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Dehydrotropylium-Co₂(CO)₆ Ion. Generation, Reactivity and Evaluation of Cation Stability

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Abstract: Dehydrotropylium-Co₂(CO)₆ ion, **1**, has been generated by the action of HBF₄ or BF₃·OEt₂ on the corresponding cycloheptadienynol complex **7**, which in turn has been prepared in four steps from a known diacetoxycycloheptyne complex. The reaction of **7** via **1** with several nucleophiles results in substitution reactions with reactive nucleophiles (N > 1) under normal conditions, and a radical dimerization reaction in the presence of less reactive nucleophiles. Competitive reactions of **7** with an acyclic trienynol complex, **12**, shows no preference for generation of **1** over acyclic cation **13**. DFT studies on **1**, specifically evaluation of its HOMA value (+0.95), homodesmotic reaction based stabilization energy (ca. 2.8 kcal/mol) and NICS(1) value (-2.9), taken together with the experimental studies suggest that **1** is weakly aromatic.

Introduction

The chemistry of propargyldicobalt cations, normally known as the Nicholas reaction,^[1] is widely used in organic synthesis because of the reliable site of reactivity of the cations, their combination of ready generation and stability approximating triphenylmethyl cation,^[2] and an electrophilicity sufficient to engage in reaction with a wide range of nucleophiles.^[3] A proposed structural model for the cations has spectroscopic and crystallographic support, and as such has gained wide acceptance.^[4] Within the synthetic utility, stability and reactivity, however, lay ambiguities in the effects of structure on these cations. Cations bearing electron withdrawing groups are often readily generated,^[5] as are those in which the cationic carbons reside in classically antiaromatic systems.^[6] Furthermore, by pK_R⁺ measurements, cations substituted by traditional conjugatively stabilizing and hyperconjugatively stabilizing groups in some cases actually result in very small destabilizations of the cations,^[2a] while in other cases such groups reduce the reactivity of the cations, but by very modest amounts.^[3a]

We, and others, have been engaged in the synthesis of cycloheptynedicobalt complexes.^[1h] These compounds have good thermal stability due to the ability of Co₂(CO)₈ complexation to result in the bending of formal CC triple bond to ca. 140 °.^[7] They may be prepared by Nicholas reactions or electrophilic attack/substitution routes,^[8] carbonylative Heck reactions,^[9] ring closing metathesis reactions,^[10] and in some cases Diels-Alder reactions;^[11] this has led to a growing body of functionalized systems that are synthetically accessible. Given the recognition of cycloheptatrienyl cation (tropylium ion) as a classic 6 π aromatic system, we considered the preparation and study of the Co₂(CO)₆ complex of dehydrotropylium ion, **1**, as an important

goal (Figure 1). In particular, matters such as whether **1** demonstrates greater stability than unfunctionalized propargyldicobalt cations, and whether its formal 6π system shows evidence of aromaticity would be important contributions to the understanding of the stabilization of propargyldicobalt cations.^[12] The Iwasawa group has prepared a small group of naphthalene- $\text{Co}_2(\text{CO})_6$ complexes^[13] and dehydrotropone- $\text{Co}_2(\text{CO})_4(\text{dppm})$ complexes;^[9] the latter group of complexes has not been transformed further. The Jones group^[14] has reported the synthesis of analogous η^2 -‘tropyne’ complexes of platinum, palladium, zirconium, and an η^2, η^7 -platinum/molybdenum complex. While a very modest bond alternation^[14a,c] of the seven membered ring is seen in the crystal structures of two of these complexes, the cation stabilization or aromaticity aspects of the compounds were not the central considerations of these studies.

Suggested location for **Figure 1**

Figure 1. Tropylium ion and dehydrotropylium- $\text{Co}_2(\text{CO})_6$ ion (**1**).

Results and Discussion

It was our belief that the precursor to **1** could be readily obtained from diacetoxycycloheptenyndicobalt complex **2**, the latter of which has been prepared in our lab previously by ring closing metathesis chemistry.^[10a] While **2** did not undergo elimination of acetic acid under acidic conditions, **2** did undergo rapid isomerization to nominally conjugated complex **3** in the presence of H_2SO_4 in acetic acid (96% yield) (Scheme 1). Attempts at acetate hydrolysis under conventional basic conditions gave competitive decomposition and hydrolysis, but reduction with excess DIBAL-H gave the diol **4**, which was immediately oxidized with MnO_2 to give β -hydroxy ketone complex **5** (62% yield, 2 steps). Acid induced elimination of water to afford the dienone (**6**) could be accomplished rapidly in moderate yield with HBF_4 (50% yield) or more slowly with *p*-TsOH. Final reduction of **6** with DIBAL-H afforded dienol complex **7** (82%), along with a small amount of **8** (5%).

Suggested location for **Scheme 1**

Scheme 1. Preparation of cycloheptadienyne- $\text{Co}_2(\text{CO})_6$ complex **7**. Yields in parentheses are based on recovered starting materials.

Generation of Cation 1. Subjecting a solution of alcohol **7** in CH_2Cl_2 at $-78\text{ }^\circ\text{C}$ to HBF_4 , followed by addition of Et_2O , or subjecting a solution of **7** in Et_2O to HBF_4 at $-78\text{ }^\circ\text{C}$, resulted in precipitation of a dark solid that was evaluated by ^1H NMR spectroscopy (in CD_2Cl_2). These spectra revealed the presence of three new compounds. Dehydrotropylium- $\text{Co}_2(\text{CO})_6$ ion (**1**) was evidenced by the signals at δ 8.47 (d, $J = 9.5\text{ Hz}$, 2H), δ 8.36 (t, $J = 9.4\text{ Hz}$, 1H), and δ 8.19 (apparent t, $J = 9.5\text{ Hz}$, 2H) (Figure 2); this species possessed limited stability, gradually degrading in solution even at $-20\text{ }^\circ\text{C}$. In addition to **1** were resonances that were ascribed to regioisomeric dimeric complexes **9a** and **9b** (vide infra). The resonances attributed to **1** are significantly upfield from those of tropylium ion itself (δ 9.16 in CH_2Cl_2).^[15] Although H atoms on sites propargylic to alkyne- $\text{Co}_2(\text{CO})_6$ alkyne complexes are often deshielded relative to those in the metal-free alkyne, these shifts nevertheless suggest a reduction of positive charge distribution on the seven membered ring in **1** relative to tropylium ion. A similar effect has been observed in the $\text{Pt}(\text{PPh}_3)_2$, $\text{Pd}(\text{PPh}_3)_2$, and $\text{ZrCp}(\text{PMe}_3)_2$ complexes of dehydrotropylium ion.^[14] Given that **1** possessed limited thermal stability and that it was not generated cleanly, ^{13}C NMR spectra were not obtained.

Suggested location for **Figure 2**.

Figure 2. Contents of CD_2Cl_2 solutions of **7** + $\text{HBF}_4\text{-OEt}_2$.

Reactivity of Alcohol 7/Cation 1 in Lewis Acid Mediated Nicholas Reactions. The reaction of $\text{Co}_2(\text{CO})_6$ complexes of propargyl alcohol derivatives and their vinylogous allylic alcohol derivatives with Lewis acids are well established to proceed through the derived cations. As a result, we investigated the Lewis acid mediated reactivity of **7** with a variety of nucleophiles possessing a range of strengths, in order gain an understanding of the ability of **1** as an electrophile (Scheme 2, Table 1). Among the nucleophiles investigated, **7** underwent ready reaction with 1,3,5-trimethoxybenzene (Mayr nucleophilicity^[3c] $N = 3.40$) in CH_2Cl_2 (3 equiv $\text{BF}_3\text{-OEt}_2$, $0\text{ }^\circ\text{C}$) to give good yields of the product of condensation at C-7 (α - site) (**10aa**, 88% yield) (entry 1). Nucleophile 2-methylaltrimethylsilane ($N = 4.41$) gave the corresponding C-7 site condensation product **10ba** accompanied by a

significant amount of C-5 (γ -site) condensation product **10by** (73% yield, **10ba:10by** = 67:33, entry 3). Allyltrimethylsilane ($N = 1.79$) (70% yield, **10ca:10cy** = 83:17, entry 4) and methylenecyclohexane ($N = 1.66$) (50% yield, **10da:10dy** = 91:9, entry 5) gave reactivity patterns approximating those of 2-methyltrimethylsilane, while 2-methylthiophene ($N = 1.26$, entry 6) gave exclusive C-7 condensation (**10ea**, 83% yield). Finally, isomeric alcohol **8** gave products identical to **7** with 1,3,5-trimethoxybenzene, although in more modest yield (**10aa**, 54%, entry 2).

Suggested location for Scheme 2

Scheme 2. Nicholas reactions of **7** via **1**.

Suggested location for Table 1.

The pattern of α - versus γ - reactivity of **7** and its derived **1** is consistent. With the exception of 1,3,5-trimethoxybenzene, which has been demonstrated to react reversibly in Nicholas reactions, the relative amount of **10a**- condensation product increases as the nucleophile strength decreases. Analogous behaviour has been observed in the Nicholas reaction chemistry of cycloheptenyne complexes, where conjugated enyne reaction products are observed to a greater degree with weaker nucleophiles.^[16]

With other nucleophiles, 3-methylanisole ($N = 0.13$), thiophene ($N = -1.01$), and mesitylene ($N < 2.5$), electrophile/nucleophile reaction combination products were not isolated in any significant amounts under the standard reaction conditions. Rather, the products of dimerization at each α - site and one α - and one γ - site, **9a** and **9b** (**9a:9b** = 33:67) respectively, were isolated as a regioisomeric mixture in 26%, 34%, and 50% yield, respectively. A small amount (4%) of condensation product (**10fa**) could be isolated in the case of thiophene. Repetition of this procedure using thiophene as solvent enabled the isolation of **10fa** in more substantial amounts (45% yield, Table 1, entry 7). In addition, subjecting **7** to the otherwise standard reaction conditions in the absence of any recognized nucleophile did result in the formation of a small amount (9%) of the same **9a/9b** mixture (**9a:9b** = 33:67).

The homodimerization products **9a** and **9b** are likely products of a dimerization of radical **11**. The conversion of propargyldicobalt cations to their corresponding radicals is well precedented, particularly by the Melikyan group, and can be mediated by electron rich aromatics, ethereal solvents, and other alkynedicobalt complexes.^[17] Given the more significant amounts of **9a/9b** in the presence of arenes and in the ¹H NMR spectroscopic samples relative to the case with no arene, each of these mediators appears to be operating to some degree in the current system. Compound **9a** could be detected only as one diastereomer, which has been assigned as *syn*- based on extensive precedent for high *syn*- diastereoselectivity in intermolecular propargyldicobalt radical dimerizations.^[17] As thiophene is known to undergo C-2 reaction with radicals,^[18] it is possible both that the small amount of **10fa** may also be accounted for by **11**; however we favour the interpretation that the electrophile – nucleophile combination is still occurring, but a rate much slower than the conversion to the radical process at the standard concentrations of these reactions (0.01 M).

Suggested location for structures 11, 13, 18.

The results of the nucleophile/electrophile combinations are therefore unusual for Nicholas reaction chemistry. The bulk of propargyl cation-Co₂(CO)₆ complexes have electrophilicities in the $E = -1.2 - -2.2$ range,^[3a] making them normally compatible in reaction with nucleophiles as weak as $N \approx -3 - -4$. In the case of cycloheptadienyne complex **7** and its resultant dehydrotropylium ion **1**, successful reaction as an electrophile only occurs reliably with nucleophiles of $N > 1$; use of high concentrations of nucleophile pushes this limit only down to $N \geq -1$. While this may be interpreted as implicating lower reactivity and perhaps greater stability of dehydrotropylium ion complex **1**, the ready conversion to radical reactivity suggests a stability of **11** close to **1**, and therefore a lack of any special stability for **1**. Therefore, this question was pursued further, by competition experiments and by calculational studies.

Reactivity comparison of 7 with acyclic dienyl 12. Given the shortcomings of using an evaluation of compatible nucleophiles for an accurate estimation of the stability of dehydrotropylium ion-Co₂(CO)₆, we considered a reactivity comparison with a similar but non-aromatic propargyl cation complex important. As a result, propargyl dienyl alcohol complex **12** was chosen as a target for synthesis and reactivity studies, since the resultant cation (**13**) would approximate the dienynyl cation

portion of **1**, and the remote alkene function in **12** would mimic the sp^2 -hybridized carbon on both ends of the alkyne- Co_2 portion of **1**. To this end, sorbaldehyde (2,4-hexadienal) was reacted with the lithium acetylide of trimethylsilylethyne, to give the relatively unstable **14** (Scheme 3). While this compound could be isolated (31% yield), it underwent substantial decomposition during purification, and it was more efficient to carry on unpurified **14** to further steps. Alcohol **14** was subjected to one pot fluoride-mediated desilylation and immediate Sonogashira reaction with bromoethene to give a similarly unstable **15**; immediate complexation with $Co_2(CO)_8$ afforded **12** (14% overall yield from sorbaldehyde).

Suggested location for Scheme 3

Scheme 3. Preparation of acyclic dienynyl propargyl alcohol **12**.

The Lewis acid mediated Nicholas reactions of **12** were investigated briefly, in order to have an understanding of the range of compatible nucleophiles and the regiochemistry of substitution (Scheme 4, Table 2). Allyltrimethylsilane ($N = 1.79$) reacted in straightforward fashion, giving condensation predominantly at the dienyl terminus remote from the alkynedicobalt (C-9), along with small amounts of two other regioisomers (**16a**, 85%) (isomer ratio 82:12:6, entry 1). This regiochemical preference towards attack at the most remote site is consistent with that of allyl propargyldicobalt cations.^[16b] Each of the remaining condensation products were from exclusive reaction at C-9. 2-Methylthiophene ($N = 1.26$) afforded **16b** in 65% yield (entry 2). 3-Methylanisole ($N = 0.13$) reacted similarly, but in more modest yield and as a mixture of arene regioisomers (**16c**, 22%, **16c'**, 17%, entry 3). Allyltriphenylsilane ($N = -0.13$) also gave **16a** in modest yield (37%, entry 4), while anisole itself ($N = -1.18$) required its presence as a significant excess to give reasonable amounts of condensation products (**16e**, 56%, **16e'**, 4.5%, entry 6). Under the standard conditions, thiophene ($N = -1.01$) was able to undergo condensation with **12**, but the monopropargylated product **16d** was sufficiently reactive that 2,5-disubstitution product **17** was isolated predominantly (**17**, 45%; **16d**, 7%, entry 5) None of the less reactive nucleophiles employed, including cyclopentene ($N = -1.55$), 1-methylnaphthalene ($N = ca. -2.4$), and mesitylene ($N < -2.5$), afforded any isolable condensation product, nor was there evidence of significant amount of a dimerization product present in these cases.

Suggested location for Scheme 4

Scheme 4. Nicholas reactions of **12** via cation **13**.

Suggested location for Table 2.

From these results it is clear that the cation **13** derived from **12** enters electrophile-nucleophile combination reactions with nucleophiles of $N > -1.5$, a value less than the majority of propargyldicobalt cations, but a cation that does not switch over to radical dimerization chemistry to the degree observed with **1**. While this gives greater confidence in contending that this is consistent with an electrophilicity of $E \approx -3.5$, it is not rigorous proof of this value; nevertheless, the way was now paved for competitive substitution reactions with dehydrotropylum cation precursor **7**. To accomplish these competition reactions, equimolar amounts of **7** and **12** and an appropriate nucleophile were dissolved together in CH_2Cl_2 . To this mixture, excess $BF_3 \cdot OEt_2$ was added, and the product mixture evaluated. In each of the cases of allyltrimethylsilane and 2-methylthiophene nucleophiles, the predominant product isolated was that of condensation of **12**, by ratios of 1.7:1 (allyltrimethylsilane) and 2.8:1 (2-methylthiophene) (Scheme 5). The discrepancy of the ratios raised the possible concern that 2-methylthiophene was showing some signs of reversibility in its reaction, and so the competition with this nucleophile was conducted at $-50^\circ C$. The preferential formation of **16b** over **10e** (1.9:1) now was obtained in a ratio approximately consistent with that of the allyltrimethylsilane reaction.

Suggested location for Scheme 5

Scheme 5. Competition reactions between **7** and **12**.

The most straightforward interpretation of these results is that pentadienyl cation (**13**) is being generated slightly more rapidly than the dehydropentadienyl ion **1**, thereby giving products **16a** and **16b** preferentially. A potential caveat for this interpretation stems from the fact that examples of second step rate determining S_N1 processes have been demonstrated recently by Mayr.^[19] Nevertheless, we have observed that phenyl and vinyl substituents at the propargylic site in propargyl acetate- $\text{Co}_2(\text{CO})_6$ complexes result in more rapid reaction with nucleophiles such as allyltrimethylsilane,^[20] giving confidence to the assertion that the traditional rate determining step in this S_N1 process is operating here. Furthermore, it is clear that the reactivities of **7** and **12** are relatively close, and that the activation energies to the formation of **1** and **13** differ only slightly, so that no great additional stabilization of **1** is apparent.

With the possibility that dehydropentadienyl ion **1** possesses any aromaticity questionable, we chose to investigate the matter computationally by commonly employed three methods:^[21] the Harmonic Oscillator Model (HOMA); by evaluation of homodesmotic reactions involving **1**, and by the Nucleus Independent Chemical Shift (NICS(1)). The structure of **1** obtained at the B3LYP/6-311 + G(d,p) + ZPVE level^[22] is shown in Figure 3.^[23] The seven membered ring system is close to planar, with the C1,C2,C3,C4 dihedral angle 5.8° . The Co-Co axis and C7,C1,C2,C3 plane are bent significantly from perpendicular (angle = 72.5°), reflecting the bending of the propargylic centres towards a cobalt atom consistent with the accepted bonding models in propargylium- $\text{Co}_2(\text{CO})_6$ complexes.^[4]

Suggested location for Figure 3.

Figure 3. Optimized structure of **1**. Selected bond lengths C1-C2 1.374 Å, C2-C3 = C7-C1 1.403 Å, C3-C4 = C6-C7 1.394 Å, C4-C5 = C5-C6 1.406 Å.

HOMA. The Harmonic Oscillator Model of Aromaticity (HOMA),^[24] is one of the simplest measures of aromaticity, taking into account both deviations from ideal aromatic bond lengths (EN) and bond alternation (GEO). The minimal nature of bond alternation (≤ 0.012 Å, excluding the formal alkyne) for the carbocycle in **1** is immediately apparent. HOMA calculations were carried out for this system, with the exclusion of the formal triple bond due to its understandable deviation from ideal benzenoid bond length. The HOMA was calculated both including and excluding the formal alkyne-propargyl carbon bond lengths. Including these bonds gives a HOMA of 0.950 (EN = 0.044, GEO = 0.007), while excluding the bonds immediately adjacent to the alkynedicycobalt function gives a HOMA of 0.954 (EN = 0.037, GEO = 0.009); each value suggests a high degree of aromaticity according to these geometric parameters. Nevertheless, purely geometric indicators of aromaticity, although useful, are not direct indicators of ring current or aromatic stabilization.^[25]

Homodesmotic Reactions.^[26] A choice of reactions on which to evaluate for calculated aromatic stabilization required a careful selection of systems in order to equalize bond types as much as possible; ultimately two reactions were chosen. Equation 1 (Scheme 6) possesses an extra *s-cis* relationship on starting material side of the equation, which is known to have an energetic cost of ca. 3.4 kcal/mol. Consequently, we have also chosen equation 2 for study, as this equation possesses an extra *s-cis* relationship on the product side, with the intent on considering the two reactions together. Using DFT calculations (B3LYP/6-311+G(d,p) + ZPVE), the energetic differences were calculated as follows: equation 1, + 0.50 kcal/mol; equation 2, + 5.13 kcal/mol. Taken together, these two equations predict an aromatic stabilization for **1** of 2.8 kcal/mol; approximately equivalent to phosphole, which is considered to be weakly aromatic,^[27] or occasionally non-aromatic. By a more relevant comparison, the stabilization is considerably reduced (ca. 24%) relative to tropylium ion itself, which gives an aromatic stabilization of 11.6 kcal/mol by the analogous homodesmotic reactions (see Supporting Information); other authors have calculated a stabilization energy at 15.2 – 15.7 kcal/mol.^[28]

Suggested location for Scheme 6

Scheme 6. Homodesmotic reactions for **1**.

NICS(1). The NICS(0) and NICS(1) values^[29] were calculated, at the HF/6-311+G(d,p)//B3LYP/6-311+G(d,p) level, for **1**. The NICS(0) value, which is actually positive (+1.58), was considered less relevant due to effects of the sigma framework. Given the fact that in the optimized structure of dehydropentadienyl complex **1** the cobalt – cobalt vertex and the seven membered ring are not perpendicular, it is possible to place an imaginary proton at two different sites 1 Å above the ring, and therefore two different NICS(1) values may be calculated. Nevertheless, the two calculated values for the isotropic GIAO shielding tensor are essentially identical (-2.92 and -2.93). This is compared with tropylium ion itself, which gives NICS(1) values of -9.2 – -11.2,^[30]

depending upon basis set and functional (-10.5 in our hands at the identical level to **1**), and like the homodesmotic reactions reflects a significantly reduced ring current (ca. 28% of tropylium ion) in the current system.

In evaluation of the four methods of measuring aromaticity, there are 3 distinct results. The competition reactions between **7** and acyclic dienyl cation precursor **12** shows no evidence of aromatic stabilization for **1**, while the HOMA calculations show a very high degree of aromatic character. The homodesmotic reaction and NICS(1) calculations each show a reduced but extant aromaticity, about 25% that of tropylium ion. We have more confidence in these latter two measures. In the **7** versus **12** competition reactions there are sufficient discrepancies in bond types (conjugated diene in **7**, possible hyperconjugative stabilization in **13**, an extra conjugated enyne complex in **7**) to compensate for a small aromatic stabilization in **1**. With respect to the calculated HOMA values, these are exceptionally high, and therefore the minimized structure for the corresponding nominally antiaromatic cycloheptadienyl anion- $\text{Co}_2(\text{CO})_6$ complex **18** was calculated (B3LYP/6-311+G(d,p)) (see Supporting Information). While the bond alternation in **18** excluding the formal triple bond ($\leq 0.029 \text{ \AA}$) was somewhat greater than for **1**, it was still quite modest, as reflected to the high HOMA values (HOMA = 0.879, EN = 0.077, GEO = 0.055). Consequently we consider it likely that the HOMA value for **1** does not reflect its aromatic stabilization as accurately as the homodesmotic and NICS(1) values.

Conclusion

The dehydrotropylium ion- $\text{Co}_2(\text{CO})_6$ complex **1** may be generated from alcohol **2**, its ^1H NMR spectrum acquired, and reacted *in situ* with nucleophiles. More reactive nucleophiles undergo electrophile- nucleophile combination reactions with **1** predominantly at the propargylic site, whereas in the presence of weaker nucleophiles, conversion to a radical and subsequent dimerization occurs. Taking competitive reactivity with dienyl analogue **12**, HOMA calculations, homodesmotic reactions and NICS(1) calculations into consideration, **1** is best described as showing a very weak aromaticity, approximately one quarter of that of tropylium ion.

Experimental Section

Experimental procedures and characterization data for **10ba/by**, **10da/dy**, **10fa**, **16c/c'**, **16d**, **16d/d'**, and **17**, are given in the Supporting Information.

Hexacarbonyl[μ - η^4 -(5,7-diacetoxycyclohept-1-en-3-yne)]dicobalt (3**):** To a solution of **2** (1.419 g, mmol) in $\text{CH}_3\text{CO}_2\text{H}$ (20 mL) was added H_2SO_4 (10 drops). Following stirring for 1.5 h, water was added, and the mixture was subjected to a conventional extractive workup (hexanes). The organic layers were dried over MgSO_4 , and concentrated under reduced pressure. Flash chromatography (10:1 petroleum ether : Et_2O) afforded **3** (1.356 g, 96% yield) as a single diastereomer; (**3**); ^1H NMR (CDCl_3) δ 6.77 (d, $J = 10.0$ Hz, 1H, vinyl-*CH*), 6.27 (dd, $J = 10.3$ Hz, 3.7 Hz, 1H, *CH-OAc*), 6.14 (dd, $J = 10.0$ Hz, 6.3 Hz, 1H, vinyl-*CH*), 5.57 (apparent t, $J = 6.8$ Hz, 1H, *CH-OAc*), 2.40 (m, 1H, *CHH*), 2.16 (s, 3H, *C(O)-CH_3*), 2.05 (m, 1H, *CHH*), 2.03 (s, 3H, *C(O)-CH_3*); ^{13}C NMR (CDCl_3) $\delta = 198.9$ (br), 170.2, 170.0, 130.6, 130.3, 93.9, 81.4, 71.0, 67.3, 35.0, 21.0, 20.8; IR (neat, NaCl) $\nu = 3030, 2928, 2095, 2056, 2029, 1741 \text{ cm}^{-1}$; MS (EI, 20 eV) m/e 466 ($\text{M} - \text{CO}^+$), 438 ($\text{M} - 2\text{CO}^+$), 354 ($\text{M}^+ - 5\text{CO}$), 326 ($\text{M}^+ - 6\text{CO}$); HRMS (TOF) m/e for $\text{C}_{17}\text{H}_{12}\text{Co}_2\text{O}_{10}$ calcd. 465.9145 ($\text{M} - \text{CO}^+$), found 465.9159.

Hexacarbonyl[μ - η^4 -(6-hydroxycyclohept-2-en-4-ynone)]dicobalt (5**):** Compound **3** (0.3572 g, 0.723 mmol) was dissolved in Et_2O and cooled to -78°C . DIBAL-H (3.0 mL of a 1 M solution in Et_2O , 4 equiv) was added and the solution stirred for 1.5 h. Saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ was added and the reaction mixture was subjected to a conventional extractive workup (Et_2O). Removal of the volatiles under reduced pressure afforded a crude mixture containing **4**, which was dissolved in CH_2Cl_2 . MnO_2 (excess) was added, and the mixture stirred 12 h. Filtration through silica gel and concentration under reduced pressure gave a residue, which was subjected to flash chromatography (4:1 petroleum ether : Et_2O) to afford **5** (0.1829 g, 62%); (**5**); ^1H NMR (CDCl_3) δ 7.36 (d, $J = 10.4$ Hz, 1H, vinyl-*CH*), 6.26 (d, $J = 10.4$ Hz, 1H, vinyl-*CH*), 5.17 (m, 1H, *CH-OH*), 3.02 (m, 2H, *CH_2*), 2.20 (d, $J = 5.0$ Hz, 1H, *OH*); ^{13}C NMR (CDCl_3) $\delta = 198.3$ (br, obscured), 198.3, 139.5, 132.2, 97.8, 78.4, 68.7, 52.3; IR (neat, NaCl) $\nu = 3417, 3027, 2925, 2099, 2059, 2030, 1651 \text{ cm}^{-1}$; MS (EI, 20 eV) m/e 408 (M^+), 380 ($\text{M} - \text{CO}^+$), 352 ($\text{M} - 2\text{CO}^+$), 324 ($\text{M} - 3\text{CO}^+$), 296 ($\text{M} - 4\text{CO}^+$); HRMS (TOF) m/e for $\text{C}_{13}\text{H}_6\text{Co}_2\text{O}_8$ calcd. (M^+) 407.8727, found 407.8705.

Hexacarbonyl[μ - η^4 -(cyclohepta-2,6-dien-4-ynone)]dicobalt (6**):** To a solution of **5** (0.200 g, 0.490 mmol) in CH_2Cl_2 (10 mL) was added HBF_4 (0.5 mL, 54 wt. % in Et_2O , excess) in a dropwise fashion. After 20 min saturated $\text{NaHCO}_3_{(\text{aq})}$ was added, and followed by a conventional extractive workup (CH_2Cl_2). Flash chromatographic purification (5:1 petroleum ether : Et_2O) afforded **6** (0.095 g, 50% yield); (**6**); ^1H NMR (CDCl_3) $\delta = 7.61$ (d, $J = 10.0$ Hz, 2H, vinyl-*CH*), 6.59 (d, $J = 10.0$ Hz, 2H, vinyl-*CH*) ppm; ^{13}C NMR (CDCl_3) $\delta = 198.0$ (br), 191.1, 140.5, 135.3, 80.5 ppm; IR (neat, NaCl) $\nu = 3031, 2927, 2102, 2064, 2032, 1699 \text{ cm}^{-1}$; MS (EI, 20 eV) m/e 390 (M^+), 362 ($\text{M} - \text{CO}^+$), 334 ($\text{M} - 2\text{CO}^+$), 306 ($\text{M} - 3\text{CO}^+$), 278 ($\text{M} - 4\text{CO}^+$), 250 ($\text{M} - 5\text{CO}^+$), 222 ($\text{M} - 6\text{CO}^+$); HRMS (TOF) m/e for $\text{C}_{13}\text{H}_6\text{Co}_2\text{O}_7$ calcd. (M^+) 389.8621, found 389.8625.

Hexacarbonyl[μ - η^4 -(cyclohepta-2,6-dien-4-ynol)]dicobalt (7**) and Hexacarbonyl[μ - η^4 -(cyclohepta-2,4-dien-6-ynol)]dicobalt (**8**):** To a solution of **6** (0.0768 g, 0.197 mmol) in Et_2O (10 mL) at -78°C was added DIBAL-H (0.5 mL of 1M solution, 0.5 mmol). After stirring 2 h at -78°C , saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ was added, and the reaction subjected to a conventional extractive workup (Et_2O). Flash chromatographic purification (100% petroleum ether - 5:1 petroleum ether: Et_2O) gave the sequential elution of recovered **6** (0.0036 g, 5% recovery), alcohol **8** (0.0038 g, 5% yield), and **7** (0.0633 g, 82% yield, 86% based on recovered **6**); (**7**); ^1H NMR (CDCl_3) $\delta = 6.79$ (dd, $J = 10.0$ Hz, 1.8 Hz, 1H, vinyl-*CH*), 5.93 (dd, $J = 10.0$ Hz, 3.8 Hz, 1H, vinyl-*CH*), 4.94 (br, 1H, *CH-OH*), 2.21 (br, 1H, *OH*) ppm; ^{13}C NMR (CDCl_3) 199.1, 133.0, 127.5, 84.8, 70.3 ppm; IR (neat, NaCl) ν_{max} 3324, 3021, 2923, 2099, 2053, 2053, 2028, 2009 cm^{-1} ; MS (EI, 20 eV) m/e 392 (M^+); HRMS (TOF) m/e for $\text{C}_{13}\text{H}_6\text{Co}_2\text{O}_7$ calcd. 391.8763 (M^+), found 391.8764. Compound (**8**); ^1H NMR (CDCl_3) $\delta = 6.88$ (d, $J = 9.8$ Hz, 1H, vinyl-*CH*), 6.17 (m, 1H, vinyl-*CH*), 5.92-5.98 (m, 2H, 2 vinyl-*CH*), 5.55 (d, $J = 6.2$ Hz, 1H, *CH-OH*), 2.18 (br, 1H, *OH*) ppm; ^{13}C NMR (CD_2Cl_2) $\delta = 199.8$ (br), 135.7, 131.4, 127.2, 126.4, 102.5,

83.1, 72.5 ppm; IR (neat, NaCl) ν = 3400 (br), 3022, 2095, 2054, 2022 cm^{-1} ; MS (EI, 20 eV) m/e 364 (M - CO⁺), 336 (M - 2CO⁺), 308 (M - 3CO⁺), 280 (M - 4CO⁺), 252 (M - 5CO⁺), 224 (M - 6CO⁺); HRMS (TOF) m/e for C₁₃H₆Co₂O₇ calcd. 363.8981 (M⁺ - CO), found 363.8994.

Hexacarbonyl[μ - η^4 -(7-(2,4,6-trimethoxyphenyl)cyclohepta-1,3-dien-5-yl)]dicobalt (10aa): To a solution of compound **7** (0.023 g, 0.059 mmol) and 1,3,5-trimethoxybenzene (0.050 g, 0.29 mmol) in CH₂Cl₂ (5 mL) at 0 °C was added BF₃·OEt₂ (21 μ L, 0.18 mmol). After 15 min, saturated NaHCO_{3(aq)} was added and the mixture subjected to a conventional extractive workup (CH₂Cl₂). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. Flash chromatography (10:1 petroleum ether : Et₂O) afforded **10aa** (0.028 g, 88% yield); (**10aa**): ¹H NMR (CDCl₃) δ = 6.74 (d, J = 9.6 Hz, 1H, vinyl-CH), 6.17 (s, 2H, aryl-CH), 6.12 (dd, J = 9.6, 7.5 Hz, 1H, vinyl-CH), 5.95 (dd, J = 11.9 Hz, 1.9 Hz, 1H, vinyl-CH), 5.83 (m, 1H, vinyl-CH), 5.59 (br s, 1H, alkyl-CH), 3.86 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃) ppm; ¹³C NMR (CDCl₃) δ = 199.8 (br), 160.3, 159.7, 158.2, 137.7, 129.3, 127.4, 124.7, 110.8, 106.4, 90.7, 90.1, 85.6, 55.3, 55.2, 54.5, 40.0 ppm; IR (neat, NaCl) ν = 3019, 2924, 2090, 2050, 2020 cm^{-1} ; MS (EI, 20 eV) m/e 514 (M - CO⁺), 486 (M - 2CO⁺), 458 (M - 3CO⁺), 430 (M - 4CO⁺), 402 (M - 5CO⁺), 374 (M - 6CO⁺); HRMS (TOF) m/e for C₂₂H₁₆Co₂O₉ calcd. (M - 2CO⁺) 485.9560, found 485.9538.

Hexacarbonyl[μ - η^4 -(7-allylcyclohepta-1,3-dien-5-yl)]dicobalt (10ca) and Hexacarbonyl[μ - η^4 -(7-allylcyclohepta-1,5-dien-3-yl)]dicobalt (10cy): Reaction of **7** (0.028 g, 0.071 mmol) with allyltrimethylsilane (56 μ L, 0.36 mmol) under the standard conditions afforded **10c** (0.021 g, 70%) as a 83:17 mixture of **10ca**:**10cy** following purification by flash chromatography (100% hexanes); (**10c**): ¹H NMR (CDCl₃) (major isomer) δ = 6.79 (d, J = 10.0 Hz, 1H, vinyl-CH), 6.11 (dd, J = 10.0 Hz, 7.5 Hz, 1H, vinyl-CH), 5.96 (m, 1H, vinyl-CH), 5.90 (m, 1H, vinyl-CH), 5.74 (ddd, J = 12.0 Hz, 3.0 Hz, 1.0 Hz, 1H), 5.22 (dd, J = 17.0 Hz, 1.5 Hz, 1H, =CHH), 5.17 (dd, J = 10.5 Hz, 1.5 Hz, 1H, CHH), 3.74 (m, 1H, alkyl-CH), 2.67 (m, 1H, CHH), 2.51 (m, 1H, CHH) ppm; (minor isomer) 6.69 (dd, J = 9.5 Hz, 2.0 Hz, 2H, vinyl-CH), 5.79 (m, 1H, vinyl-CH), 5.64 (dd, J = 9.5 Hz, 4.3 Hz, 2H, 2 vinyl-CH), 5.10 (d, J = 9.4 Hz, 1H, vinyl-CH), 5.09 (d, J = 17.7 Hz, 1H, vinyl-CH), 3.16 (m, 1H, alkyl-CH), 2.37 (apparent t, J = 6.8 Hz, 2H, CH₂) ppm; ¹³C NMR (CDCl₃) (major isomer) δ = 199.6 (br), 136.0, 135.0, 130.2, 127.7, 127.1, 117.4, 104.9, 85.8, 43.5, 41.3 ppm; resonances from the minor isomer could be detected at 135.5, 133.8, 127.4, 42.5, 41.1 ppm; (neat, KBr) ν = 2923, 2090, 2054, 2024 cm^{-1} ; MS (EI, 20 eV) m/e 418 (M⁺), 388 (M - CO⁺), 360 (M - 2CO⁺), 332 (M - 3CO⁺), 304 (M - 4CO⁺), 276 (M - 5CO⁺), 248 (M - 6CO⁺); HRMS (TOF) m/e for C₁₆H₁₀Co₂O₆ calcd. (M - CO⁺) 387.9192, found 387.9166.

Hexacarbonyl[μ - η^4 -(7-(5-methyl-2-thienyl)cyclohepta-1,3-dien-5-yl)]dicobalt (10ea): Reaction of **7** (0.018 g, 0.046 mmol) with 2-methylthiophene (23 μ L, 0.23 mmol) under the standard conditions afforded **10ea** (0.018 g, 83% yield) following purification by flash chromatography (100% hexanes); (**10ea**): ¹H NMR (CDCl₃) δ = 6.84 (d, J = 9.0 Hz, 1H, vinyl-CH), 6.76 (d, J = 3.0 Hz, 1H, thienyl-CH), 6.61 (d, J = 3.0 Hz, 1H, thienyl-CH), 6.18 (m, 1H, vinyl-CH), 6.00-6.08 (m, 2H, 2 vinyl-CH), 5.16 (s, 1H, alkyl-CH), 2.46 (s, 3H, CH₃) ppm; ¹³C NMR (CDCl₃) δ = 199.0 (br), 145.0, 139.0, 134.3, 131.0, 127.9, 126.6, 124.7, 124.4, 105.9, 84.5, 45.7, 15.4 ppm; IR (neat, NaCl) ν = 3020, 2923, 2091, 2052, 2022 cm^{-1} ; MS (EI, 20 eV) m/e 472 (M⁺), 444 (M - CO⁺), 416 (M - 2CO⁺), 388 (M - 3CO⁺), 360 (M - 4CO⁺), 332 (M - 5CO⁺), 304 (M - 6CO⁺); HRMS (TOF) m/e for C₁₈H₁₀Co₂O₆S calcd. (M⁺) 471.8862, found 471.8851.

Hexacarbonyl[μ^4 - η^2 , η^2 , η^2 , η^2 -(1,1'-bi(cyclohepta-2,4-dien-6-yl))tetracobalt (9a) and Hexacarbonyl[μ^4 - η^2 , η^2 , η^2 , η^2 -(7-(cyclohepta-2,6-dien-4-ynyl)cyclohepta-1,3-dien-5-yl)]tetracobalt (9b): To a solution of **7** (0.028 g, 0.071 mmol) and mesitylene (49 μ L, 0.36 mmol) in CH₂Cl₂ (5 mL) at 0 °C was added BF₃·OEt₂ (26 μ L, 0.21 mmol). After 15 min, saturated NaHCO_{3(aq)} was added and the mixture subjected to a conventional extractive workup (CH₂Cl₂). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. Flash chromatography (100% hexanes) afforded **9** (0.0133 g, 50%) as a 33:67 mixture of **9a**:**9b**. Compound **9b** slowly decomposed in solution in CDCl₃; (**9**): ¹H NMR (CDCl₃) (major isomer) δ = 6.96 (dd, J = 9.8 Hz, 2.6 Hz, 1H, vinyl-CH), 6.94 (dd, J = 9.3 Hz, 2.6 Hz, 1H, vinyl-CH), 6.87 (d, J = 9.6 Hz, 1H, vinyl-CH), 6.17 (dd, J = 9.6 Hz, 7.3 Hz, 1H, vinyl-CH), 6.0-6.08 (m, 2H, 2 vinyl-CH), 5.96 (dd, J = 9.3 Hz, 3.6 Hz, 1H, vinyl-CH), 5.77 (ddd, J = 11.9 Hz, 3.1 Hz, 1.0 Hz, 1H, vinyl-CH), 3.96 (m, 1H, alkyl-CH), 3.38 (m, 1H, alkyl-CH) ppm; resonances from the minor isomer could be detected at 6.89 (d, J = 9.7 Hz, 2H, vinyl-CH), 6.25 (dd, J = 9.7 Hz, 7.3 Hz, 2H, vinyl-CH), 6.13 (m, 2H, vinyl-CH), 6.00 (ddd, J = 12.0 Hz, 2.5 Hz, 1.0 Hz, 2H, vinyl-CH), 4.16 (br s, 2H, alkyl-CH) ppm; ¹³C NMR (CDCl₃) δ = 199.3 (br), 133.4 (major), 132.8 (major), 132.3 (major), 131.6 (minor), 130.8 (major), 130.5 (major), 130.2 (minor), 129.8 (minor), 129.6 (major), 127.7 (minor), 126.9 (major), 104.2, 86.4, 48.5 (minor), 46.7 (major) ppm; IR (neat, NaCl) ν = 3020, 2923, 2091, 2053, 2023 cm^{-1} ; MS (EI, 20 eV) m/e 638 (M - 4CO⁺), 610 (M - 5CO⁺), 582 (M - 6CO⁺), 554 (M - 7CO⁺), 526 (M - 8CO⁺), 498 (M - 9CO⁺), 470 (M - 10CO⁺), 442 (M - 11CO⁺), 414 (M - 12CO⁺); HRMS (TOF) m/e for C₂₆H₁₀Co₄O₁₂ calcd. (M⁺) 749.7500, found 749.7515.

(4E,6E)-1-(Trimethylsilylocta-4,6-dien-1-yn-3-ol (14): To a -75 °C solution of trimethylsilylacetylene (0.71 mL, 5 mmol) in diethyl ether (11 mL) was added MeLi (3.14 mL, 1.6 M solution in Et₂O, 5 mmol). After stirring for 1 h, sorbaldehyde (0.50 mL, 4.5 mmol) was added and the reaction stirred at -75 °C for 1 h. A saturated solution of NH₄Cl(aq) was added slowly, and the mixture was allowed to warm up to room temperature. A conventional extractive workup (Et₂O) gave a crude residue, which was taken on to subsequent steps without purification. In a separate run, the crude residue was subjected to flash column chromatography on neutralized silica (400:40:1 petroleum ether : Et₂O : Et₃N) afforded **14** (0.270 g, 31% yield); (**14**) ¹H NMR δ = 6.35 (dd, J = 10.5 Hz, 15.0 Hz, 1H), 6.07 (m, 1H), 5.80 (m, 1H), 5.64 (dd, J = 6.0 Hz, 15.0 Hz, 1H), 4.88 (d, J = 6.0 Hz, 1H), 1.78 (d, J = 6.5 Hz, 3H), 0.18 (s, 9H) ppm; resonances from minor isomers could be observed at 6.75 (m, 1H), 4.93 (d, J = 5.5 Hz, 1H), 1.92 (d, J = 6.5 Hz, 3H) ppm; ¹³C NMR δ = 132.6, 131.7, 130.2, 128.5, 104.5, 90.9, 63.2, 18.1, -0.2 ppm; IR (neat, KBr) ν = 3383, 3022, 2961, 2173, 1624, 1251 cm^{-1} ; MS (TOF) m/e 194 (M⁺); HRMS m/e for C₁₁H₈OSi calcd. (M⁺) 194.1127, found 194.1117.

(6E,8E)-Deca-1,6,8-trien-3-yn-5-ol (15): To a solution of unpurified **14** (ca. 0.5 g, ca. 2.5 mmol) in THF (15 mL) was added TBAF (7.5 mL of a 1M solution in THF, 7.5 mmol), and the mixture was stirred at room temperature for 1 h. Water was added and a conventional extractive workup (Et₂O) performed. The crude residue was dissolved in diethylamine (5 mL), vinyl bromide (3.9 mL of a 1.0 M solution in THF), Pd(PPh₃)₄ (0.039 g, 1 mol%) and CuI (0.030 g, 3 mol%) were added to the solution, and the mixture stirred under N₂ for 18 h. Saturated NH₄Cl(aq) was added, and a conventional extractive workup (Et₂O) was performed, to give a crude product as brown oil, which was carried on to the subsequent step. In a separate run, subjecting the crude residue to flash column chromatography on neutralized silica (400:40:1 petroleum ether : Et₂O : Et₃N) was accompanied with the formation of several new bands and loss of product; but gave a small amount of (**15**): (**15**) ¹H NMR δ = 6.36 (dd, J = 15.0 Hz, 11.0 Hz, 1H), 6.07 (dd, J = 14.0 Hz, 10.0 Hz, 1H), 5.80-5.83 (m, 2H), 5.67 (m, 2H), 5.51 (d, J = 11.0 Hz, 1H), 5.01 (d, J = 6.0 Hz, 1H), 1.90 (br, 1H), 1.77 (d, J = 6.5 Hz, 3H) ppm; resonances from minor isomers could be observed at 6.72 (m, 1H), 5.06 (d, J = 6.5, 1H) ppm; ¹³C NMR δ = 132.5, 131.9, 130.1, 128.5, 127.7, 116.5, 88.7, 84.7, 63.1, 18.2 ppm; IR (neat, KBr) ν = 3355, 3020, 2227, 1660, 1610 cm^{-1} ; MS (TOF) 148 (M⁺).

Hexacarbonyl[μ , η^4 -(6E,8E)-deca-1,6,8-trien-3-yn-5-ol]dicobalt (12): The crude mixture containing compound **15** was dissolved in CH₂Cl₂ and Co₂(CO)₈ (excess) was added to the solution. The mixture was stirred for 1 h, and subsequently concentrated under reduced pressure and subjected to flash column chromatography (5:1 petroleum ether : Et₂O) to give **12** (0.275 g, 14% yield from sorbaldehyde); (**12**) ¹H NMR δ = 6.83 (dd, J = 16.5 Hz, 10.0 Hz, 1H), 6.34 (dd, J = 15.0 Hz, 10.5 Hz, 1H), 6.04 (app dt, J = 10.5 Hz, 1.5 Hz, 1H), 5.79 (m, 1H), 5.65 (dd, J = 15.0 Hz, 10.5 Hz, 1H), 5.61 (dd, J = 16.5 Hz, 1.5 Hz, 1H), 5.50 (dd, J = 10.5 Hz, 1.5 Hz, 1H), 5.35 (app t, J = 5.5 Hz, 1H), 1.94 (d, J = 4.5 Hz, 1H), 1.77 (dd, J = 6.5 Hz, 1.3 Hz, 3H) ppm; resonances from minor isomers could be observed at 6.70 (dd, J = 15.1 Hz, 10.9 Hz, 1H), 6.28 (m, 1H), 5.51 (dd, J = 10.4 Hz, 1.6 Hz, 1H), 5.62 (dd, obscured, 1H), 5.42 (apparent t, J = 5.5 Hz, 1H), 1.99 (d, J = 4.7 Hz, 1H), 1.81 (dd, obscured, 3H) ppm; ¹³C NMR δ = 199.2, 133.4, 131.6, 131.5, 131.3, 130.2, 120.2, 101.1, 89.6, 73.1, 18.1 ppm; IR (neat, KBr) ν = 3449, 2928, 2856, 2092, 2053,

2023, 1859, 1628 cm⁻¹; MS (TOF) m/e 406 (M - CO⁺), 378 (M - 2CO⁺), 350 (M - 3CO⁺), 322 (M - 4CO⁺), 294 (M - 5CO⁺), 266 (M - 6CO⁺); HRMS (TOF) m/e for C₁₆H₁₂Co₂O₇ calcd. (M - CO⁺) 405.9298 found 405.9279.

Hexacarbonyl[μ,η⁴-(5E,7E)-9-methyldodeca-1,5,7,11-tetraen-3-yne]dicobalt (16a). To a solution of alcohol **12** (0.033 g, 0.076 mmol) and allyltrimethylsilane (40 μL, 0.25 mmol) in CH₂Cl₂ (5 mL) was added BF₃·OEt₂ (31 μL, 0.25 mmol) at 0 °C. The mixture was stirred for 0.5 h before the addition of saturated solution of NaHCO_{3(aq)}. Following a conventional extractive workup (CH₂Cl₂), subjecting the crude mixture to flash column chromatography (100% hexanes) gave **16a** (0.030 g, 85 % yield); (**16a**) ¹H NMR δ = 6.91 (dd, *J* = 16.0 Hz, 10.5 Hz, 1 H), 6.56–6.63 (m, 2H), 6.16 (dd, *J* = 15.5 Hz, 9.0 Hz, 1H), 5.73–5.83 (m, 2H), 5.62 (dd, *J* = 16.5 Hz, 1.5 Hz, 1 H), 5.49 (dd, *J* = 10.0 Hz, 1.5 Hz, 1H), 5.00–5.07 (m, 2 H), 2.31 (m, 1H), 2.14 (m, 1H), 2.08 (m, 1H), 1.04 (d, *J* = 6.5 Hz, 3H) ppm; resonances from minor isomers could be observed at 6.83 (dd, *J* = 16.4 Hz, 10.1 Hz, 1H), 6.47 (d, *J* = 15.1 Hz, 1H), 5.98–6.10 (3H), 5.56 (dd, *J* = 16.0 Hz, 1.5 Hz, 1H), 5.40–5.48 (m, 3H), 5.04–5.12 (m, 2H), 1.74 (d, *J* = 6.9 Hz, 3H), 1.70 (d, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR δ = 199.3, 142.2, 136.7, 136.2, 134.1, 128.4, 127.0, 119.7, 116.1, 91.6, 90.7, 41.0, 36.8, 19.5 ppm; resonances from minor isomers could be observed at 136.0, 134.0, 132.0, 130.7, 119.6, 116.9, 47.1, 41.4, 39.6, 18.1; IR (neat, KBr) ν = 2966, 2927, 2089, 2051, 2020, 1639 cm⁻¹; MS (TOF) m/e 458 (M⁺), 430 (M - CO⁺), 402 (M - 2CO⁺), 374 (M - 3CO⁺), 346 (M - 4CO⁺), 318 (M - 5CO⁺), 286 (M - 6CO⁺); HRMS (TOF) m/e for C₁₉H₁₆Co₂O₆ calcd. (M⁺) 457.9611 found 457.9612.

Under analogous conditions, a solution of alcohol **12** (0.037 g, 0.085 mmol), allyltriphenylsilane (0.0900 g, 0.299 mmol), and BF₃·OEt₂ (31 μL, 0.25 mmol) afforded **16a** (0.015 g, 38% yield).

Hexacarbonyl[μ,η⁴-(2-(3E,5E)-deca-3,5,9-trien-7-yn-2-yl)-5-methylthiophene]dicobalt (16b). To a solution of alcohol **12** (0.027 g, 0.062 mmol) and 2-methylthiophene (18 μL, 0.25 mmol) in CH₂Cl₂ (5 mL) was added BF₃·OEt₂ (26 μL, 0.18 mmol) at 0 °C. The mixture was stirred for 0.5 h before the addition of saturated solution of NaHCO_{3(aq)}. Following a conventional extractive workup (CH₂Cl₂), subjecting the crude mixture to flash column chromatography (100% hexanes) gave **16b** (0.020 g, 65% yield); (**16b**) ¹H NMR δ = 6.91 (dd, *J* = 16.6, 10.2, 1H), 6.58–6.68 (m, 4H), 6.22 (dd, *J* = 15.1 Hz, 9.9 Hz, 1H), 5.98 (dd, *J* = 15.1 Hz, 7.3 Hz, 1H), 5.63 (dd, *J* = 16.6 Hz, 1.4 Hz, 1H), 5.50 (dd, *J* = 10.1 Hz, 1.4 Hz, 1 H), 3.73 (m, 1H), 2.45 (s, 3H), 1.45 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR δ = 199.2, 146.6, 140.3, 137.8, 135.6, 134.0, 128.8, 128.1, 124.7, 122.9, 119.7, 91.6, 90.6, 38.3, 21.8, 15.3 ppm; IR (neat, KBr) ν = 2996, 2924, 2870, 2089, 2050, 2019, 1631 cm⁻¹; MS (TOF) m/e 514 (M), 486 (M - CO⁺), 458 (M - 2CO⁺), 430 (M - 3CO⁺), 402 (M - 4CO⁺), 374 (M - 5CO⁺), 346 (M - 6CO⁺); HRMS (TOF) m/e for C₂₁H₁₆Co₂O₆S calcd. (M⁺) 513.9332 found 513.9328

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Scheme and Figure Legends

Figure 1. Tropylium ion and dehydrotropylium-Co₂(CO)₆ ion (**1**).

Scheme 1. Preparation of cycloheptadienyol-Co₂(CO)₆ complex **7**. Yields in parentheses are based on recovered starting materials.

Figure 2. Contents of CD₂Cl₂ solutions of **7** + HBF₄-OEt₂.

Scheme 2. Nicholas reactions of **7** via **1**.

Scheme 3. Preparation of acyclic dienyne propargyl alcohol **12**.

Scheme 4. Nicholas reactions of **12** via cation **13**.

Scheme 5. Competition reactions between **7** and **12**.

Figure 3. Optimized structure of **1**. Selected bond lengths C1-C2 1.374 Å, C2-C3 = C7-C1 1.403 Å, C3-C4 = C6-C7 1.394 Å, C4-C5 = C5-C6 1.406 Å.

Scheme 6. Homodesmotic reactions for **1**.

Tables

Table 1. Condensation reactions of **7**.

Entry	Nu (N ^[a])	Product	Yield (%)	α -: γ -
1	1,3,5-trimethoxybenzene (3.40)	10a	88	100:0
2 ^[b]	1,3,5-trimethoxybenzene (3.40)	10a	54	100:0
3	2-methyltrimethylsilane (4.41)	10b	73	67:33
4	allyltrimethylsilane (1.79)	10c	70	83:17
5	methylcyclohexane (1.66)	10d	50	91:9

6	2-methylthiophene (1.26)	10e	83	100:0
7	thiophene ^[c] (-1.01)	10f	45	100:0

[a] Nucleophilicity N value. [b] Starting from **8**. [c] Using thiophene as solvent.

Table 2. Condensation reactions of dienyl cation precursor **12**.

Entry	Nu (N value)	Product	Yield (%)
1	allyltrimethylsilane (1.79)	16a	85
2	2-methylthiophene (1.26)	16b	65
3	3-methylanisole (0.13)	16c, 16c'	22, 17
4	allyltriphenylsilane (-0.13)	16a	37
5	thiophene (-1.01)	16d, 17	7, 45
6	Anisole (-1.18)	16e, 16e'	56, 4.5

Headline, and Entry for the Table of Contents

Aromatic, but only weakly

The dehydrotropylium- $\text{Co}_2(\text{CO})_6$ cation complex has been generated from the corresponding alcohol. Its reactivity in the presence of nucleophiles has been studied and its ^1H NMR spectrum acquired. The aromatic stabilization of this cation has been evaluated (competitive reaction with an acyclic analogue, and HOMA, NICS(1) homodesmotic reaction calculations); a weak aromaticity of approximately one quarter of that of tropylium ion is found.

Keywords: Aromatic compd. • Cycloalkynes • Carbocations • Propargylic compd. • Organometallic compd.