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Generation and Reactions of a Benzodehydrotropylium Ion−$Co_2(CO)_6$ Complex

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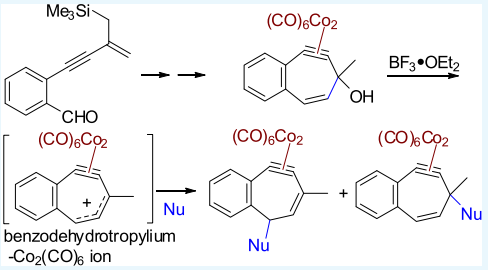
Supporting Information

ABSTRACT: A series of 7-methylenedehydrobenzo[7]annulen-5-ol hexacarbonyldicobalt complexes were generated by Hosomi−Sakurai reactions of allylsilanes containing *o*-alkynylarylaldehyde-$Co_2(CO)_6$ complexes. One of the cyclization products was converted into its corresponding dihydrobenzo[7]annulen-7-ol hexacarbonyldicobalt complex, an immediate precursor to a benzodehydrotropylium−$Co_2(CO)_6$. The cation was generated in situ and reacted with four nucleophiles, and its aromatic stabilization was determined by computational methods.



INTRODUCTION

The propargylium cation−$Co_2(CO)_6$ complex (**1**, Figure 1) has become one of the most important species in metal-

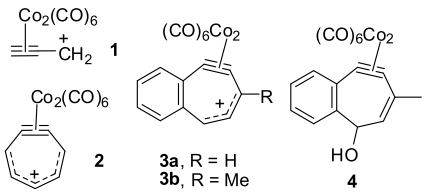


Figure 1. Propargyldicobalt cations and the target precursor.

stabilized carbocation chemistry, by virtue of its excellent stability and reactivity that is both good and predictable; its transformations are normally known as Nicholas reactions.[1] Among its noteworthy features is the fact that the alkynedicobalt unit contributes sufficiently to the overall carbocation picture such that simple substitution at the propargylic center gives very limited change in carbocation stability, and in many cases cations that would be difficult to generate in the absence of the $Co_2(CO)_6$ unit are generated readily in its presence.[2,3] Furthermore, the bending of alkynyl carbon bond angles to ca. 140° allows the Nicholas reaction to work well in medium-ring-size-generating reactions. As a result, and in conjunction with reliable reductive decomplexation protocols, the ready preparation and manipulation of cycloheptynedicobalt complexes has been exploited extensively in total synthesis.[4,5]

In addition to purely synthetic ends, the presence of an adjacent alkynedicobalt unit has been shown to have significant effects on the properties of nominally aromatic or antiaromatic carbocations.[3] The development of the aforementioned multiple cycloheptynedicobalt preparation methods has allowed our group to make contributions to the study of metal complexes of the putatively aromatic 1,2-dehydrotropylium ion (henceforth referred to simply as a dehydrotropylium ion). We have reported the generation, trapping, and evaluation of a dehydrotropylium ion −$Co_2(CO)_6$ complex (**2**) and found a reduced level of aromatic stabilization in that system, approximately 25% of that of a tropylium ion, employing NICS(1) calculations and homodesmotic reactions as the primary measures.[6,7] By contrast, a dehydrotropylium ion itself only has been proposed as a mass spectral fragment of 2-acylbenzofurans and benzothiophene,[8] and neither has it been prepared synthetically nor has had its properties investigated.[9] The η^2-platinum(0), palladium(0), and zirconium(II) complexes of a dehydrotropylium ion or related cations have been prepared by the Jones group and show no to modest C−C bond alternation.[7] Dehydrotropone−$Co_2(CO)_4$(dppm) shows considerable bond alternation.[10]

In the tropylium ion system, the effect of ring fusion to another aromatic ring has been reported to have contradictory effects, with benzo-fused systems less stable[11] but with azulene and heteroaromatic systems giving enhanced stability.[12] A benzodehydrotropylium ion has been proposed solely as a mass spectral fragment ion, without any insight on its properties.[8] Dehydrobenzotropone−$Co_2(CO)_4$ (dppm) complexes have not been converted to tropylium ion derivatives.[10] Given the limitations of the above information, we were interested in developing methods for access to the benzo-fused analogue of the dehydrotropylium ion−$Co_2(CO)_6$ complex (**3a**), to assess the viability of the cation itself.

RESULTS AND DISCUSSION

We envisioned that a benzodehydrotropylium cation−$Co_2(CO)_6$ complex (**3**), specifically as methyl-substituted **3b**, would be most readily obtained through benzocycloheptynol

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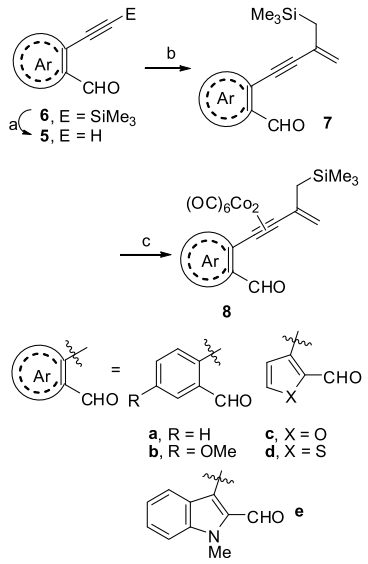
complex **4**, which in turn would be prepared in several steps from 2-ethynylbenzaldehyde (**5a**) (Scheme 1). 2-Ethynylbenzaldehyde (**5a**), itself available by a literature Sonogashira-desilylation protocol from 2-bromobenzaldehyde via **6a**,[13,14] was subjected to a Sonogashira reaction with 2-bromoallyltrimethylsilane to give enyne **7a** (71% yield, Table 1). Upon treatment with $Co_2(CO)_8$, complex **8a** formed in 80% yield. Generation of the cycloheptynol complex could then be accomplished by subjecting **8a** to an equimolar amount of BF_3-OEt_2 at 0 °C in CH_2Cl_2 (0.016 M in **8a**) for 20 min; the resulting Hosomi–Sakurai reaction gave exo-methylene benzocycloheptynol–$Co_2(CO)_6$ complex **9a** in 75% yield (Scheme 2). The identity of **9a** was evident from the ^{1}H resonances of the exo-methylene function (5.86 ppm and 5.70), the benzylic carbinol methine (4.98 ppm), and the diastereotopic methylene function (3.11 and 2.88 ppm).

While other reaction fates and other ring size preparations are known,[15,16] this is the first example of a cycloheptynoldicobalt complex preparation by a Hosomi–Sakurai reaction. As a result, we wished to explore the generality of this method for benzocycloheptynedicobalt complex preparation and investigated this protocol on a series of related compounds, including those derived from 2-ethynyl-5-methoxybenzaldehyde (**5b**), 3-ethynyl-2-furancarboxaldehyde (**5c**), 3-ethynyl-2-thiophenecarboxaldehyde (**5d**), and 3-ethynyl-1-methyl-1*H*-indole-2-carboxaldehyde (**5e**). The Sonogashira reaction of **5b–e** with 2-bromoallyltrimethylsilane afforded **7b–e** in a straightforward fashion (**7b**, 73%; **7c**, 66%; **7d**, 63%; **7e**, 72%) (Table 1). The reaction of **7b–7d** with $Co_2(CO)_8$ formed the hexacarbonyldicobalt complexes **8b** (75% yield), **8c** (85%), and **8d** (77%) in good yield. Conversely, alkyne **7e** gave an alkyne complex (**8e**), which had limited stability to chromatography; consequently, **8e** was carried forward to the subsequent cyclization reaction without rigorous purification.

The enyne complexes **8b–e** were subjected to reaction with BF_3-OEt_2 under conditions analogous to the **8a–9a** cyclization reaction. In each of the cases, the fused bicyclic exo-methylene cycloheptynol complex could be formed in reasonable to excellent yield, with the methoxy-substituted **9b** (5 min, 72% yield) being formed somewhat more rapidly than **9a** and the 5,7-systems **9c** (59% yield) and **9d** (92% yield) forming somewhat more slowly (ca. 1 h) than **9a**. Compound **9e** was formed, also over 1 h, in 44% yield, for the two-step process and based on the amount of metal-free alkyne **7e**. Each of **9b–9e** gave characteristic ^{1}H NMR spectral resonances closely analogous to those for **9a**; for instance, in the case of **9d**, the resonances for the exo-methylene appeared at 5.85 and 5.70 ppm, the carbinol methine at 5.05 ppm, and the diastereotopic methylene at 3.00 and 2.87 ppm. Despite the more modest yield for **9e**, these results demonstrate that this Hosomi–Sakurai-reaction-based protocol is an effective general method for the preparation of exo-methylene-substituted cycloheptynol–$Co_2(CO)_6$ complexes.

With the goal of ultimate generation of the dehydrotropylium ion–$Co_2(CO)_6$ complex, compound **9a** was selected for further manipulation. A Swern oxidation[17] afforded ketone **10** with minimal decomposition (89% yield) (Scheme 3), as evidenced by the appearance of a shifted CH_2 singlet at 3.76 ppm in the ^{1}H NMR spectrum and ketone carbonyl ^{13}C NMR spectral resonance at 198.3 ppm. While this material could also be obtained with MnO_2 oxidation, the yields were inferior (28%, 43% by recovered starting material). With the ketone function in place, the exo-methylene group of **10** could be

Scheme 1. Preparation of Hosomi–Sakurai Precursors[a]



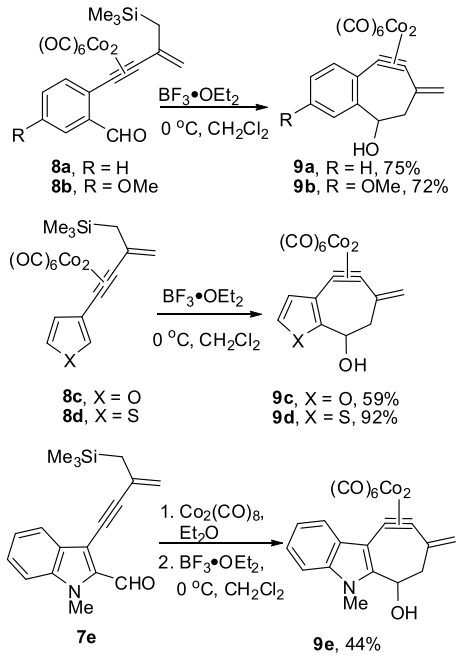
[a](a) K_2CO_3, MeOH, or *n*-Bu_4NF, THF; (b) $H_2C{=}CH(Br){-}CH_2SiMe_3$, $Pd(PPh_3)_4$, CuI, *i*-Pr_2NH–THF; (c) $Co_2(CO)_8$, 0 °C, Et_2O.

Table 1. Hosomi–Sakurai Precursor Preparation

	7 (%)	8 (%)
a	71	80
b	73	75
c	66	85
d	63	77
e	72	[a]

[a]Yield determined after a two-step complexation/cyclization process.

Scheme 2. Hosomi–Sakurai Reactions



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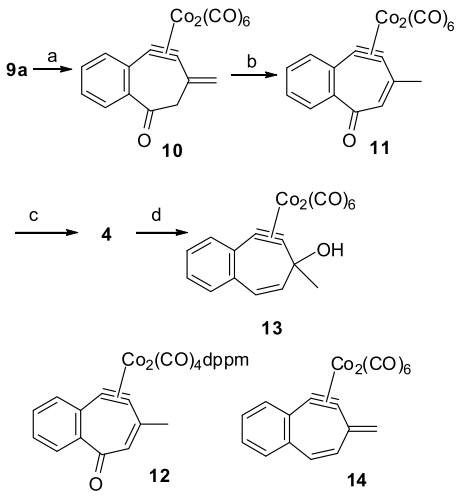
Scheme 3. Preparation of a Dehydrotropylium Ion Complex Precursor[a]

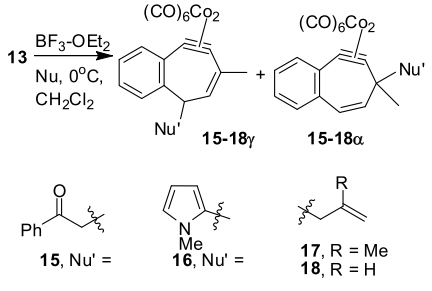


[a](a) $CH_3S(O)CH_3$, ClC(O)C(O)Cl, CH_2Cl_2, −78 °C; then **9a**, Et_3N, −78 to −20 °C, 89% (b) H_2SO_4, CH_2Cl_2, 0 °C, 88%; (c) DIBAL-H, THF, −78 °C; (d) silica gel, 68% (**13**) + 29% (**14**).

induced to isomerize into conjugation with the carbonyl by a catalytic amount of H_2SO_4, giving enone **11** in 88% yield. The formation of this conjugated ketone was evidenced by the disappearance of the exo-methylene function of **10** in the ^{1}H NMR spectrum and the appearance of a single vinyl proton resonance at 6.68 ppm and a methyl group at 2.43 ppm. It is noteworthy that the analogous $Co_2(CO)_4$−dppm complex, **12**, has been prepared previously by a carbonylative Heck reaction,[10] but this process is not tolerant for the $Co_2(CO)_6$ complex. Finally, reduction of **11** with DIBAL-H gave a crude reaction product whose ^{1}H NMR spectral resonances were consistent with **4**, but this material underwent prompt isomerization on silica gel; following chromatographic purification, **13** was isolated in 68% yield, along with a small amount of the elimination product **14** (29%). The appearance of two vinyl protons at 6.39 and 6.15 ppm (each J = 12.5 Hz) in the ^{1}H NMR spectrum was the most distinctive evidence for this isomerization product. Since **13** was equally serviceable relative to **4** as a precursor to the dehydrotropylium ion−$Co_2(CO)_6$ complex, compound **13** was considered appropriate for further study (Scheme 4).

The reactivity of **13** was investigated with a series of nucleophiles, chosen as being representatives of the groups of nucleophiles commonly incorporated in Lewis-acid-mediated reactions of metal-stabilized carbocations and in view of their relative nucleophilicities as measured on the Mayr N scale.[18]

Scheme 4. Nicholas Reactions of Cation Precursor 13



The reaction of **13**, BF_3-OEt_2, and acetophenone trimethylsilyl enol ether (N = 6.22) gave **15** (94% yield) as a 9:1 regioisomeric mixture of **15*γ*** and **15*α*** (Table 2). *N*-

Table 2. Nicholas Reactions of 13

Nu (Mayr N value)	product, yield (%)	γ:α
acetophenone TMS enol ether (6.22)	**15**, 94	9.0:1
N-methylpyrrole (5.82)	**16**, 81	>30:1
methallyltrimethylsilane (4.41)	**17**, 89	13:1
allyltrimethylsilane (1.68)	**18**, 82	7.5:1

Methylpyrrole (N = 5.85) gave condensation product **16** (81% yield) with only the γ-regioisomer apparent (**16*γ*:16*α*** > 30:1). Methallyltrimethylsilane (N = 4.41) afforded **17** (89% yield) as a 13:1 mixture of **17*γ*** and **17*α***, whereas allyltrimethylsilane itself (N = 1.68) afforded **18** (82% yield) as a similar regioisomeric mixture (**18*γ*:18*α*** = 7.5:1). The major isomers (**15**−**18*γ***) were distinguished in the ^{1}H NMR spectra by the single endocyclic vinyl proton (5.85 ppm in **15*γ***), whereas the minor isomer (**15*α***, **16**−**18*α***), when present, was distinguished by the two doublets or AB pattern for the two endocyclic vinyl protons (6.39 ppm, and 6.30, AB, J = 12.3 Hz in **15*α***). In addition, resonances for the incorporated nucleophile [i.e., 5.79 (m), 5.13 ppm (d, J = 17.1 Hz,), 5.09 (d, J = 10.2 Hz) for the vinyl protons of the allyl unit of **18*γ***] were diagnostic. Attempts to incorporate less reactive nucleophiles, with N < 1 (i.e., thiophene, N = −1.01), resulted in the formation of elimination product **14**, whereas radical homocoupling products were not seen in any of these reactions, in contrast to analogous reactions on dehydrotropylium−$Co_2(CO)_6$ ion (**2**) precursors.[6]

From these results, it is clear that the benzodehydrotropylium ion−$Co_2(CO)_6$ **3b** is generated readily. In previous work, Nicholas reactions of cations that are allylic in addition to being propargylic to an alkyne−$Co_2(CO)_6$ group have been shown to favor attacks at the γ-site [i.e., the terminus remote to the alkyne−$Co_2(CO)_6$ unit] over the α-site for the majority of nucleophiles (with a greater selectivity for lower reactivity nucleophiles), for reasons that are not entirely well-understood. This observation has been found to apply to both acyclic[19] and cyclic systems.[20] Here, this situation is much less straightforward, as the γ-site of **3b** is benzylic, whereas the α-site is substantially more hindered than in the literature cases.

With the isolation of the benzodehydrotropylium ion **3b** complex not readily available, due to the elimination pathway, the structural aspects of **3b** were addressed computationally. The putative aromaticity of **3b** was also addressed in terms of geometric, ring current, and energetic factors, namely, HOMA values,[21] NICS(1) values,[22] and appropriate homodesmotic reactions,[23] for comparison to **1** and to tropylium ion. At the B3LYP/6-311+G(d,p) + ZPVE level, the minimized structure of **3b** reveals a 7-membered ring that is nearly planar (Figure 2), with dihedral angles in the 7-membered ring averaging 8.4° and no individual dihedral angle in the ring being >18.5° (see the Supporting Information). Very modest bond alternation is apparent, with bond lengths ranging from 1.385 to 1.437 Å, excluding the formal triple bond. Within the harmonic oscillator model of aromaticity, these bond lengths correspond to a HOMA of 0.636 (EN = 0.256, GEO = 0.108). While this figure is coincident with molecules of substantial aromaticity, it is lower than the dehydrotropylium ion−$Co_2(CO)_6$ complex 0.950 (EN = 0.044, GEO = 0.007). However, this earlier

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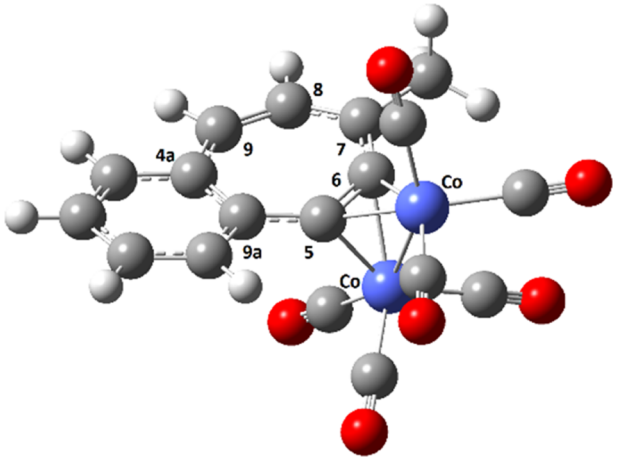


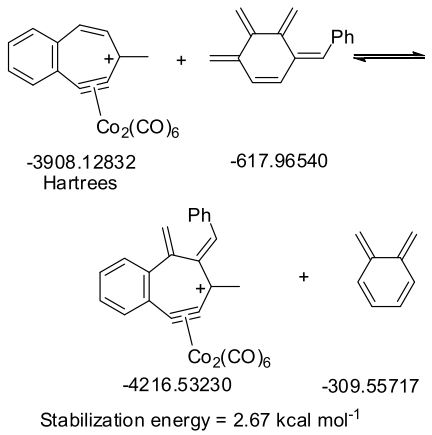
Figure 2. Optimized structure of **3b**. Selected by lengths [Å]: C5−C6 1.364, C6−C7 1.403, C7−C8 1.415, C8−C9 1.385, C9−C4a 1.436, C4a−C9a 1.437.

work[6a] also demonstrated that HOMA was a poor measure of aromaticity in these charged systems in comparison with other methods.

The NICS(1) values of **3b** were calculated to evaluate aromaticity by ring current criteria (see the Supporting Information). These calculations resulted in two different values for the 7-membered ring, with (arbitrarily) above the ring top face giving a value of −4.88 and the opposite face yielding a value of −2.03. A strict averaging of these numbers gives a value of −3.46, somewhat higher than the dehydrotropylium−$Co_2(CO)_6$ cation (**1**) (−2.92) and approximately one-third of that of the tropylium ion itself (−10.5 with the identical functional and basis set). Nevertheless, it is apparent that the proximity of each $Co(CO)_3$ unit is likely affecting these numbers, and they should be taken with caution.

After careful consideration of potential homodesmotic measures of aromaticity, the equation in Scheme 5 was chosen

Scheme 5. Homodesmotic-Reaction-Based Evaluation of 3b



as the most appropriate reaction, given the nature of **3b** as both a propargyldicobalt cation and as a benzylic cation. Employing DFT calculations (B3LYP/6-311+G(d,p) + ZPVE), cation **3b** was evaluated as being aromatic by 2.7 kcal mol^{-1} (see the Supporting Information). Given the apparent issues with the HOMA and NICS(1) calculations, we consider this the most reliable of the measures of the aromaticity of **3b**. This value is nearly identical (≤0.1 kcal mol^{-1} less) to that resulting from the dehydrotropylium ion complex **2** (2.8 kcal mol^{-1}) and ca. 23% of the value arrived at for the tropylium ion itself (11.6 kcal mol^{-1}).[6a]

In summary, we have prepared the alcohol precursor to a dehydrobenzotropylium ion−$Co_2(CO)_6$ by a Hosomi−Sakurai reaction and carried out subsequent manipulation of the exo-methylene benzocycloheptynol complex into a benzocycloheptenynol complex. The Hosomi−Sakurai reaction to generate the benzocycloheptyne−$Co_2(CO)_6$ ring system has been demonstrated to have some generality. The dehydrobenzotropylium ion−$Co_2(CO)_6$ complex **3b** may be generated in solution and reacts with nucleophiles of Mayr nucleophilicities of $N > 1$. The cation itself is modestly aromatic, having approximately the same aromatic stabilization as dehydrotropylium ion−$Co_2(CO)_6$ and roughly one quarter of that of tropylium ion.

EXPERIMENTAL SECTION

General Considerations.[25] Reagents were obtained from commercial sources unless otherwise stated. Reactions were conducted under an inert atmosphere (N_2) using glassware dried in an oven (110 °C, >1 h). The solvent for each reaction was acquired from a solvent purification system (Innovative Technologies). BF_3-OEt_2 was distilled prior to use and stored under an inert atmosphere (N_2). Reactions were subject to a "conventional workup" by partitioning the reaction mixture between an aqueous phase and a diethyl ether or dichloromethane phase, combining the organic phases, followed by drying ($MgSO_4$), filtration, and concentration of the organic phase. Flash chromatography was performed according to the method of Still.[26] High-resolution mass spectrometry (HRMS) results were obtained via a direct insertion probe-electron ionization method (70 eV) on a GCT time-of-flight (ToF) mass spectrometer at the McMaster Regional Centre for Mass Spectrometry and in the University of Windsor Mass Spectrometry lab with a ToF mass spectrometer using the atmospheric solids analysis probe (ASAP) and a corona discharge to facilitate ionization. Elemental analysis was performed by Guelph Chemical Laboratories, Guelph, ON (Canada). ^{1}H NMR spectra were recorded on 300 or 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm), relative to the 7.26 ppm resonance for the residual $CHCl_3$ in $CDCl_3$, unless otherwise indicated. Coupling constants are reported in Hertz (Hz). ^{13}C NMR data were obtained at either 75 or 125 MHz. Infrared spectra (IR) were recorded on a FT-IR spectrophotometer using KBr plates. 2-Bromo-3-(trimethylsilyl)-1-propene and[24] alkynes **6a**,[14] **5a**,[14] **6b**,[14] **5b**,[14] **6c**,[27] **5c**,[13] **6d**,[27] **5d**,[27] and **6e**[28] were prepared by literature methods.

*3-Ethynyl-1-methyl-1H-indole-2-carbaldehyde (**5e**).* To a solution of **6e** (0. 741 g, 2.90 mmol) in anhydrous THF (25 mL) was added a solution of TBAF (1.0 M in THF, 2.9 mL, 1 equiv) at room temperature. The solution was stirred for 5 min, and a solution of aqueous NH_4Cl (sat) was added. The mixture was subjected to conventional extractive workup using diethyl ether to give the material satisfactory for further use. Compound **5e** was isolated as a yellow solid (0.5122 g, 95% yield), mp 122−123 °C. IR (KBr) ν_{max} 3284, 2102, 1669, 1476 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.84 (dt, J = 1.0, 8.0 Hz, 1H), 7.47 (apparent td, J = 1.0, 8.0 Hz, 1H), 7.40 (apparent dt, J = 1.0, 8.5 Hz, 1H), 7.26 (td, J = 1.0, 7.5

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Hz, 1H), 4.09 (s, 3H), 3.53 (s, 1H); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.20 (s, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.49−7.43 (m, 2H), 7.26 (td, J = 7.0, 1.0 Hz, 1H), 4.07 (s, 3H), 3.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 139.3, 136.5, 128.0, 127.8, 122.1, 121.9, 110.6, 110.3, 84.7, 74.8, 31.8; HRMS m/e for $C_{12}H_9NO$ [M^+] calcd 183.0684, found 183.0684.

*2-(3-((Trimethylsilyl)methyl)but-3-en-1-yn-1-yl)-benzaldehyde (**7a**).* General Method I: To a solution of 2-ethynylbenzaldehyde (**6a**, 0.543 g, 4.18 mmol) and 2-bromo-3-(trimethylsilyl)-1-propene (0.807 g, 4.18 mmol) in a degassed (5:1) mixture of diisopropylamine/THF (40 mL) were added $Pd(PPh_3)_4$ (0.241 g, 5 mol %) and CuI (0.080 g, 10 mol %). The solution was stirred for 2 h at room temperature. An aqueous solution of NH_4Cl (sat) was added, and the mixture was subjected to a conventional extractive workup using diethyl ether. The crude material was subjected to flash chromatography (25:1 petroleum ether/Et_2O) to give product **7a** (0.719 g, 71%) as a yellow oil; IR (KBr) ν_{max} 2927, 1700, 1599 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.53 (d, J = 0.5 Hz, 1H), 7.91 (m, 1H), 7.53 (m, 2H), 7.41 (m, 1H), 5.37 (d, J = 2.0 Hz, 1H), 5.18 (d, J = 1.5 Hz, 1H), 1.79 (d, J = 0.5 Hz, 2H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 135.9, 133.9, 133.2, 128.6, 128.4, 127.3, 127.2, 120.8, 98.7, 83.8, 28.1, −1.5; HRMS m/e for $C_{15}H_{18}OSi$ [M^+] calcd 242.1127, found 242.1130.

*5-Methoxy-2-(3-((trimethylsilyl)methyl)but-3-en-1-yn-1-yl)benzaldehyde (**7b**).* 2-Ethynyl-5-methoxybenzaldehyde (**6b**, 0.147 g, 0.918 mmol, 1.1 equiv) and 2-bromo-3-(trimethylsilyl)-1-propene (0.1616 g, 0.836 mmol) were subjected to the conditions of General Method I. Flash chromatography (5:1 petroleum ether/Et_2O) gave product **7b** (0.166 g, 73%) as a yellow oil; IR (KBr) ν_{max} 2955, 2200, 1690, 1601, 1493 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 3.0 Hz, 1H), 7.10 (dd, J = 3.0, 8.5 Hz, 1H), 5.33 (s, 1H), 5.14 (s, 1H), 3.86 (s, 3H), 1.78 (s, 2H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 191.3, 159.8, 137.2, 134.5, 132.0, 128.6, 121.3, 119.6, 109.8, 96.9, 83.6, 55.7, 27.9, −2.0; HRMS m/e for $C_{16}H_{20}O_2Si$ [M^+] calcd 272.1233, found 272.1239.

*3-(3-((Trimethylsilyl)methyl)but-3-en-1-yn-1-yl)furan-2-carbaldehyde (**7c**).* 3-Ethynylfuran-2-carbaldehyde (**6c**, 0.0737 g, 0.614 mmol) and 2-bromo-3-(trimethylsilyl)-1-propene (0.1185 g, 0.613 mmol) were subjected to the conditions of General Method I. Flash chromatography (5:1 petroleum ether/Et_2O) gave compound **7c** (0.0939 g, 66% yield) as a yellow oil; IR (KBr) ν_{max} 2956, 1683, 1420, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (d, J = 1.0 Hz, 1H), 7.61 (apparent dd, J = 1.5, 2.8 Hz, 1H), 6.58 (d, J = 3.0 Hz, 1H), 5.38 (d, J = 1.5 Hz, 1H), 5.21 (d, J = 1.5 Hz, 1H), 1.77 (d, J = 0.5 Hz, 2H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.2, 153.0, 148.0, 128.6, 121.4, 120.0, 115.5, 99.8, 77.5, 28.1, −1.7; HRMS m/e for $C_{13}H_{16}O_2Si$ [M^+] calcd 232.0920; found: 232.0925.

*3-(3-((Trimethylsilyl)methyl)but-3-en-1-yn-1-yl)-thiophene-2-carbaldehyde (**7d**).* 3-Ethynylthiophene-2-carbaldehyde (**6d**, 0.1425 g, 1.05 mmol) and 2-bromo-3-(trimethylsilyl)-1-propene (0.2035 g, 1.05 mmol) were subjected to the conditions of General Method I, with the exception of the reaction mixture being stirred for 2 h at 50 °C. Flash chromatography (2:1 petroleum ether/ether) afforded compound **7d** (0.165 g, 63% yield) as a yellow oil; IR (KBr) ν_{max} 2955, 2925, 2195, 1668, 1418, 1248 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (d, J = 1.0 Hz, 1H), 7.66 (dd, J = 1.0, 5.0 Hz, 1H), 7.15 (d, J = 5.0 Hz, 1H), 5.38 (d, J = 1.5 Hz, 1H), 5.20 (d, J = 1.5 Hz, 1H), 1.78 (s, 2H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 143.4, 134.0, 131.6, 128.2, 121.3, 110.3, 98.3, 80.5, 28.1, −1.5; HRMS m/e for $C_{13}H_{16}OSSi$ [M^+] calcd 248.0691, found 248.0673.

*1-Methyl-3-(3-((trimethylsilyl)methyl)but-3-en-1-yn-1-yl)-1H-indole-2-carbaldehyde (**7e**).* 3-Ethynyl-1-methyl-1*H*-indole-2-carbaldehyde (**6e**, 0.512 g, 2.79 mmol) and 2-bromo-3-(trimethylsilyl)-1-propene (0.539 g, 2.79 mmol) were subjected to the conditions of General Method I, with the exception of the reaction mixture being stirred for 30 min at room temperature. Flash chromatography (5:1 petroleum ether/Et_2O) gave product **7e** (0.595 g, 72%) as a yellow oil; IR (KBr) ν_{max} 2954, 2200, 1668, 1476 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.46 (td, J = 1.0, 7.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.24 (m, 1H), 5.39 (d, J = 2.0 Hz, 1H), 5.17 (s, 1H), 4.08 (s, 3H), 1.84 (s, 2H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.4, 139.6, 135.4, 128.8, 127.8, 127.7, 122.3, 121.6, 119.7, 112.2, 110.5, 99.3, 79.2, 31.8, 28.3, −1.5; HRMS m/e for $C_{18}H_{21}NOSi$ [M^+] calcd 295.1392, found 295.1384.

*Hexacarbonyl[μ-η^4-(2-(3-((trimethylsilyl)methyl)but-3-en-1-yn-1-yl)benzaldehyde)]dicobalt (**8a**).* General Method II: To a solution of **7a** (0.132 g, 0.545 mmol) in anhydrous Et_2O at 0 °C was added an unweighed amount of dicobalt octacarbonyl (excess). The solution was stirred for 1.5 h at 0 °C and was subsequently concentrated under reduced pressure at 0 °C. The crude brown-colored material was added to the top of a plug of silica and washed with hexanes, followed by diethyl ether. The concentration of the Et_2O washings afforded compound (**8a**) as a dark-brown oil (0.230 g, 80% yield); IR (KBr) ν_{max} 2925, 2852, 2092, 2055, 2022, 1693, 1593 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.61 (td, J = 1.25, 7.5 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 5.48 (d, J = 1.0 Hz, 1H), 5.35 (d, J = 1.0 Hz, 1H), 1.72 (d, J = 1.0 Hz, 2H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 191.1, 143.7, 141.5, 134.7, 133.5, 132.6, 128.2, 117.3, 101.9, 88.6, 26.5, −0.8; HRMS m/e for $C_{21}H_{18}Co_2O_7Si$ [M^+ − 2CO] calcd 471.9587, found 471.9604.

*Hexacarbonyl[μ-η^4-(5-methoxy-2-(3-((trimethylsilyl)-methyl)but-3-en-1-yn-1-yl) benzaldehyde)]dicobalt (**8b**).* A solution of **7b** (0.155 g, 0.57 mmol) in anhydrous Et_2O (40 mL) was subjected to General Method II to afford product **8b** (0.238 g, 75% yield) as a dark-brown oil; IR (KBr) ν_{max} 2959, 2090, 2055, 1689, 1599, 1481 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 2.5 Hz, 1H), 7.18 (dd, J = 2.5, 8.5 Hz, 1H), 5.48 (s, 1H), 5.34 (s, 1H), 3.89 (s, 3H), 1.71 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 190.9, 159.7, 143.8, 135.2, 133.8, 133.5, 122.5, 117.3, 110.6, 101.6, 89.1, 55.8, 26.4, −0.8; HRMS m/e for $C_{22}H_{20}Co_2O_8Si$ [M^+ − 4CO] calcd 445.9795, found 445.9785.

*Hexacarbonyl[μ-η^4-(3-(3-((trimethylsilyl)methyl)but-3-en-1-yn-1-yl)furan-2-carbaldehyde)]dicobalt (**8c**).* A solution of **7c** (0.0305 g, 0.131 mmol) in anhydrous Et_2O (35 mL) was subjected to General Method II to afford product **8c** (0.058 g, 85% yield) as a dark-brown oil; IR (KBr) ν_{max} 2958, 2094, 2056, 2026, 1679, 1477, 1251 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (d, J = 0.6 Hz, 1H), 7.65 (apparent dd, J = 0.6, 1.8 Hz, 1H), 6.64 (d, J = 1.8 Hz, 1H), 5.46 (d, J = 0.9 Hz, 1H), 5.29 (d, J = 0.9 Hz, 1H), 1.78 (d, J = 0.6 Hz, 2H), 0.10 (s,

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9H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 199.0, 176.2, 147.9, 146.6, 143.5, 136.1, 116.5, 115.6, 100.1, 77.9, 26.0, −1.3; HRMS *m/e* for $C_{19}H_{16}Co_2O_8Si$ [M^+ − CO] calcd 489.9329, found 489.9312.

*Hexacarbonyl[μ-η^4-(3-(3-((trimethylsilyl)methyl)but-3-en-1-yn-1-yl)thiophene-2-carbaldehyde)]dicobalt (**8d**).* A solution of **7d** (0.0165 g, 0.066 mmol) in anhydrous Et_2O (15 mL) was subjected to General Method II to afford product **8d** (0.0273 g, 77% yield) as a dark-brown oil; IR (KBr) ν_{max} 2957, 2925, 2855, 2092, 2056, 2026, 1721, 1664, 1461 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.09 (d, *J* = 1.2 Hz, 1H), 7.72 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.23 (d, *J* = 5.0 Hz, 1H), 5.49 (d, *J* = 0.7 Hz, 1H), 5.34 (m, 1H), 1.77 (d, *J* = 0.9 Hz, 2H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 182.4, 147.2, 143.4, 137.1, 134.7, 132.9, 117.0, 99.8, 81.4, 26.2, −1.0; HRMS *m/e* for $C_{19}H_{16}Co_2O_7SSi$ [M^+ − CO] calcd 505.9101, found 505.9100.

*Hexacarbonyl[μ-(8,9-dehydro-7-methylene-6,7-dihydro-5H-benzo[7]annulen-5-ol)]dicobalt (**9a**).* General Method III: To a solution of **8a** (0.2177 g, 0.412 mmol) in anhydrous CH_2Cl_2 (25 mL) at 0 °C was added BF_3-OEt_2 (0.051 mL, 0.41 mmol, 1.0 equiv). After stirring for 20 min at 0 °C, aqueous $NaHCO_3$ (sat) was added to the mixture, which was then subjected to a conventional extractive workup using CH_2Cl_2. The resulting residue was subjected to flash chromatography (2:1 petroleum ether/Et_2O) to afford alcohol (**9a**) as a dark-brown solid (0.1415 g, 75% yield), mp 91−93 °C; IR (KBr) ν_{max} 3438, 2090, 2055, 2022, 1633 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.41 (m, 1H), 7.31−7.36 (m, 2H), 5.87 (s, 1H), 5.71 (s, 1H), 4.99 (dd, *J* = 4.0, 7.5 Hz, 1H), 3.12 (d of 1/2 AB, *J* = 8.0, 14.5 Hz, 1H), 2.90 (1/2 AB, *J* = 14.5 Hz, 1H), 1.82 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 143.0, 141.3, 135.8, 134.3, 129.4, 129.2, 128.5, 123.4, 88.4, 88.0, 73.3, 41.3; HRMS *m/e* for $C_{18}H_{10}Co_2O_7$ [M^+] calcd 455.9090, found 455.9085. Anal. calcd for $C_{18}H_{10}Co_2O_7$: C, 47.40; H, 2.21; found: C, 47.16; H, 1.95.

*Hexacarbonyl[μ-(8,9-dehydro-3-methoxy-7-methylene-6,7-dihydro-5H-benzo[7]annulen-5-ol)]dicobalt (**9b**).* Following General Method III, a solution of compound **8b** (0.1445 g, 0.259 mmol) in anhydrous CH_2Cl_2 (30 mL) was treated with BF_3-OEt_2 (33 μL, 0.26 mmol, 1.0 equiv). The reaction was conducted for 5 min (with monitoring by TLC). The crude material was subjected to flash chromatography (5:1 petroleum ether/Et_2O) to afford compound **9b** (0.0901 g, 72% yield) as a dark-brown solid, mp 76−78 °C; IR (KBr) ν_{max} 3413, 2923, 2088, 2051, 2021 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 2.7, 8.4 Hz, 1H), 6.89 (d, *J* = 2.7 Hz, 1H), 5.84 (s, 1H), 5.67 (d, *J* = 0.9 Hz, 1H), 4.91 (dd, *J* = 4.5, 7.5 Hz, 1H), 3.85 (s, 3H), 3.09 (d of 1/2 AB, *J* = 7.8, 14.5 Hz, 1H), 2.88 (1/2 AB, *J* = 14.5 Hz, 1H), 1.84 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 159.9, 143.1, 135.9, 127.4, 123.1, 114.7, 114.5, 88.8, 88.6, 73.3, 55.5, 41.7; HRMS *m/e* for $C_{19}H_{12}Co_2O_8$ [M^+] calcd 485.9196, found 485.9202.

*Hexacarbonyl[μ-(7,8-dehydro-6-methylene-6H-cyclohepta[b]furan-8-ol)]dicobalt (**9c**).* A solution of compound **8c** (0.0410 g, 0.079 mmol) in anhydrous CH_2Cl_2 (15 mL) was treated with BF_3-OEt_2 (9.8 μL, 0.079 mmol, 1.0 equiv) as described in General Method III. The reaction was conducted for 1 h (with monitoring by TLC). The crude material was subjected to flash chromatography (2:1 petroleum ether/Et_2O) to afford compound **9c** (0.0208 g, 59% yield) as a viscous brown oil; IR (KBr) ν_{max} 3390, 2094, 2056, 2026 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.9 Hz, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 5.86 (s, 1H), 5.71 (s, 1H), 5.03 (m, 1H), 3.00 (d of 1/2 AB, *J* = 6.3, 14.1 Hz, 1H), 2.78 (1/2 AB, *J* = 14.1 Hz, 1H), 1.93 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 152.1, 143.7, 141.6, 124.8, 118.6, 112.7, 91.0, 79.7, 65.1, 39.6; HRMS *m/e* for $C_{16}H_8Co_2O_8$ [M^+ − 2CO] calcd 389.8985, found 389.8989.

*Hexacarbonyl[μ-(7,8-dehydro-6-methylene-6H-cyclohepta[b]thiophen-8-ol)]dicobalt (**9d**).* A solution of compound **8d** (0.0165 g, 0.031 mmol) in anhydrous CH_2Cl_2 (8 mL) was treated with BF_3-OEt_2 (3.5 μL, 0.031 mmol, 1.0 equiv) as described in General Method III. The reaction was conducted for 1 h (with monitoring by TLC). The crude material was subjected to flash chromatography (2:1 petroleum ether/Et_2O) to afford compound **9d** (0.0131 g, 92% yield) as a viscous brown oil; IR (KBr) ν_{max} 3398, 2926, 2855, 2090, 2055, 2022, 1715, 1625 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 5.5 Hz, 1H), 7.25 (d, *J* = 5.0 Hz, 1H), 5.85 (s, 1H), 5.70 (s, 1H), 5.05 (dd, *J* = 6.5, 8.2 Hz, 1H), 3.00 (d of 1/2 AB, *J* =8.2, 14.0 Hz, 1H), 2.87 (1/2 AB, *J* = 14.0 Hz, 1H), 2.04 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 143.5, 142.3, 133.4, 130.9, 125.7, 124.1, 89.3, 82.1, 68.2, 41.7; HRMS *m/e* for $C_{16}H_8Co_2O_7S$ [M^+] calcd 461.8655, found 461.8652.

*Hexacarbonyl[μ-(9,10-dehydro-5-methyl-8-methylene-5,6,7,8-tetrahydrocyclo-hepta[b]indol-6-ol)]dicobalt (**9e**).* A solution of **7e** (0.0415 g, 0.141 mmol) in CH_2Cl_2 (30 mL) was subjected to General Method II. Following removal of volatiles under reduced pressure, the residue containing **8e** was dissolved in anhydrous CH_2Cl_2 (15 mL) and treated with BF_3-OEt_2 (18 μL, 0.14 mmol, 1.0 equiv) as described in Method III. The reaction was conducted for 1 h (with monitoring by TLC). The crude material was subjected to flash chromatography (2:1 petroleum ether/Et_2O) to afford compound **9e** (0.0315 g, 44% yield) as a black solid, mp > 250 °C; IR (KBr) ν_{max} 3561, 2921, 2086, 2036, 2000, 1720 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34 (td, *J* = 1.0, 7.0 Hz, 1H), 7.27 (td, *J* = 1.0, 7.0 Hz, 1H), 5.91 (s, 1H), 5.71 (d, *J* = 1.5 Hz, 1H), 5.22 (m, 1H), 3.84 (s, 3H), 3.15 (d of 1/2 AB, *J* = 5.5, 14.0 Hz, 1H), 2.90 (1/2 AB, *J* = 14.0 Hz, 1H), 1.70 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 142.1, 138.3, 137.7, 128.4, 123.7, 123.3, 121.0, 119.8, 110.1, 109.6, 92.1, 83.0, 63.5, 40.3, 29.6; HRMS *m/e* for $C_{21}H_{13}Co_2NO_7$ [M^+] calcd 508.9356, found 508.9352.

*Hexacarbonyl[μ-(8,9-dehydro-7-methylene-6,7-dihydro-5H-benzo[7]annulen-5-one)]dicobalt (**10**).* To a solution of oxalyl chloride (60 μL, 0.69 mmol) in CH_2Cl_2 (15 mL) at −78 °C was added DMSO (60 μL, 0.84 mmol). After 30 min, a solution of **9a** (0.1130 g. 0.248 mmol) in CH_2Cl_2 (4 mL) was added. After stirring at −78°C for 45 min, Et_3N (0.30 mL, 2.2 mmol) was added, and the solution was gradually allowed to warm to −20 °C over 45 min. Addition of NH_4Cl(aq) and a conventional extractive workup (CH_2Cl_2), followed by flash chromatography (10:1 petroleum ether:Et_2O), gave **10** (0.1005 g, 89%) as a red-brown oil; IR (KBr) ν_{max} 2926, 2095, 2057, 2026, 1682, 1596 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.68 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.56 (td, *J* = 1.5, 7.7 Hz, 1H), 7.41 (td, *J* = 1.0, 7.7 Hz, 1H), 5.77 (s, 1H), 5.75 (s, 1H), 3.76 (s, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 198.7, 198.3, 139.1, 138.6, 136.8, 133.4,

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132.6, 128.9, 128.4, 122.3, 87.8, 87.4, 51.9; HRMS *m/e* for $C_{18}H_8Co_2O_7$ [M^+] calcd 453.8934, found 453.8914.

*Hexacarbonyl[μ-(8,9-dehydro-7-methyl-5H-benzo[7]-annulen-5-one)]dicobalt (**11**).* To a solution of **10** (80.9 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (10 mL) at 0 °C was added H_2SO_4 (3 drops in 2 mL of anhydrous CH_2Cl_2) in a dropwise fashion over a period of 20 min. The solution was stirred for 2 h at 0 °C, after which water was added, and the mixture was subjected to a conventional extractive workup using dichloromethane. The crude material was subjected to flash chromatography (5:1 petroleum ether/Et_2O) to afford **11** (70.8 mg, 88% yield) as a brown solid, mp 77−79 °C; IR (KBr) ν_{max} 2918, 2095, 2057, 2031, 1730, 1605, 1582 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 1.2, 8.1 Hz, 1H), 7.87 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.66 (td, *J* = 1.2, 7.5 Hz, 1H), 7.53 (td, *J* = 1.2, 7.5 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 2.43 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.5, 189.3, 149.5, 137.8, 136.7, 133.6, 133.5, 132.4, 131.4, 129.1, 85.4, 83.7, 23.6; HRMS *m/e* for $C_{18}H_8Co_2O_7$ [M^+] calcd 453.8934, found 453.8941.

*Hexacarbonyl[μ-(8,9-dehydro-7-methyl-7H-benzo[7]-annulen-7-ol)]dicobalt (**13**).* To a solution of compound **11** (52 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (7 mL) at −78 °C was added DIBAL-H (0.46 mL of a 1.0 M solution in THF, 0.46 mmol, 4 equiv) in a dropwise manner. The solution was stirred for 1 h at −78 °C. An aqueous solution of NH_4Cl (sat) was added, and the reaction mixture was subjected to a conventional extractive workup using dichloromethane. Following removal of the volatiles under reduced pressure, flash chromatography (10:1 petroleum ether/Et_2O) afforded elimination product **14** (14.0 mg, 29% yield) followed by alcohols **13** and **4** (inseparable by chromatography). The isolated mixture containing (**13**) and (**4**) was dissolved in hexanes, and silica gel was added. After stirring for 1 h, the silica was removed by filtration and the collected filtrate was concentrated under reduced pressure to afford alcohol (**13**) (35.5 mg, 68% yield from ketone **11**). Compound **13**; a red-brown solid; mp 80−81 °C (dec); IR (KBr) ν_{max} 3448, 2924, 2853, 2092, 2055, 2024, 1723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.30−7.40 (m, 2H), 7.20 (m, 1H), 6.39 (d, *J* = 12.5 Hz, 1H), 6.15 (d, *J* = 12.5 Hz, 1H), 2.31 (s, 1H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 139.8, 135.5, 132.0, 133.0, 131.81, 131.79, 128.9, 128.7, 128.2, 107.1, 86.5, 73.7, 32.0; HRMS *m/e* for $C_{18}H_{10}Co_2O_7$ [M^+ − 2CO] calcd 399.9192, found 399.9196. Compound **14**; a red-brown viscous oil; IR (KBr) ν_{max} 3016, 2086, 2033, 2017, 2000, 1624 $cm^{-1;}$ ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (m, 1H), 7.27−7.31 (m, 2H), 7.15 (m, 1H), 6.37 (1/2 AB, *J* = 12.6 Hz, 1H), 6.34 (1/2 AB, *J* = 12.6 Hz, 1H), 5.71 (s, 1H), 5.63 (s, 1H); ^{13}C NMR (125 MHz) 198.7, 143.8, 137.0, 133.13, 133.10, 133.05, 130.9, 130.1, 128.9, 128.6, 121.6, 88.2, 87.3; HRMS (ASAP) *m/e* for $C_{18}H_8Co_2O_6$ [M^+ + H] calcd 438.9063, found 438.9059. Resonances for **4** could be observed in the ^1H NMR spectra of the crude reaction product at δ 7.74 (dd, *J* = 1.0, 7.4, Hz, 1H), 7.54 (d, *J* = 7.6, 1H), 7.44 (apparent dt, *J* = 1.2, 7.5 Hz, 1H), 7.40 (apparent dt, *J* = 1.1, 7.4, 1H), 6.05 (m, 1H), 5.12 (br s, 1H), 2.21 (s, 3H), 1.97 (d, *J* = 4.3, 1H).

General Method IV: To a solution of (**13**) in anhydrous dichloromethane at 0 °C was added an excess amount of the nucleophile (5−8 equiv). BF_3-OEt_2 (3 equiv) subsequently was added dropwise while maintaining the temperature at 0 °C. The solution was stirred for 30 min (with monitoring by TLC). Aqueous $NaHCO_3$ (sat) was added, followed by a conventional extractive workup using dichloromethane. Flash chromatography (100:1 petroleum ether/Et_2O) afforded the final product.

*Hexacarbonyl[μ-(8,9-dehydro-2-(7-methyl-5H-benzo[7]-annulen-5-yl)-1 phenylethanone)]dicobalt (**15γ** and **15α**).* A solution of alcohol compound **13** (68.0 mg, 0.149 mmol) in CH_2Cl_2 (10 mL) was subjected to General Method IV with trimethyl((1-phenylvinyl)oxy)silane (143 mg, 0.745 mmol, 5 equiv) and BF_3-OEt_2 (57 μL, 0.45 mmol, 3 equiv), followed by flash chromatography (20:1 petroleum ether: Et_2O), to afford a 9.0:1 mixture of **15γ** and **15α** (0.0780 g, 94% yield) as a red-brown viscous oil; IR (KBr) ν_{max} 2923, 2853, 2088, 2050, 2017, 1688, 1449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (major product, **15γ**) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.73 (m, 1H), 7.58 (m, 1H), 7.42−7.49 (m, 2H), 7.28−7.36 (m, 2H), 5.85 (dd, *J* = 5.9, 1.4 Hz, 1H), 4.05 (m, 1H), 3.5d (dd, J = 16.8, 8.6 Hz, 1H), 3.46 (d, *J* = 16.8, 4.5 Hz, 1H), 2.14 (s, 3H); resonances from the minor product (**15α**) could be observed at 7.88 (d, *J* = 7.5 Hz, 1H), 7.67 (m, 1H), 6.36 (1/2 AB, *J* = 12.3 Hz, 1H), 6.30 (1/2 AB, *J* = 12.2 Hz, 1H), 3.40 (d, *J* = 16.3 Hz, 1H), 3.26 (d, *J* = 16.3 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (major product, **15γ**) δ 199.6, 197.6, 138.5, 137.1, 136.7, 135.1, 133.4, 133.2, 130.5, 128.9, 128.6, 128.0, 127.4, 126.8, 91.8, 88.6, 44.1, 40.2, 23.3; resonances from the minor isomer could be observed at 197.1, 140.4, 135.5, 131.4, 131.3, 129.4, 128.4, 51.8, 42.5, 28.8; HRMS *m/e* for $C_{26}H_{16}Co_2O_7$ [M^+ − 6CO] calcd 389.9865, found 389.9844.

*Hexacarbonyl[μ-(8,9-dehydro-1-methyl-3-(7-methyl-5H-benzo[7]annulen-5-yl)-1H-pyrrole)]dicobalt (**16γ**).* A solution of alcohol compound **13** (10.2 mg, 0.0224 mmol) in CH_2Cl_2 (5 mL) was subjected to General Method IV with *N*-methylpyrrole (9.1 mg, 0.11 mmol, 5 equiv), resulting in the isolation of **16γ** (9.4 mg, 81% yield) as a viscous brown oil; IR (KBr) ν_{max} 3434, 2918, 2090, 2051, 2021, 1641 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.71 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.28 (m, 1H), 7.21 (td, *J* = 1.8, 7.5 Hz, 1H), 6.64 (apparent t, *J* = 2.1 Hz, 1H), 6.34 (m, 1H), 6.30 (m, 1H), 6.25 (m, 1H), 6.19 (td, *obscured*, 1H), 4.38 (d, *J* = 2.1 Hz, 1H), 3.20 (s, 3H), 2.21 (t, *J* = 2.8 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 200.4, 199.1, 139.7, 137.1, 136.3, 132.8, 132.7, 130.2, 128.7, 127.2, 126.5, 122.0, 108.1, 106.9, 92.8, 89.3, 41.8, 33.5, 22.8; HRMS *m/e* for $C_{23}H_{15}Co_2NO_6$ [M^+ − 2CO] calcd 462.9665, found 462.9662.

*Hexacarbonyl[μ-(8,9-dehydro-7-methyl-5-(2-methylallyl)-5H-benzo[7]annulene)]dicobalt (**17γ** and **17α**).* A solution of alcohol compound **13** (61.5 mg, 0.135 mmol) in CH_2Cl_2 (10 mL) was subjected to General Method IV with methallyltrimethylsilane (0.12 mL, 0.67 mmol, 5 equiv) and BF_3-OEt_2 (51 μL, 0.40 mmol) to afford a (13:1) mixture of **17γ** and **17α** (59.1 mg, 89% yield **17γ** + **17α**) as a viscous red-brown oil; IR (KBr) ν_{max} 2956, 2922, 2852, 2094, 2055, 2011, 1601, 1463 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (major product, **17γ**) δ 7.70 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.29−7.35 (m, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 5.74 (dd, *J* = 4.7, 1.4 Hz, 1H), 4.88 (s, 1H), 4.79 (s, 1H), 3.26 (m 1H), 2.58−2.73 (m, 2H), 2.16 (s, 3H), 1.70 (s, 3H); resonances from the minor product (**17α**) could be detected at 7.65 (m, 1H), 7.15 (m, 1H), 6.39 (d, *J* = 12.1 Hz, 1H), 5.97 (d, *J* = 12.1 Hz, 1H), 4.98 (s, 1H), 4.83 (s, 1H), 2.42 (d, *J* = 12.5 Hz, 1H), 2.22 (d, *J* = 12.5 Hz, 1H), 1.86 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (major product, **17γ**) δ 200.1, 199.4, 143.0, 139.4, 137.5, 135.3, 133.1, 133.0, 131.1, 128.5, 127.0, 125.9, 113.2, 92.7, 89.4, 42.2, 40.8, 23.0,

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22.2; resonances from the minor product could be observed at 142.2, 141.0, 131.4, 129.6, 128.3, 127.9, 116.1, 53.2, 43.2, 29.0, 25.2; HRMS *m/e* for $C_{22}H_{16}Co_2O_6$ [M^+ − 2CO] calcd 437.9713, found 437.9720.

*Hexacarbonyl[μ-(8,9-dehydro-5-allyl-7-methyl-5H-benzo-[7]annulene)]dicobalt (**18γ** and **18α**).* A solution of alcohol compound **13** (11.4 mg, 0.0250 mmol) in CH_2Cl_2 (7 mL) was subjected to General Method IV with allyltrimethylsilane (22.8 mg, 0.201 mmol, 8 equiv) to afford a (7.5:1) mixture of **18γ** and **18α** (9.9 mg, 82% yield **18γ** + **18α**) as a viscous brown oil; IR (KBr) ν_{max} 2924, 2854, 2088, 2048, 2015, 1445, 1102 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (major product, **18γ**) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.30−7.35 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 5.79 (m, 1H), 5.75 (d, *J* = 5.3 Hz, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.09 (d, *J* = 10.2 Hz, 1H), 3.15 (m, 1H), 2.63−2.72 (m, 2H), 2.14 (s, 3H); resonances from the minor product (**18α**) could be detected at 7.63 (m, 1H), 7.14 (m, 1H), 6.39 (d, *J* = 12.2 Hz, 1H), 5.95 (m, 1H), 5.88 (d, *J* = 12.2 Hz, 1H), 2.47 (m, 1H), 2.35 (m, 1H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (major product, **18γ**) δ 200.0, 199.5, 139.2, 137.3, 136.4, 135.4, 132.9, 131.4, 128.5, 127.0, 126.1 117.0, 92.7, 89.3, 43.5, 38.2, 22.9; resonances from the minor product could be observed at 140.2, 133.9, 129.7, 127.9, 118.7, 49.4, 29.2; HRMS *m/e* for $C_{21}H_{14}Co_2O_6$ [M^+] calcd 479.9454, found 479.9440.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02390.

^1H and ^{13}C NMR data of all new compounds; final coordinates for computationally determined structures; magnetic shielding tensors for **3b** (PDF)

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Notes

The authors declare no competing financial interest.

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