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Tetraarylcyclobutadienecyclopentadienylcobalt Complexes: Synthesis, Electronic Spectra, Magnetic Circular Dichroism, Linear Dichroism, and TD DFT Calculations

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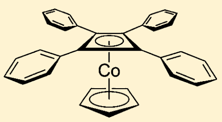
S *Supporting Information*

ABSTRACT: The known (tetraphenyl-η^4-cyclobutadiene)-η^5-cyclopentadienylcobalt (**1**) and a series of its new substituted derivatives have been prepared. The electronic states of a few representatives have been characterized by absorption and magnetic circular dichroism. Time-dependent density functional theory has been used to arrive at spectral assignments for several prominent low-energy bands. The absorption spectra of the radical ions of **1** have also been recorded.



INTRODUCTION

For some time, we have been interested in the development of a molecular Tinkertoy[1] construction set permitting nanometer-scale assembly of rods[2,3] and connectors,[4,5] especially for use in the construction of molecular rotors.[6−12] For a project in molecular electronics, we sought rigid cross-shaped connectors with tunable and reversible redox properties that could be easily substituted at different positions for coupling into a grid. (Tetraaryl-η^4-cyclobutadiene)-η^5-cyclopentadienylcobalt ($Ar_4CbCoCp$) complexes[13,14] are an interesting class of molecules for this purpose, due to their thermal and air stability and resistance to a wide range of chemical reagents. They are colored, but little is known about their excited states. CbCoCp complexes have applications as building blocks in oligomers[15] and polymers,[16−18] as catalysts,[19−35] and as structural units in other systems.[36−43] Structural analyses of such complexes have shown the Cb and Cp rings to be parallel and the Cb ring to be square,[44−47] making them interesting connectors. In addition, the aryl rings on both rings can be substituted, providing a broad synthetic scope. The parent complex, $Ph_4CbCoCp$ (**1**), is readily available by the reaction of two equivalents of diphenylacetylene (tolane) and cyclopentadienylcobalt(I) dicarbonyl in xylenes.[48−50] A variety of 4,4′-diphenylacetylenes have been found to give the corresponding (p-RPh)$_4$CbCoCp complexes[47] (R = Br, I, COOEt, p-$CB_{10}H_{10}CH$). More recently, several groups have reported the synthesis of such complexes using microwave heating.[51,52] A number of groups have also shown that substitution on the Cp ring is possible.[47,49,50,53−56] In general, most reports in the literature concern the synthesis of symmetrically substituted $Ar_4CbCoCp$ complexes, in which all four aryl groups are equivalent. Unsymmetrical complexes have been studied much less[52,57] but promise potentially interesting electronic and structural properties.

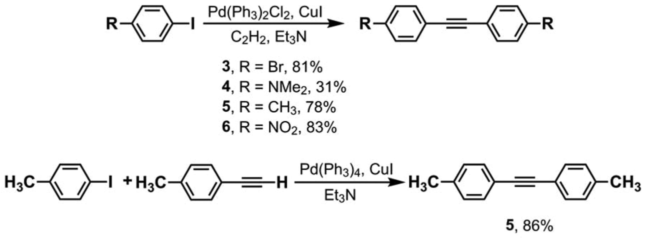
The primary purpose of this paper is to report the synthesis of additional symmetrical and unsymmetrical derivatives of **1**. In addition, we illustrate the excited states of a few of them by electronic spectroscopy, magnetic circular dichroism, linear dichroism, and DFT calculations. Since in molecular electronics electron transfer to or from a building unit is often of interest, we have also obtained the spectra of the radical ions of **1**.

RESULTS

Synthesis. Tolanes. Typically, tolanes (diphenylacetylenes) are synthesized by coupling an aryl halide with acetylene or its derivative, using the procedures developed by Sonogashira and Hagihara.[58−62] 4-Iodoaniline was converted to 4-bromoiodobenzene on a 150 g scale by a Sandmeyer reaction and into 4-iodo-*N,N*-dimethylaniline by phase-transfer-catalyzed methylation, avoiding quaternization.[63,64]

Scheme 1 shows the preparation of the symmetrical tolanes by the coupling of two aryl iodide derivatives with acetylene in the presence of a palladium catalyst and copper cocatalyst and triethylamine as a base, giving tolanes **3**−**6** in 31−83% yield.

Scheme 1



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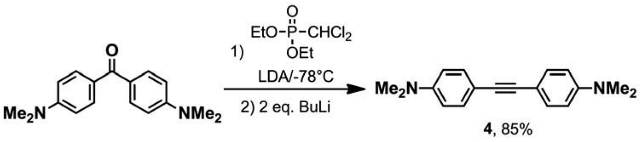
The tolane **5** was also obtained in higher yield (86%) by coupling with commercially available 4-ethynyltoluene.

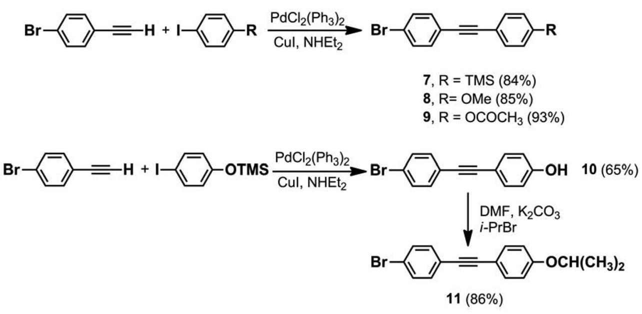
The low yield (31%) of 4,4′-*N,N*-dimethylaminodiphenylacetylene (**4**) was observed even at high catalyst loadings and long reaction times. We therefore abandoned the palladium coupling in favor of the higher yielding and less time-consuming conversion of 4,4′-bis(*N,N*-dimethylamino)-benzophenone (Michler's ketone) to **4** via a vinylidene rearrangement, which proceeds in 85% yield (Scheme 2).[65,66]

Scheme 2



The unsymmetrical tolanes were prepared by coupling the corresponding aryl iodide to 4-ethynylbromobenzene as shown in Scheme 3. Tolanes **7**−**9** were prepared in 84−93% yield.

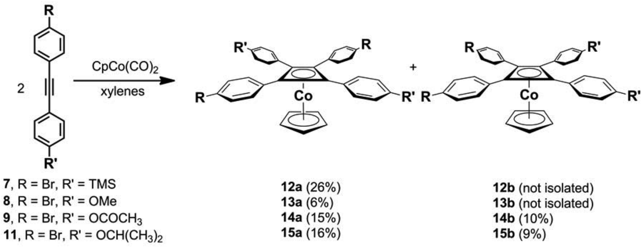
Scheme 3



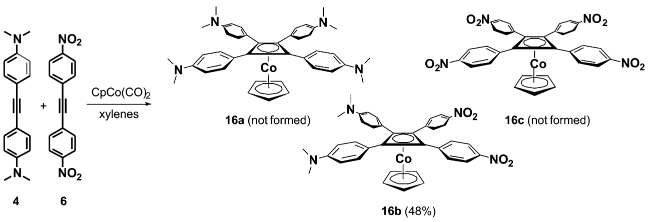
When using the trimethylsilyl-protected phenol, in situ hydrolysis gave **10** in 65% yield. The product **10** was subsequently converted to the isopropoxy derivative **11** in 86% yield (Scheme 3).

Cobalt Complexes. The tolane derivatives were converted into (tetraaryl-η^4-cyclobutadiene)-η^5-cyclopentadienylcobalt ($Ar_4CbCoCp$) complexes using the procedure developed by Rausch and co-workers[49,50] with two equivalents of the tolane cyclizing to form the cyclobutadiene ring in the presence of $CpCo(CO)_2$ (Schemes 4−7). Complexes **12**−**15** were prepared from the unsymmetrical tolanes **7**−**11**, respectively, permitting the formation of cis and trans isomers. For complexes **14** and **15**, both isomers were isolated, but in the case of **12** and **13**, only the trans isomer (**12a** and **13a**[52]) was isolated. Mixtures of two symmetrical tolanes can give three products (two symmetrical and one asymmetrical, the cis form) as shown in Scheme 5. However, when tolanes **4** and **6** reacted in the correct proportions, only the asymmetrical product **16b** was formed in an isolated yield of 48%. The complex **16a** was formed independently by reaction of two equivalents of **4** with $CpCo(CO)_2$, and **1** was synthesized according to the literature procedure[50] for use as a model system (Scheme 6).

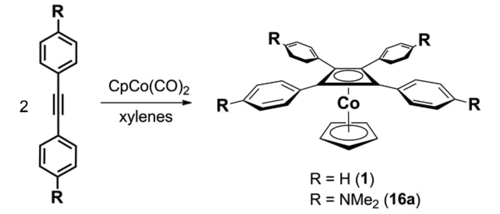
Scheme 4



Scheme 5



Scheme 6

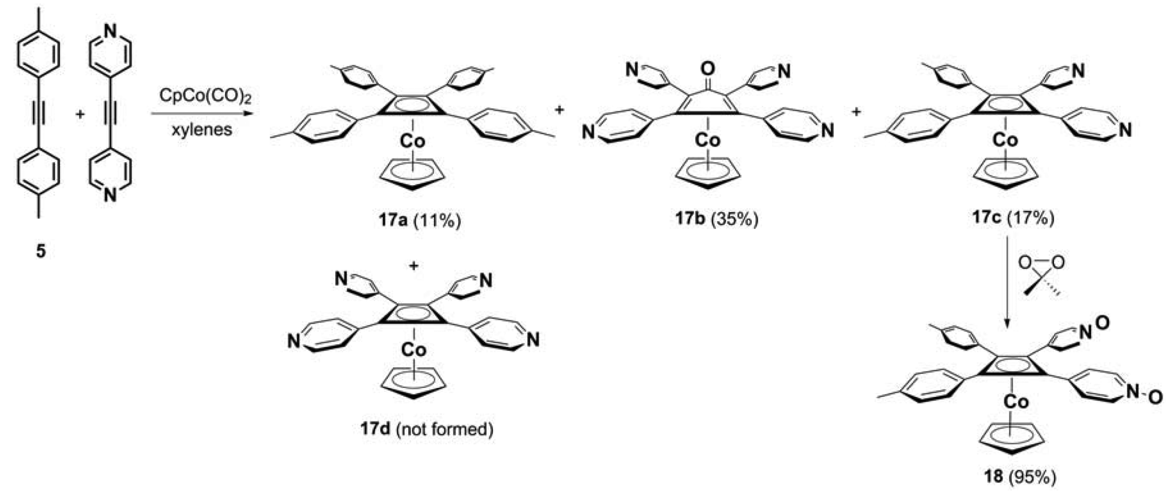


Finally, tolane **4** was cyclized with 4,4′-bipyridylacetylene to form a mixture of the symmetrically substituted product **17a** (11%), the unsymmetrical cis complex **17c** (17%), and the carbonyl insertion product **17b** (35%)[47] (Scheme 7; complex **17d** was not observed and has previously been shown to form only in low yield[47]). Cobalt complex **17c** was difficult to purify but was oxidized with dimethyldioxirane to the *N*-oxide **18** in a nearly quantitative yield, and the latter was obtained analytically pure.

Electronic Spectra. We have chosen three symmetrically (**1**, **17d**, **16a**) and two unsymmetrically (**16b**, **18**) substituted cobalt complexes to illustrate the UV−visible and magnetic circular dichroism (MCD) spectra (Figures 1−5, respectively, and Table 1) of these compounds. For the parent system **1** we also measured linear dichroism (LD) of a sample aligned in stretched polyethylene, and the absorption spectra of its radical cation $1^{\bullet+}$ and radical anion $1^{\bullet-}$ were obtained by pulse radiolysis (Figure 6). A detailed spectroscopic and theoretical study of all the new compounds lies beyond the scope of this paper, which focuses on their synthesis.

All the complexes listed above show three or four major absorption bands in the UV−vis region with high absorption coefficients (ε_{max} = 20 000−55 000 M^{-1} cm^{-1}). For the parent complex **1**, the maximum occurs at 31 800 cm^{-1} (ε_{max} = 17 600 M^{-1} cm^{-1}). The presence of four dimethylamino groups (**16a**) produces a small red shift to 31 500 cm^{-1} and triples the molar absorptivity (53 400 M^{-1} cm^{-1}). Replacing the four phenyl units by pyridine rings (**17d**) shifts the principal peak to 33 500 cm^{-1} (ε_{max} = 22 700 M^{-1} cm^{-1}). The MCD spectra are considerably more structured and leave little doubt that a fair number of electronic transitions are present. The results of TD-DFT calculations indeed indicate the presence of a large number of distinct transitions. The transition moments obtained from these calculations mostly fall into two categories: those oriented approximately along an axis *z* that connects the centers of the four-membered and the five-membered rings and passes through or close to the cobalt atom ("*z* polarized") and

Scheme 7



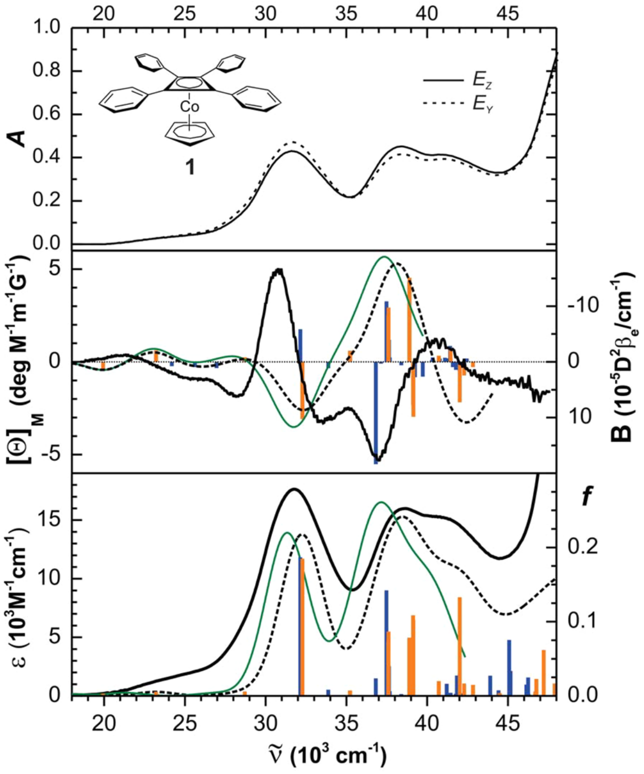


Figure 1. Optical spectra of **1**. Bottom: Absorption in THF overlaid over TD-DFT(B3LYP/DZP)-calculated oscillator strengths (blue: *z* polarized; orange: *x,y* polarized) and simulated spectra (black dashed line: B3LYP/DZP, compared with B3LYP/TZP, green line). The simulated spectra are scaled by a factor of 0.25. Center: MCD spectrum in THF overlaid over TD-DFT(B3LYP/DZP)-calculated *B* terms (blue: *z* polarized; orange: *x,y* polarized) and B3LYP/DZP-simulated MCD spectrum (black dashed line), compared with simulated B3LYP/TZP spectrum (green line) for limited number of states. The simulated spectra are scaled by a factor of 0.5. Top: Polarized absorption spectra in stretched polyethylene measured parallel (E_Z) and perpendicular (E_Y) to the stretching direction *Z*.

those oriented along a direction that lies approximately perpendicular to *z* ("*x,y* polarized"). However, certain transition moments lie at a direction intermediate between these two.

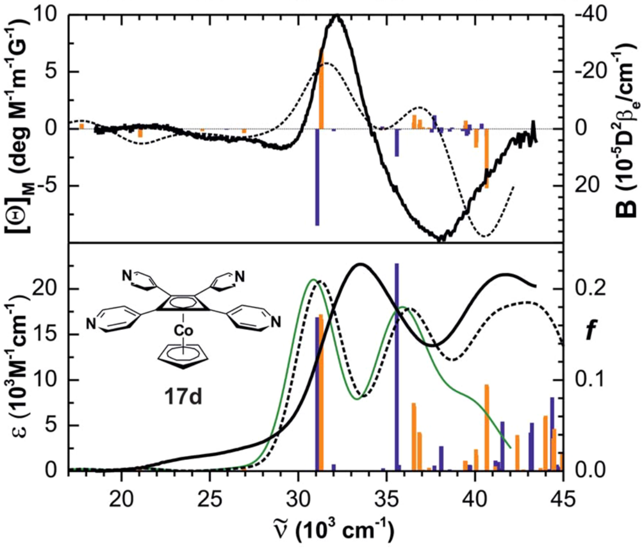


Figure 2. Optical absorption and MCD spectra of **17d** recorded in DCM. Bottom: Absorption overlaid on TD-DFT(B3LYP/DZP)-calculated oscillator strengths (blue: *z* polarized; orange: *x,y* polarized) and simulated spectra (black dashed line: B3LYP/DZP, compared with B3LYP/TZP, green line). The simulated spectra are scaled by a factor of 0.4. Top: MCD spectrum overlaid on TD-DFT(B3LYP/DZP)-calculated *B* terms (blue: *z* polarized; orange: *x,y* polarized) and B3LYP/DZP-simulated MCD spectrum (black dashed line). The simulated spectra are scaled by a factor of 0.75.

Linear dichroism of **1** in stretched polyethylene shows that the transition moments of the three high-energy bands (Table 1, Figure 1) are preferentially aligned with the stretching direction, while that of the band at 31 800 cm^{-1} is oriented perpendicular to it.

Pulse Radiolysis. The radical cation and anion of **1** were formed by standard pulse radiolysis techniques,[67] and their visible and near-infrared spectra are shown in Figure 6. The cations were formed in 1,2-dichloroethane and the anions in THF. The oxidized form shows transitions at ~17 500 cm^{-1} (ε_{max} = 10 600 M^{-1} cm^{-1}) and 14 500 cm^{-1} (ε_{max} = 7700 M^{-1} cm^{-1}), with a weak transition just below 11 400 cm^{-1} (ε_{max} = 400 M^{-1} cm^{-1}). The radical anion shows less intense transitions with a shoulder barely in the observation window

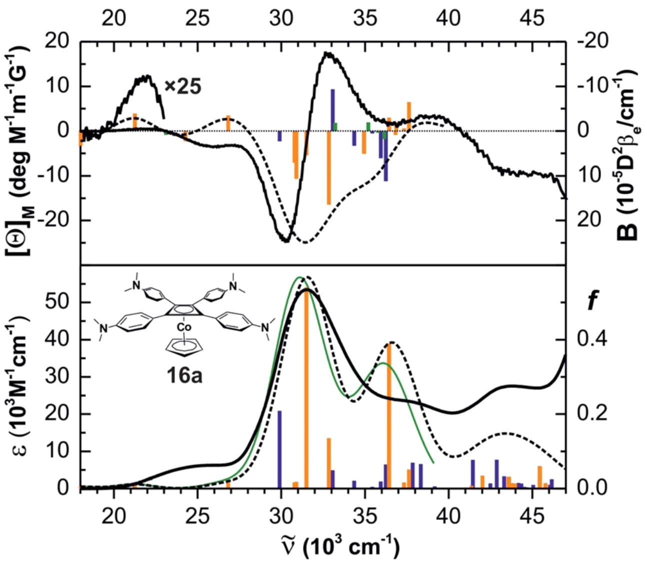


Figure 3. Optical absorption and MCD spectra of **16a** recorded in THF. Bottom: Absorption overlaid on TDDFT(B3LYP/DZP)-calculated oscillator strengths (blue: *z* polarized; orange: *x,y* polarized, green: mixed polarization) and simulated spectra (black dashed line: B3LYP/DZP, compared with B3LYP/TZP, green line). The simulated spectra are scaled by a factor of 0.4. Top: MCD spectrum overlaid on TD-DFT(B3LYP/DZP)-calculated *B* terms (blue: *z* polarized; orange: *x,y* polarized, green: mixed polarization) and B3LYP/DZP-simulated MCD spectrum (black dashed line). The simulated spectra are scaled by a factor of 1.3.

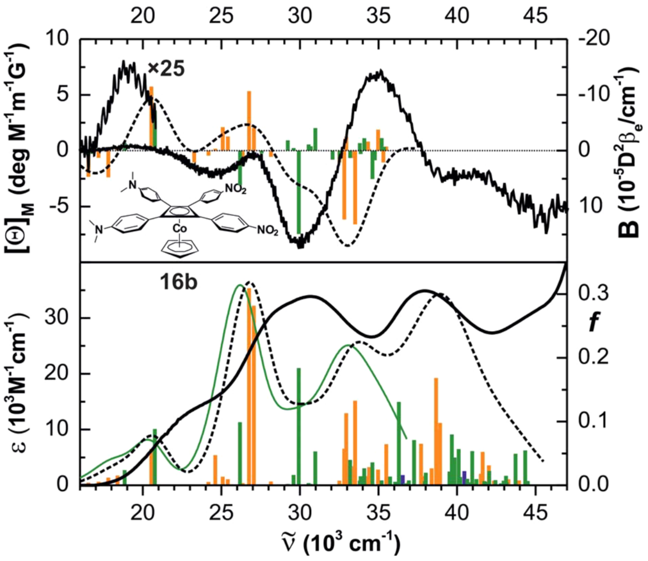


Figure 4. Optical absorption and MCD spectra of **16b** recorded in MeCN. Bottom: Absorption overlaid on TDDFT(B3LYP/DZP)-calculated oscillator strengths (blue: *z* polarized; orange: *x,y* polarized, green: mixed polarization) and simulated spectra (black dashed line: B3LYP/DZP, compared with B3LYP/TZP, green line). The simulated spectra are scaled by a factor of 0.5. Top: MCD spectrum overlaid on TD-DFT(B3LYP/DZP)-calculated *B* terms (blue: *z* polarized; orange: *x,y* polarized, green: mixed polarization) and B3LYP/DZP-simulated MCD spectrum (black dashed line). The simulated spectra are scaled by a factor of 0.9.

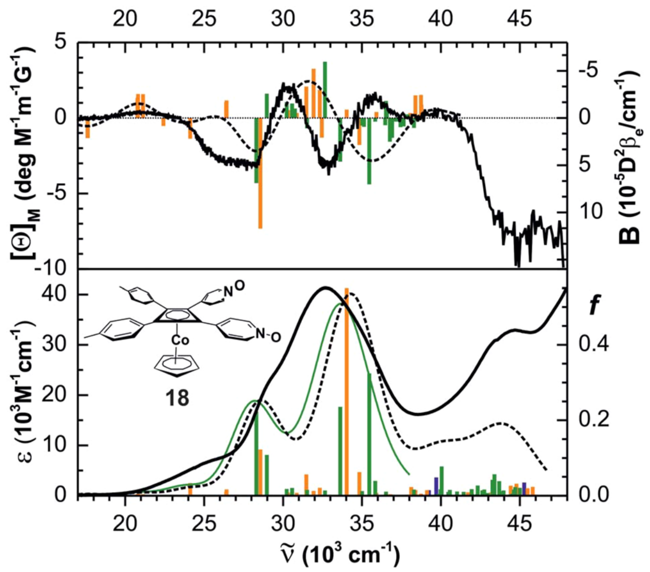


Figure 5. Optical absorption and MCD spectra of **18** recorded in MeCN. Bottom: Absorption overlaid on TDDFT(B3LYP/DZP)-calculated oscillator strengths (blue: *z* polarized; orange: *x,y* polarized, green: mixed polarization) and simulated spectra (black dashed line: B3LYP/DZP, compared with B3LYP/TZP, green line). The simulated spectra are scaled by a factor of 0.4. Top: MCD spectrum overlaid on TD-DFT(B3LYP/DZP)-calculated *B* terms (blue: *z* polarized; orange: *x,y* polarized, green: mixed polarization) and B3LYP/DZP-simulated MCD spectrum (black dashed line). The simulated spectra are scaled by a factor of 0.5.

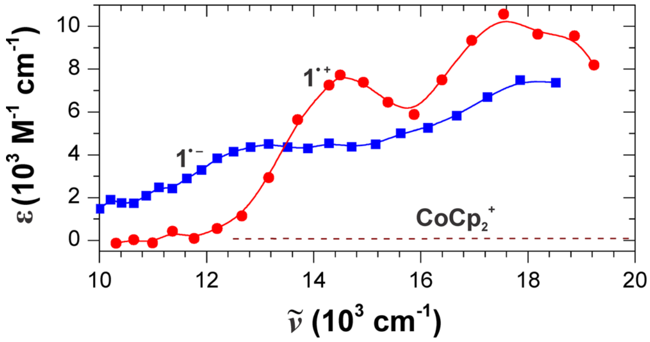


Figure 6. Optical absorption spectra of the radical ions of **1** recorded ~100 ns after pulse radiolysis of **1** in THF to form the anion or in 1,2-dichloroethane to form the cation. The lines represent interpolations between the measured points. The spectrum of cobalticenium in acetonitrile is shown for comparison.

at 18 100 cm^{-1} ($\varepsilon_{\max}$ = 7700 M^{-1} cm^{-1}) and another broad transition centered at ~13 200 cm^{-1} ($\varepsilon_{\max}$ = 4400 M^{-1} cm^{-1}). An attempt to reproduce the spectra at the same TDDFT level that gave satisfactory results for the uncharged closed-shell systems failed.

Molecular Orbitals. The frontier orbitals of **1**, calculated at the optimized geometry by the DFT-B3LYP/TZP method, and their energies are given in Figure 7 and in the Supporting Information. The orbitals shown are those that contribute to configurations present with a weight of at least 10% in one of the low-energy electronic transitions discussed below. Although the molecule is not symmetric, one-half having a local 5-fold axis and the other half a local 4-fold axis, and the phenyl substituents on the cyclobutadienyl ring being twisted by about 40°, the molecular orbitals are close to symmetric and the metal *d* orbitals form approximate symmetry sets in a way typical for C_{5v} transition metal complexes. The HOMO−4 is a mixed Cb/metal *d* (z^2) orbital of approximate "a" symmetry, the nearly

Table 1. UV−Vis and MCD Transitions of Cobalt Sandwich Complexes

			Absorption				MCD				
R_1=R_2[a]	R_3=R_4[a]	Cmpd.	$\tilde{\nu}_{max}/10^3cm^{-1}$ ($\varepsilon_{max}/10^3M^{-1}\ cm^{-1}$)				$\tilde{\nu}_{max}/10^3cm^{-1}$ ($[\Theta]_M$/deg $M^{-1}\ m^{-1}\ G^{-1}$)				
H	H	**1**[b]	40.9 (15.2)	38.6 (16.0)	31.8 (17.6)	24.0 (1.5)	44.0 (-0.9)	40.6 (1.2)	37.0 (-5.2)	35.1 (-2.5)	33.3 (-3.3)
							30.7 (5.0)	28.2 (-1.9)	25.1 (-0.8)	21.2 (0.4)	-
aza	aza	**17d**[c]	41.8 (21.6)	-	33.5 (22.7)	23.4 (1.4)	38.0 (-9.6)	32.1 (10.0)	29.0 (-1.7)	21.3 (0.3)	-
NMe_2	NMe_2	**16a**[b]	43.8 (27.5)	37.4 (23.6)	31.5 (53.4)	25.2 (6.1)	43.7 (-9.8)	39.1 (3.5)	36.6 (1.3)	32.8 (17.3)	30.3 (-24.9)
							27.2 (-3.1)	25.8 (-3.5)	21.8 (0.4)	-	-
NMe_2	NO_2	**16b**[d]	-	38.0 (34.9)	30.7 (33.9)	23.5 (14.0)	45.0 (-6.8)	41.1 (-1.6)	39.2 (-2.7)	34.9 (7.1)	29.8 (-8.1)
							27.0 (-0.007)	24.4 (-2.3)	18.9 (0.4)	-	-
Me	aza-oxide	**18**[d]	44.6 (32.9)	32.7 (41.3)	29.4 (23.9)	25.8 (7.3)	45.4 (-8.4)	40.0 (0.5)	38.5 (-0.2)	35.7 (1.6)	32.9 (-3.8)
							30.3 (2.1)	27.2 (-3.3)	21.5 (0.4)	-	-

[a] R_1−R_4 are the functional groups in the para positions of the four phenyl substituents in **1**, numbered in clockwise order. [b] In THF. [c] In CH_2Cl_2. [d] In CH_3CN.

degenerate (almost *e* symmetry) pair HOMO−3 and HOMO−2 are virtually pure metal *d* orbitals (*xy* and $x^2 - y^2$), and the essentially exactly degenerate (nearly "e" symmetry) pair HOMO−1 and HOMO are mixed Cp/Cb/*d* (*xz* and *yz*) orbitals. The Cb contribution has the form of the Cb nonbonding orbital. The almost exactly degenerate LUMO and LUMO+1 pair is well described as the nonbonding orbital pair of Cb, with very small contributions from Cp and metal *d* (*xz* and *yz*) orbitals.

Electronic Transitions. Electronic absorption spectra were calculated at ground-state DFT-B3LYP/TZP-optimized geometries by the TDDFT method using DZP and TZP Slater-type basis sets. The calculated vertical excitation energies and oscillator strengths for **1**, **16a**, **16b**, **17d**, and **18** are depicted in Figures 1−5.

The B3LYP/DZP results of calculations of the spectrum of **1** are presented in more detail in Table 2. Like the molecular orbitals, the transitions, their oscillator strengths, and the dominant configurations of the excited states reflect the approximate symmetry of the molecule. The first nine transitions are well described as metal *d* to Cb (LUMO, LUMO+1) transitions of very low intensity. Three of them are composed of pairs of nearly exactly degenerate excitations, polarized equatorially (in the Cb and Cp planes), and are stronger than the remaining three. They correspond to transitions from the *xy* and $x^2 - y^2$ orbitals and are calculated at 19 930, 23 210, and 28 710 cm^{-1}. The first really intense transitions are calculated to lie just above 32 000 cm^{-1}. One is an equatorially polarized pair of excitations into the almost exactly degenerate states produced by electron promotion from the HOMO pair (HOMO, HOMO−1) to an orbital LUMO+2 that looks like the antibonding orbital of Cb but is also delocalized onto the attached phenyl rings. The second intense transition in this region is the nondegenerate combination of approximately *z* (axially) polarized excitations from the HOMO pair to the LUMO pair. Above these three intense transitions, many weak transitions are calculated. The next intense transitions are predicted near 38 000 cm^{-1} and represent excitation from metal *d* orbitals to orbitals located on Cb and

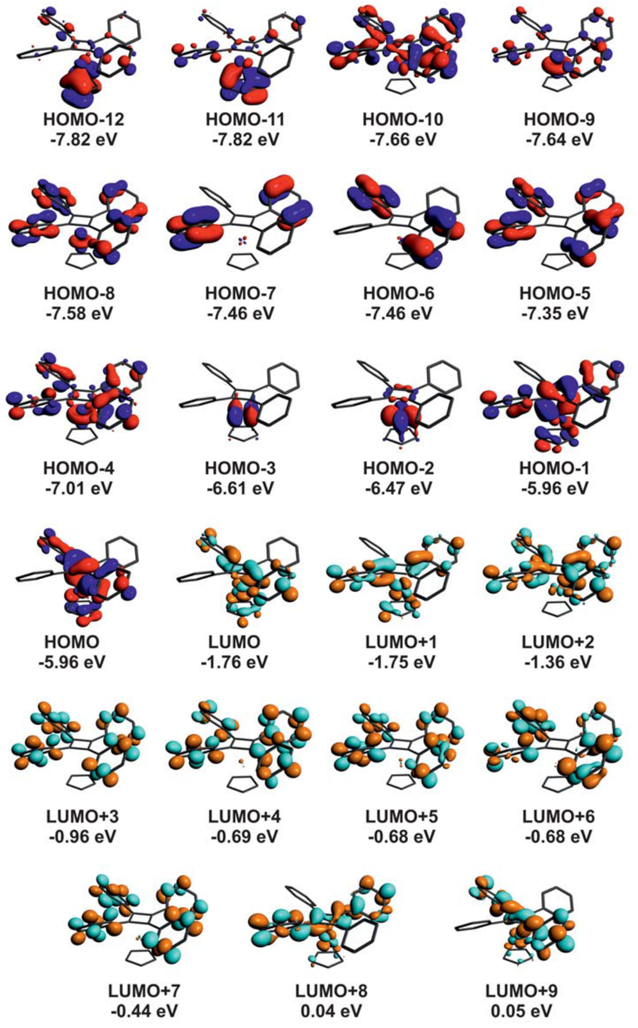


Figure 7. B3LYP/DZP frontier orbitals of **1**.

its phenyl substituents. Most are nearly degenerate and approximately *x,y* (equatorially) polarized.

Dimethylamino substitution in the para positions of the four phenyl groups (**16a**) does not affect the excitation energy of the first observed absorption band noticeably, but its intensity is almost tripled. This increase is well reproduced by the calculations. In the parent **1** the first intense calculated band consists of three excitations of almost identical energy, one polarized along *z* and two along *x,y*. In **16a**, the *z*-polarized component has a similar excited-state composition and oscillator strength as in **1** and is red-shifted by ~1500 cm^{-1}. The oscillator strength of the pair of almost degenerate *x,y*-polarized transitions is tripled relative to the parent **1**, and the excited state contains one additional important configuration. This corresponds to an electron promotion from the orbital HOMO−2 of **16a**, with a large amplitude on the amino nitrogen atoms (Supprting Information, Figure S2), to the LUMO pair and transfers electron density from the amino groups to Cb, Co, and Cp, roughly equally.

The substitution of parent **1** by donor and acceptor groups, dimethylamino and nitro (**16b**), destroys significantly its original approximate symmetry. This is reflected in the mixed polarization of most calculated transitions. The observed intensity of the band near 30 000 cm^{-1} is 1.5 times higher, and this is reproduced by the calculated increase of the oscillator strength of the *x,y*-polarized pair of excitations predicted at about 27 000 cm^{-1}. Inspection of the orbitals involved in these transitions shows significant charge transfer from amino groups and from *d* orbitals of Co into the nitro groups. The calculated *z*-polarized transition of the parent **1** is difficult to trace due to a large mixing caused by the asymmetric substitution.

■ DISCUSSION

Synthesis. Diphenylacetylene and its derivatives (tolanes) have been known for almost a hundred years, but it was not until the development of Hagihara−Sonogashira coupling conditions[58−62] that a relatively cheap and functional group tolerant approach for their synthesis became available. Since aryl iodides undergo oxidative addition to palladium much faster than aryl bromides, we exclusively used the iodides. While many are commercially available, 1-bromo-4-iodobenzene and 4-iodo-*N,N*-dimethylaniline were prepared in high yield on multigram scale from 4-iodoaniline (Scheme 1), the former via a Sandmeyer reaction and the latter via methylation under phase-transfer-catalysis conditions, which avoided quaternary byproducts.[63,64]

Most tolanes were prepared in high yield using the palladium coupling procedures developed by Hagihara and Sonogashira. As shown in Scheme 1, tolanes **3**, **5**, and **6** formed in yields of ~80% or higher by reaction of two equivalents of the corresponding aryl iodide with acetylene gas in the presence of Pd^{II} and Cu^{I}, with all reactions performed on multigram scale. A slightly higher yield (86%) of **5** was obtained when using commercially available 1-ethynyl-4-methylbenzene with 1-iodo-4-methylbenzene (Scheme 1). However, in the case of dimethylaminotolane **4**, the coupling of 4-iodo-*N,N*-dimethylaniline with acetylene gas gave poor yields and was abandoned. Another procedure, which relies on a vinylidene to alkyne rearrangement, was developed by Savignac and co-workers (Scheme 2).[65,66] Using the Horner modification of the Wittig reaction,[68−70] benzophenone derivatives can be converted to 1,1-dichloro-2,2-diarylalkenes by treatment with a phosphonate.[71] Reaction of the *gem*-dichloride with a lithium reagent generates the vinylidene, which rearranges to give the tolane.

Unsymmetrical tolanes have been studied less[7,72,73] and can be prepared by coupling an appropriate arylacetylene with an aryl iodide as shown in Scheme 3. Here we employed 4-bromophenylacetylene[74] to prepare a number of unsymmetrical tolanes (**7**−**10**) in good to excellent yields. Coupling of 4-bromophenylacetylene with the protected 4-trimethylsilyloxyiodobenzene led to in situ deprotection to give tolane **10**, which in this case was desirable, as **10** was alkylated with isopropyl bromide to give **11**.

As mentioned above, cyclization of the unsymmetrical tolanes in the presence of CpCo(CO)$_2$ gives two isomers of the corresponding sandwich complexes, cis and trans with respect to the disposition of the substituent groups (Scheme 4). In the case of unsymmetrical tolanes **7** and **8**, only the trans forms **12a** and **13a** were isolated (we were able to isolate but not fully purify small quantities of **12b** and **13b**). When tolanes **9** and **11** were cyclized, a slight excess of the cis (**14a** and **15a**) over the trans (**14b** and **15b**) form was formed. The lower yields were due to difficulties in separating the isomers with flash chromatography due to their often nearly identical retention times and the resulting need for multiple chromatographic separations (see Experimental Section).

Table 2. TDDFT (B3LYP/DZP)-Calculated Vertical Transitions in 1

	$\tilde{\nu}$/cm^{-1}	*f*	*B* term[a]	dominant configurations[b]	polarization
1	19 932	0.0029	1.5972	**3→−1, 4→−2**	*x*,*y*
2	19 936	0.0029	1.5993	**3→−2, 4→−1**	
3	23 205	0.0058	−2.0614	**4→−1**, 3→−2, 10→−1	*x*,*y*
4	23 216	0.0058	−2.0567	**4→−2**, 3→−1, 10→−2	
5	24 184	0.0001	0.7686	**1→−2, 2→−1**	*z*
6	25 615	0.0000	0.9628	**2→−1, 1→−2**	*z*
7	26 957	0.0001	1.1239	**1→−1, 2→−2**	*z*
8	28 709	0.0059	−0.8210	**5→−1, 10→−1**, 4→−1	*x*,*y*
9	28 717	0.0058	−0.8045	**5→−2, 10→−2**, 4→−2	
10	32 142	0.1868	−5.8507	**2→−2, 1→−1**, 4→−3	*z*
11	32 271	0.1848	10.2793	**1→−3**	*x*,*y*
12	32 283	0.1832	10.2508	**2→−3**	
13	33 874	0.0084	1.1501	**3→−3**, 4→−3	*z*
14	35 217	0.0073	−2.0264	**1→−4**	*x*,*y*
15	35 233	0.0073	−2.0034	**2→−4**	
16	36 822	0.0237	18.3868	**4→−3**, 1→−7, 2→−6	*z*
17	37 142	0.0002	0.3158	1→−7, 2→−6, 1→−6, 2→−7	*z*
18	37 482	0.1422	−10.8875	**4→−3**, 1→−7, 2→−6	*z*
19	37 589	0.0739	−8.4849	**1→−5**	*x*,*y*
20	37 604	0.0867	−9.7680	**2→−5**, 2→−6	
21	37 636	0.0401	−3.9135	**1→−6, 2→−7**, 1→−7	*z*
22	37 680	0.0064	−0.7898	**2→−7, 2→−6**, 1→−7 1→−6	*z*
23	38 396	0.0026	0.6140	13→−1, 12→−2, 12→−1, 13→−2	*z*
24	38 891	0.0784	−14.4975	**1→−8, 5→−1**	*x*,*y*
25	38 903	0.0769	−15.1171	**2→−8, 5→−2**	
26	39 131	0.1087	7.7446	**1→−8**, 5→−2, 10→−1	*x*,*y*
27	39 145	0.1027	9.8763	**2→−8**, 5→−2, 10→−2	
28	39 236	0.0008	2.7667	**3→−4**	*z*
29	39 720	0.0004	2.6604	**5→−3**, 12→−1, 13→−2	*z*
30	40 294	0.0000	−0.3506	**4→−4**	*z*
31	40 334	0.0001	−0.8042	12→−2, 13→−1, 8→−1, 7→−2	*z*
32	40 715	0.0196	−1.0367	**6→−1**, 1→−8	*x*,*y*
33	40 722	0.0199	−1.1156	**6→−2**, 2→−8	
34	40 781	0.0005	−0.5867	5→−3, 12→−1, 13→−2, 3→−5, 4→−4	*z*
35	41 100	0.0003	−0.7315	**3→−5**	*z*
36	41 210	0.0163	−0.6299	**8→−2, 7→−1**, 1→−9	*z*
37	41 415	0.0030	−2.8706	7→−2, **8→−1**	*z*
38	41 444	0.0037	−2.2830	**3→−7, 3→−6**, 3→−5	*x*,*y*
39	41 453	0.0042	−0.6026	**3→−6, 3→−7**	
40	41 581	0.0001	0.9520	**8→−1, 7→−2**	*z*
41	41 772	0.0029	1.4403	**1→−9**, 7→−1	*z*
42	41 838	0.0275	1.3164	**2→−10**, 1→−9, 8→−2	*z*
43	41 993	0.0282	1.6490	2→−10, 11→−1, 7→−1, 8→−2, 1→−9	*z*
44	42 016	0.1100	6.1265	**11→−1**	*x*,*y*
45	42 019	0.1328	7.2710	**11→−2**	
46	42 253	0.0035	0.4604	**4→−5**	*z*
47	42 286	0.0168	2.4497	**9→−1**, 4→−7, 10→−1, 4→−6	*x*,*y*
48	42 294	0.0154	2.2386	**9→−2**, 4→−6, 4→−7,10→−2	
49	42 448	0.0005	−0.6079	**2→−9, 1→−10**, 4→−5	*z*
50	42 833	0.0150	0.9520	**4→−7**, 4→−6, 9→−2, 4→−5	*x*,*y*

[a] In units of 10^{-5} D$^2\beta_e$/cm^{-1}. [b] Dominant configurations with weight more than 10% (bold: weight more than 25%). 1 = HOMO, −1 = LUMO, 2 = HOMO−1, −2 = LUMO+1, etc.

For the symmetrical tolanes, no isomers are possible, but three different products can be formed: the two complexes obtained from cyclization of the same tolane and the cross-product formed by the coupling of different tolanes (Scheme 5). For these cyclizations with CpCo(CO)$_2$, the reactivity of the tolane must be taken into consideration, as those with electron-withdrawing groups tend to be less reactive. Therefore, the reactant ratio must be changed to optimize the conditions under which the mixed cobalt complex forms in highest yield. In the case of **16b**, it was found that three equivalents of the dinitrotolane **6** for every equivalent of the dimethylaminotolane **4** were necessary to optimize the yield. As shown in Scheme 5, the coupling reaction proceeds in a 48% yield, without observation of either symmetrically substituted cobalt complex. It should be noted that tetrakis(*N*,*N*-dimethylaminophenyl)-CbCoCp (**16a**) is observed when the ratio of the tolanes deviates from three-to-one. However, the tetrakis(nitrophenyl)-CpCoCp complex (**16c**) is never observed under the reaction conditions, and unreacted dinitrotolane **6** could be recovered after the reaction. Compound **16a** was also synthesized independently by the reaction of two equivalents of **4** with CpCo(CO)$_2$ in 56% yield, as shown in Scheme 6.

The products from the reaction of two equivalents of 4,4′-dipyridylacetylene with one equivalent of dimethyltolane **5** and one equivalent of CpCo(CO)$_2$ were mostly the cyclopentadienone complex **17b** (35%) and little of the desired compound **17c** (17%). Brotin et al.[47] have previously shown that treating two equivalents of 4,4′-dipyridylacetylene with CpCo(CO)$_2$ in refluxing xylenes gives a low yield (15%) of the tetrapyridyl complex **17d** along with a significant amount (50%) of the tetrapyridylcyclobutadienone complex **17b**. Complex **17d** was not observed in our reaction mixture, while the tetratolylcyclobutadienylcyclopentadienecobalt complex **17a** was formed in an 11% yield (Scheme 7). Attempts to optimize the formation of **17c** over the formation of **17b** failed to increase the yields significantly. The use of CpCo-(cyclooctadiene), devoid of a carbonyl group that could insert into the cyclobutadiene ring, did not produce any reaction. Likewise, attempts to purge CO from the reaction mixture with bubbling argon did not significantly decrease the amount of **17b** formed. Therefore, the carbonyl insertion product was deemed to be a more stable electronic structure unique in the presence of the pyridine groups. Rausch and Genetti[50] had previously reported the formation of the tetraphenylcyclopentadienone CoCp complex in the cyclization of diphenylacetylene, but in much lower yields (<10%). Due to difficulties in our attempts to purify **17b**, it was converted to the *N*-oxide with dimethyldioxirane in nearly quantitative yield (Scheme 7) to give compound **18**.

Electronic Spectra. The absorption spectra shown in Figures 1−5 show remarkable similarity, and only that of **16b** differs significantly from the others. We focus primarily on the absorption and MCD spectra of the parent complex **1**.

In the low-energy region, they agree remarkably well with expectations from the TDDFT calculations. Below 30 000 $\mathrm{cm^{-1}}$, where three moderately weak equatorially polarized nearly degenerate transitions and three extremely weak axially polarized transitions are calculated and the absorption curve shows only an indistinct shoulder, the MCD curve is very helpful. It shows a negative *B* term and two positive *B* terms at the expected locations, easily assignable to the three predicted transitions. A nearly degenerate transition could also exhibit an apparent A term, but those seem to be weak since there is no indication of any in the spectral curve. The agreement with the DFT-calculated *B* terms is poor.

The linear dichroism of these three transitions could not be measured reliably, and we were unable to obtain an independent confirmation of their equatorial (x,y) polarization. Nevertheless, it seems that these electron promotions from metal d orbitals (xy and $x^2 - y^2$) to the nonbonding orbitals of the Cb ligand are correctly described by the TDDFT calculation. The same three transitions appear in the MCD spectra of the substituted derivatives, except for **18**, where both calculations and spectra indicate a more complicated situation, with a larger number of transitions present.

The first intense band at 32 000 $\mathrm{cm^{-1}}$ looks deceptively simple, and only the spectra of some of the derivatives, especially **18**, suggest that it contains more than one transition. According to the calculations, it should contain one nearly degenerate pair of equatorially polarized transitions plus another transition at nearly the same spectral location, polarized axially, all of comparable intensity. Its weakly negative linear dichroism ($E_Z < E_Y$) suggests that either the molecule of **1** orients in an unexpected way in stretched polyethylene, given its shape,[75] or the axially polarized transition is actually stronger than the equatorially polarized ones. In any event, the weakness of the LD signal agrees with expectations. Even if the molecule oriented well, the presence of overlapping transitions of both polarizations would cause LD to be weak. The shape of the MCD curve is compatible with a negative *A* term overlapped at the high-energy end with a negative *B* term, and this would be in perfect accord with the calculations, but the actually predicted spectral shape does not agree with the observed spectrum. The pseudo-*A* term of the nearly degenerate transition should be negative[76] if the pair of transitions can indeed be described as a promotion of an electron from the nearly degenerate (HOMO, HOMO−1) orbital pair, the nonbonding orbital on Cb, into the antibonding orbital on Cb, as the TDDFT calculation suggests.

The next intense band, located near 40 000 $\mathrm{cm^{-1}}$, shows evidence of its complex nature in both the absorption and the MCD spectra. Calculations suggest that the lower energy peak is due to the overlap of three intense and several other transitions, and the higher energy shoulder is due primarily to one transition, with many others contributing weakly. The calculated polarization of all the intense transitions in this region is equatorial, and this agrees with the observed positive linear dichroism if the molecules orient in the expected fashion. We thus conclude that they apparently do and that in the lower energy band near 32 000 $\mathrm{cm^{-1}}$ the axially polarized transition is actually stronger than the overlapping equatorially polarized ones. In the 40 000 $\mathrm{cm^{-1}}$ region, substituents modify the spectra more strongly, and it is difficult to draw simple conclusions.

In summary, it appears that in the lower energy region the TDDFT calculations provide a quite reasonable description of the energies and relative intensities of electronic excitations in **1**, although the finer details of substituent-induced shifts are not reproduced well or at all. Given the large number of transitions present, the MCD spectra that reflect their mixing by the magnetic field are obviously quite challenging to reproduce computationally. The DFT procedure used, which is the best available at the moment for molecules of this size, is not up to the task, although in certain parts of some of the spectra some agreement can be detected.

The visible absorption spectra of the radical ions of **1** (Figure 6) are relatively featureless. Both the cation and anion have absorptions with extinction coefficients ε of several thousand in the visible region, in contrast to the case of cobalticenium, which has almost no significant absorption in the visible. We expect the bands of the radical ions of **1** to be useful for the detection of charge transfer events if **1** finds use as a connector or as an active redox element in studies directed at molecular electronics.

■ SUMMARY

Efficient synthetic procedures have been described for derivatives of **1** substituted symmetrically or unsymmetrically in the phenyl rings, and an initial examination of their electronically excited states has been performed. Some information on the low-energy excited states of the parent **1** and their response to substitution has been obtained by a combination of time-dependent density functional theory with absorption, linear dichroism, and magnetic circular dichroism spectroscopy on the parent and four of its derivatives. An attempt to reproduce the absorption and MCD spectra by DFT computations has met with only partial success, particularly in the case of MCD. The absorption spectra of the radical ions of **1** have been recorded.

■ EXPERIMENTAL SECTION

Measurements. Most measurements were conducted with standard commercial instruments as detailed in the Supporting Information. Linear dichroism spectra were measured in stretched polyethylene sheets with a JASCO J-720 spectropolarimeter in the linear dichroism mode. Polyethylene sheets were cut from commercial polyethylene bags and cleaned by soaking in chloroform for several hours before washing with clean chloroform and drying. The clean sheets were stretched in a homemade stretcher to approximately five times their original length. The sheet was doped by placing a drop of a saturated sample solution in chloroform on the stretched sheet in a closed, chloroform-saturated environment. After 1 h, the sheet was removed and the chloroform was allowed to evaporate. Excess sample that was not absorbed into the polymer was washed from the sheet with methanol, and the sheet was dried. The doped, stretched sheet was placed in the spectrometer in an orientation such that the photoelastic modulator produced light that alternated between polarizations parallel and perpendicular to the stretching direction. As a baseline, an identical stretched sheet without incorporation of the sample, but otherwise handled in the identical manner, was measured before measurement of the doped sheet.

Pulse Radiolysis. These experiments were done at the Brookhaven National Laboratory. Solutions of 0.7 μM of cations in 1,2-dichloroethane or anions in THF were produced by pulse radiolysis. About 0.7 mM solutions of **1** in 1,2-dichloroethane (cations) or THF (anions) were exposed to <50 ps pulses of 9 MeV electrons at the LEAF accelerator, and the spectra were recorded 100 ns after the pulse. The uncertainty in the scale factors used to obtain molar extinction coefficients from the observed absorbances is ±30%.

Computations. Calculations were performed by the DFT-B3LYP method using the program ADF, version 2013.[77] The internally stored Slater-type basis sets[78] DZP (excitation spectra, MCD) and TZP (geometry optimization, in selected calculations of excitation spectra and MCD for comparison) were used. Description of the B3LYP funtional[79−81] is available. Geometry optimizations were performed without constraints. Electronic excitation was calculated using the time-dependent DFT method.[82] MCD *B* terms[83] were calculated for the lowest 50 states by the iterative conjugate gradient procedure. Excitation and MCD spectra were simulated by a home-developed code, using Gaussian shape functions with square-root band broadening ($w_i = w\sqrt{(\nu_i/30\,000)}$, $w = 3000$ cm^{-1}). The orbitals were plotted using ADF-GUI.

Synthetic Procedures. Compound **4**,[65,66] dimethyldioxirane,[84] 4-iodophenyltrimethylsilane,[74] 4-bromophenylacetylene,[74] 4,4′-bipyridylacetylene,[85] **1**,[48−50] and **17d**[47] were prepared according to the literature. Cyclopentadienylcobalt(I) dicarbonyl and tetrakis(triphenylphosphine)palladium(0) were from Strem Chemicals, and the former was distilled prior to use. Dichlorobis(triphenylphosphine)palladium(II) (Aldrich) was used as received. All other reagents were purchased and used as received. All reactions were carried out under an argon atmosphere with dry solvent, freshly distilled under anhydrous conditions,[86] unless otherwise noted. Xylenes, THF, and diethyl ether were dried over and distilled from sodium benzophenone ketyl. Triethylamine was dried over and distilled from calcium hydride. Standard Schlenk- and vacuum-line techniques were employed for all manipulations with air- or moisture-sensitive compounds. Yields refer to isolated, chromatographically and spectroscopically homogeneous materials, unless otherwise stated.

1-Bromo-4-iodobenzene. A three-neck flask equipped with a mechanical stirrer and containing $NaNO_2$ (54.5 g, 0.79 mol) was evacuated, placed under argon, and cooled to 0 °C. Under mechanical stirring, H_2SO_4 (concd, 300 mL) was added slowly to minimize the formation of nitrogen oxides. Acetic acid (concd, 500 mL) was then added from an addition funnel, and the mixture was stirred for 30 min. In the meantime, 4-bromoaniline (100 g, 0.58 mol) was dissolved in acetic acid. Under stirring at 0 °C, H_2SO_4 (concd, 45 mL) was added slowly. The resulting white precipitate was dissolved by addition of a minimum of ice. This solution was transferred to a cooled addition funnel and added dropwise very slowly to the $NaNO_2/H_2SO_4$ solution at 0 °C. After 2 h of continued stirring, the reaction mixture was transferred to an ice-cooled addition funnel and added dropwise but rapidly under vigorous stirring to a solution of KI (230 g, 1.36 mol), I_2 (202 g, 0.79 mol), and urea (30.5 g) in 1000 mL of water and 450 mL of chloroform at 0 °C. The reaction mixture was stirred overnight while warming to room temperature. The two layers were separated in a separation funnel, and the aqueous layer was extracted with chloroform (4 × 250 mL). The organic phases were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was flash chromatographed (silica gel, hexanes/chloroform, 4:1) to yield 137.2 g (0.48 mol, 84%) of 1-bromo-4-iodobenzene (**1**) as a white solid. Mp: 89 °C (lit.[87] 92 °C).

4-Iodo-N,N-dimethylaniline. 4-Iodoaniline (20.0 g, 91 mmol) was charged into a dry two-necked flask, and toluene (200 mL) was added under an argon atmosphere. NaOH (7.3 g, 182 mmol) was finely pulverized and added to the solution at once. Tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1, 1.4 mL, 4.3 mmol) was then added from a syringe. Under vigorous stirring, iodomethane (11.4 mL, 182 mmol) was added dropwise to the solution, and the reaction mixture was warmed to 50 °C for 6 h while a dry ice condenser was attached. More NaOH (7.3 g, 182 mmol) and more TDA-1 (1.4 mL, 4.3 mmol) were added, and the solution was stirred until ^{1}H NMR showed complete conversion of the starting material. The reaction mixture was then filtered, and the solid residue thoroughly rinsed with toluene. The filtrate was washed with dilute NaOH (2 M, 3 × 50 mL). The combined organic layers were dried over sodium sulfate, and the solvent was evaporated. The solid residue was dissolved in 2 M hydrochloric acid (150 mL) and extracted with hexanes (3 × 50 mL). Then, concentrated NaOH was added to the aqueous layer until the solution was strongly basic and a white precipitate appeared. After extraction with hexanes (3 × 100 mL), the combined organic layers were dried over sodium sulfate and the solvent was evaporated to yield 18.5 g (75 mmol, 82%) of **2** as a white solid. Mp: 64 °C (lit.[88] 66−67 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.90 (s, 6 H, CH_3), 6.47 (dt, J = 9.0 Hz, J = 2.1 Hz, 2 H, Ar), 7.54 (dt, J = 9.0 Hz, J = 2.1 Hz, 2 H, Ar).

*4,4′-Dibromodiphenylacetylene (**3**).* 1-Bromo-4-iodobenzene (125 g, 0.44 mol), CuI (265 mg, 1.1 mmol), and $Pd(PPh_3)_2Cl_2$ (1.05 g, 1.1 mmol) were charged into a dry 1 L three-necked flask under an argon atmosphere. Freshly distilled triethylamine (600 mL) was added from a syringe, and the solution was cooled to 10 °C with an ice/water bath. Then a steady stream of acetylene was bubbled through the solution until ^{1}H NMR showed complete conversion of the starting material after 3 h. The reaction mixture was poured into 4 M hydrochloric acid (500 mL) and extracted with chloroform (4 × 200 mL). After drying over sodium sulfate, the solvents were evaporated and the crude product was flash chromatographed (silica gel, chloroform/hexane, 1:3). 4,4′-Dibromodiphenylacetylene (**3**) was recrystallized from chloroform/hexanes: 59.8 g (0.18 mol, 81%). Mp: 181 °C (lit.[89] 182−184 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 (dt, J = 8.7 Hz, J = 1.8 Hz, 4 H, Ar), 7.47 (dt, J = 8.7 Hz, J = 1.8 Hz, 4 H, Ar).

*4,4′-N,N-Dimethylaminodiphenylacetylene (**4**).* 4-Iodo-*N*,*N*-dimethylaniline (**2**) (2.1 g, 8.5 mmol), CuI (26 mg, 0.13 mmol), and $Pd(PPh_3)_2Cl_2$ (100 mg, 0.13 mmol) were charged to a dry 100 mL three-necked flask under an argon atmosphere. Freshly distilled dry triethylamine (80 mL) was added from a syringe, and a steady stream of acetylene was bubbled through the solution under vigorous stirring in the dark. After 12 h, a second portion of $Pd(PPh_3)_2Cl_2$ (100 mg, 0.13 mmol) was added, and the gas flow was continued until ^{1}H NMR showed the complete conversion of starting material after 48 h. The reaction mixture then was poured into 4 M NaOH (100 mL) and extracted with toluene (3 × 50 mL). The organic layers were combined and dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The crude product (525 mg, 47%) was chromatographed (silica gel: toluene) and recrystallized from THF to yield 348 mg (1.3 mmol, 31%) of **4** as large pale red cubes. Mp: 242 °C (lit.[90] 240−243 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.96 (s, 12 H, CH_3), 6.64 (dt, J = 9.0 Hz, J = 2.1 Hz, 4 H, Ar), 7.37 (dt, J = 9.0 Hz, J = 2.1 Hz, 4 H, Ar).

*4,4′-Dimethyldiphenylacetylene (**5**).* *Method A*: 1-Iodo-4-methylbenzene (5.0 g, 23 mmol) and CuI (108 mg, 0.57 mmol) were charged into a dry 100 mL three-neck flask under an argon atmosphere. Freshly distilled 1-ethynyl-4-methylbenzene (2.9 mL, 23 mmol) and freshly distilled, dry triethylamine (80 mL) were added from a syringe, and the solution was degassed by three freeze−pump−thaw cycles. Subsequently, $Pd(PPh_3)_4$ (670 mg, 0.57 mmol) was added from a tip tube. The reaction mixture was warmed to 50 °C and stirred for 5 h in the dark. After ^{1}H NMR showed a full conversion of the starting material, the solution was poured into dilute hydrochloric acid (2 M, 250 mL) and extracted with toluene (3 × 100 mL). The organic layers were combined and dried over sodium sulfate. After evaporation of the solvent, the crude reaction mixture was chromatographed (silica gel, chloroform/hexane, 1:5). The desired product **5** was recrystallized from hexane to yield 3.9 g (20 mmol, 86%) of **5** as white plates. Mp: 135 °C (lit.[91] 136 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.27 (s, 6 H, CH_3), 6.91 (dt, J = 8.1 Hz, J = 1.8 Hz, 4 H, Ar), 7.54 (dt, J = 8.1 Hz, J = 1.8 Hz, 4 H, Ar). *Method B*: 1-Iodo-4-methylbenzene (5.0 g, 23 mmol), CuI (29 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (110 mg, 0.15 mmol) were charged into a dry 100 mL three-necked flask under an argon atmosphere. Freshly distilled triethylamine (80 mL) was added from a syringe. A steady stream of acetylene was then bubbled through the solution until ^{1}H NMR showed complete conversion of the starting material after 12 h. The reaction mixture was poured into dilute hydrochloric acid (2 M, 250 mL) and extracted with chloroform (3 × 100 mL). After drying over sodium sulfate, the solvents were evaporated and the crude product was chromatographed (silica gel, chloroform/hexane, 1:5), yielding **5** as a white solid: 3.6 g (17 mmol, 74%).

*4,4′-Dinitrodiphenylacetylene (**6**).* 4-Iodo-1-nitrobenzene (5.0 g, 20 mmol), CuI (26 mg, 0.13 mmol), and $Pd(PPh_3)_2Cl_2$ (100 mg, 0.13 mmol) were charged into a dry 100 mL three-necked flask under an argon atmosphere. Freshly distilled triethylamine (80 mL) was added from a syringe. A steady stream of acetylene was then bubbled through the solution until ^{1}H NMR showed complete conversion of the starting material after 68 h. The reaction mixture was poured into 2 M hydrochloric acid (250 mL) and extracted with chloroform (3 × 100 mL). After drying over sodium sulfate, the solvents were evaporated and the crude product was chromatographed (silica gel, chloroform/hexane, 1:3). The product was recrystallized from hexanes to yield 4.5 g (17 mmol, 83%) of **6** as pale yellow needles. Mp: 208 °C (lit.[92] 205−207 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (dt, J = 8.7 Hz, J = 1.8 Hz, 4 H, Ar), 8.23 (dt, J = 8.7 Hz, J = 1.8 Hz, 4 H, Ar).

*1-(4-Bromophenyl)-2-(4-trimethylsilylphenyl)acetylene (**7**).* 4-Iodophenyltrimethylsilane (9.93 g, 36.0 mmol), 4-bromophenylacetylene (7.15 g, 39.5 mmol), CuI (110 mg, 6 mmol), $PdCl_2(PPh_3)_2$ (840 mg, 1.2 mmol), and diethylamine (185 mL) were charged to a 500 mL three-neck flask and stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue dissolved in diethyl ether and washed twice with water. The organic layer was dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was triturated with hexanes and filtered on sintered glass, which removed a white solid. The filtrate was concentrated under reduced pressure, giving an orange residue, which was chromatographed on silica gel (eluent: hexanes) to give **7** as a white solid (10 g, 30 mmol, 84%), which was recrystallized from cold pentane. Mp: 82 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.58 (m, 2 H, Ar), 7.34 (m, 2 H, Ar), 7.08 (m, 4 H, Ar), 0.14 (s, 9 H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 MHz): δ −1.34 (Si−C), 89.42. 91.33, 122.58, 122.81, 123.86, 131.08, 131.87, 133.29, 133.72, 141.44. MS (EI+): m/z (rel int) 328 ([M]$^+$, 40), 272 ([M − CH_3]$^+$, 100). Anal. Calcd for $C_{17}H_{17}SiBr$: C, 62.00; H, 5.20. Found: C, 61.84; H, 5.35.

*1-(4-Bromophenyl)-2-(4-methoxyphenyl)acetylene (**8**).* 4-Bromophenylacetylene (5 g, 27.6 mol), 4-iodoanisole (6.15 g, 26.2 mmol), $PdCl_2(PPh_3)_2$ (0.646 g, 0.92 mmol), CuI (90 mg, 0.46 mmol), and triethylamine (120 mL) were charged to a 500 mL three-neck flask. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the solid residue was dissolved in CH_2Cl_2, washed twice with water, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crystalline product was chromatographed on silica gel (dichloromethane/hexanes, starting at 25:75 and gradually increasing the proportion of dichloromethane) to give **8** as white crystals (6.4 g, 22 mmol, 85%). It was recrystallized from dichloromethane and hexanes. Mp: 154−155 °C (lit.[93] 150−152 °C; lit.[94] 155 °C).

*1-(4-Acetoxyphenyl)-2-(4-bromophenyl)acetylene (**9**).* 4-Acetoxyiodobenzene (0.5 g, 1.9 mmol), 4-bromophenylacetylene (0.36 g, 2.0 mmol), CuI (6 mg, 0.032 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 0.064 mmol), and triethylamine (20 mL) were charged to a 100 mL three-neck flask and stirred for 3 h at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in dichlormethane and washed twice with water. The organic layer was dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (eluent: acetone/hexanes, 1:1) to give **9** as a gray-white solid (0.56 g, 1.8 mmol, 93%). It was then recrystallized from acetone and hexanes. Mp: 136−137 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.37 (m, 2 H, Ar), 7.08 (s, 4 H, Ar), 6.88 (m, 2 H, Ar), 1.68 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 MHz): δ 20.42 (CH_3), 88.89. 90.33, 120.75, 122.14, 122.46, 122.83, 131.90, 132.92, 133.22, 151.37, 167.97 (C═O). MS (EI+): m/z (rel int) 314 ([M]$^+$, 10), 272 ([M − $COCH_3$]$^+$, 100), 165 (18), 43 ($OCCH_3$, 27). Anal. Calcd for $C_{16}H_{11}O_2Br$: C, 60.98; H, 3.52. Found: C, 60.86; H, 3.23.

*1-(4-Bromophenyl)-2-(4-hydroxyphenyl)acetylene (**10**).* 4-Trimethylsilyliodobenzene (4.23 g, 14.5 mmol), 4-bromophenylacetylene (2.75 g, 15.0 mmol), CuI (20.0 mg, 0.11 mmol), $PdCl_2(PPh_3)_2$ (0.105 g, 0.15 mmol), and triethylamine (100 mL) were charged to a 250 mL three-neck flask and stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue dissolved in dichloromethane and washed once with 1 M HCl and twice with water. The organic layer was dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (eluent: dichloromethane) to give **10** as a gray-white solid (2.6 g, 9.5 mmol, 65%), which was then recrystallized from dichloromethane and hexanes. Mp: 149−150 °C (change of color) (lit.[95] 148−149 °C; lit.[96] 182 °C). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.34 (m, 2 H, Ar), 7.08 (m, 4 H, Ar), 6.32 (m, 2 H, Ar), 3.9 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR (DMSO, 300 MHz): δ 86.30, 91.25. 112.07, 115.75, 121.45, 122.14, 131.67, 132.93, 133.06, 158.25. MS (EI+): m/z (rel int) 272 ([M]$^+$, 100), 165 (30), 139 (10).

*1-(4-Bromophenyl)-2-(4-isopropoxyphenyl)acetylene (**11**).* Compound **10** (2.11 g, 7.73 mmol), 2-bromopropane (1.14 g, 9.3 mmol), potassium carbonate (2.7 g, 19.5 mmol), and dry DMF (75 mL) were charged to a 250 mL three-neck flask. The mixture was heated to 120 °C for 3 h. Then 2-bromopropane (1.14 g, 9.3 mmol) was added, and the mixture was stirred overnight at 120−130 °C under an argon atmosphere. The mixture was poured into a 1 M HCl solution (100 mL) and extracted with chloroform (3 × 30 mL). The combined organic layers were washed with water (3 × 30 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (eluent: chloroform/hexanes, 60:40) to give **11** as a white solid (2.1 g, 6.7 mmol, 86%). Mp: 117−118 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.46 (m, 2 H, Ar), 7.10 (m, 4 H, Ar), 6.66 (m, 2 H, Ar), 4.04 (hept, J = 6.0 Hz, 1 H, CH), 1.03 (d, J = 6.0 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 MHz): δ 21.84 (CH_3), 69.62 (CH), 87.59, 91.49, 115.13, 115.98, 122.30, 123.11, 131.84, 133.12, 133.48, 158.70. MS (EI+): m/z (rel int) 314−316 ([M]$^+$, 25), 272 (100), 163 (22), 43 (12). Anal. Calcd for $C_{17}H_{15}OBr$: C, 64.77; H, 4.80. Found: C, 64.64; H, 4.63.

*[1,3-Bis(4-bromophenyl)-2,4-bis(4-trimethylsilylphenyl)cyclobutadiene]cyclopentadienylcobalt (**12a**).* Compound **7** (1.62 g, 4.9 mmol), freshly distilled $CpCo(CO)_2$ (0.44 g, 2.47 mmol), and degassed xylenes (100 mL) were charged to a 200 mL three-neck flask and refluxed overnight in the dark. After cooling, the dark solution was poured onto a dry column of silica gel and eluted with hexanes. An orange band was collected, and the solvent was removed under reduced pressure. The solid was collected on a frit and washed with copious amounts of hexanes and a few milliliters of acetone. Compound **12a** was recrystallized from a mixture of dichloromethane and acetonitrile (0.5 g, 0.64 mmol, 26%). Single crystals were obtained from a mixture of benzene and acetonitrile. Mp: 285−295 °C (dec). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.38 (m, 8 H, Ar), 7.33 (m, 8 H, Ar), 4.62 (s, 5 H, Cp), 0.28 (s, 18 H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 MHz): δ −1.12 (Si−C), 74.24 (Cb), 75.42 (Cb), 83.62 (Cp), 120.04 (Ar), 128.32 (Ar), 133.70 (Ar), 131.45 (Ar), 133.48 (Ar), 136.06 (Ar), 136.59 (Ar), 139.06 (Ar). MS (FAB+, 3-NOBA): m/z 780 (maximum at 782). HRMS calcd for $C_{39}H_{39}Si_2Br_2Co$: 780.0289. Found: 780.0269. Anal. Calcd for $C_{39}H_{39}Si_2Br_2Co\cdot 1/2CH_2Cl_2$: C, 57.50; H, 4.89. Found: C, 57.26; H, 4.81.

*[1,3-Bis(4-bromophenyl)-2,4-bis(4-methoxyphenyl)cyclobutadiene]cyclopentadienylcobalt (**13a**).* The procedure described for **12a** was followed, using **8** (2.48 g, 8.7 mmol), $CpCo(CO)_2$ (0.78 g, 4.3 mmol), and degassed xylenes (100 mL) in a 250 mL three-neck flask and refluxing overnight in the absence of light. After cooling, the dark solution was poured onto a dry column of silica gel, and an orange band eluted with dichloromethane. The first fraction (150 mL) contains mainly the desired isomer. The solvent was removed under reduced pressure, and the brown residue was collected on a frit and washed with diethyl ether. The product was then purified by flash chromatography on silica gel (eluent: chloroform/pentane, 60:40). The desired isomer (top spot on TLC) was collected, and the same purification procedure was applied to the other fractions. Compound **13a** was then washed with diethyl ether (0.33 g, 0.43 mmol, 6%) and

recrystallized from DMSO as dark red crystals. Mp: 308−310 °C. MS (ESI+): *m/z* 696 (maximum at 698). Anal. Calcd for $C_{35}H_{27}O_2Br_2Co$: C, 60.20; H, 3.90. Found: C, 60.31; H, 3.71. The NMR data agree with those reported.[52]

*[1,3-Bis(4-acetoxyphenyl)-2,4-bis(4-bromophenyl)cyclobutadiene]cyclopentadienylcobalt (**14a**).* The procedure described for **12a** was followed, using **9** (2.87 g, 9.1 mmol), $CpCo(CO)_2$ (0.82 g, 4.5 mmol), and degassed xylenes (150 mL) in a 500 mL three-neck flask and refluxing for 20 h in the absence of light. After cooling, the dark solution was poured onto a dry column of silica gel (*h* = 30 cm), and an orange band eluted with chloroform. The first fraction (200 mL) contains mainly the desired isomer. The solvent was removed under reduced pressure, the product was rechromatographed on silica gel (eluent: chloroform), and the fractions containing the desired isomer (top spot on TLC) were collected. The second fraction (200 mL) contains a mixture of the two isomers. The same purification procedure was applied to isolate both isomers. After removing the solvent, all the fractions corresponding to the expected isomer were combined and rechromatographed on silica gel (eluent: chloroform) to give **14a** as a yellow-orange solid (0.52 g, 0.69 mmol, 15%). The product was then recrystallized from a mixture of dichloromethane and hexanes. Single crystals were obtained from a mixture of THF and ethanol. Mp: 244−246 °C. ^1H NMR (DMSO, 300 MHz): δ 7.45 (m, 4 H, Ar), 7.37 (m, 4 H, Ar), 7.27 (m, 4 H, Ar), 7.04 (m, 4 H, Ar), 4.70 (s, 5 H, Cp), 2.27 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz): δ 21.31 (CH_3), 74.13 (Cb), 74.59 (Cb), 83.67 (Cp), 120.26 (Ar), 121.86 (Ar), 129.95 (Ar), 130.66 (Ar), 131.64 (Ar), 133.62 (Ar), 135.61 (Ar), 149.66 (2C, Ar), 169.59 (C═O). MS (FAB+, 3-NOBA): *m/z* 752 (maximum at 754). Anal. Calcd for $C_{37}H_{27}O_4Br_2Co$: C, 58.91; H, 3.61. Found: C, 58.50; H, 3.37.

*[1,2-Bis(4-acetoxyphenyl)-3,4-bis(4-bromophenyl)cyclobutadiene]cyclopentadienylcobalt (**14b**).* The third fraction (300 mL) contains mainly the second isomer (second spot by TLC). The same purification procedure was applied. After removing the solvent, all the fractions corresponding to this isomer were combined and flash chromatographed on silica gel (eluent: chloroform) to give **14b** as a yellow-orange solid (0.33 g, 0.43 mmol, 10%). The product was then recrystallized from a mixture of chloroform and hexanes. Mp: 258−260 °C. ^1H NMR (DMSO, 300 MHz): δ 7.46 (m, 4 H, Ar), 7.36 (m, 4 H, Ar), 7.28 (m, 4 H, Ar), 7.04 (m, 4 H, Ar), 4.70 (s, 5 H, Cp), 2.26 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz): δ 21.31 (CH_3), 73.94 (Cb), 74.81 (Cb), 83.68 (Cp), 120.27 (Ar), 121.85 (Ar), 129.95 (Ar), 130.68 (Ar), 131.65 (Ar), 133.64 (Ar), 135.62 (Ar), 149.66 (2C, Ar), 169.61 (C═O). MS (ESI+): *m/z* 752 (maximum at 754). Anal. Calcd for $C_{37}H_{27}O_4Br_2Co$: C, 58.91; H, 3.61. Found: C, 58.90; H, 3.42.

*[1,3-Bis(4-bromophenyl)-2,4-bis(4-isopropoxyphenyl)cyclobutadiene]cyclopentadienylcobalt (**15a**).* The procedure described for **12a** was followed, using **11** (1.65 g, 5.2 mmol), $CpCo(CO)_2$ (0.47 g, 2.6 mmol), and degassed xylenes (100 mL) in a 250 mL three-neck flask and refluxing for 20 h in the dark. After cooling, the dark solution was poured onto a dry column of silica gel, and an orange band eluted with chloroform. The first fraction (200 mL) contains mainly the desired isomer. The solvent was removed under reduced pressure, the product was rechromatographed on silica gel (eluent: chloroform/hexanes, 50:50), and the fractions containing the desired isomer (top spot on TLC) were collected. The second fraction contains a mixture of the two isomers. The same purification procedure was repeated twice to isolate **15a** as a yellow-orange solid (0.32 g, 0.42 mmol, 16%). Single crystals have been obtained from a mixture of THF and ethanol. Mp: 252−256 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.40 (m, 4 H, Ar), 7.33 (m, 4 H, Ar), 7.17 (m, 4 H, Ar), 6.73 (m, 4 H, Ar), 4.45 (s, 5 H, Cp), 4.21 (hept, *J* = 6.0 Hz, 2 H, CH), 1.12 (d, *J* = 6.0 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz): δ 22.26 (CH_3), 70.18 (CH), 73.25 (Cb), 75.81 (Cb), 83.38 (Cp), 115.66 (Ar), 119.68 (Ar), 127.34 (Ar), 130.26 (Ar), 130.64 (Ar), 131.42 (Ar), 136.65 (Ar), 157.17 (2C, Ar). MS (ESI+): *m/z* 752 (maximum at 754). Anal. Calcd for $C_{39}H_{35}O_2Br_2Co$: C, 62.09; H, 4.68. Found: C, 62.06; H, 4.60.

*[1,2-Bis(4-bromophenyl)-3,4-bis(4-isopropoxyphenyl)cyclobutadiene]cyclopentadienylcobalt (**15b**).* All fractions corresponding to the second isomer were combined and flash chromatographed twice on silica gel (eluent: chloroform/hexanes, 50:50) to give **15b** as a yellow solid (0.17 g, 0.23 mmol, 9%). Mp: 170−180 °C (dec). ^1H NMR (C_6D_6, 300 MHz): δ 7.46 (m, 4H, Ar), 7.26 (m, 4 H, Ar), 7.17 (m, 4 H, Ar), 6.73 (m, 4 H, Ar), 4.45 (s, 5 H, Cp), 4.19 (hept, *J* = 6.0 Hz, 2 H, CH), 1.11 (d, *J* = 6.0 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz): δ 22.26 (CH_3), 70.15 (CH), 72.93 (Cb). 76.06 (Cb), 83.37 (Cp), 115.62 (Ar), 119.81 (Ar), 127.52 (Ar), 130.33 (Ar), 130.58 (Ar), 131.48 (Ar), 136.51 (Ar), 157.08 (2C, Ar). MS (ESI+): *m/z* 751 (maximum at 753). Anal. Calcd for $C_{39}H_{35}O_2Br_2Co$: C, 62.09; H, 4.68. Found: C, 62.49; H, 4.46.

*[1,2-Bis(4-nitrophenyl)-3,4-bis(4-N,N-dimethylaminophenyl)-cyclobutadiene]cyclopentadienylcobalt (**16b**).* Compound **4** (500 mg, 1.9 mmol) and compound **6** (1.5 g, 5.7 mmol) were suspended in 100 mL of degassed xylenes in a 250 mL three-neck flask with stir bar and condenser. The mixture was subsequently heated to 80 °C, at which time both components dissolved, and 1.0 g (5.7 mmol) of freshly distilled $CpCo(CO)_2$ was added via syringe. The reaction was heated to reflux overnight in the dark. After cooling, the reaction mixture was poured onto a plug of silica gel on a glass frit and eluted with ethyl acetate. The solvent was removed under reduced pressure to give a black oil. The oil was chromatographed on silica gel [gradient: hexanes (100−80)/ethyl acetate (0−20)], first eluting a yellow band containing unreacted **6** (214 mg). Compound **16b** eluted in a second, red band, which gave an indigo-colored solid upon removal of the solvent. The product was crystallized by slow evaporation of CH_2Cl_2 from a ~3:1 $MeOH/CH_2Cl_2$ solution to give 532 mg (0.91 mmol, 48%) of pure **16b**. Mp: 268−270 °C. ^1H NMR (CD_2Cl_2, 500 MHz): δ 2.97 (s, 12 H, N−CH_3), 4.59 (s, 5 H, Cp), 6.59 (d, *J* = 8 Hz, 4 H, Ar), 7.27 (d, *J* = 8 Hz, 4 H, Ar), 7.55 (d, *J* = 8 Hz, 4 H, Ar), 8.06 (d, *J* = 8 Hz, 4 H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 500 MHz): δ 40.52 (N−CH_3), 83.39 (Cb), 112.10 (Cp), 123.65 (Ar), 128.85 (Ar), 130.08 (Ar), 145.63 (Ar), 146.76 (Ar). MS (EI^+) *m/z* (rel int): 956 ($[M]^+$, 100), 388 (15), 250 (10), 220 (15), 69 (30). IR (KBr, cm^{-1}): 554, 729, 736, 782, 808, 827, 854, 945, 1067, 1107, 1168, 1194, 1224, 1340, 1511, 1444, 1511, 1589, 1609, 2800, 1442. UV−vis (solvent): λ (ε) 200 (79 000), 260 (35 000), 320 (34 000), 352 (sh, 30 000), 450 (12 000) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{37}H_{33}N_4O_4Co$: C, 67.68; H 5.07; N, 8.53. Found: C, 67.78; H, 5.26; N, 8.21. HRMS (ESI+): calcd for $C_{37}H_{33}N_4O_4Co$: 656.1828. Found: 656.1841.

*Tetrakis(4-N,N-dimethylaminophenyl)cyclobutadienecyclopentadienylcobalt (**16a**).* To 80 mg (0.30 mmol) of **4** dissolved in 20 mL of dry, degassed xylenes in a 50 mL three-neck flask with stir bar and condenser was added 27 mg (0.152 mmol) of $CpCo(CO)_2$. The reaction mixture was brought to reflux for 3 h, at which point TLC (4:1 hexanes/ethyl acetate) showed the absence of starting material. After cooling, the reaction was poured over a plug of silica gel on a glass frit and eluted with ethyl acetate. The solvent from the eluent was removed under reduced pressure, and the resulting dark solid was chromatographed on silica gel (4:1 hexanes/ethyl acetate) to yield 64 mg (0.10 mmol, 66%) of **16a** as a gold solid. The product was crystallized by slow evaporation of CH_2Cl_2 for a ~3:1 $MeOH/CH_2Cl_2$ solution. Mp: >285 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.93 (s, 24 H, $N(CH_3)_2$), 4.55 (s, 5 H, Cp), 6.57 (d, *J* = 8 Hz, 8 H, Ar), 7.36 (d, *J* = 8 Hz, 8 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 40.65 ($N(CH_3)_2$), 74.63 (Cb), 82.61 (Cp), 112.05 (Ar), 125.24 (Ar), 129.80 (Ar), 148.46 (Ar). MS (EI^+) *m/z* (rel int): 652 ($[M]^+$, 20), 388 ($[M-\mathbf{4}]^+$, 10), 264 ($[\mathbf{4}]^+$,100), 205 (25), 129 (30). IR (KBr, cm^{-1}): 664, 800, 1029, 1103, 1262, 1348, 1511, 1600, 2792, 2850, 2928, 2963, 3449. UV−vis (solvent): λ (ε) 229 (27 500), 262 (sh, 23 000), 318 (53 500), 410 (br, 6000) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{41}H_{45}N_4Co$: C, 75.45; H, 6.95; N, 8.58. Found: C, 75.65; H, 7.02; N, 8.42.

*[1,2-Bis(4-pyridyl)-3,4-bis(4-methylphenyl)cyclobutadiene]cyclopentadienylcobalt (**17c**).* 4,4′-Dipyridylacetylene (1.75 g, 9.7 mmol) and compound **5** (1.0 g, 4.85 mmol) were suspended in 50 mL of degassed xylenes in a 100 mL three-neck flask. The mixture was heated to 80 °C, at which time both components went into solution, and 1.75 g (9.71 mmol) of $CpCo(CO)_2$ was added from a syringe. The reaction mixture was heated to reflux overnight in the dark. After cooling, the solvent was removed under reduced pressure, and the dark red solid

was dissolved in methylene chloride and poured over silica gel on a glass frit. Elution with methylene chloride brought off **17a** as a yellow band. The silica gel was then eluted with methanol to give a mixture of **17c** and **17b** as a dark red solid after removal of the methanol. The solid was triturated with methanol, and an orange solid was collected on a glass frit. The dark red filtrate contained only compound **17b** (800 mg, 35% crude yield). The orange solid, which contained mostly **17c**, was crystallized from $CHCl_3$/MeOH to give 420 mg (0.82 mmol, 17%) of **17c** as a yellow-orange powder. The product was oxidized without further purification. Mp > 200 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.32 (s, 6 H, CH_3), 4.65 (s, 5 H, Cp), 7.07 (d, J = 7.2 Hz, 4 H, Ar), 7.30 (d, J = 7.8 Hz, 4 H, Ar), 7.31 (m, 4 H, Ar), 8.41 (m, 4 H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 21.61 (CH_3), 70.53 (Cb), 83.71 (Cp), 123.10 (Ar), 128.98 (Ar), 129.19 (Ar), 131.62 (Ar), 137.09 (Ar), 146.24 (Ar), 149.70 (Ar). MS (EI$^+$) m/z (rel int): 510 (M, 95), 317 (22), 206 (10), 124 (52), 84 (48), 69 (20), 57 (28), 31 (100). IR (KBr, cm^{-1}): 484, 526, 531, 596, 618, 629, 642, 663, 724, 818, 832, 991, 1001, 1061, 1106, 1180, 1215, 1412, 1507, 1515, 1541, 1590, 1597, 3021, 3442.

*Tetrakis(4-methylphenyl)cyclobutadienecyclopentadienylcobalt (**17a**).* This material was formed during the synthesis of **17c**. After elution on silica gel, the solvent was removed under reduced pressure, and the resulting yellow solid triturated with methanol. The resulting solid was recrystallized from hexanes to give pure **17a** (280 mg, 0.52 mmol, 11%). Mp: 308−310 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.28 (s, 12 H, CH_3), 4.57 (s, 5 H, Cp), 6.99 (d, J = 7.6 Hz, 8 H, Ar), 7.32 (d, J = 7.6 Hz, 8 H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 21.58 (CH_3), 74.86 (Cb), 83.27 (Cp), 128.82 (Ar), 128.95 (Ar), 133.80 (Ar), 135.84 (Ar). MS (EI$^+$) m/z (rel int): 536 ([M]$^+$, 100), 330 ([M − **5**]$^+$, 40), 206 ([**5**]$^+$, 25), 124 (55). IR (KBr, cm^{-1}): 404, 483, 516, 553, 592, 632, 703, 722, 735, 807, 828, 841, 93, 1001, 1018, 1110, 1179, 1516, 1608, 1714, 1902, 2857, 2914, 3017, 3053. UV−vis (CH_2Cl_2): λ (ε) 312 sh (21 000), 269 (39 000), 243 (33 000) nm (L mol^{-1} cm $^{-1}$). Anal. Calcd for $C_{37}H_{33}Co$: C, 82.82; H, 6.20. Found: C, 82.83; H, 6.12.

*[1,2-Bis(4-pyridine-N-oxide)-3,4-bis(4-methylphenyl)cyclobutadiene]cyclopentadienylcobalt (**18**).* Compound **17c** (1.0 g, 2.0 mmol) was dissolved in 40 mL of dichloromethane and cooled to 0 °C in an ice water bath. To the solution was added dropwise an excess of dimethyldioxirane in acetone.[97] After warming to room temperature, 40 mL of water was added and the layers were separated. The aqueous layer was washed twice more with dichloromethane (20 mL). After drying over sodium sulfate the solvent was removed under reduced pressure to yield 1.0 g (1.9 mmol, 95%) of compound **18**. Mp: >280 °C (dec). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.29 (s, CH_3, 6 H, CH_3), 4.62 (s, 5 H, Cp), 7.08 (d, J = 7.9 Hz, 4 H, Ar), 7.21 (d, J = 8.1 Hz, 4 H, Ar), 7.23 (d, J = 7.0 Hz, 4 H, Ar), 7.96 (d, J = 7.3 Hz, 4 H, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz): δ 21.52 (CH_3), 69.15 (Cb), 77.88 (Cb), 83.55 (Cp), 124.21 (Ar), 128.75 (Ar), 129.38 (Ar), 130.69 (Ar), 136.39 (Ar), 137.56 (Ar), 139.08 (Ar). IR (KBr, cm^{-1}): 743, 821, 846, 995, 1023, 1087, 1106, 1163, 1244, 1452, 1485, 1505, 1614, 2862. UV−vis (solvent): λ (ε) 227 (33 000), 229 (41 500), 345 (22 000), 400 (6500) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{33}H_{27}N_2O_2Co$: C, 73.06; H, 5.02; N, 5.16. Found: C, 72.95; H, 4.99; N, 5.01.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational methods and optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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