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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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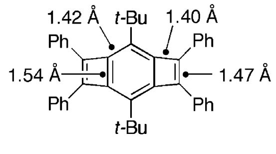
Theoretical and synthetic studies of the tricyclic 10π-electron hydrocarbon cyclobuta[1,2:3,4]-dicyclopentene (**1**), a nominally aromatic structure that has never been synthesized, are described. Geometry optimization by density-functional-theory calculations (B3LYP/6-31G(d,p)) predict that **1** is a D_{2h} 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-didehydronaphthalene (**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[5.3.0.0^{2,6}]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 methyllithium 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 η^2-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 π-systems and the study of the "aromatic" properties associated with these systems date to the very beginnings of organic chemistry as a discipline.[1] Tricyclic 10π aromatic systems, exemplified by the hydrocarbon cyclobuta[1,2:3,4]dicyclopentene ($C_{10}H_6$, **1**), are largely unknown,[2] whereas bicyclic (naphthalene, azulene) and monocyclic (1,6-didehydro[10]annulene, **2**)[3] 10π aromatic systems have been well-studied (Figure 1).

More than 10 tricyclic 10π structures of formula $C_{10}H_6$ can be envisioned (Figure 1). All are unknown in unsubstituted form; only the substituted benzo[1,2:4,5]dicyclobutadiene **3** has been synthesized.[4a] Crystallographic analysis has shown that **3** has a planar structure of 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]



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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

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(1) Garratt, P. J. *Aromaticity*; John Wiley & Sons: New York, 1986; and references therein.

(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.; Butenschön, H. *Synlett.* **1992**, 22.

(3) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 10986.

(4) Synthesis of **3**: (a) Toda, F.; Ohi, M. *J. Chem. Soc., Chem. Commun.* **1975**, 506. Crystal structure of **3**: (b) Boese, R.; Benet-Buchholz, J.; Stranger, A.; Tanaka, K.; Toda, F. *J. Chem. Soc., Chem. Commun.* **1999**, 319.

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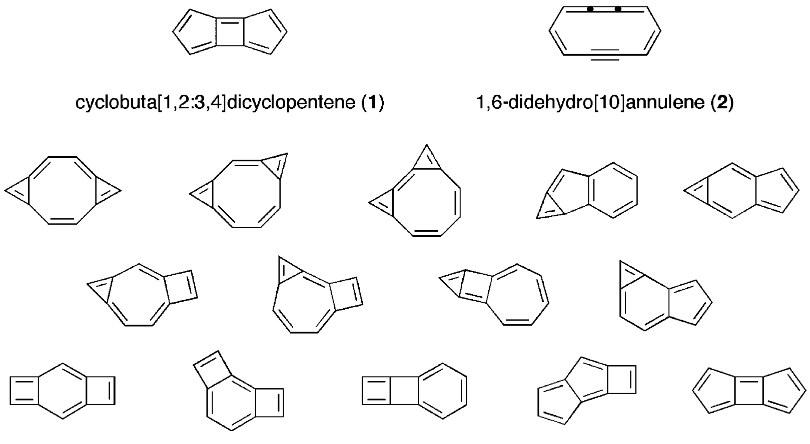
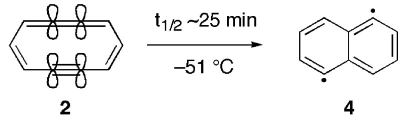


FIGURE 1. Cyclobuta[1,2:3,4]dicyclopentene (**1**), 1,6-didehydro[10]annulene (**2**), and tricyclic, 10π structures of formula $C_{10}H_6$.

isomerization of **2** to 1,5-didehydronaphthalene (**4**) occurs at −51 °C, $t_{1/2}$ ~25 min, eq 1]. While extensively studied theoretically, neither **1** nor any substituted structure containing the tricyclic 10π 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.



(1)

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[5] or nonaromatic molecule,[6a,c−e] another, using the SINDO 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_{2v} symmetry and a carbon skeleton with alternant C−C single and double bonds, the calculated structure was found to be planar with nonalternant bonds and D_{2h} symmetry, consistent with a delocalized 10π-electron system (Figure 2). The calculated structure of **2** was also planar with nonalternant bonds and D_{2h} 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_{2h} symmetry" at −90 °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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[5] (a) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371. (b) Gastmans, J. P.; Ferraz, M. H. M. *Tetrahedron* **1977**, *33*, 2205. (c) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1971**, *36*, 3418.

[6] (a) Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455. (b) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344. (c) Toyota, A. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1152. (d) Nakajima, T. *Pure Appl. Chem.* **1971**, *28*, 219. (e) Dewar, M. J. S.; Trinajastic, N. *Tetrahedron Lett.* **1967**, *8*, 3121.

[7] Borden, W. T. *Modern Molecular Orbital Theory for Organic Chemists*; Prentice-Hall: Englewood Cliffs, NJ, 1975; Chapter 5.

[8] Anh, N. T.; Frison, G.; Solladie-Cavallo, A.; Metzner, P. *Tetrahedron* **1998**, *54*, 12841.

[9] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennuci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malik, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98;* Gaussian, Inc.: Pittsburgh, PA, 1998.

[10] For an alternative calculation method for the determination of aromaticity (NICS), see: Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.

[11] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[12] Lee, C.; Yang, G.; Parr, R. G.; *Phys. Rev. B* **1988**, *37*, 785.

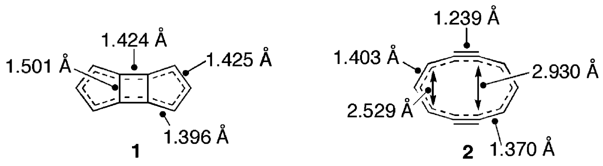
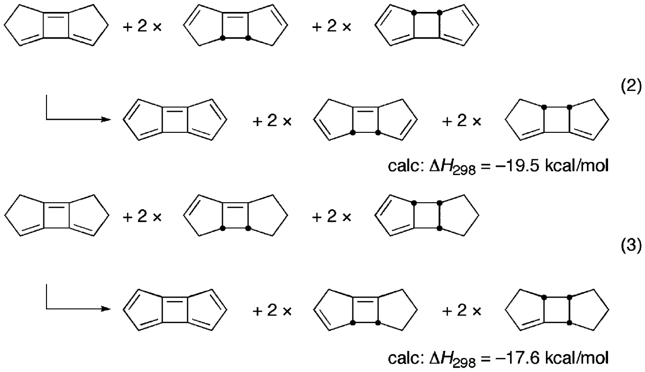
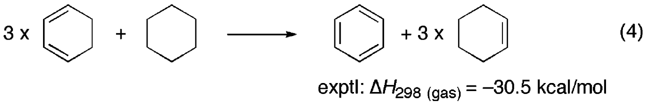


FIGURE 2. B3LYP/6-31G(d,p)-optimized geometries of cyclobuta[1,2:3,4]dicyclopentene (**1**) and 1,6-didehydro[10]annulene (**2**). Both structures were determined to be planar with nonalternant bonds and D_{2h} symmetry.

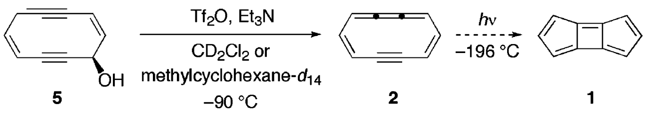
SCHEME 1. B3LYP/6-31G(d,p) Calculated RSE of 1 Based on Enthalpic Changes (ΔH_{298}) of Two Strain-Balanced Homodesmotic Reactions



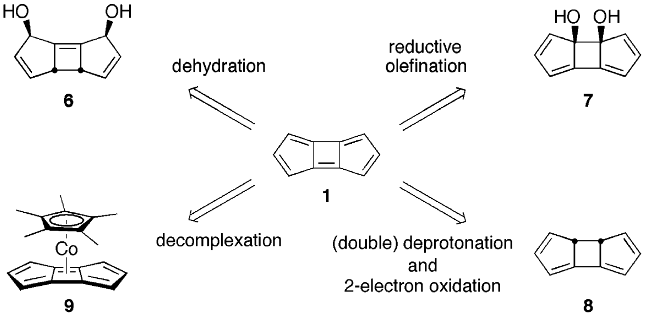
of the strain-balanced homodesmotic reactions shown in eqs 2 and 3 (Scheme 1). Homodesmotic reactions are hypothetical transformations that maintain equal numbers and types of chemical bonds in reactants and products, but which differ in the connectivities between atoms.[13a] They provide a means to 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.[13b] 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.[14] 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-molecule 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.



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



SCHEME 3. Potential Synthetic Precursors to 1[a]



[a] 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 cyclobuta[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,[3] involving as a final step the low-temperature (−90 °C) dehydration of the alcohol **5** (Scheme 2). Frozen matrixes of **2** in dichloromethane-d_2 (opaque) and methylcyclohexane-d_{14} (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) ^{1}H NMR spectroscopy.[15] 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**,[16] our efforts were focused on the development of a multistep 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

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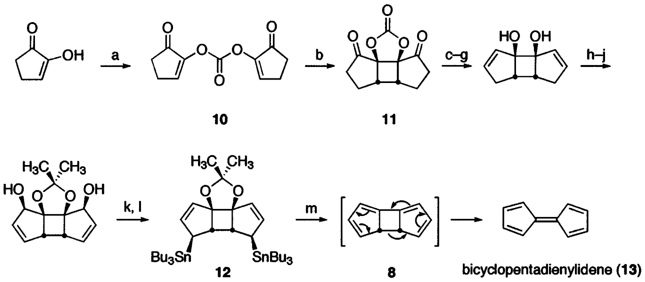
[13] (a) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. (b) Ponomarev, P. A.; Takhistov, V. V. *J. Chem. Educ.* **1997**, *74*, 201.

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

[15] Arvedson, S. P. M.S. Thesis, California Institute of Technology, Pasadena, CA, 1997.

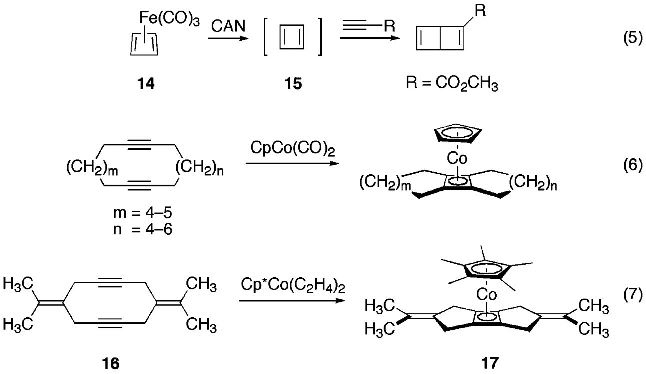
[16] We note that according to our calculations the transformation of **2** to **1** is endergonic by 4.7 kcal/mol. If this is correct, then the conversion of **2** to **1** could only have occurred under photostationary conditions (cf. cyclobutene in the photochemical ring-closure of 1,3-butadiene).

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



[a] Reagents and conditions: (a) triphosgene (0.62 equiv), pyridine (1.4 equiv), dichloromethane (CH_2Cl_2), 23 °C; (b) *hν* (medium pressure, quartz mercury lamp with a Pyrex immersion well), CH_2Cl_2, 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), CH_2Cl_2, −60 → 0 °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), CH_2Cl_2, 0 → 23 °C, 78% (two steps); (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; (i) 1,1,1-trifluoroacetone (3.0 equiv), Oxone (5.0 equiv), sodium bicarbonate (11 equiv), water−acetonitrile (3:1), 0 °C, 88% (two steps); (j) lithium diethylamide (10 equiv), tetrahydrofuran (THF), 0 → 23 °C, 60%; (k) acetic anhydride (4.6 equiv), pyridine (9.3 equiv), 4-(dimethylamino)pyridine (0.21 equiv), CH_2Cl_2, 23 °C, 98 %; (l) *n*-butyllithium (5.2 equiv), copper cyanide (2.6 equiv), tri-*n*-butyltin hydride (5.2 equiv), ethyl ether, −78 °C, 52%; (m) boron fluoride ethyl etherate (2.2 equiv), CD_2Cl_2, −78 °C.

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



intermediates in this series suffered from difficulties associated with the 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 refunctionalization reactions to transform **11** into the distannane **12**, as detailed in Scheme 4. Many more direct approaches to **12** proved unsuccessful, revealing the idiosyncratic 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 bicyclopentadienylidene (**13**) was produced,[17] a result that could be explained by invoking the rearrangement 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 (e.g., **12** → **8**), an alternative synthetic strategy was pursued where these carbons were introduced as part of a metal−cyclobutadiene complex. Metal−cyclobutadiene complexes have been widely used as precursors to reactive cyclobutadienes, as first demonstrated by Pettit and co-workers, who showed that the stable transition-metal complex (tricarbonyl)(η^4-cyclobutadiene)iron (**14**) produced free cyclobutadiene (**15**) upon oxidative decomplexation in the presence of ceric ammonium nitrate (eq 5, Scheme 5).[18] Metal−cyclobutadiene complexes can be prepared by metal-induced dimerization of alkynes,[19] and there is extensive precedence establishing the feasibility of cobalt-induced transannular cyclizations of cycloalkadiyne substrates (10−15-membered rings) as a means of forming tricyclic products containing a central metal−cyclobutadiene complex (eqs 6 and 7, Scheme 5).[20] The preparation of the tricyclic cobalt complex **17** from the reaction of 4,9-diisopropylidene-1,6-cyclodecadiyne (**16**) and bis(ethylene)(η^{5-}pentamethylcyclopentadienyl)cobalt (Cp*Co-

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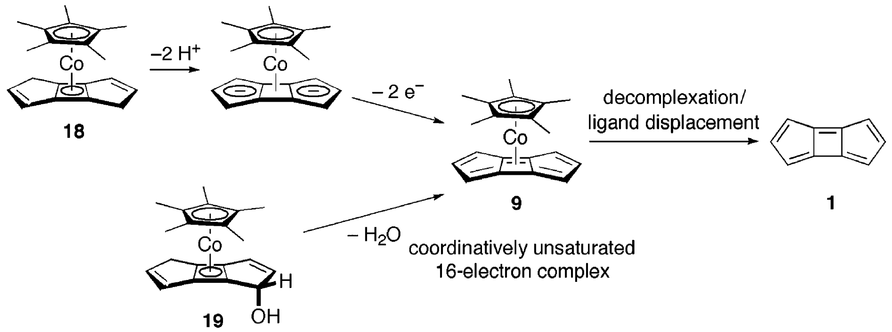
[17] Synthesis of bicyclopentadienylidene (**13**): (a) Escher, A.; Ritsch, W.; Neuschwander, M. *Helv. Chim. Acta* **1986**, *69*, 1644. NMR spectroscopic data of **13**: (b) *Helv. Chim. Acta* **1986**, *69*, 1052.

[18] Wutts, L.; Fitzpatrick, J. D.; Pettit, R.; *J. Am. Chem. Soc.* **1965**, *87*, 3253.

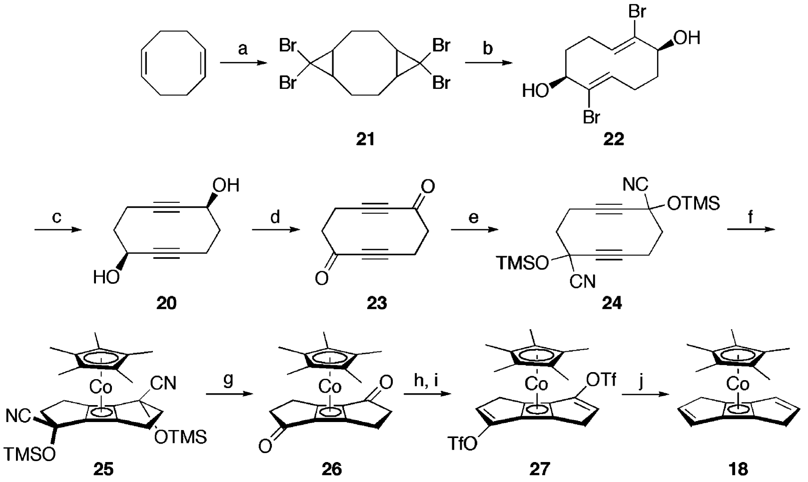
[19] Review on metal-cyclobutadiene complexes: Efraty, A. *Chem. Rev.* **1977**, *77*, 691.

[20] (a) King, R. B.; Efraty, A.; *J. Am. Chem. Soc.* **1970**, *92*, 6071; **1972**, *94*, 3021. (b) Gleiter, R.; Merger, M.; Irgartinger, H.; Nuber, B. *J. Org. Chem.* **1993**, *58*, 2025.

SCHEME 6. Two Proposed Pathways for the Formation of 9



SCHEME 7. Synthesis of 18[a]



[a] Reagents and conditions: (a) bromoform (2.1 equiv), potassium *tert*-butoxide (2.5 equiv), *n*-hexane, 0 → 23 °C, 43%; (b) silver tetrafluoroborate (3.0 equiv), acetone−water (4:1), 23 °C, 36%; (c) sodium hydride (10 equiv), THF−DMF (1:1), 23 °C, 90%; (d) Dess−Martin periodinane (2.3 equiv), CH_2Cl_2, 23 °C, 82%; (e) trimethylsilyl cyanide (3.0 equiv), zinc iodide (0.2 equiv), CH_2Cl_2, 0 → 23 °C; (f) $Cp^*Co(C_2H_4)_2$ (1.0 equiv), *n*-hexane, 60 °C; (g) tetra-*n*-butylammonium fluoride (2.4 equiv), THF, 0 °C, 79% (three steps); (h) *tert*-butyldimethylsilyl trifluromethanesulfonate (TBSOTf, 2.4 equiv), 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (3.0 equiv), CH_2Cl_2, −78 °C; (i) cesium fluoride (8.0 equiv), *N*-phenyltrifluoromethanesulfonimide (3.4 equiv), 1,2-dimethoxyethane (DME), 23 °C, 63% (two steps); (j) tetrakis(triphenylphosphine)palladium(0) (0.4 equiv), tri-*n*-butyltin hydride (2.0 equiv), lithium chloride (10 equiv), THF, 60 °C, 65%.

$(C_2H_4)_2$) (eq 7), as described by Gleiter et al.,[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 tetraene **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.[21] The highly insoluble *gem*-dibromocyclopropanes formed in this reaction (**21**) were then subjected to solvolytic ring-expansion using silver tetrafluoroborate (in lieu of silver perchlorate)[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)[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).[23] Oxidation of **20** with 2.3 equiv of the

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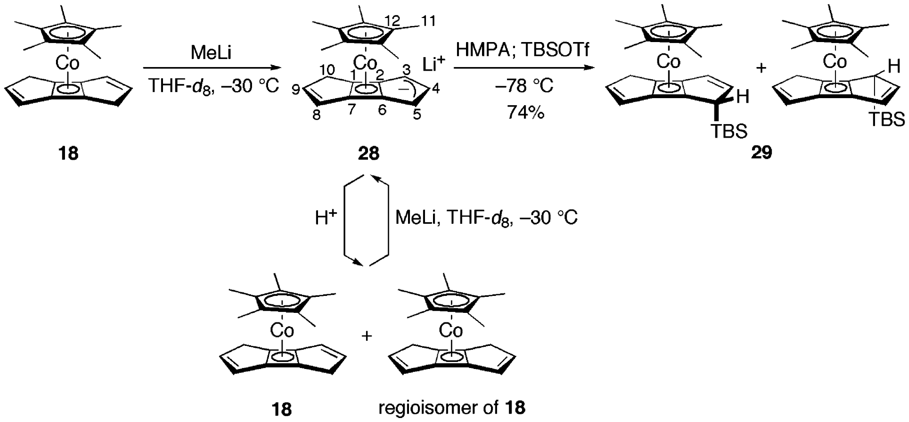
(21) Skattebøl, L. *Acta Chem. Scand.* **1963**, *17*, 1683.

(22) (a) Reese, C. B.; Shaw, A. *J. Chem. Soc., Perkins I* **1975**, 2422. (b) *J. Chem. Soc., Perkins I* **1976**, 890.

(23) Lütjens, H.; Nowotny, S.; Knochel, P. *Tetrahedron: Asymmetry* **1995**, *6*, 2675.

SCHEME 8. Deprotonation of 18 To Form 28 and Its Trapping with Electrophiles



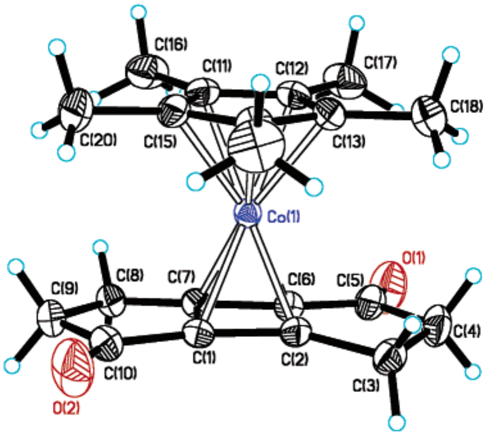


FIGURE 3. Thermal ellipsoid drawing of the dione cyclobutadiene–cobalt complex **26**, showing the ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Co(1)–C(1), 1.99; Co(1)–C(11), 2.07; C(1)–C(2), 1.47; C(2)–C(6), 1.44; C(11)–C(12), 1.43; Co(1)–Cp*, 1.87; Co(1)–(cyclobutadiene), 1.66; C(7)–C(1)–C(2), 90.5; C(6)–C(2)–C(1), 89.5; C(15)–C(11)–C(12)–C(13), −1.3; C(7)–C(1)–C(2)–C(6), −2.9; C(10)–C(1)–C(2)–C(6), −177.9; C(1)–C(2)–C(6)–C(5), −176.0; Cp*–(cyclobutadiene), 3.4.

Dess–Martin periodinane afforded the light-sensitive, crystalline diketone **23**, in 82% yield.[24] The carbonyl groups of **23** were temporarily masked as the corresponding trimethylsilyl cyanohydrins (TMSCN, 3.0 equiv; zinc iodide, 0.2 equiv),[25] and the resulting mixture of the diastereomeric trimethylsilyl cyanohydrins **24** was allowed to react with Cp*Co(C_2H_4)$_2$ (1.0 equiv) at 60 °C. Direct subjection of the cobalt complexes (**25**) to tetra-*n*-butylammonium fluoride furnished the highly crystalline, bright orange dione cobalt–cyclobutadiene complex **26** in 79% yield for the three steps. The structure of this product was established unequivocally by X-ray analysis (Figure 3). To transform the dione **26** to the diene **18**, it was necessary to employ a two-step procedure for enol triflate formation (63% yield) that involved as a second step the recent Corey protocol for enol triflate formation from *tert*-butyldimethylsilyl enol ethers.[26] Palladium-catalyzed reduction of the resulting bistriflate **27** with tri-*n*-butyltin hydride then provided **18** in 65% yield.[27] 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 cyclobutadiene–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 methyllithium (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 hexamethylphosphoric triamide (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 (^{1}H, ^{13}C, HMQC) of the product obtained upon treatment of **18** with MeLi in THF-d_8 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, ^{1}H NMR chemical shifts for H3, H4, and H5 were δ 4.60, 6.60, and 4.67 ppm, respectively, while ^{13}C NMR chemical shifts for C3, C4, and C5 were δ 81.3, 124.0, and 82.0 ppm, respectively (the assignments were unambiguously determined by HMQC experiments).[28] Also, when the mixture of the diene **18** and its regioisomer was deprotonated with MeLi in THF-d_8, ^{1}H NMR analysis showed that the monoanion **28** had been cleanly regenerated.

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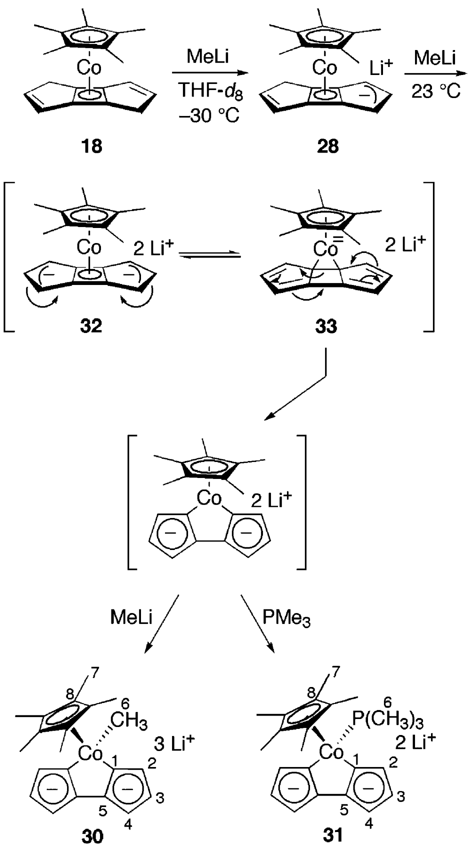
(24) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.

(25) (a) Higuchi, K.; Onaka, M.; Izumi, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1035. (b) Gassman, P. G.; Talley, J. J. *Org. Synth.* **1980**, *60*, 14.

(26) Mi, Y.; Schreiber, J. V.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *120*, 11290.

(27) Yamamoto, K.; Heathcock, C. H. *Org. Lett.* **2000**, *2*, 1709.

SCHEME 9. Proposed Mechanism of Formation of 30 and 31



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 (^{1}H NMR analysis) to react slowly to form a new species. Extensive NMR characterization (^{1}H, ^{13}C, HMQC, HMBC, NOESY1D) of the product formed led us to the conclusion that it was not the dianion arising from direct deprotonation of **28**. Rather, we propose that the product formed was the novel cobaltacyle **30**, formally an 18-electron, trianionic species (Scheme 9). In the proposed structure, cobalt has inserted into a C−C bond of the central, four-membered ring, both cyclopentadiene rings are deprotonated, and one molecule of MeLi has added to the cobalt center. The proposed structure (**30**) is supported by an extensive series of NMR spectroscopic data. Whereas the ^{1}H NMR spectrum of the monolithiated species **28** shows five distinct peaks corresponding to H3, H4, H5, H8, and H9 in the region δ 4.60−6.60 ppm, the ^{1}H NMR spectrum of the cobaltacycle **30** shows only three broad peaks in this region, δ 5.79, 5.61, and 5.55 ppm, assigned as H2, H3, and H4, respectively. An HMQC spectroscopic experiment established the connectivity of each proton with its corresponding carbon; the ^{13}C NMR chemical shifts were δ 109.0, 92.9, and 97.2 ppm for C2, C3, and C4, respectively. An HMBC spectroscopic experiment revealed that the quaternary carbons C1 and C5 have ^{13}C NMR chemical shifts of δ 143.2 and 134.3 ppm, respectively. These ^{13}C NMR data are clearly inconsistent with the presence of a cobalt−cyclobutadiene complex, but they do support the proposed cobaltacyclic structure **30**.[29] The NMR chemical shift data are in good agreement with corresponding values in lithium cyclopentadienide, for example.[30] 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-d_3; 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. 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 HMPA (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 (PMe_3, 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 ^{13}C NMR spectrum (due to a large heteronuclear coupling to the phosphorus atom of the PMe_3 ligand), the carbon resonance of the cobalt-bound carbon of the cyclopentadienide ligand (C1) was unambiguously located by an HMBC experiment; its chemical shift (δ 132.45 ppm) and coupling to phosphorus were consistent with the proposed cobaltacyclic structure **31**, but not with any cobalt−cyclobutadiene complex. Further support for structure **31** was obtained by irradiation of the protons of the Cp*

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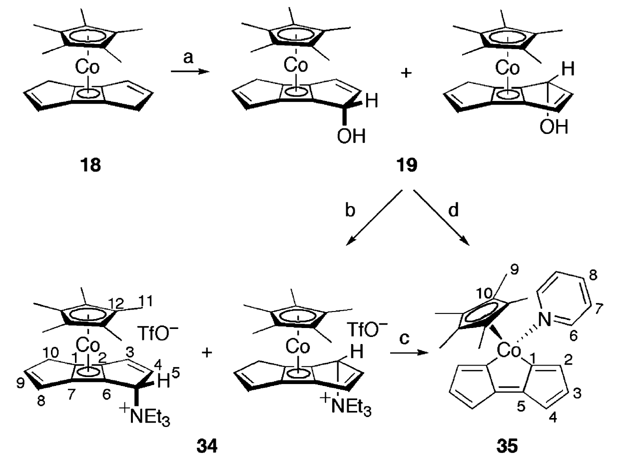
(28) For examples of σ- and π-allyllithium species, see: (a) Glaze, W. H.; Hanicak, J. E.; Moore, M. L.; Chaudhuri, J. *J. Organomet. Chem.* **1972**, *44*, 39. (b) Frankel, G.; Halaas, A. F.; Mochel, V.; Stumpe, R.; Tate, D. *J. Org. Chem.* **1985**, *50*, 4563. (c) West, P.; Purmort, J. I.; Mckinley, S. V.; *J. Am. Chem. Soc.* **1968**, *90*, 797. (d) O'Brien, D. H.; Hart, A. J.; Russel, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

(29) Several related cobaltacyclic structures have been reported where the cobalt-bound quaternary carbons are strongly deshielded. (a) Brabdt, L.; Green, M.; Parkins, A. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1046. (b) A similar situation has been reported wherein a peak corresponding to the cobalt-bound carbon of a cobaltacyclic complex could not be observed in the ^{13}C NMR spectrum due to a large coupling to the phosphorous atom of a cobalt-bound PMe_3 ligand. Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016. (c) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *124*, 8247. (d) Dosa, P. I.; Whitener, G. D.; Vollhardt, K. P. C.; Bond, A. D.; Teat, S. J. *Org. Lett.* **2002**, *4*, 2075.

(30) Lithium cyclopentadienide was purchased from Strem Chemical Co., and its ^{1}H and ^{13}C NMR spectra were measured: ^{1}H NMR (500 MHz, THF-d_8) δ 5.66 (s, 5H); ^{13}C NMR (125 MHz, THF-d_8) δ 103.42 (5C).

SCHEME 10. Preparation of 19 and Its Dehydration To Form 35[a]



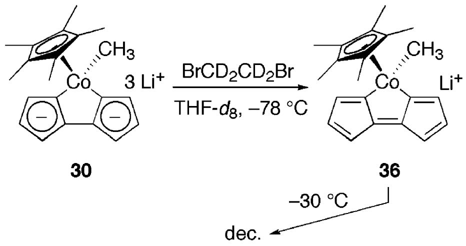
[a] Regents and conditions: (a) (i) MeLi (1.1 equiv), 12-crown-4 (1.4 equiv), HMPA (11 equiv), DME, −78 °C; (ii) (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine (1.5 equiv), −12 °C, 44%; (b) Tf_2O (2.0 equiv), Et_3N (4.0 equiv), CD_2Cl_2, −78 °C; (c) pyridine (3.5 equiv), −78 → −50 °C; (d) Martin sulfurane (2.0 equiv), pyridine (4.0 equiv), CD_2Cl_2, −78 °C.

ligand in a NOESY1D 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(C_2H_4)$_2$ 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 π-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 Et_3N (4.0 equiv) and Tf_2O (2.0 equiv) to a cold (−78 °C) solution of **19** in CD_2Cl_2 (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, ^{13}C, HMQC, HMBC, NOESY1D) 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 $J \sim 0$ 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]

SCHEME 11. Transformation of 30 to 36



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-d_4 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 Jones and coworkers that Cp*Co(C_2H_4)$_2$ inserts into the C−C bond of biphenylene to form the dicobalt complex **37**; further heating of **37** in the presence of PMe_3 forms the cobaltacyclic complex **38**, which is closely analogous to the dicyclopentadienide complex **31** we prepared (Scheme 12).[29b] Somewhat related cobaltacyclic products have also been reported to arise by cobalt(I)-induced dimerization of alkynes.[29c,d]

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

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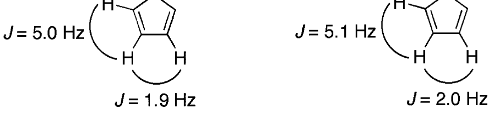
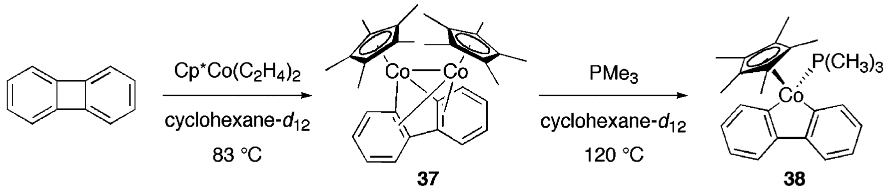
[31] (a) Morrissey, M. M. The Asymmetric Oxygenation of Chiral Imide Enolates. Ph.D. Thesis, Harvard University, Cambridge, MA, 1986. (b) Davis, F. A.; Mancinelli, P. A.; Balasubramanian, K.; Nadir, U. K. *J. Am. Chem. Soc.* **1979**, *101*, 1044.

[32] Scalar couplings in cyclopentadienyl systems are typically much larger between adjacent protons linked by a C−C double bond (vs a single bond); see: cyclopentadiene (**48**) and 5-methylene-1,3-cyclopentadiene (**49**). Pretsch, E.; Bühlmann, P.; Affolter, C. *Structure Determination of Organic Compounds*; Springer-Verlag: New York, 2000; page 176.

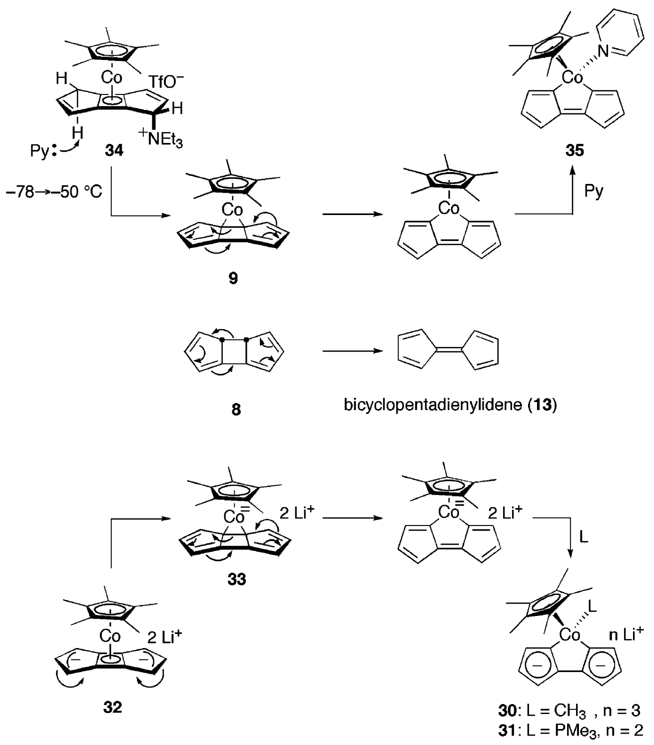


cyclopentadiene (**48**) 5-methylene-1,3-cyclopentadiene (**49**)

SCHEME 12. Formation of 38, a Species Closely Analogous to 31



SCHEME 13. Comparison of Proposed Mechanisms for Electrocyclic Ring-Opening of the Four-Membered Ring of 8, 9 and 33



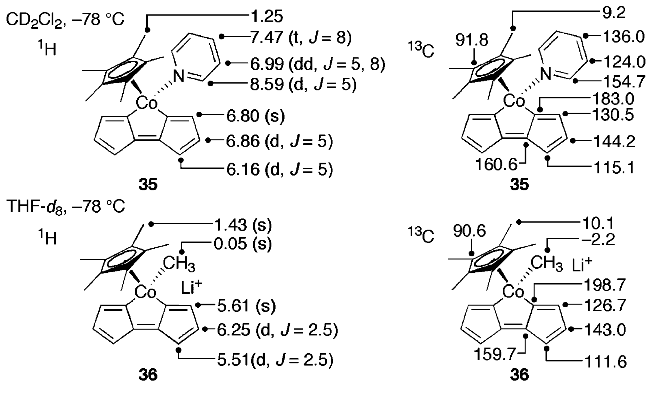


FIGURE 4. ^{1}H and ^{13}C NMR data of the closely related cobaltacyclic complexes **35** and **36**; the data are presented as chemical shift in ppm (multiplicity, coupling constant in hertz).

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 η^2-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).

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged. M.S. acknowledges predoctoral fellowship support from Eli Lilly and Co. S.P.A. acknowledges predoctoral fellowship support from the National Science Foundation.

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[33] Cyclopropane and ethylene are sterically nondemanding hydrocarbons and are known to interact with activated transition metals; cyclopropane is subject to C−C insertion, and ethylene forms π-complexes. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Sausalito, CA, 1987; pp 149−155, 461−155.

We thank Dr. Richard J. Staples, for X-ray analysis of compound **26**, and Dr. Shaw Huang and Mr. William Collins, for their assistance with NMR experiments. We thank Prof. Robert G. Bergman (University of California, Berkeley) for his suggestions concerning quantum calculations.

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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