Synthetic and Theoretical Studies of Cyclobuta[1,2,3,4]dicyclopentene. Organocobalt Intermediates in the Construction of the Unsaturated Carbon Skeleton and Their Transformation into Novel Cobaltacyclic Complexes by C–C Insertion

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Theoretical and synthetic studies of the tricyclic 10π-electron hydrocarbon cyclobuta[1,2,3,4]dicyclopentene (1), a nominally aromatic structure that has never been synthesized, are described. Geometry optimization by density-functional-theory calculations (B3LYP/6-31G(d,p)) predict that 1 is a D2h symmetric structure with nonalternant C–C single and double bonds. The calculations also predict that 1 is 4.7 kcal/mol higher in energy than the isomeric hydrocarbon 1,6-didehydro-[10]annulene (2), a molecule known to isomerize to 1,5-didehydroanthracene (4) above −50 °C. Calculated enthalpic changes of homodesmotic reactions support the notion that 1 is an aromatic molecule with a resonance stabilization energy (RSE) about half to two-thirds that of benzene on a per-molecule basis. Investigations of potential synthetic pathways to 1 initially utilized as starting material the tricyclic carbonate 11, the product of an intramolecular [2 + 2]-photocyclization reaction. In these studies, 11 was transformed in several steps to the distannane 12, which upon treatment with boron fluoride ethyl etherate is believed to have formed the unstable hydrocarbon bicyclopentadienylidene (13). In an effort to avoid cleavage of the central, four-membered ring of unsaturated tricyclo[5.3.0.02,6]decane intermediates (perhaps the result of 10-electron electrocyclic ring opening of the tetraene 8), synthetic approaches to 1 employing cobalt–cyclobutadiene complexes 18 and 19 were pursued. Treatment of 18 with excess methylolithium led to the novel cobaltacyclic product 30, and dehydration of 19 in the presence of pyridine produced the ring-opening cobaltacyclic product 35. It is proposed that both processes may occur by a 10-electron electrocyclic ring-opening reaction of γ-organocobalt intermediates. These processes may be related to the hypothetical transformation of tetraene 8 to bicyclopentadienylidene (13).

Introduction
The synthesis of molecules with delocalized, planar \( \pi \)-systems and the study of the “aromatic” properties associated with these systems date to the very beginnings of organic chemistry as a discipline. Tricyclic 10\( \pi \) aromatic systems, exemplified by the hydrocarbon cyclobuta[1,2,3,4]dicyclopentene (1), are largely unknown, whereas bicyclic (naphthalene, azulene) and monocyclic (1,6-didehydro[10]annulene, 2) 3 10\( \pi \) aromatic systems have been well-studied (Figure 1).

More than 10 tricyclic 10\( \pi \) structures of formula C\( _{10} \)H\(_{6} \) can be envisioned (Figure 1). All are unknown in unsubstituted form; only the substituted benzoc[1,2,4,5]dicyclobutadiene 3 has been synthesized.\(^{45} \) Crystallographic analysis has shown that 3 has a planar structure of \( \text{D}_{2h} \) symmetry with carbon–carbon bond lengths of 1.40–1.47 Å along the 10-membered envelope ring and abnormally long carbon–carbon bonds of 1.54 Å at the two ring-fusion sites.\(^{4b} \)

Cyclobuta[1,2,3,4]dicyclopentene (1) and 1,6-didehydro-[10]annulene (2) are isomers. Formally, 1 can be derived from 2 by intramolecular [2 + 2]-cycloaddition, forming the central, four-membered ring of 1 by transannular bonding of opposing sp-hybridized carbons of 2. Transannular electronic repulsion between opposing sp-hybridized carbon atoms of 2 is felt to play a large role in the extraordinary thermal instability of 2 [the unimolecular

(2) For previous efforts towards the synthesis of 1 see: (a) Eaton, P. D. J. Am. Chem. Soc. 1962, 84, 2344. (b) Bister, H.-J.; Butenschoen, H. Synlett. 1992, 22.

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isomerization of 2 to 1,5-didehydro[10]naphthalene (4) occurs at \(-51^\circ\text{C}, t_{1/2} \sim 25\text{ min}\), eq 1. While extensively studied theoretically, neither 1 nor any substituted structure containing the tricyclic \(10\pi\) skeleton of 1 has been synthesized. Interesting and unresolved issues concerning the aromaticity of 1 (vide infra), its reactivity, and its thermal stability led us to undertake both experimental and theoretical studies in an effort to access and characterize structure 1; these studies ultimately leave open the question of whether 1 is capable of existing as an independent chemical entity.

**Theoretical Studies**

Although cyclobuta[1,2;3,4]dicyclopentene (1) has not been prepared in the laboratory, it has been the subject of several theoretical studies. Both Hückel\(^{5}\) and semiempirical molecular orbital methods\(^{6}\) were employed in studies seeking to determine if 1 is properly categorized as an aromatic molecule. Unfortunately, little consensus has emerged from the prior theoretical studies of 1. While some authors have concluded that 1 is an antiaromatic\(^{6a}\) or nonaromatic molecule,\(^{5c,d}\) another, using the SIINDO approximation method, categorized 1 as a “moderately aromatic” compound.\(^{6b}\) Given the limitations of the HMO method in predicting the aromaticity of hydrocarbons (in part, because it ignores electrostatic effects)\(^7\) and the difficulties associated with parametrization in semiempirical methods,\(^8\) it is perhaps not surprising that no clear picture of the aromatic properties of 1 has arisen from theoretical studies that have employed these methods.

To further explore the question of whether 1 should be characterized as an aromatic molecule and to estimate its heat of formation, we undertook theoretical studies using the Gaussian 98 suite of programs.\(^{9,10}\) In addition to structure 1, we investigated its isomer, 1,6-didehydro[10]annulene (2), as well as other related structures (vide infra). Molecular geometries were optimized with Becke’s three-parameter hybrid density-functional/Hartree–Fock method\(^{11}\) using the correlation functional of Lee, Yang, and Parr\(^{12}\) and the 6-31G(d,p) basis set (B3LYP/6-31G(d,p)). Frequency calculations were also conducted at this level of theory. In each case, the absence of imaginary frequencies confirmed that the structure we calculated was a local minimum.

Although our input geometry for 1 had \(C_2\)_\text{v} symmetry and a carbon skeleton with alternating C—C single and double bonds, the calculated structure was found to be planar with nonalternant bonds and \(D_{3h}\) symmetry, consistent with a delocalized \(10\pi\)-electron system (Figure 2). The calculated structure of 2 was also planar with nonalternant bonds and \(D_{3h}\) symmetry. The latter calculation is consistent with low-temperature solution NMR experiments, which provided evidence for a diamagnetic ring current in 2 and which led to the conclusion that 2 has “static or time-averaged \(D_{3h}\) symmetry” at \(-90^\circ\text{C}.\)\(^3\) Our calculations show that 1 is 4.7 kcal/mol higher in energy than 2, which is perhaps not surprising given the undoubtedly greater strain energy of 1 versus 2.

To provide an estimate of the resonance stabilization energy (RSE) of 1, we calculated the enthalpic changes.

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**References**

in Scheme 1, the calculated (B3LYP/6-31G(d,p)) enthalpic employed to estimate the RSE of benzene. As shown reasonable to conclude from these values that the RSE somewhat subjective exercise, we believe that it is reaction enthalpies to specific molecular features is a

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example, the homodesmotic reaction of eq 4, with an

SCHEME 1. B3LYP/6-31G(d,p) Calculated RSE of 1 Based on Enthalpic Changes (ΔH298) of Two Strain-Balanced Homodesmotic Reactions

of the strain-balanced homodesmotic reactions shown in eqs 2 and 3 (Scheme 1). Homodesmotic reactions are hypothetical transformations that maintain equal numbers and types of chemical bonds in reactants and products, but which differ in the connectivities between atoms. They provide a means to estimate deviations in measured heats of formation from values calculated by simple bond energy additivity methods, deviations which are then typically ascribed to some molecular feature such as RSE, strain energy, or the like. For example, the homodesmotic reaction of eq 4, with an enthalpic change of −30.5 kcal/mol, has been widely employed to estimate the RSE of benzene. As shown in Scheme 1, the calculated (B3LYP/6-31G(d,p)) enthalpic changes of eqs 2 and 3 are −19.5 and −17.6 kcal/mol, respectively. Although the attribution of homodesmotic reaction enthalpies to specific molecular features is a somewhat subjective exercise, we believe that it is reasonable to conclude from these values that the RSE of 1 is about half to two-thirds that of benzene on a per-atom basis. To summarize our theoretical studies of 1, both geometry optimization calculations and homodesmotic reaction enthalpies support the conclusion that 1 is a delocalized structure with significant aromatic character.

(14) The vibrational, translational, and rotational energies at 298 K were obtained from frequency calculations.

The vibrational, translational, and rotational energies at 298 K were obtained from frequency calculations.

FIGURE 2. B3LYP/6-31G(d,p)-optimized geometries of cyclodobuta[1,2,3,4]dicyclopentene (1) and 1,6-didehydro[10]annulene (2). Both structures were determined to be planar with nonalternant bonds and C2v symmetry.

SCHEME 2. Attempted Synthesis of 1 by Intramolecular [2 + 2]-Photocyclization of 2

SCHEME 3. Potential Synthetic Precursors to 1a

* Intermediate 9 is distinguished from compounds 6-8 by the hybridization of the carbon atoms of its central, four-membered ring.

Synthetic Studies

Our efforts to synthesize cyclodobuta[1,2,3,4]dicyclopentene (1) began with an investigation of the hypothetical photochemical transformation of 2 to 1, potentially a one-step synthesis of 1 from a known, albeit highly thermally unstable precursor. 1,6-Didehydro[10]annulene (2) was synthesized by the procedure we had previously reported, involving as a final step the low-temperature (−90 °C) dehydration of the alcohol 5 (Scheme 2). Frozen matrixes of 2 in dichloromethane-d2 (opaque) and methylcyclohexane-d14 (glass) in quartz NMR tubes were irradiated at −196 °C for 8 h and then were warmed to −90 °C, and the resulting cold solutions were analyzed by low-temperature (−90 °C) 1H NMR spectroscopy. Remarkably, 2 was found to be unchanged in these experiments. Further efforts to explore the photochemistry of 2 were complicated by the extremely facile unimolecular thermal rearrangement of 2 to 4 that occurred above −90 °C (eq 1). Failing this admittedly improbable but potentially direct synthesis of 1 from 2, our efforts were focused on the development of a multi-step synthetic route to 1 using different starting materials.

Retrosynthetic analysis of 1 at this point focused on the identification of molecules that might serve as immediate precursors to 1, a target of unknown stability, and the reactions by which these precursors might be transformed into 1. Four potential precursors were identified and are shown in Scheme 3. Because intermediates 6−8 were envisioned to arise from a closely related series of tricyclic precursors, we elected to pursue synthetic pathways to these intermediates first. However, each of the routes directed toward the synthesis of

(16) We note that according to our calculations the transformation of 2 to 1 is endergonic by 4.7 kcal/mol. If this is correct, then the conversion of 2 to 1 could only have occurred under photostationary conditions (cf. cyclobutene in the photochemical ring-closure of 1,3-butadiene).
of the expected hydrocarbon product 8 in a 10-electron electrocyclic ring-opening process (Scheme 4). Such a process would in part be driven by release of strain energy. After the fact, the facility of this (unproven) rearrangement reaction is perhaps not surprising. If correct, it immediately casts doubt upon the feasibility of our proposed route to 1 using 7 as a synthetic precursor. For this reason, this route was abandoned, as were routes involving 8 as a synthetic intermediate. Only routes involving the tricyclic intermediate 6 remain viable in the light of the proposed skeletal rearrangement; however, to date, we have been unable to produce 6 by any means we have examined. Double dehydration of 6 is felt to remain a feasible option for the synthesis of 1, should a route to 6 become available.

Because many of the complications that we encountered in our initial routes directed toward the synthesis of 1 were related to rehybridization of the carbon atoms of the central, four-membered ring, necessitating consideration of a fourth, organocobalt-based pathway (vide infra). The specific case of our attempted route to intermediate 8 (Scheme 4) shows the basic assembly of the carbon skeleton in this series and is instructive, in that it reveals what may be an underlying reactivity problem that could compromise many approaches to the synthesis of 1.

As shown in Scheme 4, intramolecular [2 + 2]-photocyclization of the carbonate 10, prepared by the dimerization of 1,2-cyclopentanedione with triphosgene, produced the tricyclic product 11, comprising the basic carbon skeleton of 1, albeit with a fully saturated four-membered ring. Although the yield of 11 in this two-step sequence was not high (42%), the process could be conducted on the gram scale and was indispensable in our early investigations of routes to intermediates 6–8.

Considerable effort was required to develop an effective series of refuctionalization reactions to transform 11 into the distannane 12, as detailed in Scheme 4. Many more direct approaches to 12 proved unsuccessful, revealing the idsynrhythmic nature of synthetic intermediates in this tricyclic series. Significantly, when the distannane 12 was exposed to boron fluoride ethyl etherate at −78 °C, 1H NMR spectral evidence suggested that bicyclopentadienyldiene (13) was produced, a result that could be explained by invoking the rearrangement of the central, four-membered ring.

SCHEME 4. Attempted Synthesis of 1, Leading Instead to Fragmentation of the Four-Membered Ring

![Scheme 4](image_url)

* Reagents and conditions: (a) triphosgene (0.62 equiv), pyridine (1.4 equiv), dichloromethane (CH₂Cl₂), 23 °C; (b) hν (medium pressure, quartz mercury lamp with a Pyrex immersion well), CH₂Cl₂, 23 °C, 42% (two steps); (c) sodium borohydride (3.2 equiv), ethanol, −10 °C; (d) trifluoromethanesulfonic anhydride (4.0 equiv), 2-chloropyridine (8.0 equiv), CH₂Cl₂, −60 °C, 57% (two steps); (e) benzeneselenol (3.0 equiv), cesium carbonate (3.7 equiv), N,N-dimethylformamide (DMF), 0 °C; (f) hydrogen peroxide (10 equiv), pyridine (5.8 equiv), CH₂Cl₂, 0 °C, 73 °C; (g) potassium carbonate (3.0 equiv), water–methanol (1:4), 23 °C, 77% (h) 2-methoxypropene (10 equiv), 10-camphorsulfonic acid (0.17 equiv), DMF, 0 °C; (l) 1,1,1-trifluoroacetaone (3.0 equiv), Oxone (5.0 equiv), sodium bicarbonate (11 equiv), water–acetonitrile (3:1), 0 °C, 88% (two steps); (i) lithium ethylamide (10 equiv), tetrahydrofuran (THF), 0 °C, 73%; (k) acetic anhydride (4.6 equiv), pyridine (9.3 equiv), 4-(dimethylamino)pyridine (0.21 equiv), pyridine (5.8 equiv), CH₂Cl₂, 0 °C, 88% (two steps); (m) boron fluoride ethyl etherate (2.2 equiv), CD₂Cl₂, 78 °C.


![Scheme 5](image_url)

SCHEME 5. Use of Metal–Cyclobutadiene Complexes as Precursors to Reactive Cyclobutadiene and Precedence for the Transannular Cyclization of Cycloalkadiynes To Form Cobalt–Cyclobutadiene Complexes

* Reagents and conditions: (a) triphosgene (0.62 equiv), pyridine (1.4 equiv), dichloromethane (CH₂Cl₂), 23 °C; (b) hν (medium pressure, quartz mercury lamp with a Pyrex immersion well), CH₂Cl₂, 23 °C, 42% (two steps); (c) sodium borohydride (3.2 equiv), ethanol, −10 °C; (d) trifluoromethanesulfonic anhydride (4.0 equiv), 2-chloropyridine (8.0 equiv), CH₂Cl₂, −60 °C, 57% (two steps); (e) benzeneselenol (3.0 equiv), cesium carbonate (3.7 equiv), N,N-dimethylformamide (DMF), 0 °C; (f) hydrogen peroxide (10 equiv), pyridine (5.8 equiv), CH₂Cl₂, 0 °C, 73 °C; (g) potassium carbonate (3.0 equiv), water–methanol (1:4), 23 °C, 77% (h) 2-methoxypropene (10 equiv), 10-camphorsulfonic acid (0.17 equiv), DMF, 0 °C; (l) 1,1,1-trifluoroacetaone (3.0 equiv), Oxone (5.0 equiv), sodium bicarbonate (11 equiv), water–acetonitrile (3:1), 0 °C, 88% (two steps); (i) lithium ethylamide (10 equiv), tetrahydrofuran (THF), 0 °C, 73%; (k) acetic anhydride (4.6 equiv), pyridine (9.3 equiv), 4-(dimethylamino)pyridine (0.21 equiv), pyridine (5.8 equiv), CH₂Cl₂, 0 °C, 88% (two steps); (m) boron fluoride ethyl etherate (2.2 equiv), CD₂Cl₂, 78 °C.
(C_2H_4)_2) (eq 7), as described by Gleiter et al.,\textsuperscript{20b} is especially noteworthy in the context of our synthetic problem.

To apply cobalt-based approaches to the synthesis of \(1\), we considered two closely related cobalt-cyclobutadiene complexes as potential precursors to \(1\), the diene \(18\), and the diene alcohol \(19\) (Scheme 6). Elimination of water from \(19\) was envisioned to produce the complex \(9\) as an intermediate, which we hypothesized might undergo decomplexation/ligand displacement to liberate \(1\). Alternatively, we imagined that the substrate \(18\) might undergo double deprotonation followed by two-electron oxidation to form \(9\). Both routes relied upon the formation of the intermediate \(9\), where it was anticipated that cobalt would effectively be coordinatively unsaturated and might therefore be susceptible to ligand replacement.

As we will show, evidence suggests that, upon dehydration, the substrate \(19\) does form \(9\) or a closely related intermediate, but an unexpected metal-insertion process intercedes, one perhaps related to the putative transformation of tetracene \(8\) to bicyclopentadienylidene (\(13\)) (vide infra). Formation of a similar metal-insertion product was also observed upon double deprotonation of \(18\), as will be discussed in detail.

The brown-orange diene cobalt-cyclobutadiene complex \(18\) was synthesized by the route outlined in Scheme 7. The first three steps of the route, leading to the known cyclodecadiyne diol \(20\), were adapted from literature procedures. The reaction of 1,5-cyclooctadiene with excess dibromocarbene was conducted according to the original Skattebøl protocol.\textsuperscript{21} The highly insoluble gem-dibromo-cyclopropanes formed in this reaction (\(21\)) were then subjected to solvolytic ring-expansion using silver tetrafluoroborate (in lieu of silver perchlorate)\textsuperscript{22a} in aqueous acetone to furnish the 10-membered ring diol dibromide \(22\), in 36% yield after crystallization from acetonitrile. The structure of the product \(22\) was confirmed by X-ray analysis. Although dehydrobromination of a diol-protected form of \(22\) by literature methods (potassium tert-butoxide, DMSO)\textsuperscript{22b} was not successful, the desired transformation could be achieved by stirring \(22\) with sodium hydride in a 1:1 mixture of THF and DMF at 23 °C (90% yield).\textsuperscript{23} Oxidation of \(20\) with 2.3 equiv of the (21) Skattebøl, L. Acta Chem. Scand. 1963, 17, 1683.
This crystalline cobalt complex was found to be somewhat sensitive to both acid and oxygen but, with appropriate precautions, proved to be a suitable intermediate for two different approaches to the target complex 9.

Having developed a viable route to the diene cyclobuta[1,2:3,4]dicyclopentene—cobalt complex 18, we next investigated its deprotonation in the presence of various strong bases, with the goal of forming a doubly deprotonated species for subsequent two-electron oxidation to form 9, as proposed in Scheme 6. We found that 18 rapidly formed the monoanion 28 at −78 °C in the presence of n-butyllithium or tert-butyllithium as base, whereas deprotonation to form 28 using methylthium (MeLi), a weaker base, did not occur at −78 °C, but did proceed smoothly at −30 °C (Scheme 8). Evidence that the monoanion 28 was formed in these deprotonation reactions was obtained in two different types of quenching experiments, as well as in direct NMR studies. Sequential addition of hexamethylphosphoramide (HMPA) (5.0 equiv) and TBSOTf (1.7 equiv) to a solution of the monoanion 28 at −78 °C led to the formation of a 2.5:1 mixture of the two regioisomeric allyl silanes 29 arising from trapping of the allyl anion 28 on its exo-face (the anion 28 was unreactive in the absence of HMPA). Trapping of the monoanion 28 with a proton source (HMPA was not required) produced a mixture of 18 and the regioisomeric diene. More direct evidence for the formation of 28 was obtained by NMR spectroscopic analysis (1H, 13C, HMQC) of the product obtained upon treatment of 18 with MeLi in THF-d8 at −30 °C. Proton spectra of 28 were invariant over the temperature range from −78 to 22 °C, and both proton and carbon spectra were indicative of a delocalized π-allyl anion species, as represented in structure 28. In particular, 1H NMR chemical shifts for H3, H4, and H5 were 4.60, 6.60, and 4.67 ppm, respectively, while 13C NMR chemical shifts for C3, C4, and C5 were 81.3, 124.0, and 82.0 ppm, respectively (the assignments were unambiguously determined by HMQC experiments). Also, when the mixture of the diene 18 and its regioisomer was deprotonated with MeLi in THF-d8, 1H NMR analysis showed that the monoanion 28 had been cleanly regenerated.

Although monodeprotonation of 18 with alkyllithium reagents was facile, further reaction of the monoanion (28) with alkyllithium bases required more forcing conditions. Whereas 28 was found to be inert to alkyllithium reagents in THF below 0 °C, at 23 °C in the presence of excess MeLi (other alkyllithium reagents are known to deprotonate the solvent at this temperature) 28 was observed (1H NMR analysis) to react slowly to form a new species. Extensive NMR characterization (1H, 13C, HMOC, HMQC, NOESY1D) of the product formed led us to the conclusion that it was not the dianion arising from direct deprotonation of 18 toward oxygen. An unresolved issue concerning structure 30 is a fluxional behavior that is apparent from the broadness of its proton peaks at 22 °C, whereas, at −78 °C, two well-resolved sets of peaks are observed in a ratio of 1:1.7. Addition of HMPO (5.9 equiv) to a cold (−78 °C) solution of 30 causes these peaks to merge to form a single set of sharp peaks. We suggest that these data may reflect structural differences associated with the position of the lithium cations in 30 and/or differences in aggregation state.

When the monolithiated species 28 was deprotonated in the presence of trimethylphosphine (PMMe₃, ca. 20 equiv), a different cobaltacyclic product was formed, assigned as structure 31 (Scheme 9). This assignment followed from a series of spectroscopic experiments that are closely paralleled by those described above for the determination of structure 30. Although not visible in the 13C NMR spectrum (due to a large heteronuclear coupling to the phosphorus atom of the PMMe₃ ligand), the carbon resonance of the cobalt-bound carbon of the cyclopentadienide ligand (C1) was unambiguously located by an HMBC spectroscopic experiment; its chemical shift (109.0 ppm) is clearly inconsistent with the presence of a cobalt-cyclobutadiene complex, but they do support the proposed cobaltacyclic structure 30. The NMR chemical shift data are in good agreement with corresponding values in lithium cyclopentadienide, for example. Additional evidence in support of the structure 30 was obtained in NOESY1D experiments; irradiation of protons of the Cp⁺ ligand led to a significant NOE (7.3%) of H2, but not of H3 nor of H4. This same experiment also induced a large NOE of protons assigned to the cobalt-bound methyl group (9.3%, δ −1.21 ppm). The latter assignment was confirmed when the transformation of 18 to 30 was conducted using MeLi-d₄; the assigned peak (δ −1.21 ppm) was absent in the product spectrum. This result also confirmed that the cobalt-bound methyl group originated from the base used in the deprotonation reaction. All efforts to crystallize the product 30 were unsuccessful, largely due to the extraordinary instability of 30 toward oxygen.

29 Several related cobaltacyclic structures have been reported where the cobalt-bound quaternary carbons are strongly deshielded.

(30) Lithium cyclopentadienide was purchased from Strem Chemical Co., and its 1H and 13C NMR spectra were measured: 1H NMR (500 MHz, THF-d₈) δ 5.66 (s, 5H); 13C NMR (125 MHz, THF-d₈) δ 103.42 (SC).
ligand in a NOESY 1D experiment, leading to significant NOEs of H2 (4.3%) and the protons of the PMe 3 group (9.0%).

As an alternative pathway to the cobalt complex 9, the proposed precursor to 1, we pursued a different strategy involving dehydration of the cobalt – cyclobutadiene complex 19, as presented in Scheme 6. We initially attempted to prepare 19 by cobalt-induced transannular cyclization of hydroxyl-protected forms of the known alcohol 5 (the precursor to 1,6-didehydro[10]annulene (2), Scheme 2); however, treatment of these substrates with Cp*Co(C2H4)2 produced only naphthalene. Ultimately, we were able to hydroxylate the monoanion 28 from our initial route to 9 to access the desired substrate 19 (Scheme 10).

To achieve this, it was necessary to use a highly reactive form of the monoanion 28, obtained by the addition of both HMPA and 12-crown-4 to a solution of 28 in DME; addition of (±)-trans-2-(phenylsulfonyl)-3-phenyloxaziridine to the resulting complex afforded a ~1:1 mixture of the two possible diastereomeric alcohols arising from exo-face addition of the oxygen electrophile to the α-allyl anion (19, 44% yield).31

Although the diastereomers 19 could be separated by repeated column chromatography on silica gel, this proved to be unnecessary, for both isomers transformed identically under subsequent conditions of dehydration. These involved the sequential addition of Et3N (4.0 equiv) and Tf2O (2.0 equiv) to a cold (~78 °C) solution of 19 in CD2Cl2 (Scheme 10). Low-temperature 1H NMR analysis (~78 °C) of the product solution suggested that a 1:2:1 mixture of the two exo-oriented triethylammonium salts 34 had been formed. Addition of pyridine to the product mixture at ~78 °C and warming of the resulting solution to ~50 °C led to the formation of a new product, proposed to be the cobaltacyclic complex 35 on the basis of low-temperature (~78 °C) NMR analysis (Scheme 10).32 This same product was formed when 19 was treated with the Martin sulfurane reagent in the presence of pyridine at ~78 °C, albeit less cleanly. Although stable for extended periods of time at ~78 °C, the product 35 was observed to decompose slowly at ~10 °C. Selected data from an extensive series of low-temperature (~78 °C) NMR experiments (1H, 13C, HMBC, NOESY 1D) by which we characterized 35 are proton chemical shifts of δ 6.80, 6.86, and 6.16 ppm for H2, H3, and H4, respectively, and scalar couplings of J = 5.0 Hz between H3 and H4, and of J ~ 0 Hz between H2 and H3. The coupling constants are consistent with the localization of C–C double and single bonds proposed in the assigned structure 35.32

It is interesting to note that the reaction of the trianionic cobaltacyclic complex 30 (produced as an intermediate in the previous cobalt-based route) with 1,2-dibromoethane–d4 afforded the cobaltacyclic complex 36, structurally related to 35, in a net two-electron oxidation of the dicyclopentadienide framework (Scheme 11). Like the complex 35, 36 exhibited 1H–1H coupling constants that were consistent with the localization of C–C double and single bonds as shown. However, the chemical shift values for the two complexes varied (see Figure 4 for details) in a manner attributable to overall charge differences (35 is a neutral complex, whereas 36 is anionic) and to anisotropic effects of the pyridine ligand in 35. Like 35, the complex 36 was found to be temperature sensitive and readily decomposed above ~30 °C.

The process most closely related to our findings of which we are aware is the observation by J ones and coworkers that Cp*Co(C2H4)2 inserts into the C–C bond of biphenylene to form the dicobalt complex 37; further heating of 37 in the presence of PMe3 forms the cobaltacyclic complex 38, which is closely analogous to the dicyclopentadienide complex 31 we prepared (Scheme 12).32c,d Somewhat related cobaltacyclic products have also been reported to arise by cobalt(I)-induced dimerization of alkynes.32c,d

It is fascinating to consider that two fundamentally distinct synthetic approaches to the desired cobalt-

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containing precursor to 1 (complex 9) led instead to the formation of closely related cobaltacyclic products wherein cobalt formally inserted into a C–C bond of the central, four-membered ring. Mechanistically, the processes may be related and, we suggest, may also relate to the putative rearrangement of the hydrocarbon 8 to bicyclopentadienylidene (13), discussed above. Side-by-side comparisons of our mechanistic proposals are presented in Scheme 13. As shown, elimination within the complex 34 is proposed to lead to the desired cobalt complex 9 as an intermediate, but rearrangement of this complex, a process that we view as a 10-electron electrocyclic ring-opening reaction (cf. 8 → 13), occurs instead, forming ultimately the pyridine-containing complex 35. Attempts to divert the course of this reaction by the incorporation of ethylene or cyclopropane into the reaction mixture had no effect on the reaction outcome.33 The transformation of the putative dianion 32 (Schemes 9 and 13) to the cobaltacyclic complexes 30 and 31 could follow a related pathway if a transient π*-species such as 33 were formed (33 is an 18-electron complex that is formally related to 9 by the addition of two electrons), but other pathways to cobaltacyclic products from 32 can also be envisioned. Although the possibility that anionic or neutral reaction pathways to cobaltacyclic products (Schemes 9 and 10) had formed 1 reversibly in solution cannot be ruled out, this is considered unlikely at present.

**Conclusion**

Our theoretical studies of cyclobuta[1,2;3,4]dicyclopentene (1) suggest that 1 is a D_{2h} symmetric structure with nonalternant C–C single and double bonds, and is 4.7 kcal/mol higher in energy than the isomeric hydrocarbon 1,6-didehydro[10]annulene (2). Calculations of enthalpic changes of homodesmotic reactions support the conclusion that 1 is an aromatic molecule, that is, that the π-system of 1 is substantially stabilized by electron delocalization. Our ultimate goals of synthesizing 1 and studying its properties remain elusive. The various synthetic approaches to 1 that we pursued, both cobalt-based and non-cobalt-based, met with unexpected ring-opening reactions of the central, four-membered ring of molecules comprising the tricyclic skeleton of 1. Our studies of these fragmentations in the cobalt-based routes led us to discover novel pathways to the formation of cobaltacyclic products from cobalt-cyclobutadiene complexes. It is proposed that these transformations may take place by a novel 10-electron electrocyclic ring-opening process, which may also relate to the putative transformation of the tetraene 8 to bicyclopentadienylidene (13) (Scheme 4).

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Studies of Cyclobuta[1,2:3,4]dicyclopentene

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Supporting Information Available: Experimental procedures, characterization of the products, and X-ray data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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