{1-3} = 3.2 Hz, H$_3$), 5.07 (ddd, 1H, J_{3-4} = 7.2 Hz, J_{4-5} = 9.0 Hz, J_{4-6eq} = 1.4 Hz, H$_4$), 4.31 (ddd, 1H, J_{4-5} = 9.0 Hz, J_{5-6ax} = 5.5 Hz, J_{5-6eq} = 3.3 Hz, H$_5$), 4.12 (dq, 1H, J_{gem} = 9.6 Hz, J_{vic} = 7.0 Hz, -OC*H*$_2$CH$_3$), 3.97 (dq, 1H, J_{gem} = 9.6 Hz, J_{vic} = 7.0 Hz, −OC*H*$_2$CH$_3$), 3.75 (dd, 1H, J_{1-7} = 3.8 Hz, J_{1-3} = 3.2 Hz, H$_1$), 2.03 (ddd, 1H, J_{5-6ax} = 5.5 Hz, $J_{6ax-6eq}$ = 15.9 Hz, J_{6ax-7} = 6.8 Hz, H$_{6ax}$), 1.82 (s, 15H, CpMe$_5$), 1.64 (m, 1H, J_{5-6eq} = 3.3 Hz, $J_{6ax-6eq}$ = 15.9 Hz, H$_{6eq}$), 1.40 (t, 3H, J = 7.0 Hz, −OCH$_2$C*H*$_3$), 1.15 (d, 3H, J_{7-CH_3} = 5.4 Hz, C$_7$−CH$_3$), 1.11 (m, 1H, J_{1-7} = 3.8 Hz, J_{7-CH_3} = 5.4 Hz, J_{6ax-7} = 6.8 Hz, H$_7$). ^{1}H NMR (400 MHz, chloroform-*d*): minor isomer **3c**′, δ 6.40 (t$_{app}$d, 1H, J_{2-3} = 6.9 Hz, J_{3-4} = 7.6 Hz, J_{3-5} = 1.0 Hz, H$_3$), 4.87 (d, 1H, J_{2-3} = 6.9 Hz, H$_2$), 4.79 (ddm, 1H, J_{3-4} = 7.6 Hz, J_{4-5} = 6.4 Hz, H$_4$), 4.04 (t$_{app}$dd, 1H, J_{4-5} = 6.4 Hz, J_{5-6ax} = 8.0 Hz, J_{5-6eq} = 4.7 Hz, J_{3-5} = 1.0 Hz, H$_5$), 1.95 (m, 1H, J_{5-6ax} = 8.0 Hz, $J_{6ax-6eq}$ = 15.2 Hz, H$_{6ax}$), 1.77 (s, 15H, CpMe$_5$), 1.67 (m, 1H, J_{7-CH_3} = 6.8 Hz, H$_7$), 1.40 (t, 3H, J = 7.0 Hz, −OCH$_2$C*H*$_3$), 1.32 (td, 1H, J_{5-6eq} = 4.7 Hz, J_{6eq-7} = 4.7 Hz, $J_{6ax-6eq}$ = 15.2 Hz, H$_{6eq}$), 1.17 (d, 3H, J_{7-CH_3} = 6.8 Hz, C$_7$−CH$_3$). ^{1}H−^{1}H GCOSY (400 MHz, chloroform-*d*): major isomer **3c**, δ 6.24 ↔ δ 5.07, δ 3.75; δ 5.07 ↔ δ 4.31; δ 4.31 ↔ δ 2.03, δ 1.64; δ 4.12 ↔ δ 3.97, δ 1.40; δ 3.97 ↔ δ 1.40; δ 3.75 ↔ δ 1.11; δ 2.03 ↔ δ 1.64, δ 1.11; δ 1.64 ↔ δ 1.11; δ 1.15 ↔ δ 1.11. ^{1}H−^{1}H GCOSY (400 MHz, chloroform-*d*): minor isomer **3c**′, δ 6.40 ↔ δ 4.87, δ 4.79; δ 4.79 ↔ δ 4.04; δ 4.04 ↔ δ 1.95, δ 1.32; δ 3.81 ↔ δ 3.79, δ 1.40; δ 3.79 ↔ δ 1.40; δ 1.95 ↔ δ 1.67, δ 1.32; δ 1.67 ↔ δ 1.32, δ 1.17; δ 1.32 ↔ δ 1.17. ^{13}C NMR (100 MHz, chloroform-*d*): major isomer **3c**, δ 139.7 (C$_2$), 98.3 (C$_5$Me$_5$), 94.8 (C$_4$), 89.0 (C$_5$), 84.8 (C$_3$), 77.2 (C$_1$), 67.3 (-OCH$_2$CH$_3$), 43.6 (C$_6$), 36.1 (C$_7$), 22.7 (C$_7$−CH$_3$), 14.5 (−OCH$_2$CH$_3$), 9.9 (C$_5$*Me*$_5$); ^{13}C NMR (100 MHz, chloroform-*d*) Minor Isomer **3c**′: δ 151.2 (C$_1$), 97.0 (C$_5$Me$_5$), 95.6 (C$_4$), 91.8 (C$_3$), 79.5 (C$_5$), 78.2 (C$_2$), 66.2 (-OCH$_2$CH$_3$), 42.4 (C$_7$), 41.2 (C$_6$), 18.2 (C$_7$−CH$_3$), 14.3 (−OCH$_2$CH$_3$), 9.4 (C$_5$*Me*$_5$); HMQC (400 MHz, chloroform-*d*): major isomer **3c**, δ 94.8 ↔ δ 5.07; δ 89.0 ↔ δ 4.31; δ 84.8 ↔ δ 6.24; δ 77.2 ↔ δ 3.75; δ 67.3 ↔ δ 4.12, δ 3.97; δ 43.6 ↔ δ 2.03, δ 1.64; δ 36.1 ↔ δ 1.11; δ 22.7 ↔ δ 1.15; δ 14.5 ↔ δ 1.40; δ 9.9 ↔ δ 1.82. HMQC (400 MHz, chloroform-*d*): minor isomer **3c**′, δ 95.6 ↔ δ 4.79; δ 91.8 ↔ δ 6.40; δ 79.5 ↔ δ 4.04; δ 78.2 ↔ δ 4.87; δ 66.2 ↔ δ 3.81, δ 3.79; δ 42.9 ↔ δ 1.67; δ 41.2 ↔ δ 1.95, δ 1.32; δ 18.2 ↔ δ 1.17; δ 14.3 ↔ δ 1.40; δ 9.4 ↔ δ 1.77. Electrospray high-resolution mass spectrometry: mass calculated for C$_{20}$H$_{30}$CoO 345.16231, found 345.16234. Anal. Calcd for C$_{20}$H$_{30}$CoOPF$_6$: C, 48.99; H, 6.17. Found: C, 50.15; H, 6.24.

Cp*Co(η^5-7-methyl-2-propylcycloheptadienyl)$^+$PF$_6^-$ (3d) and Cp*Co(η^5-7-methyl-1-propylcycloheptadienyl)$^+$PF$_6^-$ (3d′). A glass bomb was charged with a solution of **1a** (17.8 mg, 0.0424 mmol) in freshly distilled dichloromethane (~1 mL). 1-Pentyne (25 μL, ~0.25 mmol) was added via syringe, the bomb was sealed, and the solution was maintained at 42 °C for 17 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent and subsequent drying under high vacuum, a 69:31 mixture (as determined by ^{1}H NMR integration) of **3d** and **3d**′ (18.8 mg, 0.0385 mmol, 91%) was obtained. Although pinhole diffusion of diethyl ether into dichloromethane afforded analytically pure material, efforts to grow X-ray-quality crystals proved fruitless. The product was characterized as a mixture, although the NMR data for **3d** and **3d**′ are presented individually. IR (microscope, cm^{-1}): 2967 (s), 2934 (s), 2874 (s), 1578 (w), 1464 (s), 1384 (s), 1335 (w), 1316 (w), 1306 (w), 1241 (w), 1203 (w), 1156 (w), 1083 (m), 1026 (m), 968 (w), 936 (m), 906 (m), 857 (s), 775 (m), 741 (m), 724 (m). ^{1}H NMR (600 MHz, chloroform-d_3): major isomer **3d**, δ 6.38 (dd, 1H, J_{3-4} = 7.0 Hz, J_{1-3} = 1.6 Hz, H$_3$), 4.96 (ddm, 1H, J_{3-4} = 7.0 Hz, J_{4-5} = 9.1 Hz, H$_4$), 4.40 (ddd, 1H, J_{4-5} = 9.1 Hz, J_{5-6ax} = 4.8 Hz, J_{5-6eq} = 3.3 Hz, H$_5$), 3.61 (dd, 1H, J_{1-7} = 3.5 Hz, J_{1-3} = 1.6 Hz, H$_1$), 2.51 (m, 1H, −C*H*$_2$CH$_2$CH$_3$), 2.27 (ddd, 1H, J_{5-6ax} = 4.8 Hz, $J_{6ax-6eq}$ = 16.7 Hz, J_{6ax-7} = 8.8 Hz, H$_{6ax}$), 1.95 (m, 1H, J_{5-6eq} = 3.3 Hz, $J_{6ax-6eq}$ = 16.7 Hz, H$_{6eq}$), 1.84 (s, 15H, CpMe$_5$), 1.8−1.7 (m, 3H, −C*H*$_2$CH$_2$CH$_3$ (1H) and −CH$_2$C*H*$_2$CH$_3$ (2H)), 1.08 (d, 3H, J_{7-CH_3} = 6.8 Hz, C$_7$−CH$_3$), 1.00 (t, 3H, J = 7.1 Hz, −CH$_2$CH$_2$C*H*$_3$), 0.85 (m, 1H, J_{7-CH_3} = 6.8 Hz, H$_7$). ^{1}H NMR (600 MHz, chloroform-d_3): minor isomer **3d**′, δ 6.52 (app td, 1H, J_{2-3} = 7.0 Hz, J_{3-4} = 7.2 Hz, J_{3-5} = 1.2 Hz, H$_3$), 5.19 (app t, 1H, J_{3-4} = 7.2 Hz, J_{4-5} = 6.5 Hz, H$_4$), 4.93 (d, 1H, J_{2-3} = 7.0 Hz, H$_2$), 4.28 (dddd, 1H, J_{4-5} = 6.5 Hz, J_{5-6ax} = 7.5 Hz, J_{5-6eq} = 5.0 Hz, J_{3-5} = 1.2 Hz, H$_5$), 2.38 (ddd, 1H, J_{gem} = 12.7 Hz, J_{vic} = 10.0 Hz, J_{vic} = 4.6 Hz, −C*H*$_2$CH$_2$CH$_3$), 1.94 (m, 1H, J_{7-CH_3} = 6.8 Hz, H$_7$), 1.82 (s, 15H, CpMe$_5$), 1.7 (m, 1H, −CH$_2$C*H*$_2$CH$_3$), 1.51 (ddd, 1H, J_{5-6ax} = 7.5 Hz, $J_{6ax-6eq}$ = 13.7 Hz, J_{6ax-7} = 2.8 Hz, H$_{6ax}$), 1.45 (m, 1H, −CH$_2$C*H*$_2$CH$_3$), 1.41 (d, 3H, J_{7-CH_3} = 6.8 Hz, C$_7$−CH$_3$), 1.34 (ddd, 1H, J_{gem} = 12.7 Hz, J_{vic} = 10.6 Hz, J_{vic} = 6.2 Hz, −C*H*$_2$CH$_2$CH$_3$), 0.98 (t, 3H, J = 7.3 Hz, −CH$_2$CH$_2$C*H*$_3$), 0.49 (m, 1H, J_{5-6eq} = 5.0 Hz, $J_{6ax-6eq}$ = 13.7 Hz, H$_{6eq}$). ^{1}H−^{1}H GCOSY (500 MHz, chloroform-d_3): major

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isomer **3d**, δ 6.38 ↔ δ 4.96, δ 4.40, δ 3.61; δ 4.96 ↔ δ 4.40, δ 1.95; δ 4.40 ↔ δ 2.27, δ 1.95; δ 3.61 ↔ δ 0.85; δ 2.51 ↔ δ 1.8, δ 1.7, δ 1.00; δ 2.27 ↔ δ 1.95, δ 0.85; δ 1.95 ↔ δ 0.85; δ 1.8 ↔ δ 1.7, δ 1.00; δ 1.7 ↔ δ 1.00; δ 1.08 ↔ δ 0.85. ^{1}H−^{1}H GCOSY (500 MHz, chloroform-d_3): minor isomer **3d′**, δ 6.52 ↔ δ 5.19, δ 4.93, δ 4.28; δ 5.19 ↔ δ 4.93, δ 4.28, δ 0.49; δ 4.28 ↔ δ 1.51, δ 0.49; δ 2.38 ↔ δ 1.7, δ 1.45, δ 1.34; δ 1.94 ↔ δ 1.51, δ 1.41, δ 0.49; δ 1.7 ↔ δ 1.45, δ 1.34, δ 0.98; δ 1.51 ↔ δ 0.49; δ 1.45 ↔ δ 1.34, δ 0.98. ^{13}C NMR (125 MHz, chloroform-d_3): major isomer **3d**, δ 113.5 (C_2), 99.0 (C_3), 98.5 (C_5Me_5), 97.6 (C_4), 91.1 (C_5), 90.4 (C_1), 46.3 (C_6), 38.1 (−$CH_2CH_2CH_3$), 36.0 (C_7), 25.6 (−$CH_2CH_2CH_3$), 22.4 (C_7−CH_3), 13.5 (−$CH_2CH_2CH_3$), 9.7 (C_5Me_5). ^{13}C NMR (125 MHz, chloroform-d_3): minor isomer **3d′**, δ 116.4 (C_1), 99.8 (C_4), 98.2 (C_2), 97.9 (C_5Me_5), 97.2 (C_3), 85.5 (C_5), 46.2 (C_7), 41.0 (−$CH_2CH_2CH_3$), 36.2 (C_6), 23.2 (−$CH_2CH_2CH_3$), 22.0 (C_7−CH_3), 14.1 (−$CH_2CH_2CH_3$), 9.6 (C_5Me_5). HMQC (500 MHz, chloroform-d_3): major isomer **3d**, δ 99.0 ↔ δ 6.38; δ 97.6 ↔ δ 4.96; δ 91.1 ↔ δ 4.40; δ 90.4 ↔ δ 3.61; δ 46.3 ↔ δ 2.27, δ 1.95; δ 38.1 ↔ δ 2.51, δ 1.7; δ 36.0 ↔ δ 0.85; δ 25.6 ↔ δ 1.8, δ 1.7; δ 22.4 ↔ δ 1.08; δ 13.5 ↔ δ 1.00; δ 9.7 ↔ δ 1.84. HMQC (500 MHz, chloroform-d_3): minor isomer **3d′**, δ 99.8 ↔ δ 5.19; δ 98.2 ↔ δ 4.93; δ 97.2 ↔ δ 6.52; δ 85.5 ↔ δ 4.28; δ 46.2 ↔ δ 1.94; δ 41.0 ↔ δ 2.38, δ 1.34; δ 36.2 ↔ δ 1.51, δ 0.49; δ 23.2 ↔ δ 1.7, δ 1.45; δ 22.0 ↔ δ 1.41; δ 14.1 ↔ δ 0.98; δ 9.6 ↔ δ 1.82. Electrospray high-resolution mass spectrometry: mass calculated for $C_{21}H_{32}Co$ 343.18305, found 343.18330. Anal. Calcd for $C_{21}H_{32}CoPF_6$: C, 51.65; H, 6.60. Found: C, 51.30; H, 6.35.

[Cp*Co(η^5-1-phenylcycloheptadienyl)]$^+$$BF_4^-$ (3f). [Cp*Co(η^5-1-phenylpentadienyl)]$^+$$BF_4^-$ (105 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (3 mL) in a reaction bomb and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature for 3 days. During this time, the color was seen to gradually change from dark red to orange-red. The bomb was then heated at 60 °C in an oil bath for 1 day, and the color changed back to dark red. The solvent was removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 111 mg (100%) of product as a thick, red oil. A sample suitable for combustion analysis was obtained by crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O to yield a light, orange powder. IR (CH_2Cl_2 cast, cm^{-1}): 3029 (w), 2917 (w), 1601 (w), 1493 (w), 1456 (w), 1384 (w), 1284 (w), 1056 (s), 878 (w), 762 (w), 732 (w), 704 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 2H, Ph), 7.27 (m, 1H, Ph, overlaps solvent signal), 7.12 (m, 2H, Ph), 6.90 (t, $J_{3-2} = J_{3-4} = 6.3$ Hz, 1H, H_3), 5.42 (t, $J_{2-1} = J_{2-3} = 7.1$ Hz, 1H, H_2), 5.16 (t, $J_{4-3} = J_{4-5} = 8.6$ Hz, 1H, H_4), 4.52 (dt, $J_{5-4} = 9.3$ Hz, $J_{5-6endo} = J_{5-6exo} = 3.7$ Hz, 1H, H_5), 4.32 (ddd, $J_{1-2} = 8.1$ Hz, $J_{1-7} = 4.5$ Hz, $J_{1-3} = 1.1$ Hz, 1H, H_1), 2.99 (ddd, $J_{6endo-6exo} = 16.7$ Hz, $J_{6endo-7} = 10.4$ Hz, $J_{6endo-5} = 4.2$ Hz, 1H, H_{6endo}), 2.30 (br app dt, $J_{6exo-6endo} = 16.7$ Hz, $J_{6exo-5} = J_{6exo-7} = 3.7$ Hz, 1H, H_{6exo}), 1.91 (s, 15H, C_5Me_5), 1.78 (dt, $J_{7-6endo} = 11.6$, $J_{7-1} = J_{7-6exo} = 5.2$ Hz, 1H, H_7). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 7.36 (Ph) ↔ δ 7.27 (Ph), 7.12 (Ph); δ 7.27 (Ph) ↔ δ 7.12 (Ph); δ 6.90 (H_3) ↔ δ 5.42 (H_2), 5.16 (H_4), 4.32 (H_1); δ 5.42 (H_2) ↔ δ 4.32 (H_1); δ 5.16 (H_4) ↔ δ 4.52 (H_5); δ 4.52 (H_5) ↔ δ 2.99 (H_{6endo}), 2.30 (H_{6exo}); δ 4.32 (H_1) ↔ δ 1.78 (H_7); δ 2.99 (H_{6endo}) ↔ δ 2.30 (H_{6exo}), 1.78 (H_7); δ 2.30 (H_{6exo}) ↔ δ 1.78 (H_7). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.8, 129.1, 127.3, 126.9, 101.1, 99.0, 98.1, 97.7, 95.1, 88.8, 49.0, 45.6, 9.8. Electrospray MS: *m*/*z* calculated for $C_{23}H_{28}Co$ ($M^+ - BF_4$), 363.15175, found 363.15171 (100%). Anal. Calcd for $C_{23}H_{28}CoBF_4$: C, 61.36; H, 6.27. Found: C, 61.05; H, 6.03.

[Cp*Co(η^5-1-phenyl-2,3-dimethylcycloheptadienyl)]$^+$$BF_4^-$ (3g). [Cp*Co(η^5-1-phenylpentadienyl)]$^+$$BF_4^-$ (101 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (4 mL) in a reaction bomb and degassed with argon for 5 min. To this was added 2-butyne (100 μL, 1.28 mmol). The bomb was sealed and allowed to stand at room temperature for 3 days. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 110 mg (96%) of product as a thick, red oil. A sample suitable for combustion and X-ray analysis was prepared by crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O to yield red crystals. IR (CH_2Cl_2 cast, cm^{-1}): 2920 (m), 1491 (w), 1456 (m), 1432 (w), 1384 (m), 1054 (s), 775 (m), 732 (m), 706 (m), 520 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30−7.17 (m, 3H, Ph, overlaps solvent signal), 6.95 (m, 2H, Ph), 6.75 (d, $J_{1-2} = 7.4$ Hz, 1H, H_1), 4.83 (t, $J_{2-1} = J_{2-3} = 8.3$ Hz, 1H, H_2), 4.52 (dt, $J_{3-2} = 9.2$ Hz, $J_{3-4endo} = J_{3-4exo} = 3.4$ Hz, 1H, H_3), 3.25 (ddd, $J_{4endo-4exo} = 16.5$ Hz, $J_{4endo-5} = 12.8$ Hz, $J_{4endo-3} = 3.1$ Hz, 1H, H_{4endo}), 2.39 (brapp dt, $J_{4exo-4endo} = 16.6$ Hz, $J_{4exo-5} = J_{4exo-3} = 4.8$ Hz, 1H, H_{4exo}, other couplings which do not resolve well are also seen), 2.23 (s, 3H, Me), 1.80 (s, 15H, C_5Me_5), 1.30 (dd, $J_{5-4endo} = 12.8$ Hz, $J_{5-4exo} = 4.0$ Hz, 1H, H_5), 0.84 (s, 3H, Me). ^{1}H−^{1}H GCOSY (300 MHz, $CDCl_3$): δ 7.30−7.17 (Ph) ↔ δ 6.95 (Ph); δ 6.75 (H_1) ↔ δ 4.83 (H_2); δ 4.83 (H_2) ↔ δ 4.52 (H_3), 2.39 (H_{4endo}); δ 4.52 (H_3) ↔ δ 3.25 (H_{4endo}), 2.39 (H_{4exo}); δ 3.25 (H_{4endo}) ↔ δ 2.39 (H_{4exo}), 1.30 (H_5); δ 2.39 (H_{4exo}) ↔ δ 1.30 (H_5). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.7, 128.57, 128.55, 127.3, 108.5, 100.3, 99.7, 97.9, 96.5, 86.6, 47.1, 46.6, 21.7, 17.0, 9.1. Electrospray MS: *m*/*z* calculated for $C_{25}H_{32}Co$ ($M^+ - BF_4$) 391.18305, found 391.18328 (100%). Anal. Calcd for $C_{25}H_{32}CoBF_4$: C, 62.78; H, 6.74. Found: C, 62.95; H, 6.73.

[Cp*(η^5-1-phenyl-3-trimethylsilylcycloheptadienyl)]$^+$$BF_4^-$ (3h). [Cp*Co(η^5-1-phenylpentadienyl)]$^+$$BF_4^-$ (102 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (4 mL) in a reaction bomb and degassed with argon for 5 min. To this was added TMS-acetylene (200 μL, 1.42 mmol). The bomb was sealed and heated at 40 °C for 2 days. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 98 mg of product as a thick, red oil which still contained significant impurities. The product yield (26%) was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Over several reactions, the yield was inexplicably seen to range from as low as 26% to as high as 55%. A sample suitable for combustion and X-ray analysis was prepared by crystallizing three times via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O to yield red crystals. IR (CH_2Cl_2 cast, cm^{-1}): 3390 (w), 2957 (w), 2915 (w), 1601 (w), 1493 (m), 1454 (m), 1430 (m), 1383 (m), 1252 (m), 1057 (s), 918 (w), 883 (w), 842 (s), 762 (m), 732 (w), 703 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, $J = 7.4$ Hz, 2H, Ph), 7.26 (t, $J = 7.3$ Hz, 1H, Ph, overlaps solvent signal), 7.07 (d, $J = 7.3$ Hz, 2H, Ph), 6.73 (d, $J_{3-4} = 6.9$ Hz, 1H, H_3), 5.25 (dd, $J_{4-5} = 8.8$ Hz, $J_{4-3} = 7.5$ Hz, 1H, H_4), 4.79 (dt, $J_{5-4} = 9.5$ Hz, $J_{5-6endo} = J_{5-6exo} = 3.6$ Hz, 1H, H_5), 3.93 (dd, $J_{2-1} = 4.2$ Hz, $J_{2-3} = 0.7$ Hz, 1H, H_2), 3.06 (ddd, $J_{6endo-6exo} = 17.1$ Hz, $J_{6endo-1} = 11.1$ Hz, $J_{6endo-5} = 4.2$ Hz, 1H, H_{6endo}), 2.36 (br app dt, $J_{6exo-6endo} = 17.0$ Hz, $J_{6exo-1} = J_{6exo-5} = 3.6$ Hz, 1H, H_{6exo}), 1.90 (s, 15H, C_5Me_5), 1.48 (dt, $J_{1-6endo} = 10.8$ Hz, $J_{1-2} = J_{1-6exo} = 4.8$ Hz, 1H, H_1), 0.35 (s, 9H, $SiMe_3$). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 7.36 (Ph) ↔ δ 7.26 (Ph), 7.07 (Ph); δ 6.73 (H_3) ↔ δ 5.25 (H_4), 3.93 (H_2); δ 5.25 (H_4) ↔ δ 4.79 (H_5); δ 4.79 (H_5) ↔ δ 3.06 (H_{6endo}), 2.36 (H_{6exo}); δ 3.93 (H_2) ↔ δ 1.48 (H_1); δ 3.06 (H_{6endo}) ↔ δ 2.36 (H_{6exo}), 1.48 (H_1); δ 2.36 (H_{6exo}) ↔ δ 1.48 (H_1); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.1, 129.1, 127.2, 126.6, 107.1, 102.3, 99.1, 98.0, 92.7, 91.6, 47.5, 47.2, 10.2, −0.7. Electrospray MS: *m*/*z* calculated for $C_{26}H_{36}SiCo$ ($M^+ - BF_4$) 435.19128, found 435.19152 (100%). Anal. Calcd for $C_{26}H_{36}SiCoBF_4$: C, 59.78; H, 6.95. Found: C, 59.98; H, 7.07.

Cp*Co(η^5-7-ethylcycloheptadienyl)$^+$$BF_4^-$ (3i). An NMR tube was charged with a solution of **2d** (11.1 mg, 0.161 mmol) in dichloromethane-d_2 (~750 μL). The tube was tightly sealed, and the reaction mixture was heated at 60 °C for 1 h, at which point ^{1}H NMR interrogation revealed an approximately 8% conversion to η^5-cycloheptadienyl product **3i**. Heating at 60 °C was resumed; NMR analysis revealed an approximately 75% conversion after 19 h and complete conversion after 66 h. The deuterated solvent was removed in vacuo, and the red-orange residue was chromatographed on silica gel with 3% methanol/dichloromethane, furnishing **3i** as an analytically pure powder (11.0 mg, 0.160 mol, 99%) after drying under high vacuum. IR (microscope, cm^{-1}): 2968 (m), 2918 (m), 2877 (m), 1496 (m), 1463 (m), 1434 (m), 1406 (s), 1380 (m), 1345 (w), 1313 (w), 1138 (w), 1076 (w), 1027 (m), 980 (w), 911 (w), 882 (s), 843 (s), 779 (w), 740 (w). ^{1}H NMR (400 MHz, chloroform-*d*): δ 6.61 (app td,

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1H, J_{2-3} = 6.7 Hz, J_{3-4} = 6.9 Hz, J_{1-3} = 1.3 Hz, H_3), 5.26 (ddm, 1H, J_{1-2} = 8.1 Hz, J_{2-3} = 6.7 Hz, H_2), 4.90 (ddm, 1H, J_{3-4} = 6.9 Hz, J_{4-5} = 9.3 Hz, H_4), 4.33 (ddd, 1H, J_{4-5} = 9.3 Hz, J_{5-6ax} = 4.3 Hz, J_{5-6eq} = 3.3 Hz, H_5), 4.04 (ddd, 1H, J_{1-2} = 8.1 Hz, J_{1-7} = 4.0 Hz, J_{1-3} = 1.3 Hz, H_1), 2.37 (ddd, 1H, J_{5-6ax} = 4.3 Hz, $J_{6ax-6eq}$ = 16.7 Hz, J_{6ax-7} = 9.4 Hz, H_{6ax}), 2.10 (dddd, 1H, J_{4-6eq} = 1.4 Hz, J_{5-6eq} = 3.3 Hz, $J_{6ax-6eq}$ = 16.7 Hz, J_{6eq-7} = 5.3 Hz, H_{6eq}), 1.88 (s, 15H, $CpMe_5$), 1.46 (dp, 1H, J_{gem} = 14.6 Hz, $J_{CH_2-CH_3}$ = 7.3 Hz, J_{7-CH_2} = 7.3 Hz, $-CH_2CH_3$), 1.36 (dp, 1H, J_{gem} = 14.6 Hz, $J_{CH_2-CH_3}$ = 7.3 Hz, J_{7-CH_2} = 7.3 Hz, $-CH_2CH_3$), 0.82 (t, 3H, $J_{CH_2-CH_3}$ = 7.3 Hz, $-CH_2CH_3$), 0.55 (m, 1H, J_{1-7} = 4.0 Hz, J_{6ax-7} = 9.4 Hz, J_{6eq-7} = 5.3 Hz, J_{7-CH_2} = 7.3 Hz, H_7). $^1H-^1H$ GCOSY (400 MHz, chloroform-*d*): δ 6.61 ↔ δ 5.26, δ 4.90, δ 4.04; δ 5.26 ↔ δ 4.04; δ 4.90 ↔ δ 4.33, δ 2.10; δ 4.33 ↔ δ 2.37, δ 2.10; δ 4.04 ↔ δ 0.55; δ 2.37 ↔ δ 2.10, δ 0.55; δ 2.10 ↔ δ 0.55; δ 1.46 ↔ δ 1.36, δ 0.82, δ 0.55; δ 1.36 ↔ δ 0.82, δ 0.55. ^{13}C NMR (100 MHz, chloroform-*d*): δ 100.3 (C_3), 98.3 (C_5Me_5), 97.7 (C_2), 97.6 (C_4), 94.9 (C_1), 88.8 (C_5), 46.4 (C_6), 41.4 (C_7), 29.3 ($C_7-CH_2CH_3$), 12.0 ($C_7-CH_2CH_3$), 9.7 (C_5Me_5). HMQC (400 MHz, chloroform-*d*): δ 100.3 ↔ δ 6.61; δ 97.7 ↔ δ 5.26; δ 97.6 ↔ δ 4.90; δ 94.9 ↔ δ 4.04; δ 88.8 ↔ δ 4.33; δ 46.4 ↔ δ 2.37, δ 2.10; δ 41.4 ↔ δ 0.55; δ 29.3 ↔ δ 1.46, δ 1.36; δ 12.0 ↔ δ 0.82; δ 9.7 ↔ δ 1.88. HMBC (400 MHz, chloroform-*d*): δ 100.3 ↔ δ 4.33, δ 4.04; δ 98.3 ↔ δ 1.88; δ 97.7 ↔ δ 6.61, δ 4.90; δ 97.6 ↔ δ 6.61, δ 5.26, 2.37; δ 94.9 ↔ δ 6.46, δ 1.46, δ 1.36; δ 88.8 ↔ δ 6.46, δ 2.37; δ 46.4 ↔ δ 4.90, δ 4.04, δ 1.46, δ 1.36; δ 41.4 ↔ δ 5.26, δ 2.37, δ 1.46, δ 1.36, δ 0.82; δ 29.3 ↔ δ 4.04, δ 2.37, δ 0.82; δ 12.0 ↔ δ 1.46, δ 1.36. Electrospray high-resolution mass spectrometry; mass calculated for $C_{19}H_{28}Co$ 315.15188, found 315.15175. Anal. Calcd for $C_{19}H_{28}CoPF_6$: C, 49.58; H, 6.13. Found: C, 49.52; H, 6.02.

[CpCo(η^2,η^3-1-methylcycloheptadienyl)]$^+BF_4^-$ (8a). Complex **7a** (100 mg, 0.3425 mmol) was dissolved in CH_2Cl_2 (3 mL) and placed in a reaction bomb. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 20 min in order to ensure saturation. Then, ∼2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at 40 °C over 3 days. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The dark red fraction was collected and dried, providing 59.7 mg (55%) of total product as a dark, red powder. By ^1H NMR spectroscopy, this fraction contained **8a** with a small quantity of cobaltocenium by-product. Crystals suitable for an X-ray diffraction analysis were grown from pinhole diffusion (dichloromethane/diethyl ether) at room temperature. IR (microscope, cm^{-1}): 3401 (w), 3116 (w), 2936 (w), 2860 (w), 1636 (w), 1416 (s), 1299 (w), 1284 (w), 1054 (brs), 867 (s). ^1H NMR (400 MHz, acetone-d_6): δ 5.75 (s, 5H, Cp); 5.10 (m, 1H, H_3); 4.70 (m, 1H, H_1); 4.10 (t, 1H, H_2); 3.85 (dd, 1H, H_5); 3.39 (m, 1H, H_6); 3.12 (m, 1H, H_{4endo}); 2.55 (m, 1H, H_{7exo}); 2.28 (m, 1H, H_{4exo}); 1.53 (d, 3H, $H_{8endoMe}$). GCOSY (400 MHz, acetone-d_6): δ 5.10 (H_3) ↔ 4.10 (H_2), 3.12 (H_{4endo}), 2.28 (H_{4exo}); 4.70 (H_1) ↔ 4.10 (H_2), 2.55 (H_{7exo}); 3.85 (H_5) ↔ 3.39 (H_6), 3.12 (H_{4endo}), 2.28 (H_{4exo}); 3.39 (H_6) ↔ 2.55 (H_{7exo}); 3.12 (H_{4endo}) ↔ 2.28 (H_{4exo}); 2.55 (H_{7exo}) ↔ 1.53 ($H_{8endoMe}$). ^1H NMR (400 MHz, $CDCl_3$): δ 5.61 (s, 5H, Cp); 5.04 (ddd, 1H, H_3); 4.58 (dd, J = 3.7 Hz, J = 7.3 Hz, 1H, H_1); 4.01 (t, J = 7.5 Hz, 1H, H_2), 3.73 (dd, J = 7.0 Hz, 1H, H_5); 3.14–3.24 (m, 2H, H_6 + H_{4endo}); 2.39 (dd, 1H, H_{7exo}); 2.14 (dd, 1H, H_{4exo}); 1.52 (d, 3H, $H_{8endoMe}$). GCOSY (400 MHz, $CDCl_3$): δ 5.04 (H_3) ↔ 4.01 (H_2), 3.14 (H_{4endo}), 2.14 (H_{4exo}); 4.58 (H_1) ↔ 4.01 (H_2), 2.39 (H_{7exo}); 3.73 (H_5) ↔ 3.24 (H_6); 3.24 (H_6) ↔ 2.39 (H_{7exo}); 3.14 (H_{4endo}) ↔ 2.14 (H_{4exo}); 2.39 (H_{7exo}) ↔ 1.52 ($H_{8endoMe}$). Electrospray MS: *m*/*z* calculated for $C_{13}H_{16}Co$ (M^+) 231.05785, found 231.05809.

[CpCo(η^2,η^3-1,2,3-trimethylcycloheptadienyl)]$^+BF_4^-$ (8b). A glass reaction bomb was charged with a solution of **7a** (100 mg, 0.3425 mmol) in dichloromethane (∼3 mL). An aliquot of 2-butyne (∼268 μL, 3.425 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, was comprised primarily of the desired product but contained traces (less than 5% each by ^1H NMR integration) of minor impurities. Analytically pure **8b** (51 mg, 43%) was obtained using pinhole diffusion crystallization (dichloromethane/diethyl ether). IR (microscope, cm^{-1}): 3388 (br, 3113 (w), 2972 (w), 1709 (w), 1522 (w), 1468 (m), 1435 (m), 1412 (m), 1382 (m), 1300 (w), 1053 (brs), 858 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 5.36 (m [overlapping with Cp], 1H, H_3); 5.32 (s, 5H, Cp); 4.79 (dd, J = 4.5 Hz, J = 6.7 Hz, 1H, H_1); 4.15 (t, J = 7.3 Hz, 1H, H_2); 3.14 (dd, J = 9.3 Hz, J = 14.1 Hz, 1H, H_{4endo}); 2.58 (t, J = 5.8 Hz, 1H, H_{7exo}); 2.53 (dd, J = 4.4 Hz, J = 14.1 Hz, 1H, H_{4exo}); 2.04 (s, 3H, H_{8Me}); 1.84 (s, 3H, H_{9Me}); 1.54 (d, J = 7.0 Hz, 3H, $H10_{endoMe}$). ^1H NMR (400 MHz, acetone-d_6): δ 5.48 (s, 5H, Cp); 5.32 (ddd, 1H, H_3); 4.86 (ddd, 1H, H_1); 4.14 (t, J = 7.3 Hz, 1H, H_2); 3.12 (dd, J = 9.3 Hz, J = 14.2 Hz, 1H, H_{4endo}); 2.70 (t, J = 6.2 Hz, 1H, H_{7exo}); 2.63 (dd, J = 4.6 Hz, J = 14.0 Hz, 1H, H_{4exo}); 2.09 (s, 3H, H_{8Me}); 1.92 (s, 3H, H_{9Me}); 1.52 (d, J = 7.0 Hz, 3H, $H_{10endoMe}$). GCOSY (300 MHz, acetone-d_6): δ 5.32 (H_3) ↔ 4.14 (H_2), 3.12 (H_{4endo}); 4.86 (H_1) ↔ 4.14 (H_2); 3.12 (H_{4endo}) ↔ 2.63 (H_{4exo}); 2.70 (H_{7exo}) ↔ 1.52 ($H_{10endoMe}$). ^{13}C NMR (100 MHz, acetone-d_6): δ 88.96 (Cp); 88.93 (C_3); 88.85 (C_2); 48.96 (C_1); 32.05 (C_7); 31.39 (C_4); 23.70 (C_8); 17.98 (C_{10}); 16.00 (C_9). gHSQC (400 MHz, acetone-d_6): δ 88.96 (Cp) ↔ 5.48 (Cp); 88.85 (C_2) ↔ 4.14 (H_2); 48.96 (C_1) ↔ 4.86 (H_1); 32.05 (C_7) ↔ 2.70 (H_{7exo}); 31.39 (C_4) ↔ 3.12 (H_{4endo}), 2.63 (H_{4exo}); 23.70 (C_8) ↔ 2.09 (H_8); 17.98 (C_{10}) ↔ 1.52 (H_{10}); 16.00 (C_9) ↔ 1.92 (H_9) [missing correlation: 88.93 (C_3) ↔ 5.32 (H_3)]. Electrospray MS: *m*/*z* calculated for $C_{15}H_{20}Co$ (M^+), 259.08915, found 259.08941. Anal. Calcd for $C_{15}H_{20}CoBF_4$: C, 52.06, H, 5.83; Found: C, 51.7911; H, 5.7621.

[CpCo(η^2,η^3-1-trimethylsilylcyclohepta-2,5-dien-1-yl)][BF_4] (8c). Pentadienyl complex **7b** (100 mg, 0.2856 mmol) was dissolved in CH_2Cl_2 (3 mL) and placed in a reaction bomb. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 20 min in order to ensure saturation. Then, ∼2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at 40 °C over 3 days. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 115.3 mg (94%) of **8c** as a dark red powder. ^1H NMR (400 MHz, acetone-d_6): δ 5.05 (m, 1H, H_3), 4.95 (m, 1H, H_1), 4.10 (m, 1H, H_2), 3.90 (m, 1H, H_5), 3.62 (m, 1H, H_6), 3.10 (m, 1H, H_{4endo}), 2.40 (m, 1H, H_{4exo}), 1.88 (m, 1H, H_{7exo}). GCOSY (400 MHz, acetone-d_6): δ 5.05 (H_3) ↔ 4.10 (H_2), 3.10 (H_{4endo}), 2.40 (H_{4exo}); 4.95 (H_1) ↔ 4.10 (H_2), 1.88 (H_{7exo}); 3.90 (H_5) ↔ 3.62 (H_6), 3.10 (H_{4endo}); 3.62 (H_6) ↔ 1.88 (H_{7exo}); 3.10 (H_{4endo}) ↔ 2.40 (H_{4exo}). Electrospray MS: *m*/*z* calculated for $C_{15}H_{22}CoSi$ (M^+) 289.08173, found 289.08147.

[CpCo(η^2,η^3-2,3-dimethyl-1-trimethylsilylcyclohepta-2,5-dien-1-yl)][BF_4] (8d). A glass reaction bomb was charged with a solution of **7b** (100 mg, 0.2856 mmol) in dichloromethane (∼3 mL). An aliquot of 2-butyne (224 μL, ∼2.856 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, was a powder that was identified as complex **8d** with a trace (∼5% by NMR spectroscopy) of the desilylated fully conjugated product **9b**. ^1H NMR (500 MHz, $CDCl_3$): δ 5.43 (ddd, 1H, H_3), 5.37 (s, 5H, Cp), 5.05 (dd, J = 5.9, J = 6.8 Hz, 1H, H_1), 4.29 (dd, J = 6.1, J = 7.1 Hz, 1H, H_2), 3.18 (dd, J = 9.5 Hz, J = 14.2 Hz, 1H, H_{4exo}), 2.68 (dd, J = 3.4 Hz, J = 14.4 Hz, 1H, H_{4endo}), 2.10 (s, 3H, H_{10Me}), 2.02 (s, 3H, H_{9Me}), 1.90 (d, J = 5.9 Hz, 1H, H_{7exo}), 0.40 (s, 9H, C_{8TMSMe}). GCOSY (300 MHz, $CDCl_3$): 5.43 (H_3) ↔ 4.29 (H_2), 3.18 (H_{4exo}), 2.68 (H_{4endo}); 5.05 (H_1) ↔ 4.29 (H_2), 1.90 (H_{7exo}); 3.18 (H_{4exo}) ↔ 2.68 (H_{4endo}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 88.88 (C_2), 88.09 (Cp), 62.22 (C_5), 61.29 (C_6), 44.43 (C_3), 40.84 (C_1), 31.50 (C_4), 28.12 (C_7), 22.85 (C_9), 21.22 (C_{10}), −1.76 (C_8). Electrospray MS: *m*/*z* calculated for $C_{17}H_{26}CoSi$ (M^+) 317.11298, found 317.11303.

[CpCo(η^2,η^3-1-phenylcycloheptadienyl)]$^+BF_4^-$ (8e). Complex **7c** (100 mg, 0.2825 mmol) was dissolved in CH_2Cl_2 (3 mL) and placed in a reaction bomb. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 20 min in order to ensure saturation. Then, ∼2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature over 3.5 days. The solvent was then removed in vacuo and the

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product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 74.4 mg (69%) of total product as a dark red powder. The ^{1}H NMR spectrum showed that there was a majority (ca. 83%) of starting complex **7c** and ca. 17% of **8e**. IR (microscope, cm^{-1}): 3520 (br, 3119 (m), 3026 (w), 2928 (m), 1668 (m), 1643 (m), 1619 (m), 1494 (w), 1450 (w), 1417 (w), 1286 (w), 1054 (brs), 866 (m), 753 (m), 700 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (m, 2H, Ph), 7.45 (m, 3H, Ph), 5.70 (s, 5H, Cp), 5.18 (ddd, 1H, H_1), 4.95 (dd, 1H, H_3), 4.15 (t, J = 7 Hz, 1H, H_2), 3.89 (ddd, 1H, H_6), 3.57 (dd, 1H, H_5), 3.44 (dd, 1H, H_{4endo}), 2.34 (dd, 1H, H_{7exo} or H_{4exo}), 1.60 (m, 1H, H_{4exo} or H_{7exo}). GCOSY (500 MHz, $CDCl_3$): δ 7.55 (Ph) ↔ 7.45 (Ph); 4.95 (H_3) ↔ 3.44 (H_{4endo}); 3.89 (H_6) ↔ 2.34 (H_{7exo}). Electrospray MS: m/z calculated for $C_{18}H_{18}Co$ (M^+) 293.07350, found 293.07370.

[CpCo(η^2,η^3-2,3-dimethyl-1-phenylcycloheptadienyl)]$^+$$BF_4^-$ (8f) and [CpCo(η^5-2,3-dimethyl-1-phenylcycloheptadienyl)]$^+$$BF_4^-$ (9c). A glass reaction bomb was charged with a solution of complex **7c** (100 mg, 0.2825 mmol) in dichloromethane (~4 mL). The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, provided 72.4 mg (63%) of total product as a red oily residue. The ^{1}H NMR spectrum showed that this product mixture was a majority (ca. 87%) of **8f** and only a minor amount (ca. 13%) of fully conjugated **9c**. The sample was purified by recrystallization using pinhole diffusion to provide an analytically pure sample of the mixture of isomers. Data for **9c** are as follows. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, 3H, Ph), 7.37 (t, 2H, Ph), 7.28 (m, 1H, H_3), 5.76 (m, 1H, H_4), 5.64 (s, 5H, Cp), 5.34 (m, 1H, H_5), 3.88 (m, 1H, H_{6exo}), 2.38 (m, 1H, H_{6endo}), 2.08 (s, 3H, H_8), 1.52 (m, 1H, H_{7exo}) 1.40 (s, 3H, H_9). GCOSY (500 MHz, $CDCl_3$): δ 7. 55 (d, 3H, Ph) ↔ 7.37 (t, 2H, Ph); 7.28 (m, 1H, H_3) ↔ 5.76 (m, 1H, H_4); 5.34 (m, 1H, H_5) ↔ 2.38 (m, 1H, H_{6endo}); 3.88 (m, 1H, H_{6exo}) ↔ 2.38 (m, 1H, H_{6endo}), 1.52 (m, 1H, H_{7exo}); 2.38 (m, 1H, H_{6endo}) ↔ 1.52 (m, 1H, H_{7exo}). Data for **8f** are as follows. $_1$H NMR (500 MHz, $CDCl_3$): δ 7.53 (m, 2H, Ph), 7.48 (m, 3H, Ph), 5.43 (ddd, 1H, H_3), 5.38 (s, 5H, Cp), 4.25 (t, 1H, H_2), 3.67 (dd, 1H, H_1), 3.24 (dd, 1H, H_{4endo}), 2.74 (dd, 1H, H_{4exo}), 2.38 (m, 1H, H_{7exo}), 2.06 (s, 3H, H_8), 1.39 (s, 3H, H_9). GCOSY (400 MHz, $CDCl_3$): δ 7.53 (Ph) ↔ 7.48 (Ph); 5.43 (H_3) ↔ 4.25 (H_2), 3.67 (H_1), 3.24 (H_{4endo}), 2.74 (H_{4exo}); 3.67 (H_1) ↔ 2.38 (H_{7exo}); 3.24 (H_{4endo}) ↔ 2.74 (H_{4exo}). Electrospray MS: m/z calculated for $C_{20}H_{22}Co$ (M^+) 321.10507, found 321.10480. Anal. Calcd for $C_{15}H_{17}CoBF_4$: C, 58.86; H, 5.43; Found, C, 59.1655; H, 5.5673.

[CpCo(η^2,η^3-cycloheptadienyl)]$^+$$BF_4^-$ (8g) and [CpCo(η^5-cycloheptadienyl)]$^+$$BF_4^-$ (9d). η^5-Pentadienyl complex **7d** (100 mg, 0.3601 mmol) was dissolved in CH_2Cl_2 (3 mL) and placed in a glass reaction bomb. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 20 min in order to ensure saturation. Then, ~2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and heated to 60 °C over 24 h. The solution turned from orange to red. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 68.4 mg (63%) of product as a dark red powder. The ^{1}H NMR spectrum showed that this was a mixture of the η^3:η^2 isomer and fully conjugated η^5 isomer in a 24:76 ratio. Although the product was characterized as a mixture, the NMR data are presented separately. Data for the isomeric mixture are as follows. IR (microscope, cm^{-1}): 3479 (br, 3119 (s), 2934 (w), 2856 (w), 1709 (w), 1418 (s), 1286 (m), 1054 (brs), 867 (s). Data for **9d** are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.41 (t, 1H, H_3), 5.80 (dt, 2H, H_2/H_4), 5.78 (overlap with H_2/H_4, s, 5H, Cp), 5.60 (m, 2H, H_1/H_3), 2.49 (dd, 2H, H_{6endo}/H_{7endo}), 1.25 (d, 2H, H_{6exo}/H_{7exo}). ^{1}H−^{1}H GCOSY (400 MHz, acetone-d_6): δ 7.41 (H_3) ↔ 5.80 (H_2/H_4); 5.80 (H_2/H_4) ↔ 5.60 (H_1/H_3); 5.60 (H_1/H_3) ↔ 2.49 (H_{6endo}/H_{7endo}), 1.25 (H_{6exo}/H_{7exo}); 2.49 (H_{6endo}/H_{7endo}) ↔ 1.25 (H_{6exo}/H_{7exo}). Data for **8g** are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 5.10 (m, 2H, H_1/H_3), 4.08 (t, 1H, H_2), 3.80 (m, 2H, H_6/H_7), 3.15 (m, 2H, H_{4exo}/H_{7exo}), 2.30 (dd, 2H, H_{4endo}/H_{7endo}). ^{1}H−^{1}H GCOSY (400 MHz, acetone-d_6): δ 5.10 (H_1/H_3) ↔ 4.08 (H_2), 3.15 (H_{4exo}/H_{7exo}), 2.30 (H_{4endo}/H_{7endo}); 4.08 (H_2) ↔ 3.15 (H_{4exo}/H_{7exo}), 2.30 (H_{4endo}/H_{7endo}); 3.80 (H_5/H_6) ↔ 3.15 (H_{4exo}/H_{7exo}), 2.30 (H_{4endo}/H_{7endo}); 3.15 (H_{4exo}/H_{7exo}) ↔ 2.30 (H_{4endo}/H_{7endo}). Electrospray MS: m/z calculated for $C_{12}H_{14}Co$ (M^+) 217.04220, found 217.04219.

[CpCo(η^2,η^3-1,2-dimethylcycloheptadienyl)]$^+$$BF_4^-$ (8h) and [CpCo(η^5-1,2- dimethylcycloheptadienyl)]$^+$$BF_4^-$ (9e). A glass reaction bomb was charged with a solution of **7d** (100 mg, 0.3601 mmol) in dichloromethane (~3 mL). An aliquot of 2- butyne (282 μL, ~3.601 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. Two deep red fractions were collected, and upon removal of solvent, the first fraction proved to be a mixture of the allyl-olefin product and an unknown byproduct (1:2) and the second fraction was the starting material.

The above procedure was repeated with heating to 65 °C for 72 h, isolating a single red fraction from column chromatography to provide 66.8 mg (56%) of total product as a red powder. By NMR spectroscopy, this fraction contained a mixture of the fully conjugated product **9e** and an unknown byproduct (1:3). Neither silica gel column chromatography nor pinhole diffusion crystallization (ether into dichloromethane) achieved further separation of the two compounds. Data for **8h** are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 5.45 (s, 5H, Cp); 5.40 (ddd, 2H, H_1/H_3); 4.20 (t, 1H, H_2); 3.11 (dd, 2H, H_{4endo}/H_{7endo}); 2.67 (dd, 2H, H_{4exo}/H_{7exo}); 2.20 (s, 3H, H_8/H_9). GCOSY (400 MHz, acetone-d_6): δ 5.40 (H_1/H_3) ↔ 4.20 (H_2), 3.11 (H_{4endo}), 2.67 (H_{4exo}); 3.11 (H_{4endo}) ↔ 2.67 (H_{4exo}). Data for **9e** (**A**) are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.17 (d, J_{2-3} = 7.3 Hz, 1H, H_3), 5.65 (m, 1H, H_2), 5.57 (s, 5H, Cp), 5.23 (ddd, J_{1-2} = 9.1 Hz, $J_{1-7endo}$ = 7.5 Hz, J_{1-3}= 1.5 Hz, 1H, H_1), 3.19 (dddd, $J_{7endo-7exo}$ = 19.9 Hz, $J_{7endo-6exo}$ = 11.7 Hz, $J_{7endo-1}$ = 7.7 Hz, $J_{7endo-6endo}$ = 3.5 Hz, 1H, H_{7endo}), 2.45 (s, 3H, H_8), 2.05 (m, 1H, H_{7exo}), 1.84 (s, 3H, H_9), 1.50 (ddt, $J_{6endo-6exo}$ = 12.3 Hz, $J_{6endo-7endo}$ = 7.7 Hz, $J_{6endo-7exo/9}$ = 1.5 Hz, 1H, H_{6endo}), 0.32 (dt, $J_{6exo-6endo/7exo}$ = 12.4 Hz, $J_{6exo-7exo}$ = 5.3 Hz, 1H, H_{6exo}). GCOSY (400 MHz, acetone- d_6): δ 7.17 (H_3) ↔ 5.23 (H_1), 2.45 (H_8), 1.84 (H_9); 5.65 (H_2) ↔ 5.23 (H_1), 3.19 (H_{7endo}), 2.05 (H_{7exo}), 1.50 (H_{6endo}); 5.23 (H_1) ↔ 2.05 (H_{7exo}); 3.19 (H_{7endo}) ↔ 2.05 (H_{7exo}), 1.50 (H_{6endo}), 0.32 (H_{6exo}); 2.05 (H_{7exo}) ↔ 0.32 (H_{6exo}); 1.50 (H_{6endo}) ↔ 0.32 (H_{6exo}). Data for the unknown byproduct (**B**) are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.37 (d, J = 5.4 Hz, 1H), 5.65 (s, 5H, Cp), 5.59 (m, 1H), 3.83 (d, 1H), 2.20 (s, 3H), 1.63 (d, J = 12.5 Hz, 8H). GCOSY (500 MHz, acetone-d_6): δ 7.37 ↔ 5.59, 3.83, 2.20, 1.63; 5.59 ↔ 3.83, 2.20, 1.63; 3.83, ↔ 1.63. Data for a mixture of compounds **A** and **B** are as follows. IR (microscope, cm^{-1}): 3113 (w), 2976 (w), 2942 (w), 2883 (w), 2835 (w), 1699 (w), 1458 (w), 1432 (w), 1411 (w), 1388 (w), 1285 (w), 1250 (w), 1055 (brs), 856 (w). ^{13}C NMR (125 MHz, acetone-d_6): δ 111.0, 108.0, 107.9, 99.1, 91.9, 91.2, 90.4, 89.1, 87.8, 87.6, 87.2, 86.9, 70.0, 55.7, 41.1, 33.8, 27.6, 20.4, 18.9, 18.4, 17.3, 11.8, 10.4. gHMQC (500 MHz, acetone-d_6): δ 99.3 ↔ 7.18 (B, H_2), 92.0 ↔ 7.36 (A, H_2), 87.6 ↔ 5.65 (A), 89.2 ↔ 5.56 (B), 55.9 ↔ 3.84 (B), 33.90 ↔ 1.61 (B), 27.6 ↔ 1.84 (A, Me), 19.0 ↔ 1.62, 18.3 ↔ 2.15 (A), 17.4 ↔ 1.67, 17.1 ↔ 1.60. Electrospray MS: m/z calculated for $C_{14}H_{18}Co$ (M^+) 245.07350, found 245.07387.

[CpCo(η^5-1,2,3-trimethylcycloheptadienyl)]$^+$$BF_4^-$ (9a). A glass reaction bomb was charged with a solution of **7a** (100 mg, 0.2890 mmol) in dichloroethane (~4 mL). The bomb was sealed, and the solution was maintained at 85−90 °C for 24 h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected, and upon removal of solvent, the sample was comprised primarily of the desired product but contained traces (less than 5% each by ^{1}H NMR integration) of minor impurities (99%). IR (microscope, cm^{-1}): 3115 (m), 2973 (m), 2880 (m), 1474 (s), 1431 (s), 1413 (s), 1012 (s), 857 (s). ^{1}H NMR (500 MHz, acetone-d_6): δ 7.21 (d, J_{3-2} = 7.2 Hz, 1H, H_3); 5.59 (s, 5H, Cp); 5.52 (obscured by Cp, m, 1H, H_5); 5.21 (t, $J_{4-3/5}$ = 8.1 Hz, 1H, H_4); 2.95 (ddd, $J_{6endo-6exo}$ = 17.3, $J_{6endo-5}$ = 11.7 Hz, $J_{6endo-7exo}$ = 3.4 Hz, 1H, H_{6endo}); 2.50 (s, 3H, H_8); 2.15 (dddd, $J_{6exo-6endo}$ = 17.4 Hz, $J_{6exo-7exo}$ = 4.2 Hz, J_{6exo-5} = 1.6 Hz,

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1H, H_{6exo}); 1.75 (s, 3H, H_9); 0.97 (d, $J_{10-6exo}$ = 6.8 Hz, 3H, H_{10}); 0.42 (ddd, $J_{7exo-6exo}$ = 4.6 Hz, $J_{7exo-10}$ = 6.9 Hz, 1H, H_{7exo}). GCOSY (500 MHz, acetone-d_6) δ 7.21 (H_3) ↔ 5.21 (H_4), 2.50 (H_8), 1.75 (H_9); 5.52 (H_5) ↔ 5.21 (H_4), 2.95 (H_{6endo}), 2.15 (H_{6exo}); 5.21 (H_4) ↔ 2.15 (H_{6exo}); 2.95 (H_{6endo}) ↔ 2.15 (H_{6exo}), 0.42 (H_{7exo}); 2.15 (H_{6exo}) ↔ 0.42 (H_{7exo}); 0.97 (H_{10}) ↔ 0.42 (H_{7exo}). ^{13}C NMR (125 MHz, acetone-d_6): δ 111.51 (C_2), 110.52 (C_1), 99.30 (C_3), 91.07 (C_4), 89.39 (Cp), 84.20 (C_5), 50.56 (C_6), 37.00 (C_7), 23.53 (C_9), 20.53 (C_8), 16.06 (C_{10}). gHSQC (500 MHz, acetone-d_6): δ 99.30 (C_3) ↔ 7.21 (H_3); 91.07 (C_4) ↔ 5.21(H_4); 89.39 (Cp) ↔ 5.59 (Cp); 84.20 (C_5) ↔ 5.52 (H_5); 50.56 (C_6) ↔ 2.95 (H_{6endo}), 2.15 (H_{6exo}); 37.00 (C_7) ↔ 0.42 (H_7); 23.53 (C_9) ↔ 1.75 (H_9); 20.53 (C_8) ↔ 2.50 (H_8); 16.06 (C_{10}) ↔ 0.97 (H_{10}); gHMBC (500 MHz, acetone-d_6): δ 111.51 (C_2) ↔ 2.50 (H_8), 2.15 (H_{6exo}); 110.52 (C_1) ↔ 1.75 (H_9), 0.97 (H_{10}); δ 99.30 (C_3) ↔ 2.50 (H_8); 91.07 (C_4) ↔ 2.95(H_{6endo}); 84.20 (C_5) ↔ 2.95(H_{6endo}); 50.56 (C_6) ↔ 5.21 (H_4), 1.75 (H_9), 0.97 (H_{10}), 0.42 (H_{6exo}); 37.00 (C_7) ↔ 5.52 (H_5), 2.95 (H_{6endo}), 1.75 (H_9), 0.97 (H_{10}); 20.53 (C_8) ↔ 7.21 (H_3). Electrospray MS: m/z calculated for $C_{15}H_{20}Co$ (M^+) 259.08915, found 259.08897. Anal. Calcd for $C_{15}H_{20}CoBF_4$: C, 52.06, H, 5.83; Found: C, 51.8668; H, 5.8396.

(*E*)-Dimethyl 2-(Hepta-1,4-diene-3-ol)malonate (15). Aldehyde **13** (1.6 g, 7.5 mmol), was dissolved in THF (5 mL) in a dry Schlenk flask under an argon atmosphere. The flask was cooled to −78 °C in a dry ice/acetone bath, and vinyl Grignard (0.34 M in THF, 44 mL, 15 mmol) was added via cannula. The mixture was stirred at −78 °C for 30 min and then warmed to room temperature. The flask was cooled again and the reaction quenched with aqueous NH_4Cl. This mixture was extracted with diethyl ether, washed with water and then brine, and dried over $NaSO_4$. The solvent was removed in vacuo and the product purified via triethylamine neutralized silica gel chromatography with 4:1 hexanes/EtOAc on the bench. The solvent was removed to yield 1.1 g (60%) of dienol **15** as a clear oil. IR (neat, cm^{-1}): 3447 (br m), 3008 (w), 2956 (m), 2850 (w), 1737 (s), 1438 (m), 1346 (w), 1245 (m), 1201 (m), 1158 (m), 1082 (w), 992 (m), 972 (m), 925 (w), 692 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddd, $J_{2-1trans}$ = 16.1 Hz, J_{2-1cis} = 10.3 Hz, J_{2-3} = 5.7 Hz, 1H, H_2), 5.57 (dtd, J_{5-4} = 15.5 Hz, J_{5-6} = 6.3 Hz, J_{5-3} = 0.8 Hz, 1H, H_5), 5.45 (ddt, J_{4-5} = 16.3 Hz, J_{4-3} = 5.1 Hz, J_{4-6} = 1.1 Hz, 1H, H_4), 5.16 (dt, $J_{1trans-2}$ = 17.2 Hz, $J_{1trans-1cis}$ = $J_{1trans-3}$ = 1.5 Hz, 1H, H_{1trans}), 5.04 (dt, J_{1cis-2} = 10.4 Hz, $J_{1cis-1trans}$ = J_{1cis-3} = 1.3 Hz, 1H, H_{1cis}), 4.49 (br app t, J_{3-2} = J_{3-4} = 5.6 Hz, 1H, H_3), 3.65 (s, 6H, −OMe), 3.31 (t, J_{8-7} = 7.4 Hz, 1H, H_8), 2.18 (br s, 1H, −OH), 2.01 (m, 2H, CH_2), 1.92 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.6, 139.5, 132.7, 129.8, 114.6, 73.2, 52.3, 50.7, 29.6, 27.9. Electrospray MS: m/z calculated for $C_{12}H_{18}O_5Na$ (M^+ + Na) 265.10465, found 265.10463 (100%). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.44; H, 7.60.

(*E*)-Dimethyl 2-(Octa-1,4-diene-3-ol)malonate (15). 2-(1-Penten)-dimethyl malonate (3.7 g, 18 mmol) and crotonaldehyde (4.5 mL, 54 mmol) were dissolved in CH_2Cl_2 (25 mL) in a dry three-neck round-bottom flask. Second-generation Grubbs metathesis catalyst (230 mg, 0.27 mmol) was added and the mixture heated at reflux under an argon atmosphere for 90 min, at which time full conversion to aldehyde **14** was observed via ^{1}H NMR spectroscopy. The solvent was removed in vacuo and the residue placed on the Schlenk line for 2 h to remove excess crotonaldehyde. The aldehyde product was unstable to chromatography and was therefore taken directly to the next step. The residue was taken up in THF (25 mL) and transferred to a dry addition funnel under an argon atmosphere and added dropwise to a vinyl Grignard solution (0.34 M in THF, 159 mL, 54 mmol) cooled to −78 °C in a dry ice/acetone bath. Upon complete addition, the reaction mixture was stirred for an additional 30 min at −78 °C and then warmed to room temperature. The flask was cooled again and the reaction quenched with aqueous NH_4Cl. This mixture was extracted with diethyl ether, washed with water and then brine, and dried over $NaSO_4$. The solvent was removed in vacuo and the product purified via triethylamine neutralized silica gel chromatography with 4:1 hexanes/EtOAc on the bench. The solvent was removed to yield 3.8 g (80%) of dienol **15** as a clear oil. The product upon chromatography is spectroscopically pure and sufficient to be carried forward, while additional chromatography was required to obtain analytical purity. IR (neat, cm^{-1}): 3455 (br s), 3082 (w), 2958 (s), 2850 (s), 1737 (s), 1641 (w), 1438 (s), 1346 (s), 1261 (s), 1156 (s), 1091 (s), 1016 (s), 924 (m), 873 (w), 800 (m), 699 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (ddd, $J_{2-1trans}$ = 17.2 Hz, J_{2-1cis} = 10.4 Hz, J_{2-3} = 5.8 Hz, 1H, H_2), 5.65 (dtd, J_{5-4} = 15.3 Hz, J_{5-6} = 6.5 Hz, J_{5-3} = 0.7 Hz, 1H, H_5), 5.50 (ddt, J_{4-5} = 15.5 Hz, J_{4-3} = 6.5 Hz, J_{4-6} = 1.3 Hz, 1H, H_4), 5.23 (dt, $J_{1trans-2}$ = 17.2 Hz, $J_{1trans-1cis}$ = $J_{1trans-3}$ = 1.4 Hz, 1H, H_{1trans}), 5.10 (dt, J_{1cis-2} = 10.4, $J_{1cis-1trans}$ = J_{1cis-3} = 1.4 Hz, 1H, H_{1cis}), 4.56 (br m, 1H, H_3), 3.72 (s, 6H, −OMe), 3.34 (t, J_{9-8} = 7.6 Hz, 1H, H_9), 2.06 (q, J_{6-5} = J_{6-7} = 7.1 Hz, 2H, H_6), 1.89 (m, 2H, CH_2), 1.57 (d, J_{HO-3} = 3.8 Hz, 1H, −OH), 1.40 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.6, 139.6, 131.7, 131.4, 114.7, 73.6, 52.3, 51.4, 31.6, 28.2, 26.6. Electrospray MS: m/z calculated for $C_{13}H_{20}O_5Na$ (M^+ + Na) 279.12030, found 279.12020 (100%). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 61.21; H, 7.92.

(*E*)-2-Heptenal 6-Acetal (19). Protected allyl acetone **18** (1.34 g, 9.43 mmol) and crotonaldehyde (3.9 mL, 47.15 mmol) were dissolved in CH_2Cl_2 (15 mL) under an argon atmosphere. Second-generation Grubbs catalyst (120 mg, 0.14 mmol) was added and the reaction mixture heated under reflux for 90 min. The solvent was removed in vacuo and the product purified by silica gel chromatography using 4:1 hexanes:EtOAc to provide 1.38 g (86%) of aldehyde **19** as a clear oily liquid. IR (neat, cm^{-1}): 2984 (s), 2956 (m), 2886 (s), 2736 (w), 1690 (s), 1637 (m), 1479 (w), 1449 (w), 1378 (m), 1302 (w), 1255 (s), 1222 (s), 1150 (s), 1053 (s), 979 (m), 949 (m), 867 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.49 (d, J_{1-2} = 7.9 Hz, 1H, H_1), 6.87 (dt, J_{3-2} = 15.6 Hz, J_{3-4} = 6.7 Hz, 1H, H_3), 6.10 (ddt, J_{2-3} = 15.6 Hz, J_{2-1} = 7.9 Hz, J_{2-4} = 1.6 Hz, 1H, H_2), 3.90 (m, 4H, −OCH_2CH_2O−), 2.45 (m, 2H, H_4), 1.86 (m, 2H, H_5), 1.33 (s, 3H, Me). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 9.49 (H_1) ↔ δ 6.10 (H_2); δ 6.87 (H_3) ↔ δ 6.10 (H_2), 2.45 (H_4); δ 6.10 (H_2) ↔ δ 2.45 (H_4); δ 2.45 (H_4) ↔ δ 1.86 (H_5). Electron impact MS: m/z calculated for $C_9H_{14}O_3$ (M^+) 170.09430, found 170.09481 (0.28%). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 158.4, 132.5, 109.1, 64.6, 36.9, 27.1, 23.9. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.28; H, 8.31.

(*E*)-Nona-1,4-dien-3-ol 8-Acetal (20). A solution of vinyl Grignard (0.34 M in THF, 18.2 mL, 6.18 mmol) was added to a flame-dried Schlenk flask under an argon atmosphere and cooled to −78 °C in a dry ice/acetone bath. To the resulting slurry was added slowly aldehyde **19** (1.01 g, 5.88 mmol) via syringe. The mixture was stirred at −78 °C for 30 min and then warmed slowly to room temperature and stirred for an additional 15 min. The solution was cooled again and quenched slowly with aqueous NH_4Cl. The resulting mixture was extracted with ether, washed with water and then brine, and dried over $NaSO_4$. The solvent was removed in vacuo and the product purified by silica gel chromatography with 4:1 hexane/EtOAc to provide 0.88 g (75%) of dienol **20** as a thick, pale yellow oil. IR (neat, cm^{-1}): 3440 (br s), 3080 (w), 2982 (s), 2947 (s), 2882 (s), 2678 (w), 1845 (w), 1668 (m), 1641 (m), 1477 (m), 1450 (m), 1422 (m), 1377 (s), 1344 (w), 1252 (s), 1221 (s), 1119 (s), 1058 (s), 974 (s), 949 (s), 923 (s), 862 (s), 817 (w), 787 (w), 762 (w), 668 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, $J_{2-1trans}$ = 17.2 Hz, J_{2-1cis} = 10.4 Hz, J_{2-3} = 5.8 Hz, 1H, H_2), 5.65 (dtd, J_{5-4} = 15.4 Hz, J_{5-6} = 6.6 Hz, J_{5-3} = 1.0 Hz, 1H, H_5), 5.46 (ddt, J_{4-5} = 15.4 Hz, J_{4-3} = 6.6 Hz, J_{4-6} = 1.5 Hz, 1H, H_4), 5.18 (dt, $J_{1trans-2}$ = 17.3 Hz, $J_{1trans-1cis}$ = $J_{1trans-3}$ = 1.5 Hz, 1H, H_{1trans}), 5.05 (dt, J_{1cis-2} = 10.4 Hz, $J_{1cis-1trans}$ = J_{1cis-3} = 1.4 Hz, 1H, H_{1cis}), 4.51 (br app t, J = 6.0 Hz, 1H, H_3), 3.87 (m, 4H, -OCH_2CH_2O−), 2.09 (m, 3H, H_6, −OH), 1.68 (m, 2H, H_7), 1.26 (s, 3H, H_8). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 5.82 (H_2) ↔ δ 5.18 (H_{1trans}), 5.05 (H_{1cis}), 4.51 (H_3) ; δ 5.65 (H_5) ↔ δ 5.46 (H_4), 2.09 (H_6); δ 5.46 (H_4) ↔ δ 4.51 (H_3), 2.09 (H_6); δ 5.18 (H_{1trans}) ↔ δ 5.05 (H_{1cis}), 4.51 (H_3); δ 5.05 (H_{1cis}) ↔ δ 4.51 (H_3); δ 2.09 (H_6) ↔ δ 1.68 (H_7). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.7, 131.9, 131.0, 114.5, 109.6, 73.5, 64.5, 38.2, 26.6, 23.8. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.55; H, 9.14.

[Cp*Co(η^5-1-(dimethyl-2-ethylmalonyl)pentadienyl)]$^+BF_4^-$ (21). In the drybox, Cp*Co$(C_2H_4)_2$ (0.94 g, 3.75 mmol) was dissolved in acetone (15 mL) and placed in a Schlenk tube equipped with a stir bar and septum. The sealed flask was removed to the Schlenk line and cooled to −78 °C in a dry ice/acetone bath, and HBF_4·Et_2O (517 μL,

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3.75 mmol) was added. Upon addition of HBF_4, an immediate color change from red to black was observed. The reaction mixture was stirred under argon for 15 min, then (*E*)-dimethyl 2-(hepta-1,4-diene-3-ol)malonate (1.00 g, 4.13 mmol) was added via syringe ,and the reaction mixture was warmed to room temperature overnight. A gradual color change from black to red occurred. The solvent was removed in vacuo and the product purified on the bench by silica gel chromatography using 3% $MeOH/CH_2Cl_2$. The red fraction was collected and dried to yield 1.61 g (85%) of product as a red oil. IR (neat, cm^{-1}): 3539 (w), 2956 (m), 2853 (w), 1731 (s), 1639 (w), 1438 (s), 1382 (w), 1260 (s), 1158 (s), 1078 (w), 1012 (m), 908 (w), 875 (w), 843 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.31 (t, $J_{3-2} = J_{3-4}$ = 7.0 Hz, 1H, H_3), 5.07 (dd, J_{4-5} = 11.7 Hz, J_{4-3} = 6.9 Hz, 1H, H_4), 4.96 (ddd, $J_{2-1anti}$ = 11.7 Hz, J_{2-3} = 9.8 Hz, J_{2-1syn} = 9.6 Hz, 1H, H_2), 3.74 (s, 3H, −OMe), 3.72 (s, 3H, −OMe), 3.42 (t, J_{8-7} = 7.0 Hz, 1H, H_8), 3.21 (dd, J_{1syn-2} = 9.6 Hz, $J_{1syn-1anti}$ = 3.4 Hz, 1H, H_{1syn}), 2.16−2.03 (m, 2H), 1.99 (m, 2H), 1.82 (s, 15H, C_5Me_5), 1.77 (dd, $J_{1anti-2}$ = 12.5 Hz, $J_{1anti-1syn}$ = 3.9 Hz, 1H, H_{1anti}), 1.50 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.3, 99.6, 99.0, 98.6, 95.3, 64.4, 52.6, 50.3, 30.3, 29.4, 9.6. Electrospray MS: *m/z* calculated for $C_{22}H_{32}O_4Co$ ($M^+ - BF_4$) 419.16271, found 419.16223 (100%). Anal. Calcd for $C_{22}H_{32}O_4CoBF_4$: C, 52.20; H, 6.37. Found: C, 52.29; H, 6.52.

[Cp*Co(η^5-1-(dimethyl-2-propylmalonyl)pentadienyl)]$^+BF_4^-$ (22). In the drybox, $Cp^*Co(C_2H_4)_2$ (0.720 g, 2.88 mmol) was dissolved in acetone (10 mL) and placed in a Schlenk tube equipped with a stir bar and septum. The sealed flask was removed from the Schlenk line and cooled to −78 °C in a dry ice/acetone bath, and $HBF_4{\cdot}Et_2O$ (397 μL, 2.88 mmol) was added. Upon addition of HBF_4, an immediate color change from red to black was observed. The reaction mixture was stirred under argon for 15 min, then (*E*)-dimethyl-2-(octa-1,4-diene-3-ol)malonate (0.813 g, 3.17 mmol) was added via syringe, and the reaction mixture was warmed to room temperature overnight. A gradual color change from black to red occurred. The solvent was removed in vacuo and the product purified on the bench by silica gel chromatography using 3% $MeOH/CH_2Cl_2$. The red fraction was collected and dried to yield 1.20 g (80%) of product as a red oil. Spectroscopy was not successful due to slow decomposition; therefore, this product was carried forward without further characterization.

[Cp*Co(η^2,η^3-1-(dimethyl-2-ethylmalonyl)cycloheptadienyl)]$^+BF_4^-$ (23). Pentadienyl complex **21** (127 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (10 mL) and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature for 3 days. The solvent was removed in vacuo and the product purified by silica gel chromatography using 3% $MeOH/CH_2Cl_2$. The red fraction was collected and dried, providing 119 mg (89%) of product as a thick, red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion analysis. IR (CH_2Cl_2 cast, cm^{-1}): 2957 (m), 2919 (w), 2865 (w), 1732 (s), 1455 (m), 1436 (m), 1389 (m), 1346 (w), 1285 (m), 1225 (m), 1153 (m), 1056 (s), 798 (w), 732 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 3.92 (td, $J_{3-2} = J_{3-4endo}$ = 8.3 Hz, J_{3-4exo} = 4.1 Hz, 1H, H_3), 3.71 (s, 3H, −OMe), 3.70 (s, 3H, −OMe), 3.60 (dd, J_{1-2} = 7.6 Hz, J_{1-7} = 3.8 Hz, 1H, H_1), 3.41 (t, J_{10-9} = 6.9 Hz, 1H, H_{10}), 3.30 (t, $J_{2-1} = J_{2-3}$ = 7.6 Hz, 1H, H_2), 3.10 (dt, $J_{4endo-4exo}$ = 14.1 Hz, $J_{4endo-3} = J_{4endo-5}$ = 8.5 Hz, 1H, H_{4endo}), 2.83 (td, $J_{5-4endo} = J_{5-6}$ = 7.3 Hz, J_{5-4exo} = 4.9 Hz, 1H, H_5), 2.42 (dd, J_{6-5} = 6.6 Hz, J_{6-7} = 4.5 Hz, 1H, H_6), 2.16 (tt, J_{7-8} = 7.6 Hz, $J_{7-1} = J_{7-6}$ = 3.7 Hz, 1H, H_7), 2.04 (dt, $J_{4exo-4endo}$ = 14.1 Hz, $J_{4exo-3} = J_{4exo-5}$ = 4.3 Hz, 1H, H_{4exo}), 1.90 (m, 2H, H_9), 1.82−1.78 (m, 2H, H_8, overlaps Cp* peak), 1.77 (s, 15H, C_5Me_5). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 3.92 (H_3) ↔ δ 3.60 (H_1), 3.30 (H_2), 3.10 (H_{4endo}), 2.04 (H_{4exo}); δ 3.60 (H_1) ↔ δ 3.30 (H_2), 2.16 (H_7); δ 3.41 (H_{10}) ↔ δ 1.90 (H_9); δ 3.30 (H_2) ↔ δ 2.04 (H_{4exo}); δ 3.10 (H_{4endo}) ↔ δ 2.83 (H_5), 2.42 (H_6), 2.04 (H_{4exo}); δ 2.83 (H_5) ↔ δ 2.42 (H_6), 2.04 (H_{4exo}); δ 2.42 (H_6) ↔ δ 2.16 (H_7); δ 2.16 (H_7) ↔ δ 1.82−1.78 (H_8); δ 1.90 (H_9) ↔ δ 1.82−1.78 (H_8). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.5, 97.8, 92.2, 53.1, 52.6, 50.8, 49.3, 45.8, 44.5, 31.9, 31.1, 25.3, 21.4, 9.5. Electrospray MS: *m/z* calculated for $C_{24}H_{34}O_4Co$ ($M^+ - BF_4$) 445.17836, found 445.17834 (100%).

[Cp*Co(η^2,η^3-1-(dimethyl-2-propylmalonyl)cycloheptadienyl)]$^+BF_4^-$ (24). Pentadienyl complex **22** (827 mg, 1.59 mmol) was dissolved in CH_2Cl_2 (10 mL) and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 15 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature for 3 days. The solvent was removed in vacuo and the product purified by silica gel chromatography using 3% $MeOH/CH_2Cl_2$. The red fraction was collected and dried, providing 702 mg (81%) of product as a thick, red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion and X-ray analysis. IR (CH_2Cl_2 cast, cm^{-1}): 2955 (m), 2863 (w), 1732 (s), 1653 (w), 1457 (m), 1436 (m), 1388 (m), 1282 (m), 1220 (m), 1156 (m), 1054 (s), 891 (w), 796 (w), 732 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 3.96 (td, $J_{3-2} = J_{3-4endo}$ = 8.4 Hz, J_{3-4exo} = 4.0 Hz, 1H, H_3), 3.73 (s, 6H, −OMe), 3.58 (dd, J_{1-2} = 7.6 Hz, J_{1-7} = 3.8 Hz, 1H, H_1), 3.41 (t, J_{11-10} = 7.5 Hz, 1H, H_{11}), 3.34 (t, $J_{2-1} = J_{2-3}$ = 7.6 Hz, 1H, H_2), 3.15 (dt, $J_{4endo-4exo}$ = 14.3 Hz, $J_{4endo-3} = J_{4endo-5}$ = 8.7 Hz, 1H, H_{4endo}), 2.87 (td, $J_{5-4endo} = J_{5-6}$ = 7.1 Hz, J_{5-4exo} = 5.4 Hz, 1H, H_5), 2.36 (dd, J_{6-5} = 6.3 Hz, J_{6-7} = 4.7 Hz, 1H, H_6), 2.18 (tt, J_{7-8} = 8.0 Hz, $J_{7-1} = J_{7-6}$ = 3.7 Hz, 1H, H_7), 2.10 (dt, $J_{4exo-4endo}$ = 14.4 Hz, $J_{4exo-3} = J_{4exo-5}$ = 4.1 Hz, 1H, H_{4exo}), 1.93 (q, $J_{10-9} = J_{10-11}$ = 7.7 Hz, 2H, H_{10}), 1.88−1.79 (m, 2H, H_8, overlaps Cp* peak), 1.82 (s, 15H, C_5Me_5), 1.44 (m, 2H, H_9). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 3.96 (H_3) ↔ δ 3.34 (H_2), 3.15 (H_{4endo}), 2.10 (H_{4exo}); δ 3.58 (H_1) ↔ δ 3.34 (H_2), 2.18 (H_7); δ 3.41 (H_{11}) ↔ δ 1.93 (H_{10}); δ 3.15 (H_{4endo}) ↔ δ 2.87 (H_5), 2.10 (H_{4exo}); δ 2.87 (H_5) ↔ δ 2.36 (H_6), 2.10 (H_{4exo}); δ 2.36 (H_6) ↔ δ 2.18 (H_7); δ 2.18 (H_7) ↔ δ 1.88−1.79 (H_8); δ 1.93 (H_{10}) ↔ δ 1.44 (H_9). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.6, 97.7, 92.2, 53.5, 52.5, 51.1, 49.8, 45.9, 44.7, 33.5, 31.8, 28.2, 23.7, 21.6, 9.6. Electrospray MS: *m/z* calculated for $C_{25}H_{36}O_4Co$ ($M^+ - BF_4$) 459.19401, found 459.19432 (100%). Anal. Calcd for $C_{25}H_{36}O_4CoBF_4$: C, 54.97; H, 6.64. Found: C, 54.52; H, 6.64.

[Cp*Co(η^5-1-(dimethyl-2-ethylmalonyl)cycloheptadienyl)]$^+BF_4^-$ (25). Allyl/olefin complex **23** (10 mg) was dissolved in CH_2Cl_2 (5 mL) in a reaction bomb and heated at 60 °C in an oil bath for 3 days. The solvent was removed and the residue filtered through silica gel using 3% $MeOH/CH_2Cl_2$ to remove paramagnetic impurities. ^1H NMR spectroscopy indicated quantitative conversion to the fully conjugated isomer. The spectra were identical with those previously reported.[22]

[Cp*Co(η^5-1-(dimethyl-2-propylmalonyl)cycloheptadienyl)]$^+BF_4^-$ (26). Allyl/olefin complex **24** (10 mg) was dissolved in CH_2Cl_2 (5 mL) in a reaction bomb and heated at 60 °C in an oil bath for 3 days. The solvent was removed and the residue filtered through silica gel using 3% $MeOH/CH_2Cl_2$ to remove paramagnetic impurities. ^1H NMR spectroscopy indicated quantitative conversion to the fully conjugated isomer. The spectra were identical with those previously reported.[22]

[Cp*Co(η^5-1,2-dimethyl-7-(dimethyl-2-ethylmalonyl)-cycloheptadienyl)]$^+BF_4^-$ (27). Pentadienyl complex **21** (311 mg, 0.62 mmol) was dissolved in CH_2Cl_2 (10 mL) in a reaction bomb and degassed with argon for 5 min. To this was added 2-butyne (325 μL, 4.15 mmol) via syringe. The bomb was sealed and heated at 40 °C for 3 days in an oil bath. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% $MeOH/CH_2Cl_2$. The red fraction was collected and dried, providing 241 mg (70%) of product as a thick, red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion analysis. IR (CH_2Cl_2 cast, cm^{-1}): 2956 (m), 2909 (m), 1732 (s), 1435 (s), 1384 (m), 1345 (w), 1268 (m), 1239 (m), 1199 (m), 1150 (m), 1054 (s), 910 (w), 864 (w), 732 (m), 700 (m). ^1H NMR (600 MHz, $CDCl_3$): δ 6.59 (d, J_{1-2} = 7.4 Hz, 1H, H_1), 4.69 (t, $J_{2-1} = J_{2-3}$ = 8.4 Hz, 1H, H_2), 4.36 (dt, J_{3-2} = 9.1 Hz, $J_{3-4endo} = J_{3-4exo}$ = 3.3 Hz, 1H, H_3), 3.71 (s, 3H, −OMe), 3.70 (s, 3H, −OMe), 3.21 (t, J_{8-7} = 7.1 Hz, 1H, H_8), 2.48 (ddd, $J_{4endo-4exo}$ = 16.7 Hz, $J_{4endo-5}$ = 11.9 Hz, $J_{4endo-3}$ = 2.8 Hz, 1H, H_{4exo}), 2.34 (dt, $J_{4exo-4endo}$ = 16.7 Hz,

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$J_{4exo-3} = J_{4exo-5}$ = 3.1 Hz, 1H, H_{4exo}), 2.22 (s, 3H, Me), 1.75 (s, 15H, C_5Me_5), 1.61 (m, 1H, H_7), 1.48 (dddd, $J_{7'-7}$ = 18.7 Hz, $J_{7'-6}$ = 11.8 Hz, $J_{7'-8}$ = 7.2 Hz, $J_{7'-6'}$ = 4.5 Hz, 1H, $H_{7'}$), 1.35 (tt, $J_{6-6'} = J_{6-7'}$ = 12.3 Hz, $J_{6-5} = J_{6-7}$ = 5.0 Hz, 1H, H_6), 1.29 (s, 3H, Me), 1.23 (tdd, $J_{6'-6} = J_{6'-7}$ = 13.4 Hz, $J_{6'-5}$ = 9.0 Hz, $J_{6'-7'}$ = 5.2 Hz, 1H, $H_{6'}$), 0.02 (ddt, $J_{5-4endo}$ = 12.8 Hz, $J_{5-6'}$ = 9.3 Hz, $J_{5-4exo} = J_{5-6}$ = 4.7 Hz, 1H, H_5). ^{1}H−^{1}H GCOSY (600 MHz, $CDCl_3$): δ 6.59 (H_1) ↔ δ 4.69 (H_2); δ 4.69 (H_2) ↔ δ 4.36 (H_3); δ 4.36 (H_3) ↔ δ 2.48 (H_{4endo}), 2.34 (H_{4exo}); δ 3.21 (H_8) ↔ δ 1.61 (H_7), 1.48 ($H_{7'}$); δ 2.48 (H_{4endo}) ↔ δ 2.34 (H_{4exo}), 0.02 (H_5); δ 2.34 (H_{4exo}) ↔ δ 0.02 (H_5); δ 1.61 (H_7) ↔ δ 1.48 ($H_{7'}$), 1.35 (H_6), 1.23 ($H_{6'}$); δ 1.48 ($H_{7'}$) ↔ δ 1.35 (H_6), 1.23 ($H_{6'}$); δ 1.35 (H_6) ↔ δ 1.23 ($H_{6'}$), 0.02 (H_5); δ 1.23 ($H_{6'}$) ↔ δ 0.02 (H_5). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.4, 108.7, 100.9, 99.1, 97.7, 96.1, 86.6, 52.6, 51.3, 47.9, 41.7, 28.2, 28.0, 19.2, 17.0, 9.0. Electrospray MS: *m*/*z* calculated for $C_{26}H_{38}O_4Co$ (M^+ − BF_4) 473.20966, found 473.20964 (100%). Anal. Calcd for $C_{26}H_{38}O_4CoBF_4$: C, 55.73; H, 6.84. Found: C, 55.48; H, 7.20.

[Cp*Co(η^5-1,2-dimethyl-7-(dimethyl-2-propylmalonyl)-cycloheptadienyl)]$^+$$BF_4^-$ (28). Pentadienyl complex **22** (53 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL) in a reaction bomb and degassed with argon for 5 min. To this was added 2-butyne (50 μL, 0.64 mmol) via syringe. The bomb was sealed and heated at 40 °C for 3 days in an oil bath. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 54 mg (93%) of product as a thick, red oil. Crystallization was unsuccessful for obtaining analytically pure material despite multiple attempts, due to the oily nature of the product. IR (CH_2Cl_2 cast, cm^{-1}): 2955 (m), 1732 (s), 1436 (m), 1384 (m), 1276 (m), 1232 (m), 1152 (m), 1056 (s), 909 (w), 733 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (d, J_{1-2} = 7.3 Hz, 1H, H_1), 4.68 (t, $J_{2-1} = J_{2-3}$ = 8.5 Hz, 1H, H_2), 4.34 (dt, J_{3-2} = 9.3 Hz, $J_{3-4endo} = J_{3-4exo}$ = 3.1 Hz, 1H, H_3), 3.69 (s, 3H, −OMe), 3.68 (s, 3H, −OMe), 3.23 (t, J_{9-8} = 7.4 Hz, 1H, H_9), 2.42 (ddd, $J_{4endo-4exo}$ = 16.9 Hz, $J_{4endo-5}$ = 11.7 Hz, $J_{4endo-3}$ = 2.9 Hz, 1H, H_{4endo}), 2.30 (dt, $J_{4exo-4endo}$ = 17.1 Hz, $J_{4exo-3} = J_{4exo-5}$ = 3.6 Hz, 1H, H_{4exo}), 2.20 (s, 3H, Me), 1.90−1.70 (m, 2H, H_8, overlaps Cp* peak), 1.74 (s, 15H, C_5Me_5), 1.38−1.19 (m, 2H, H_6, overlaps Me peak), 1.26 (s, 3H, Me), 1.07 (m, 1H, H_7), 0.88 (m, 1H, $H_{7'}$), 0.00 (m, 1H, H_5). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 6.58 (H_1) ↔ δ 4.68 (H_2); δ 4.68 (H_2) ↔ δ 4.34 (H_3); δ 4.34 (H_3) ↔ δ 2.42 (H_{4endo}), 2.30 (H_{4exo}); δ 3.23 (H_9) ↔ δ 1.90−1.70 (H_8); δ 2.42 (H_{4endo}) ↔ δ 2.30 (H_{4exo}), 0.00 (H_5); δ 2.30 (H_{4exo}) ↔ δ 0.00 (H_5); δ 1.90−1.70 (H_8) ↔ δ 1.07 (H_7), 0.88 ($H_{7'}$); δ 1.38−1.19 (H_6) ↔ δ 1.07 (H_7), 0.88 ($H_{7'}$), 0.00 (H_5); δ 1.07 (H_7) ↔ δ 0.88 ($H_{7'}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.5, 108.6, 101.0, 99.2, 97.5, 96.3, 86.8, 52.4, 51.2, 48.0, 41.3, 30.3, 28.5, 26.5, 19.1, 16.9, 9.0. Electrospray MS: *m*/*z* calculated for $C_{27}H_{40}O_4Co$ (M^+ − BF_4) 487.22531, found 487.22550 (100%).

[Cp*Co(η^5-1-(3-butanoyl acetal)pentadienyl]$^+$$BF_4^-$ (29). In the drybox, Cp*Co(C_2H_4)$_2$ (192 mg, 0.77 mmol) was dissolved in acetone (5 mL) and placed in a Schlenk tube equipped with a stir bar and septum. The sealed flask was removed from the Schlenk line and cooled to −78 °C in a dry ice/acetone bath, and HBF_4·Et_2O (105 μL, 0.77 mmol) was added. Upon addition of HBF_4, an immediate color change from red to black was observed. The reaction mixture was stirred under argon for 15 min, then (*E*)-nona-1,4-dien-3-ol-8-acetal (163 mg, 0.82 mmol) was added via syringe, and the reaction mixture was warmed to room temperature overnight. A gradual color change from black to red occurred. The solvent was removed in vacuo and the product purified on the bench by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried to yield 289 mg (81%) of product as a red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided a red powder suitable for combustion analysis. IR (neat, cm^{-1}): 2981 (w), 1453 (w), 1430 (w), 1383 (w), 1222 (w), 1053 (s), 950 (w), 904 (w), 863 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (t, $J_{3-2} = J_{3-4}$ = 6.9 Hz, 1H, H_3), 5.13 (dd, J_{4-5} = 11.9 Hz, J_{4-3} = 6.8 Hz, 1H, H_4), 5.03 (ddd, $J_{2-1anti}$ = 11.8 Hz, J_{2-1syn} = 9.7 Hz, J_{2-3} = 7.1 Hz, 1H, H_2), 3.94 (m, 4H, −OCH_2CH_2O−), 3.20 (dd, J_{1syn-2} = 9.5 Hz, $J_{1syn-1-anti}$ = 3.4 Hz, 1H, H_{1syn}), 2.10 (m, 1H, H_6), 1.96 (td, $J_{5-4} = J_{5-6}$ = 10.7 Hz, $J_{5-6'}$ = 4.1 Hz, 1H, H_5), 1.86 (s, 15H, C_5Me_5), 1.80−1.70 (m, 3H, H_{1anti}, H_7), 1.56 (dtd, $J_{6'-6}$ = 12.5 Hz, $J_{6'-5} = J_{6'-7}$ = 10.2 Hz, $J_{6'-7'}$ = 5.5 Hz, 1H, $H_{6'}$), 1.30 (s, 3H, Me). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 6.46 (H_3) ↔ δ 5.13 (H_4), 5.03 (H_2), 3.20 (H_{1syn}), 1.96 (H_5), 1.65 (H_{1anti}); δ 5.13 (H_4) ↔ δ 1.96 (H_5); δ 5.03 (H_2) ↔ δ 3.20 (H_{1syn}), 1.65 (H_{1anti}); δ 3.20 (H_{1syn}) ↔ δ 1.65 (H_{1anti}); δ 2.10 (H_6) ↔ δ 1.96 (H_5), 1.70 (H_7), 1.56 ($H_{6'}$); δ 1.96 (H_5) ↔ δ 1.56 ($H_{6'}$); δ 1.70 (H_7) ↔ δ 1.56 ($H_{6'}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 109.3, 99.87, 99.29, 98.7, 95.7, 87.8, 65.0, 64.9, 64.2, 40.2, 28.1, 24.2, 10.0. Electrospray MS: *m*/*z* calculated for $C_{21}H_{32}O_2Co$ (M^+ − BF_4) 375.17288, found 375.17293 (100%). Anal. Calcd for $C_{21}H_{32}O_2CoBF_4$: C, 54.57; H, 6.98. Found: C, 54.46; H, 7.02.

[Cp*Co(η^5-1-(3-butanoyl)pentadienyl)]$^+$$BF_4^-$ (30). Protected pentadienyl complex **29** (52 mg, 0.11 mmol) was placed in a round-bottom flask equipped with a reflux condenser and dissolved in off-the-shelf acetone (15 mL). To this was added HBF_4·OEt_2 (10 μL) and the mixture was heated at reflux overnight (~16 h). The solvent was removed in vacuo and the residue purified via benchtop silica gel chromatography using 3% MeOH/CH_2Cl_2 to provide 38 mg (81%) of deprotected pentadienyl complex **30**. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion and X-ray analysis. IR (neat, cm^{-1}): 2923 (m), 1709 (s), 1460 (m), 1428 (m), 1391 (m), 1366 (w), 1285 (w), 1270 (m), 1184 (w), 1165 (m), 1054 (s), 951 (w), 920 (w), 895 (w), 817 (w), 736 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (t, $J_{3-2} = J_{3-4}$ = 7.0 Hz, 1H, H_3), 5.18 (dd, J_{4-5} = 11.9 Hz, J_{4-3} = 6.8 Hz, 1H, H_4), 4.98 (ddd, $J_{2-1anti}$ = 11.5 Hz, J_{2-1syn} = 9.8 Hz, J_{2-3} = 7.2 Hz, 1H, H_2), 3.18 (dd, J_{1syn-2} = 9.6 Hz, $J_{1syn-1-anti}$ = 3.5 Hz, 1H, H_{1syn}), 2.65 (t, $J_{7-6} = J_{7-6'}$ = 6.9 Hz, 2H, H_7), 2.28 (dtd, $J_{6-6'}$ = 17.0 Hz, J_{6-7} = 6.9 Hz, J_{6-5} = 4.0 Hz, 1H, H_6), 2.08 (s, 3H, Me), 2.01 (m, 1H, H_5), 1.84 (s, 15H, C_5Me_5), 1.80 (dd, $J_{1anti-2}$ = 11.8 Hz, $J_{1anti-1syn}$ = 3.3 Hz, 1H, H_{1anti}), 1.69 (m, 1H, $H_{6'}$). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 6.33 (H_3) ↔ δ 5.18 (H_4), 4.98 (H_2), 318 (H_{1syn}), 2.01 (H_5), 1.80 (H_{1anti}); δ 5.18 (H_4) ↔ δ 2.01 (H_5); δ 4.98 (H_2) ↔ δ 3.18 (H_{1syn}), 1.80 (H_{1anti}); δ 3.18 (H_{1syn}) ↔ δ 1.80 (H_{1anti}); δ 2.65 (H_7) ↔ δ 2.28 (H_6), 1.69 ($H_{6'}$); δ 2.28 (H_6) ↔ δ 2.01 (H_5), 1.69 ($H_{6'}$); δ 2.01 (H_5) ↔ δ 1.69 ($H_{6'}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.4, 99.7, 99.3, 98.4, 95.2, 86.3, 64.3, 43.6, 30.0, 26.9, 9.7. Electrospray MS: *m*/*z* calculated for $C_{19}H_{28}OCo$ (M^+ − BF_4): 331.14666, found 331.14672 (100%). Anal. Calcd for $C_{19}H_{28}OCoBF_4$: C, 54.57; H, 6.75. Found: C, 54.56; H, 6.91.

[Cp*Co(η^2,η^3-1-(3-butanoyl)cycloheptadienyl)]$^+$$BF_4^-$ (31). Pentadienyl complex **30** (141 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (10 mL) and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 3 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature for 3 days. The solvent was removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 131 mg (88%) of product as a thick, red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion and X-ray analysis. IR (CH_2Cl_2 cast, cm^{-1}): 2919 (m), 1711 (s), 1454 (m), 1428 (m), 1384 (s), 1284 (w), 1231 (w), 1170 (w), 1056 (s), 895 (w), 846 (w), 798 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (td, $J_{3-2} = J_{3-4endo}$ = 8.4 Hz, J_{3-4exo} = 4.0 Hz, 1H, H_3), 3.69 (dd, J_{1-2} = 7.5 Hz, J_{1-7} = 3.7 Hz, 1H, H_1), 3.33 (t, $J_{2-1} = J_{2-3}$ = 7.6 Hz, 1H, H_2), 3.10 (td, $J_{4endo-4exo}$ = 14.1 Hz, $J_{4endo-3} = J_{4endo-5}$ = 8.4 Hz, 1H, H_{4endo}), 2.86 (td, $J_{5-4endo} = J_{5-6}$ = 7.2 Hz, J_{5-4exo} = 4.8 Hz, 1H, H_5), 2.69 (t, J_{9-8} = 7.2 Hz, 2H, H_9), 2.49 (dd, J_{6-5} = 6.4 Hz, J_{6-7} = 4.6 Hz, 1H, H_6), 2.21 (m, 1H, H_7, overlaps Me peak), 2.19 (s, 3H, Me), 2.11 (m, 1H, H_{4exo}, overlaps H_8), 2.08 (t, J_{8-9} = 6.8 Hz, 2H, H_8), 1.84 (s, 15H, C_5Me_5). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 3.91 (H_3) ↔ δ 3.33 (H_2), 3.10 (H_{4endo}), 2.11 (H_{4exo}); δ 3.69 (H_1) ↔ δ 3.33 (H_2), 2.21 (H_7); δ 3.33 (H_2) ↔ δ 2.21 (H_7); δ 3.10 (H_{4endo}) ↔ δ 2.86 (H_5), 2.49 (H_6), 2.11 (H_{4exo}); δ 2.86 (H_5) ↔ δ 2.49 (H_6), 2.11 (H_{4exo}); δ 2.69 (H_9) ↔ δ 2.08 (H_8); δ 2.49 (H_6) ↔ δ 2.21 (H_7). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 208.5, 97.8, 92.2, 53.4, 49.8, 45.8, 44.4, 39.8, 31.6, 30.1, 27.2, 21.6, 9.6. Electrospray MS: *m*/*z* calculated for $C_{21}H_{30}OCo$ (M^+ − BF_4): 357.16231, found 357.16251 (100%). Anal. Calcd for $C_{21}H_{30}OCoBF_4$: C, 56.78; H, 6.81. Found: C, 56.69; H, 6.83.

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[Cp*Co(η^5-1-(3-butanoyl)cycloheptadienyl)]$^+BF_4^-$ (32). Allyl/olefin complex **31** (40 mg, 0.090 mmol) was dissolved in CH_2Cl_2 (5 mL) in a reaction bomb and heated at 70 °C for 2 days. The solvent was removed in vacuo and the product purified by silica gel chromatography to provide 36 mg (90%) of the isomerized product **32** as a red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion and X-ray analysis. IR (neat, cm^{-1}): 3048 (w), 2961 (w), 2919 (w), 2852 (w), 1708 (s), 1489 (w), 1450 (m), 1420 (m), 1388 (m), 1379 (m), 1359 (w), 1318 (w), 1286 (w), 1268 (w), 1227 (w), 1193 (w), 1174 (m), 1154 (m), 1099 (s), 1057 (s), 1038 (s), 964 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 6.63 (t, $J_{3-2} = J_{3-4} = 6.5$ Hz, 1H, H_3), 5.34 (t, $J_{2-1} = J_{2-3} = 7.2$ Hz, 1H, H_2), 4.94 (t, $J_{4-3} = J_{4-5} = 8.3$ Hz, 1H, H_4), 4.34 (dt, $J_{5-4} = 9.2$ Hz, $J_{5-6endo} = J_{5-6exo} = 3.7$ Hz, 1H, H_5), 4.08 (dd, $J_{1-2} = 8.0$ Hz, $J_{1-7} = 3.8$ Hz, 1H, H_1), 2.45−2.33 (m, 3H, H_{6endo}, H_9), 2.11 (s, 3H, Me), 2.06 (br dt, $J_{6exo-6endo} = 17.0$ Hz, $J_{6exo-5} = J_{6exo-7} = 3.5$ Hz, 1H, H_{6exo}), 1.88 (s, 15H, C_5Me_5), 1.71−1.51 (m, 2H, H_8), 0.56 (br m, 1H, H_7). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 6.63 (H_3) ↔ δ 5.34 (H_2), 4.94 (H_4), 4.08 (H_1); δ 5.34 (H_2) ↔ δ 4.08 (H_1); δ 4.94 (H_4) ↔ δ 4.34 (H_5); δ 4.34 (H_5) ↔ δ 2.35 (H_{6endo}), 2.06 (H_{6exo}); δ 4.08 (H_1) ↔ δ 0.56 (H_7); δ 2.40 (H_9) ↔ δ 1.65 (H_8); δ 2.35 (H_{6endo}) ↔ δ 2.06 (H_{6exo}), 0.56 (H_7); δ 2.06 (H_{6exo}) ↔ δ 0.56 (H_7); δ 1.65 (H_8) ↔ δ 0.56 (H_7). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.3, 100.5, 98.8, 97.9, 97.7, 94.0, 88.4, 46.6, 41.2, 39.3, 30.0, 29.7, 9.7. Electrospray MS: m/z calculated for $C_{21}H_{30}OCo$ ($M^+ - BF_4$) 357.16231, found 357.16208 (100%). Anal. Calcd for $C_{21}H_{30}OCoBF_4$: C, 56.78; H, 6.81. Found: C, 56.87; H, 6.75.

[Cp*Co(η^5-1,2-dimethyl-7-(3-butanoyl)cycloheptadienyl)]$^+BF_4^-$ (33). Pentadienyl complex **30** (82 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (5 mL) in a reaction bomb and degassed with argon for 3 min. To this was added 2-butyne (100 μL, 1.28 mmol) via syringe. The bomb was sealed and heated at 40 °C for 3 days in an oil bath. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 74 mg (80%) of product as a thick, red oil that contained approximately 10% impurity, tentatively characterized as cobaltocenium type products. Crystallization was unsuccessful for obtaining analytically pure material despite multiple attempts, due to the oily nature of the product. IR (neat, cm^{-1}): 2965 (w), 2912 (w), 1711 (s), 1455 (m), 1432 (m), 1384 (s), 1282 (w), 1163 (w), 1054 (s), 910 (w), 865 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 6.49 (d, $J_{1-2} = 7.3$ Hz, 1H, H_1), 4.60 (t, $J_{2-1} = J_{2-3} = 7.8$ Hz, 1H, H_2), 4.34 (dt, $J_{3-2} = 9.1$ Hz, $J_{3-4endo} = J_{3-4exo} = 3.3$ Hz, 1H, H_3), 2.45 (ddd, $J_{4endo-4exo} = 16.7$ Hz, $J_{4endo-5} = 11.8$ Hz, $J_{4endo-3} = 3.0$ Hz, 1H, H_{4endo}), 2.25 (dt, $J_{4exo-4endo} = 16.6$ Hz, $J_{4exo-3} = J_{4exo-5} = 3.2$ Hz, 1H, H_{4exo}), 2.19 (s, 3H, Me), 2.15 (m, 1H, H_7), 2.10 (m, 1H, $H_{7'}$), 2.01 (s, 3H, Me), 1.73 (s, 15H, C_5Me_5), 1.61 (m, 1H, H_6), 1.45 (m, 1H, $H_{6'}$), 1.30 (s, 3H, Me), −0.01 (tt, $J_{5-4endo} = J_{5-6} = 9.7$ Hz, $J_{5-4exo} = J_{5-6'} = 4.5$ Hz, 1H, H_5). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 6.49 (H_1) ↔ δ 4.60 (H_2); δ 4.60 (H_2) ↔ δ 4.34 (H_3); δ 4.34 (H_3) ↔ δ 2.45 (H_{4endo}), 2.25 (H_{4exo}); δ 2.45 (H_{4endo}) ↔ δ 2.25 (H_{4exo}), −0.01 (H_5); δ 2.25 (H_{4exo}) ↔ δ −0.01 (H_5); δ 2.15 (H_7) ↔ δ 2.10 ($H_{7'}$), 1.61 (H_6), 1.45 ($H_{6'}$); δ 2.10 ($H_{7'}$) ↔ δ 1.61 (H_6), 1.45 ($H_{6'}$); δ 1.61 (H_6) ↔ δ 1.45 ($H_{6'}$), −0.01 (H_5); δ 1.45 ($H_{6'}$) ↔ δ −0.01 (H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.2, 108.6, 101.2, 99.1, 97.7, 96.2, 86.8, 47.7, 42.5, 41.2, 30.1, 24.3, 19.4, 17.1, 9.1. Electrospray MS: m/z calculated for $C_{23}H_{34}OCo$ ($M^+ - BF_4$) 385.19362, found 385.19380 (100%).

[Cp*Co(η^2,η^3-1-(3-butanoyl)cycloheptadienyl)]$^+BF_4^-$ (34). Pentadienyl complex **29** (40 mg, 0.087 mmol) was dissolved in CH_2Cl_2 (10 mL) and degassed with argon for 5 min. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test tube for 25 min in order to ensure saturation. Then, 6 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at room temperature for 3 days. The solvent was removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 34 mg (81%) of product as a thick, red oil. Crystallization via two-chambered liquid diffusion using CH_2Cl_2 and Et_2O provided red crystals suitable for combustion and X-ray analysis. IR (neat, cm^{-1}): 3063 (m), 2976 (s), 2930 (s), 1456 (s), 1383 (s), 1372 (s), 1349 (w), 1322 (w), 1280 (w), 1259 (s), 1236 (m), 1172 (w), 1144 (w), 1093 (s), 1048 (s), 1000 (m), 949 (m), 908 (m), 893 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 4H, $-OCH_2CH_2O-$), 3.93 (m, 1H, H_3, overlaps acetal peak), 3.58 (dd, $J_{1-2} = 7.5$ Hz, $J_{1-7} = 3.7$ Hz, 1H, H_1), 3.34 (t, $J_{2-1} = J_{2-3} = 7.6$ Hz, 1H, H_2), 3.12 (dt, $J_{4endo-4exo} = 14.2$ Hz, $J_{4endo-3} = J_{4endo-5} = 8.3$ Hz, 1H, H_{4endo}), 2.87 (td, $J_{5-4endo} = J_{5-6} = 7.7$ Hz, $J_{5-4exo} = 4.8$ Hz, 1H, H_5), 2.36 (dd, $J_{6-5} = 6.2$ Hz, $J_{6-7} = 4.8$ Hz, 1H, H_6), 2.17 (tt, $J_{7-8} = 7.3$ Hz, $J_{7-1} = J_{7-6} = 3.7$ Hz, 1H, H_7), 2.06 (dt, $J_{4exo-4endo} = 14.1$ Hz, $J_{4exo-3} = J_{4exo-5} = 4.2$ Hz, 1H, H_{4exo}), 1.95−1.82 (m, 2H, H_8), 1.80 (s, 15H, C_5Me_5), 1.75−1.64 (m, 2H, H_9), 1.30 (s, 3H, Me). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 3.93 (H_3) ↔ δ 3.34 (H_2), 3.12 (H_{4endo}), 2.06 (H_{4exo}); δ 3.58 (H_1) ↔ δ 3.34 (H_2), 2.17 (H_7); δ 3.12 (H_{4endo}) ↔ δ 2.87 (H_5), 2.06 (H_{4exo}); δ 2.87 (H_5) ↔ δ 2.36 (H_6), 2.06 (H_{4exo}); δ 2.36 (H_6) ↔ δ 2.17 (H_7); δ 2.17 (H_7) ↔ δ 1.95−1.82 (H_8); δ 1.95−1.82 (H_8) ↔ δ 1.75−1.64 (H_9). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 109.2, 97.6, 92.2, 64.6, 53.8, 50.3, 46.0, 44.6, 35.2, 31.9, 28.1, 23.8, 21.5, 9.6. Electrospray MS: m/z calculated for $C_{23}H_{34}O_2Co$ ($M^+ - BF_4$) 401.18853, found 401.18832 (100%). Anal. Calcd for $C_{23}H_{34}O_2CoBF_4$: C, 56.58; H, 7.02. Found: C, 56.61; H, 7.17.

[Cp*Co(η^5-1-(3-butanoyl acetal)cycloheptadienyl)]$^+BF_4^-$ (35). Allyl/olefin complex **34** (40 mg, 0.082 mmol) was dissolved in CH_2Cl_2 (5 mL) in a reaction bomb and heated at 60 °C for 16 h. The solvent was removed in vacuo and the product purified by silica gel chromatography to provide 40 mg of product as an inseparable 2:1 mixture of the isomerized product **35** and the unprotected **32** as a red oil. IR (neat, cm^{-1}): 2982 (w), 2921 (w), 1456 (w), 1430 (w), 1382 (w), 1311 (w), 1219 (w), 1054 (s), 952 (w), 857 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 6.64 (t, $J_{3-2} = J_{3-4} = 6.3$ Hz, 1H, H_3), 5.30 (t, $J_{2-1} = J_{2-3} = 7.4$ Hz, 1H, H_2), 4.94 (t, $J_{4-3} = J_{4-5} = 7.9$ Hz, 1H, H_4), 4.34 (dt, $J_{5-4} = 8.6$ Hz, $J_{5-6endo} = J_{5-6exo} = 4.0$ Hz, 1H, H_5), 4.00 (ddd, $J_{1-2} = 8.2$ Hz, $J_{1-7} = 4.1$ Hz, $J_{1-3} = 1.0$ Hz, 1H, H_1), 3.89 (m, 4H, $-OCH_2CH_2O-$), 2.32 (ddd, $J_{6endo-6exo} = 16.6$ Hz, $J_{6endo-7} = 9.6$ Hz, $J_{6endo-5} = 4.7$ Hz, 1H, H_{6endo}), 2.02 (dt, $J_{6exo-6endo} = 16.5$ Hz, $J_{6exo-5} = J_{6exo-7} = 3.7$ Hz, 1H, H_{6exo}), 1.86 (s, 15H, C_5Me_5), 1.55−1.35 (m, 4H, H_8, H_9), 1.24 (s, 3H, Me), 0.57 (m, 1H, H_7). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 6.64 (H_3) ↔ δ 5.30 (H_2), 4.94 (H_4), 4.00 (H_1); δ 5.30 (H_2) ↔ δ 4.00 (H_1); δ 4.94 (H_4) ↔ δ 4.34 (H_5); δ 4.34 (H_5) ↔ δ 2.32 (H_{6endo}), 2.02 (H_{6exo}); δ 4.00 (H_1) ↔ δ 0.57 (H_7); δ 2.32 (H_{6endo}) ↔ δ 2.02 (H_{6exo}), 0.57 (H_7); δ 2.02 (H_{6exo}) ↔ δ 0.57 (H_7); δ 1.52 (H_8) ↔ δ 1.38 ($H_{8'\text{ and }9}$), 0.57 (H_7); δ 1.38 ($H_{8'}$) ↔ δ 0.57 (H_7). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 109.3, 100.6, 98.8, 97.8, 97.7, 94.4, 88.6, 64.7, 46.5, 40.0, 37.0, 30.5, 23.8, 9.7. Electrospray MS: m/z calculated for $C_{23}H_{34}O_2Co$ ($M^+ - BF_4$) 401.18853, found 401.18860 (100%).

[Cp*Co(η^5-1,2-dimethyl-7-(3-butanoyl acetal)-cycloheptadienyl)]$^+BF_4^-$ (36). Pentadienyl complex **29** (101 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (5 mL) in a reaction bomb and degassed with argon for 5 min. To this was added 2-butyne (100 μL, 1.28 mmol) via syringe. The bomb was sealed and heated at 40 °C for 3 days in an oil bath. The solvent was then removed in vacuo and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 85 mg of a thick, red oil as an inseparable mixture of product **36** and the unprotected **33** in a 2:1 ratio. Crystallization was unsuccessful for obtaining analytically pure material despite multiple attempts, due to the oily nature of the product. IR (neat, cm^{-1}): 2878 (m), 1457 (m), 1434 (m), 1382 (m)m, 1253 (w), 1213 (m), 1138 (w), 1025 (s), 952 (s), 908 (w), 854 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.55 (d, $J_{1-2} = 7.2$ Hz, 1H, H_1), 4.66 (t, $J_{2-1} = J_{2-3} = 8.7$ Hz, 1H, H_2, overlaps H_2 of **33**), 4.35 (dt, $J_{3-2} = 9.2$ Hz, $J_{3-4endo} = J_{3-4exo} = 3.4$ Hz, 1H, H_3, overlaps H_3 of **33**), 3.85 (m, 4H, -OCH_2CH_2O-), 2.45 (ddd, $J_{4endo-4exo} = 16.8$ Hz, $J_{4endo-5} = 12.2$ Hz, $J_{4endo-3} = 3.2$ Hz, 1H, H_{4endo}, overlaps H_{4endo} of **33**), 2.30 (dt, $J_{4exo-4endo} = 16.8$ Hz, $J_{4exo-5} = J_{4exo-3} = 3.6$ Hz, 1H, H_{4exo}), 2.20 (s, 3H, Me), 1.74 (s, 15H, C_5Me_5), 1.39−1.14 (m, 4H, H_6, H_7, overlaps Me signals), 1.30 (s, 3H, Me), 1.19 (s, 3H, Me), −0.01 (tt, $J_{5-4endo} = J_{5-6} = 11.8$ Hz, $J_{5-4exo} = J_{5-6'} = 4.2$ Hz, 1H, H_5, overlaps H_5 of **33**). $^1H-^1H$ GCOSY (400 MHz, $CDCl_3$): δ 6.55 (H_1) ↔ δ 4.66 (H_2); δ 4.66 (H_2) ↔ δ 4.35 (H_3); δ 4.35 (H_3) ↔ δ 2.45 (H_{4endo}), 2.30 (H_{4exo}); δ 2.45 (H_{4endo}) ↔ δ 2.30 (H_{4exo}), −0.01 (H_5); δ 2.30 (H_{4exo}) ↔ δ −0.01 (H_5); δ 1.45 (H_6) ↔ δ 1.25 ($H_{6'}$), 1.25

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(H_9), −0.01 (H_5); δ 1.25 ($H_{6'}$) ↔ δ −0.01 (H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 108.7, 101.4, 99.2, 97.6, 97.5, 96.3, 86.8, 64.7, 48.2, 41.8, 38.4, 25.0, 23.7, 19.3, 17.0, 9.1. Electrospray MS: *m*/*z* calculated for $C_{25}H_{38}O_2Co$ ($M^+ - BF_4$) 429.21983, found 429.21965 (100%).

Cp*Co(η^2,η^2-[5.3.0]-2,2-bis(methylcarboxyl)bicyclodeca-7,10-diene) (37). Allyl/olefin complex **23** (88 mg, 0.16 mmol) was dissolved in THF (5 mL) in the glovebox and removed from the Schlenk line and cooled to −78 °C in a dry ice/acetone bath. To this solution was added Hünig's base (28 μL, 0.16 mmol). The reaction mixture was stirred for 30 min, then the solvent was removed in vacuo and the residue filtered through activity IV neutral alumina with THF in the glovebox. The solvent was removed and the product taken up in a minimal quantity of pentane and cooled to −30 °C. Material slowly came out of solution, providing 62 mg (88%) of product as a reddish brown powder. ^1H NMR (400 MHz, C_6D_6): δ 4.41 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.41 (s, 3H), 3.38 (s, 3H), 3.35 (m, 1H, obscured by other signals), 3.05 (dt, *J* = 14.2, 8.7 Hz, 1H), 2.88 (dt, *J* = 13.3, 2.7 Hz, 1H), 2.35 (m, 3H), 1.99 (td, *J* = 7.0, 2.6 Hz, 1H), 1.58 (s, 15H), remaining signals overlapping or obscured by impurities.

Cp*Co(η^4-[5.3.0]-2,2-bis(methylcarboxyl)bicyclodeca-7,10-diene) (38). Allyl/olefin complex **23** (90 mg, 0.17 mmol) was dissolved in wet MeOH (5 mL) in the glovebox. To this solution was added K_2CO_3 (26 mg, 0.19 mmol). The reaction mixture was stirred for 16 h, and then the solvent was removed in vacuo and the residue filtered through Celite with benzene in the glovebox. The solvent was removed to provide 73 mg (97%) of product as a red oil. Analytically pure orange crystals were obtained via cooling a saturated pentane solution to −30 °C. IR (neat, cm^{-1}): 3008 (w), 2986 (w), 2947 (s), 2911 (m), 2859 (m), 2817 (w), 1747 (w), 1724 (s), 1434 (w), 1425 (w), 1376 (w), 1345 (w), 1322 (w), 1262 (m), 1223 (w), 1199 (s), 1152 (m), 1102 (w), 1071 (m), 1050 (w), 1008 (w), 978 (w). ^1H NMR (300 NMR, C_6D_6): δ 4.05 (dd, J_{3-2} = 6.8 Hz, J_{3-4} = 2194.6 Hz, 1H, H_3), 3.97 (dd, J_{4-5} = 7.1 Hz, J_{4-3} = 4.6 Hz, 1H, H_4), 3.41 (s, 3H, −OMe), 3.89 (s, 3H, −OMe), 2.65 (d, J_{2-3} = 6.8 Hz, 1H, H_2), 2.49 (ddd, $J_{8-8'}$ = 13.8 Hz, *J* = 9.2 Hz, *J* = 7.8 Hz, 1H, H_8), 2.17 (dd, J_{1-7} = 9.9 Hz, J_{1-2} = 1.5 Hz, 1H, H_1), 2.15 (t, J_{5-4} = J_{5-6} = 6.9 Hz, 1H, H_5), 1.80 (ddd, $J_{8'-8}$ = 13.8 Hz, *J* = 10.9 Hz, *J* = 3.3 Hz, 1H, $H_{8'}$), 1.76 (m, 1H, $H_{6'}$), 1.71 (s, 15H, C_5Me_5), 1.60 (m, 1H, H_9), 1.14−0.94 (m, 3H, H_6, H_7, $H_{9'}$). $^1H-^1H$ GCOSY (300 MHz, C_6D_6): δ 4.05 (H_3) ↔ δ 3.97 (H_4), 2.65 (H_2), 2.15 (H_5); δ 3.97 (H_4) ↔ δ 2.65 (H_2), 2.15 (H_5); δ 2.65 (H_2) ↔ δ 2.17 (H_1); δ 2.49 (H_8) ↔ δ 1.80 ($H_{8'}$), 1.60 (H_9), 1.14−0.94 ($H_{9'}$); δ 2.17 (H_1) ↔ δ 1.14−0.94 (H_7); δ 2.15 (H_5) ↔ δ 1.76 ($H_{6'}$), 1.14- 0.94 (H_6); δ 1.80 ($H_{8'}$) ↔ δ 1.60 (H_9), 1.14−0.94 ($H_{9'}$); δ 1.76 ($H_{6'}$) ↔ δ 1.14−0.96 (H_6, H_7). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 173.0, 171.9, 89.8, 81.5, 81.4, 64.1, 54.1, 53.7, 51.6, 51.5, 50.8, 38.0, 34.9, 31.4, 29.9, 9.5. Electron impact MS: *m*/*z* calculated for $C_{24}H_{33}O_4Co$ (M^+) 444.17108, found 444.17142 (100%). Anal. Calcd for $C_{24}H_{33}O_4Co$: C, 64.86; H, 7.48. Found: C, 64.84; H, 7.73.

Cp*Co(η^2,η^2-[5.4.0]-2,2-bis(methylcarboxyl)bicycloundeca-7,10-diene) (39). Allyl/olefin complex **24** (48 mg, 0.087 mmol) was dissolved in MeCN (3 mL) in the glovebox. To this solution was added NaOMe (5.1 mg, 0.094 mmol). The reaction mixture was stirred for 15 min, and then the solvent was removed in vacuo and the residue filtered through activity IV neutral alumina with THF. The solvent was removed and the product taken up in a minimal quantity of pentane and cooled to −30 °C. Material slowly came out of solution, providing 30 mg (76%) of product as a reddish brown powder. ^1H NMR (400 MHz, C_6D_6): δ 3.52 (dd, J_{1-7} = 10.8 Hz, J_{1-2} = 4.0 Hz, 1H, H_1), 3.39 (s, 3H, −OMe), 3.32 (s, 3H, −OMe), 3.05 (dt, $J_{4endo-4exo}$ = 13.0 Hz, $J_{4endo-3}$ = $J_{4endo-5}$ = 7.8 Hz, 1H, H_{4endo}), 2.49 (m, 1H, H_{10eq}), 2.36 (dt, $J_{4exo-4endo}$ = 13.1 Hz, J_{4exo-3} = J_{4exo-5} = 4.4 Hz, 1H, H_{4exo}), 2.00 (dd, J_{2-3} = 8.1 Hz, J_{2-1} = 4.1 Hz, 1H, H_2), 1.96 (td, $J_{5-4endo}$ = J_{5-4exo} = 7.2 Hz, $J_{5-4endo}$ = 3.2 Hz, 1H, H_5), 2.02−1.92 (m, 1H, H_{9eq}, buried by H_2 and H_5), 1.84 (m, 1H, H_{8ax}), 1.68 (m, 1H, H_{9eq}), 1.64 (s, 15H, C_5Me_5), 1.62 (m, 1H, H_6), 1.70−1.62 (m, 1H, H_{10ax}, buried under Cp* peak), 1.53 (td, J_{3-2} = $J_{3-4endo}$ = 8.2 Hz, J_{3-4exo} = 3.0 Hz, 1H, H_3), 1.40 (dt, J_{7-1} = 9.4 Hz, J_{7-6} = J_{7-8ax} = 2.9 Hz, 1H, H_7), 1.35 (dd, $J_{8eq-8ax}$ = 11.9 Hz, $J_{8eq-9eq}$ = 3.7 Hz, 1H, H_{8eq}). $^1H-^1H$ GCOSY (400 MHz, C_6D_6): δ 3.52 (H_1) ↔ δ 2.00 (H_2), 1.40 (H_7); δ 3.05 (H_{4endo}) ↔ δ 2.36 (H_{4exo}), 1.96 (H_5), 1.53 (H_2); δ 2.49 (H_{10eq}) ↔ δ 2.00 (H_{9eq}), 1.65 (H_{10ax}); δ 2.36 (H_{4exo}) ↔ δ 1.96 (H_5), 1.53 (H_3); δ 1.53 (H_2) ↔ δ 1.53 (H_3); δ 1.96 (H_5) ↔ δ 1.62 (H_6); δ 2.02−1.96 (H_{9eq}) ↔ δ 1.70−1.62 (H_{9ax}), 1.35 (H_{8eq}); δ 1.84 (H_{8ax}) ↔ δ 1.40 (H_7), 1.35 (H_{8eq}), 1.70−1.62 (H_{9ax}); δ 1.70−1.62 (H_{9ax}) ↔ δ 1.35 (H_{8eq}); δ 1.62 (H_6) ↔ δ 1.40 (H_7); δ 1.40 (H_7) ↔ δ 1.35 (H_{8eq}). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 172.5, 170.7, 90.6, 67.0, 66.1, 61.0, 58.0, 51.6, 51.1, 36.5, 34.8, 33.8, 32.6, 29.6, 27.1, 24.4, 9.5. Electron impact MS: *m*/*z* calculated for $C_{25}H_{35}O_4Co$ (M^+) 458.18674, found 458.18695 (5%).

Cp*Co(η^4-[5.4.0]-bicycloundeca-8,10-dien-3-one) (42). Allyl/olefin complex **32** (108 mg, 0.24 mmol) was dissolved in MeOH (5 mL) under an argon atmosphere. To this solution was added pyrrolidine (21 μL, 0.25 mmol), and the mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the product was taken up in pentane and filtered through activity IV neutral alumina in the glovebox. The solvent was removed to yield 47 mg (54%) of product as a red oil. X-ray-quality crystals were obtained by cooling a concentrated pentane solution to −30 °C in the glovebox. ^1H NMR (400 MHz, C_6D_6): δ 3.95 (dd, J_{4-5} = 7.0 Hz, J_{4-3} = 4.5 Hz, 1H, H_4), 3.89 (dd, J_{3-2} = 6.9 Hz, J_{3-4} = 4.5 Hz, 1H, H_3), 2.52 (ddd, $J_{10eq-10ax}$ = 13.4 Hz, J_{10eq-1} = 3.9 Hz, $J_{10eq-9eq}$ = 2.3 Hz, 1H, H_{10eq}), 2.15 (ddt, $J_{9eq-9ax}$ = 13.8 Hz, $J_{9eq-8eq}$ = 4.5 Hz, $J_{9eq-8ax}$ = $J_{9eq-10eq}$ = 2.4 Hz, 1H, H_{9eq}), 2.09 (t, J_{5-4} = $J_{5-6endo}$ = 6.8 Hz, 1H, H_5), 1.80 (t, $J_{10ax-10eq}$ = J_{10ax-1} = 13.0 Hz, 1H, H_{10ax}), 1.74 (td, $J_{9ax-9eq}$ = $J_{9ax-8ax}$ = 13.9 Hz, $J_{9ax-8eq}$ = 6.8 Hz, 1H, H_{9ax}), 1.66 (d, J_{2-3} = 7.0 Hz, 1H, H_2), 1.57 (s, 15H, C_5Me_5), 1.41 (ddd, $J_{6endo-6exo}$ = 16.2 Hz, $J_{6endo-5}$ = 6.2 Hz, $J_{6endo-7}$ = 3.4 Hz, 1H, H_{6endo}), 1.26−1.18 (m, 2H, H_1, H_{8eq}), 0.94 (ddd, $J_{6exo-6endo}$ = 16.4 Hz, J_{6exo-7} = 11.6 Hz, J_{6exo-5} = 1.7 Hz, 1H, H_{6exo}), 0.89 (tdd, $J_{8ax-8eq}$ = J_{8ax-} = 13.4 Hz, J_{8ax-7} = 12.1 Hz, $J_{8ax-9eq}$ = 4.4 Hz, 1H, H_{8ax}, overlaps H_{6exo}), 0.41 (qt, J_{7-1} = J_{7-6exo} = J_{7-8ax} = 11.7 Hz, $J_{7-6endo}$ = J_{7-8eq} = 3.4 Hz, 1H, H_7). $^1H-^1H$ GCOSY (400 MHz, C_6D_6): δ 3.95 (H_4) ↔ δ 3.89 (H_3), 2.09 (H_5), 1.66 (H_2), 1.41 (H_{6endo}); δ 3.89 (H_3) ↔ δ 2.09 (H_5), 1.66 (H_2); δ 2.52 (H_{10eq}) ↔ δ 2.15 (H_{9eq}), 1.80 (H_{10ax}), 1.26−1.18 (H_1); δ 2.15 (H_{9eq}) ↔ δ 1.74 (H_{9ax}), 1.26−1.18 (H_{8eq}); δ 2.09 (H_5) ↔ δ 1.41 (H_{6endo}), 0.94 (H_{6exo}); δ 1.80 (H_{10ax}) ↔ δ 1.26−1.18 (H_1); δ 1.74 (H_{9ax}) ↔ δ 1.26−1.18 (H_{8eq}), 0.89 (H_{8ax}); δ 1.66 (H_2) ↔ δ 1.26−1.18 (H_1); δ 1.41 (H_{6endo}) ↔ δ 0.94 (H_{6exo}), 0.41 (H_7); δ 1.26−1.18 (H_1) ↔ δ 0.41 (H_7); δ 1.26−1.18 (H_{8eq}) ↔ δ 0.89 (H_{8ax}); δ 0.94 (H_{6exo}) ↔ δ 0.41 (H_7); δ 0.89 (H_{8ax}) ↔ δ 0.41 (H_7). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 208.1, 89.8, 81.7, 79.2, 58.0, 52.4, 51.9, 44.7, 41.2, 37.5, 35.5, 33.4, 9.5. Electron impact MS: *m*/*z* calculated for $C_{21}H_{29}OCo$ (M^+) 356.15503, found 356.15547 (51%).

Cp*Co(η^2,η^2-[5.4.0]-bicycloundeca-7,10-dien-3-one) (43). Allyl/olefin complex **31** (52 mg, 0.12 mmol) was dissolved in MeOH (5 mL) under an argon atmosphere. To this solution was added pyrrolidine (10 μL, 0.12 mmol), and the mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the product was taken up in pentane and filtered through activity IV neutral alumina in the glovebox. The solvent was removed to yield 33 mg (79%) of product as a red oil as a 1:1 mixture with **42** as inseparable isomers. ^1H NMR (400 MHz, C_6D_6): δ 3.16 (dt, $J_{4endo-4exo}$ = 13.1 Hz, $J_{4endo-3}$ = $J_{4endo-5}$ = 7.7 Hz, 1H, H_{4endo}), 2.95 (dddd, J_{1-10ax} = 13.8 Hz, J_{1-7} = 9.7 Hz, J_{1-2} = 4.1 Hz, J_{1-10eq} = 3.1 Hz, 1H, H_1), 2.51 (dt, $J_{4exo-4endo}$ = 13.1 Hz, J_{4exo-3} = J_{4exo-5} = 2.9 Hz, 1H, H_{4exo}), 2.46 (dt, $J_{10eq-10ax}$ = 13.7 Hz, J_{10eq-1} = $J_{10eq-9eq}$ = 2.3 Hz, 1H, H_{10eq}), 2.36 (ddt, $J_{9eq-9ax}$ = 15.2 Hz, $J_{9eq-8eq}$ = 3.9 Hz, $J_{9eq-8ax}$ = $J_{9eq-10eq}$ = 1.9 Hz, 1H, H_{9eq}), 2.11 (t, $J_{10ax-10eq}$ = J_{10ax-1} = 13.7 Hz, 1H, H_{10ax}), 1.92 (td, J_{5-6} = $J_{5-4endo}$ = 7.0 Hz, J_{5-4exo} = 2.6 Hz, 1H, H_5), 1.80 (t, $J_{9ax-9eq}$ = $J_{9ax-8ax}$ = 15.7 Hz, 1H, H_{9ax}), 1.56 (m, 2H, H_6, H_{8eq}, obscured by competing product), 1.48 (s, 15H, C_5Me_5), 1.42 (m, 1H, H_7, obscured by competing product), 1.34 (td, J_{3-2} = $J_{3-4endo}$ = 8.0 Hz, J_{3-4exo} = 2.9 Hz, 1H, H_3), 1.23 (m, 1H, H_{8ax}), 1.14 (dd, J_{2-3} = 7.8 Hz, J_{2-1} = 4.2 Hz, 1H, H_2). $^1H-^1H$ GCOSY (400 MHz, C_6D_6): δ 3.16 (H_{4endo}) ↔ δ 2.51 (H_{4exo}), 1.92 (H_5), 1.31 (H_3); δ 2.95 (H_1) ↔ δ 2.46 (H_{10eq}), 2.11 (H_{10ax}), 1.41 (H_7), 1.14 (H_2); δ 2.51 (H_{4exo}) ↔ δ 1.91 (H_5), 1.31 (H_3); δ 2.46 (H_{10eq}) ↔ δ 2.36 (H_{9eq}); δ 2.36 (H_{9eq}) ↔ δ 1.80 (H_{9ax}), 1.56 (H_{8eq}); δ 1.91 (H_5) ↔ δ 1.56 (H_6); δ 1.80 (H_{9ax}) ↔ δ 1.56

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(H_{8eq}), 1.23 (H_{8ax}); δ 1.56 (H_{8eq}) ↔ δ 1.42 (H_7); δ 1.34 (H_3) ↔ δ 1.14 (H_2).

Cp*Co(η^4-[5.4.0]-1,11-dimethylbicycloundeca-8,10-dien-3-one) (46). Cycloheptadienyl complex **33** (67 mg, 0.14 mmol) was dissolved in MeOH (5 mL) under an argon atmosphere. To this solution was added pyrrolidine (12 μL, 0.14 mmol), and the mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the product was taken up in pentane and filtered through activity IV neutral alumina in the glovebox. The solvent was removed to yield 37 mg (65%) of product as a red oil. Material of improved purity was obtained via cooling a concentrated pentane solution to −30 °C in the glovebox. ^{1}H NMR (400 MHz, C_6D_6): δ 3.98 (d, J_{1-2} = 4.9 Hz, 1H, H_1), 3.84 (dd, J_{2-3} = 7.1 Hz, J_{2-1} = 4.8 Hz, 1H, H_2), 2.65 (dd, $J_{8eq-8ax}$ = 12.8 Hz, $J_{8eq-7eq}$ = 2.4 Hz, 1H, H_{8eq}), 2.14 (ddt, $J_{7eq-7ax}$ = 13.7 Hz, $J_{7eq-6ax}$ = 4.5 Hz, $J_{7eq-6eq}$ = $J_{7eq-8eq}$ = 2.0 Hz, 1H, H_{7eq}), 1.97 (ddd, J_{3-2} = 7.6 Hz, $J_{3-4endo}$ = 5.7 Hz, J_{3-4exo} = 2.6 Hz, 1H, H_3), 1.72 (dtd, $J_{6eq-6ax}$ = 13.7 Hz, $J_{6eq-7ax}$ = $J_{6eq-7eq}$ = 7.4 Hz, J_{6eq-5} = 0.8 Hz, 1H), 1.61 (dt, $J_{8ax-8eq}$ = 12.9 Hz, $J_{8ax-7ax}$ = $J_{8ax-7eq}$ = 1.0 Hz, 1H, H_{8ax}), 1.54 (s, 15H, C_5Me_5), 1.13 (tdd, $J_{6ax-6eq}$ = $J_{6ax-5/7ax}$ = 13.6 Hz, $J_{6ax-5/7ax}$ = 12.6 Hz, $J_{6ax-7eq}$ = 4.8 Hz, 1H, H_{6ax}), 1.02−0.95 (m, 3H, H_{4endo}, H_{4exo}, H_{7ax}), 0.92 (s, 3H, Me), 0.90 (d, J_{Me-1} = 1.0 Hz, 3H, Me), 0.57 (m, 1H, H_5). ^{1}H−^{1}H GCOSY (400 MHz, C_6D_6): δ 3.98 (H_1) ↔ δ 3.84 (H_2), 0.90 (Me); δ 3.84 (H_1) ↔ δ 1.97 (H_3), 1.02−0.95 (H_{4endo}); δ 2.65 (H_{8eq}) ↔ δ 2.14 (H_{7eq}), 1.61 (H_{8ax}); δ 2.14 (H_{7eq}) ↔ δ 1.72 (H_{6eq}), 1.13 (H_{6ax}); δ 1.97 (H_3) ↔ δ 1.02−0.95 (H_{4endo}, H_{4exo}); δ 1.72 (H_{6eq}) ↔ δ 1.13 (H_{6ax}), 1.02−0.95 (H_{7ax}); δ 1.13 (H_{6ax}) ↔ δ 1.02−0.95 (H_{7ax}), 0.57 (H_5); δ 1.02−0.95 (H_{4endo}, H_{4exo}) ↔ δ 0.57 (H_5). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 208.9, 90.0, 84.5, 80.8, 66.0, 54.2, 51.7, 43.2, 41.2, 39.8, 30.9, 29.9, 23.8, 18.1, 9.9. Electron impact MS: *m*/*z* calculated for $C_{23}H_{33}OCo$ (M^+) 384.18634, found 384.18677 (99%).

***trans*-Dimethyl 2,3,3a,4-Tetrahydroazulene-1,1(8a*H*)-dicarboxylate (47).** Bicyclic cobalt complex **38** (15 mg, 0.034 mmol) was dissolved in THF (5 mL mL) in the glovebox and placed in a glass reaction bomb. To this, allyl bromide (2.9 μL, 0.034 mmol) was added, the bomb sealed and irradiated with UV light in a Rayonet carousel for 16 h resulting in a red solution. The solvent was removed in vacuo and the product purified by silica gel chromatography using 19:1 hexanes/diethyl ether, with the product dissolved in a minimal amount of CH_2Cl_2 for loading onto the column, providing 7.8 mg (92%) of bicyclic organic product **47** as a pale yellow oil. IR (CH_2Cl_2 cast, cm−1): 3016 (s), 3954 (s), 2870 (s), 1731 (s), 1610 (w), 1435 (s), 1379 (w), 1435 (s), 1329 (w), 1269 (s), 1225 (s), 1172 (s), 1079 (s), 1017 (s), 989 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (m, 1H, H_2), 5.76−5.70 (m, 3H, H_3, H_4, H_5), 3.75 (s, 3H, −OMe), 3.72 (s, 3H, −OMe), 3.03 (dq, J_{1-7} = 10.4 Hz, J_{1-2} = J_{1-3} = J_{1-9} = 1.6 Hz, 1H, H_1), 2.52 (dddd, $J_{6-6'}$ = 17.8 Hz, J_{6-7} = 6.6 Hz, J_{6-5} = 3.2 Hz, J_{6-4} =1.4 Hz, 1H, H_6), 2.41 (ddd, $J_{9-9'}$ =13.7 Hz, J_{9-8} = 8.6 Hz, $J_{9-8'}$ = 6.9 Hz, 1H, H_9), 2.38 (m, 1H, H_7), 2.30−2.10 (m, 3H, $H_{6'}$, H_8, $H_{9'}$), 1.34 (dddd, $J_{8'-8}$ = 12.8 Hz, $J_{8'-7}$ = 9.4 Hz, $J_{8'-9'}$ = 8.4 Hz, $J_{8'-9}$ = 6.0 Hz, 1H, $H_{8'}$). ^{1}H−^{1}H COSY (400 MHz, $CDCl_3$): δ 5.82 (H_2) ↔ δ 5.76−5.70 (H_3), 3.03 (H_1); δ 5.76−5.70 (H_3) ↔ δ 3.03 (H_1); δ 5.76−5.70 (H_4, H_5) ↔ δ 2.52 (H_6), 2.30−2.10 ($H_{6'}$); δ 3.03 (H_1) ↔ δ 2.38 (H_7); δ 2.52 (H_6) ↔ δ 2.38 (H_7), 2.30−2.10 ($H_{6'}$); δ 2.41 (H_9) ↔ δ 2.30−2.10 (H_8, $H_{9'}$); δ 2.38 (H_7) ↔ δ 2.30−2.10 (H_8), 1.34 ($H_{8'}$); δ 2.30−2.10 (H_8, $H_{9'}$) ↔ δ 1.34 ($H_{8'}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.8, 172.3, 132.2, 130.9, 125.0, 124.4, 64.1, 54.3, 52.8, 52.5, 41.2, 37.7, 34.1, 31.7. Electron impact MS: *m*/*z* calculated for $C_{14}H_{18}O_4$ (M^+) 250.12051, found 250.12044 (23%).

[5.4.0]-2,2-Bis(methylcarboxyl)bicycloundeca-7,10-diene (48). Bicyclic cobalt complex **39** (70 mg, 0.15 mmol) was dissolved in THF (20 mL) in the glovebox and placed in a glass reaction bomb. To this was added allyl bromide (15 μL, 0.17 mmol), and the bomb was sealed and irradiated with UV light in a Rayonet carousel for 16 h, resulting in a green solution. The solvent was removed in vacuo and the product purified by silica gel chromatography using 19:1 hexanes/diethyl ether, with the product dissolved in a minimal amount of CH_2Cl_2 for loading onto the column, providing 35 mg (85%) of bicyclic organic product **48** as a clear oil. If reactions were run at higher concentration, a red solution was obtained. Again, concentration in vacuo followed by careful chromatography would allow isolation of the organic product, followed by a red fraction, shown to be Cp*Co(η^3-CH_2CHCH_2)Br by comparison with the published spectra. IR (neat, cm^{-1}): 3008 (w), 2951 (m), 2862 (w), 1730 (s), 1434 (m), 1319 (w), 1252 (s), 1208 (m), 1151 (m), 1110 (w), 1084 (w), 1044 (w), 1035 (w), 1025 (w), 1009 (w), 965 (w), 920 (w), 873 (w), 820 (w), 786 (w), 756 (w), 665 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88−5.76 (m, 2H, H_2, H_3), 5.62 (dddd, J_{5-6} = 11.2 Hz, J_{5-4} = 6.5 Hz, $J_{5-4'}$ = 4.0 Hz, J_{5-7} = 2.3 Hz, 1H, H_5), 5.28 (dt, J_{6-5} = 11.4 Hz, $J_{6-4'}$ = J_{6-7} = 1.8 Hz, 1H, H_6), 3.76 (s, 3H, −OMe), 3.72 (s, 3H, −OMe), 2.90−2.77 (m, 2H, H_1, H_4), 2.66−2.55 (m, 2H, $H_{4'}$, H_7), 2.35 (dq, $J_{10eq-10ax}$ = 13.2 Hz, $J_{10eq-9eq}$ = $J_{10eq-9ax}$ = $J_{10eq-8eq}$ = 3.1 Hz, 1H, H_{10eq}), 1.87−1.69 (m, 3H, H_{8eq}, H_{9eq}, H_{10ax}), 1.37−1.21 (m, 2H, H_{8ax}, H_{9ax}). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 5.88−5.76 (H_3) ↔ δ 2.90−2.77 (H_4), 2.66−2.55 ($H_{4'}$); δ 5.88−5.76 (H_2) ↔ δ 2.90−2.77 (H_1); δ 5.62 (H_5) ↔ δ 5.28 (H_6), 2.90−2.77 (H_4), 2.66−2.55 ($H_{4'}$ + H_7); δ 5.28 (H_6) ↔ δ 2.66−2.55 (H_7); δ 2.90−2.77 (H_1) ↔ δ 2.66−2.55 (H_7); δ 2.90−2.77 (H_4) ↔ δ 2.66−2.55 ($H_{4'}$); δ 2.66−2.55 (H_7) ↔ δ 1.37−1.21 (H_{8ax}); δ 2.35 (H_{10eq}) ↔ δ 1.87−1.69 (H_{8eq} + H_{9eq} + H_{10ax}), 1.37−1.21 (H_{9ax}); δ 1.87−1.69 (H_{8eq} + H_{9eq}) ↔ δ 1.37−1.69 (H_{8ax} + H_{9ax}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 173.1, 171.3, 135.5, 132.2, 130.0, 126.8, 59.6, 52.7, 52.2, 45.9, 36.6, 34.1, 33.6, 26.7, 22.3. Electrospray MS: *m*/*z* calculated for $C_{15}H_{20}O_4Na$ (M^+ + Na) 287.12538, found 287.12541 (100%).

[5.4.0]-Bicycloundeca-8,10-dien-3-one (49). Bicyclic cobalt complex **42** (75 mg, 0.21 mmol) was dissolved in THF (20 mL) in the glovebox and placed in a glass reaction bomb. To this was added allyl bromide (20 μL, 0.23 mmol), and the bomb was sealed and irradiated with UV light in a Rayonet carousel for 16 h, resulting in a green solution. The solvent was removed in vacuo and the product purified by silica gel chromatography using 19:1 hexanes/diethyl ether, with the product dissolved in a minimal amount of CH_2Cl_2 for loading onto the column, providing 34 mg (100%) of bicyclic organic product **49** as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (m, 1H, H_5), 5.81 (m, 2H, H_4, H_3), 5.37 (m, 1H, H_2), 2.53 (m, 1H, H_1), 2.45 (ddd, $J_{10eq-10ax}$ = 14.4 Hz, J_{10eq-1} = 4.2 Hz, $J_{10eq-9eq}$ = 1.8 Hz, 1H, H_{10eq}), 2.37−2.34 (m, 2H, H_9, H_6), 2.32−2.26 (m, 2H, H_{10ax}, $H_{6'}$), 2.04 (m, 1H, H_8), 1.98 (m, 1H, H_7), 1.59−1.48 (m, 2H, $H_{8'}$, $H_{9'}$). ^{1}H−^{1}H COSY (400 MHz, $CDCl_3$): δ 5.89 (H_5) ↔ δ 5.81 (H_4), 2.37−2.34 (H_6); δ 5.81 (H_4, H_3) ↔ δ 5.37 (H_2), 2.53 (H_1), 2.37−2.34 (H_6); δ 5.37 (H_2) ↔ δ 2.53 (H_1); δ 2.53 (H_1) ↔ δ 2.45 (H_{10eq}), 2.32−2.26 (H_{10ax}), 1.98 (H_7); δ 2.45 (H_{10eq}) ↔ δ 2.32−2.26 (H_{10ax}); δ 2.37−2.34 (H_9) ↔ δ 1.59−1.48 ($H_{9'}$), 2.04 (H_8), 1.59−1.48 ($H_{8'}$); δ 2.04 (H_8) ↔ δ 1.59−1.48 ($H_{8'}$, $H_{9'}$), 1.98 (H_7); δ 1.98 (H_7) ↔ δ 1.59−1.48 ($H_{8'}$, $H_{9'}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 211.1, 135.3, 132.4, 125.1, 124.6, 47.4, 46.8, 40.2, 40.1, 36.1, 33.9. Electrospray MS: *m*/*z* calculated for $C_{11}H_{14}O$ (M^+): 162.10446, found 162.10431 (11%).

***trans*-9,9a-Dimethyl-3,4,4a,5-tetrahydro-1*H*-benzo[7]-annulen-2(9a*H*)-one (50).** Bicyclic cobalt complex **46** (5 mg, 0.01 mmol) was dissolved in THF (10 mL) in the glovebox and placed in a glass reaction bomb. To this was added allyl bromide (1.2 μL, 0.01 mmol), and the bomb was sealed and irradiated with UV light in a Rayonet carousel for 16 h, resulting in a green solution. The solvent was removed in vacuo and the product purified by silica gel chromatography using 19:1 hexanes/diethyl ether, with the product dissolved in a minimal amount of CH_2Cl_2 for loading onto the column, providing 2.5 mg (100%) of bicyclic organic product **50** as a pale yellow oil. IR (neat, cm^{-1}): 3023 (w), 2965 (s), 2928 (s), 1716 (s), 1611 (w), 1458 (m), 1432 (m), 1375 (w), 1354 (w), 1318 (w), 1294 (w), 1243 (w), 1218 (w), 1178 (w), 1124 (w), 1104 (w), 1000 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (m, 1H, H_3), 5.67 (dd, 1H, J_{2-3} = 7.6 Hz, J_{2-1} = 2.6 Hz, H_2), 5.61 (m, 1H, H_1), 2.53 (dd, $J_{8eq-8ax}$ = 13.3 Hz, $J_{8eq-7eq}$ = 2.1 Hz, 1H, H_{8eq}), 2.38 (d, $J_{8ax-8eq}$ = 13.3 Hz, 1H, H_{8ax}), 2.43−2.31 (m, 3H, H_4, H_{7ax}, H_{7eq}), 2.24 (tdd, J_{5-6ax} = J_{5-4} = 12.5 Hz, J_{5-6eq} = 4.0 Hz, $J_{5-4'}$ = 1.7 Hz, 1H, H_5), 2.12 (ddd, $J_{4'-4}$ = 17.8 Hz, $J_{4'-3}$ = 7.5 Hz, $J_{4'-5}$ = 1.5 Hz, 1H, $H_{4'}$), 1.97 (dddd, $J_{6eq-6ax}$ = 13.8 Hz, $J_{6eq-7eq}$ = 6.6 Hz, J_{6eq-5} = 4.0 Hz, $J_{6eq-7ax}$ = 2.6 Hz, 1H, H_{7eq}), 1.83 (s, 3H, Me), 1.77 (qd, $J_{6ax-6eq}$ = J_{6ax-5} = $J_{6ax-7ax}$ = 13.5 Hz, $J_{6ax-7eq}$ = 5.5 Hz, 1H, H_{6ax}), 1.05 (s, 3H, Me). ^{1}H−^{1}H GCOSY (400 MHz, $CDCl_3$): δ 5.77 (H_3) ↔ δ 5.67 (H_2), 2.12 ($H_{4'}$); δ 5.67 (H_2) ↔ δ 5.61 (H_1); δ 5.61 (H_1) ↔ δ 1.83 (Me); δ 2.53 (H_{8eq}) ↔ δ 2.38 (H_{8ax}), 2.43−2.31

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(H_{7eq}); δ 2.43−2.31 (H_4) ↔ δ 2.24 (H_5), 2.12 ($H_{4'}$); δ 2.43−2.31 ($H_{7ax/7eq}$) ↔ δ 1.97 (H_{6eq}), 1.77 (H_{6ax}); δ 2.24 (H_5) ↔ δ 2.12 ($H_{4'}$), 1.97 (H_{6eq}), 1.77 (H_{6ax}); δ 1.97 (H_{6eq}) ↔ δ 1.77 (H_{6ax}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 212.1, 146.1, 131.8, 124.8, 122.1, 52.7, 47.4, 42.3, 40.9, 34.4, 31.1, 23.2, 20.1. Electron impact MS: *m*/*z* calculated for $C_{13}H_{18}O$ (M^+) 190.13577, found 190.13592 (93%).

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving crystallographic data, ORTEP diagrams, crystal data collection and refinement of parameters, atomic coordinates, bond distances and angles, and isotropic displacement parameters for complexes **2f**, **3g**, **8a**, **24**, **30**−**32**, **34**, **35**, and **42**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00346.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBRVIATIONS

Cp*, (C_5Me_5); Cp, (C_5H_5); DFT, density functional theory

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