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Bis(η^5-cyclopentadienyl)[μ-(4b,5,5a-η^3:9b,10,10a-η^3)-2,3,7,8-tetrakis(trimethylsilyl)benzo[3,4]cyclobuta[1,2-*b*]biphenylene]-*syn*-dicobalt (Co–Co), a Dinuclear π-Complex of the Linear [3]Phenylene Framework

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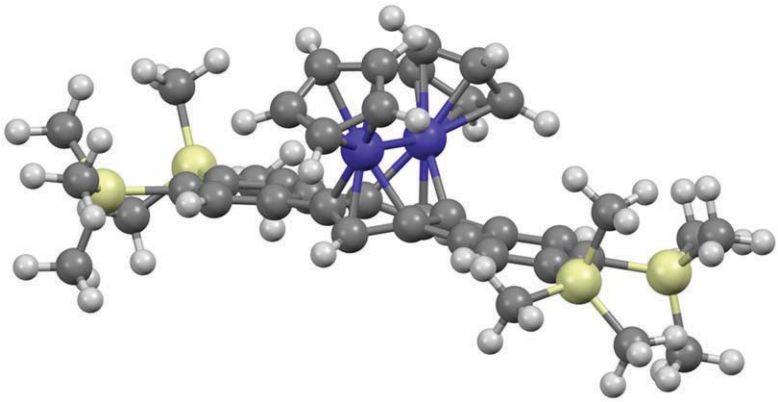

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Abstract The title compound was made by the reaction of the CpCo-complex of 2,3,7,8-tetrakis(trimethylsilyl) linear [3]phenylene, in which the metal coordinates one of the cyclobutadiene rings, with CpCo(C_2H_4)$_2$. Because of its relative stability, a *syn*-dicobalt-bound configuration is indicated rather than its *anti* alternative.

Key words aromaticity, cobalt, complexation, dinuclear complexes, phenylenes

The [*N*]phenylenes (*N* = number of benzene rings) are σ- and π-activated polycyclic hydrocarbons, in which benzene rings alternate with fused cyclobutadienes.[1] Among their various topologies (linear, angular, bent, trigonal, and helical), the linear version is distinguished by its relatively accentuated antiaromatic nature, originating from the lack of any resonance forms that avoid placing a double bond into the cyclobutadienoid fragment. As a consequence, the linear compounds emerge during their synthesis by CpCoL_2-mediated alkyne cyclotrimerization as their mono-CpCo(cyclobutadiene) complexes,[2] in turn leading to the unveiling of unprecedented inter-ring haptotropism across the entire phenylene frame (Figure 1).[2a,3] All of the known linear phenylene(CpCo) complexes share one common feature: a single CpCo unit bound to the phenylene scaffold. However, because there are one or more additional cyclobutadienoid rings in the series, the question arises as to whether it might be possible to bind more than one metal fragment to the ligand. If so, what would be the structural consequences? Would such systems be capable of haptotropism and, if so, how would the metals move relative to the ligand and to each other? This paper describes a foray into finding answers to these questions by using complex **1** (Figure 1) as a testing ground.

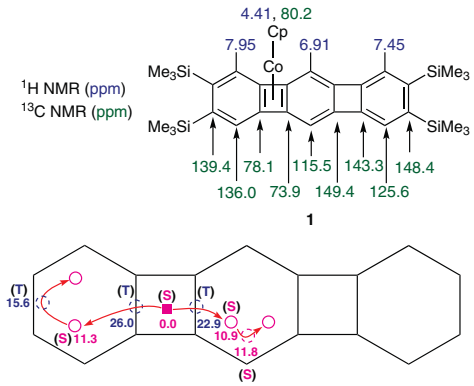

Figure 1 Top: Structure of **1** and its pertinent NMR chemical shifts. Bottom: Calculated trajectory of complexed CpCo across the [3]phenylene frame as experimentally verified on, e.g., **1** and its derivatives. S: η^4-bound singlet species, T: η^2-bound triplet. The numbers are energies (kcal/mol) relative to the ground-state CpCo(cyclobutadiene) structure.

For this system, at the outset, a bisCpCo(cyclobutadiene) array of type **2**, formally a biradical, has precedence in the unique complex **3**, for which there is X-ray structural confirmation but no other spectral information (Figure 2).[4] Further evidence for the feasibility of **2** is the isolation of side products **4** and **5** of the cyclizations engendering 2,3,8,9-tetrakis(trimethylsilyl)[4]phenylene[2c] and 2,3,9,10-tetrakis(trimethylsilyl)[5]phenylene,[2b] respectively (Figure 2), possibly through trapping the diradicals corresponding to **2** with the bis(trimethylsilyl)acetylene reagent. These considerations notwithstanding, there was a looming pos-

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sibility of conceivable insertion reactions of the metal into the four-membered rings,[5] thereby preempting the desired π-complexation chemistry.

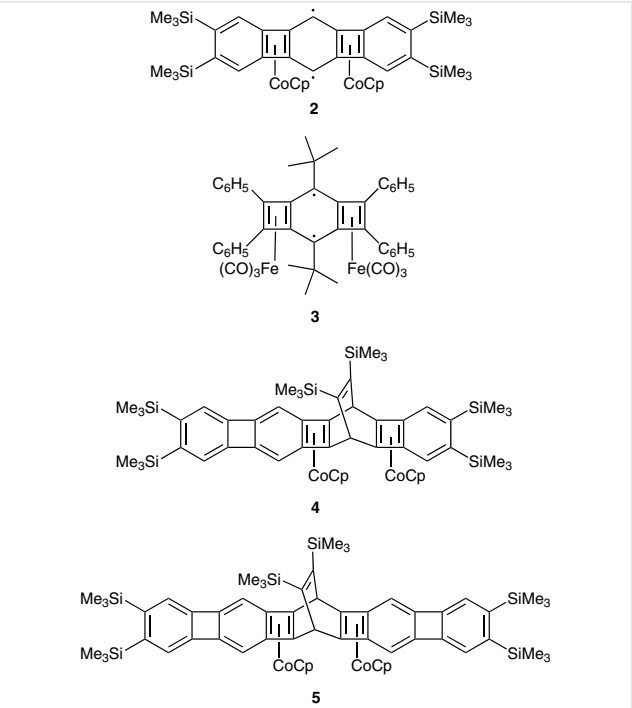
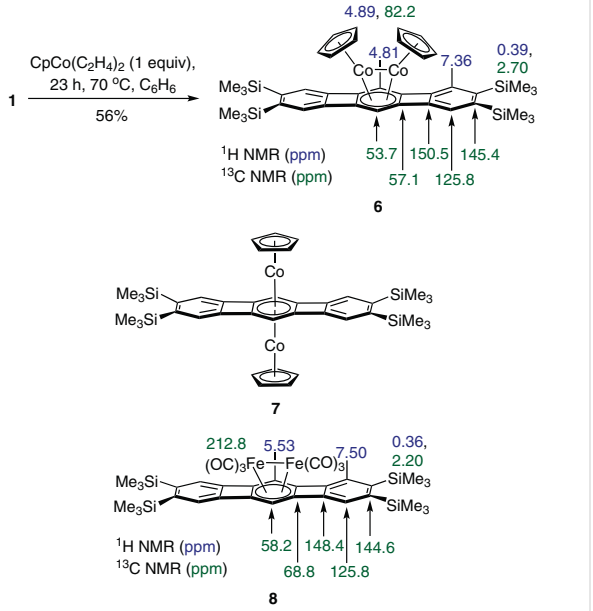


Figure 2 Potential product **2** of the metalation of **1**. Similar substructures might be responsible for the formation of compounds **3**–**5** in the synthesis of linear [4]- and [5]phenylene derivatives (see text).

In the event, complex **1** was treated with one equivalent of $CpCo(C_2H_4)_2$ in benzene at 70 °C to afford a reddish-black solid, assigned (initially tentatively) the gross structure **6** (56%), exhibiting a *syn*-dicobalt attachment mode rather than the alternative *anti*-configuration **7** (Scheme 1). The mass spectrum exhibited a molecular ion peak at *m/z* = 762, corresponding to [**1** + CpCo]. The ^{1}H NMR spectrum (acetone-d_6) revealed four sharp singlets integrating in the ratio 4:10:2:36, indicative of a highly symmetrical structure, a conclusion corroborated by the presence of only seven lines in the ^{13}C NMR spectrum. Cooling in the NMR probe to temperatures as low as –80 °C in toluene-d_8 did not produce any signs of signal decoalescence (see SI).

Two-dimensional NMR techniques (HSQC and HMBC) permitted a complete assignment of all the NMR peaks (Scheme 1) and, hence, a convincing structural diagnosis. Thus, possibility **2** is ruled out by the absence of a typically relatively deshielded aromatic singlet for a terminal benzene ring adjacent to the metallaaromatized-complexed four-membered cycle (δ = 7.9–8 ppm), as well as an absence of complexed cyclobutadiene signals [δ ≈ 74–80 ppm; see, for example, **1** (Figure 1) and its higher analogues].[1,2b,c,3] Moreover, there is one uncomplexed cyclobutadiene carbon peak (δ = 150.5 ppm). The greatly shielded (relative to the



Scheme 1 Synthesis of **6** from **1**, and NMR data for the product. Two-dimensional NMR correlations for **6** (δ_x/δ_y ppm); HSQC: 0.39/2.70, 4.81/53.7, 4.89/82.2, 7.36/125.8; HMBC: 0.36/145.4, 4.81/57.1, 150.5-7.36/57.1, 145.4, and 150.5 (see SI).

free ligand) proton (δ = 4.81 ppm) and carbon (53.7 and 57.1 ppm) resonances assigned to the central benzene ring strongly indicate that both cobalt fragments are coordinated to the phenylene ligand at this position. These NMR details are very similar to those of an iron complex obtained as a minor product in the reaction of 2,3,7,8-tetrakis(trimethylsilyl) linear [3]phenylene (the ligand in **1**) with $Fe_2(CO)_9$, for which (also tentatively) the syn arrangement **8** was proposed.[6] Unfortunately, extensive efforts to grow crystals of **6** suitable for X-ray analysis failed.

In an attempt to resolve the structural ambiguity presented by the possibility of structure **7**, we scrutinized the literature on related complexes[7] with respect to elucidating the NMR spectral features. This task was complicated by the fact that there are multiple modes of coordination to the pertinent arene ligand[8] and that there exist no directly comparable *syn*- and *anti*-diastereomers of this type. Moreover, inspection of cobalt analogues for which there is X-ray structural verification revealed that these systems all exhibit upfield shifts of the NMR signals for the dimetalated ring, comparable in magnitude to that observed for **6**/**7**.[9] For example, the fluxional *anti*-$(Cp^*Co\text{-}\eta^4\text{:}\eta^4)_2$ arenes [arene = benzene, toluene, *o*-, *m*-, or *p*-xylene, and (1-methylethyl)benzene] of type **7** show ^{1}H NMR absorptions at δ ≈ 2.7–3 ppm and ^{13}C NMR signals at δ ≈ 53–56 (CH) and 69 (C_{quat}) ppm.[9b,e] Similarly, the fluxional *syn*-$(CpCo\text{-}\eta^3\text{-}CpIr\text{-}\eta^3)$benzene presents hydrogen signals (coalesced at –50 °C) for the Co-bound benzene half at δ = 2.86 (1 H) and 4.12 (2 H) ppm. (A carbon spectrum was not presented).[9f] Finally, a fluxion-

al *syn*-(CpCo-η³)₂(*p*-disubstituted arene) displays corresponding (coalesced at 80 °C) resonances at δ = 4.12 ppm and δ = 61.7 and 60.2 ppm, respectively.[9a]

The preceding notwithstanding, there appears to be a clear distinction between the two types of Co complexes based on their chemistry. Thus, whereas the *syn* variants are unreactive, their *anti* counterparts are very labile. For example, *anti*-(Cp*Co-η⁴:η⁴)₂arenes exchange the sandwiched ligands with external π-ligands (e.g., benzene, cycloheptatriene, and cyclooctatetraene) at room temperature.[9b,c,e] In addition, a plethora of other species degrade the triple-decker structure to various Cp*Co-derivatives.[9d] In contrast, heating a sample of **6** to 120 °C in toluene-d_8 did not lead to any changes in the NMR spectra (see SI). To explore its potential photochemical activation, **6** was irradiated at various wavelengths (300–365 nm), as well as being exposed to ambient sunlight for days, leaving it unchanged in all cases. We therefore favor the *syn* structure for the title compound.

Because an X-ray analysis of **6** was unattainable, density functional theory (DFT) calculations were performed on both diastereomers to pinpoint their energetic and geometric details (see Figures 3 and 4; see SI).

Interestingly, structure **6** (Figure 3) is more stable than **7** by 1.8 kcal/mol, which, while not unequivocal, is in tune with the preferred assignment. The computed geometry of **6** encompasses a symmetrical near-D_2h array and a *syn* μ²:(η³,η³) coordination to the central ring, accentuating the bisallyl arrangement already present in the free ligand.[6,10] Compared with the latter, the bonds linking the allyl fragments are considerably elongated and the terminal rings are aromatized, as evidenced by diminished bond alternation. Moreover, the complexed six-membered ring adopts an 'elongated boat' conformation,[8] in which the dihedral angle between the planes of the allyl piece and the central carbons is 25.7°. This feature is similar to that encountered in the related *syn*-dimetal systems mentioned earlier (see above).[9a,f]

The calculated frame of **7** (Figure 4) exhibits a C_2 symmetry along the phenylene axis, an *anti*-μ²:(η⁴,η⁴) mode of attachment of the two CpCo units, and a highly distorted central arene section, describable as a twist chair, the 'twist' manifesting in the dihedral angle of its two four-membered ring bonds (38.34°). As in other *anti*-dicobalt complexes of this type (see above),[9b,e,f] the metals share a pair of ligand carbons of one of the cyclobutadiene cycles. Note that, whereas the structure is desymmetrized, this facet cannot be used as argument against its formation, because such complexes are highly fluxional.[7,9b,e,f]

To conclude, the CpCo-complex of 2,3,7,8-tetrakis(trimethylsilyl) linear [3]phenylene **1**, in which the metal coordinates one of the cyclobutadiene rings, transforms in the presence of $CpCo(C_2H_4)_2$ into the rare *syn*-bound dinuclear derivative **6**, in which the metals are connected to the central benzene ring.[11] Although not rigorously excluded as an alternative, the *anti*-diastereomeric form **7** seems an unlikely option, primarily because of the relative reactivity of analogues. Studies aimed at clarifying the details of the fluxionality by desymmetrizing the molecule, an exercise that might provide crystals suitable for X-ray analysis, and the mechanism of its formation through kinetic studies will have to await the results of future enquiry.

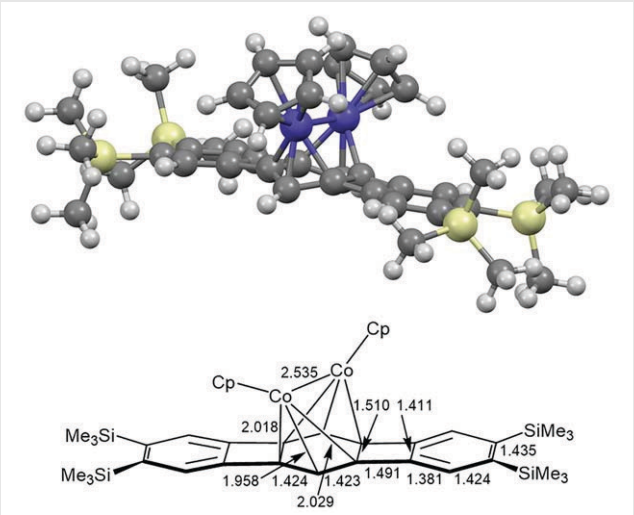


Figure 3 DFT rendition of **6** (top) and selected bond lengths (bottom)

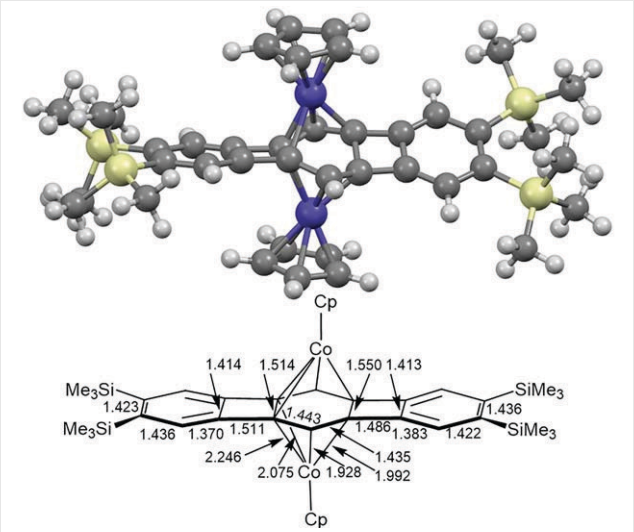


Figure 4 DFT rendition of **7** (top) and selected bond lengths (bottom)

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1659-7656.

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(11) **2,3,7,8-Tetrakis(trimethylsilyl) linear [3]phenylene(CpCo)$_2$ 6**
In a glovebox, 2,3,7,8-tetrakis(trimethylsilyl) linear [3]phenylene(CpCo) **1** (85 mg, 0.133 mmol) and CpCo(C_2H_4)$_2$ (25 mg, 0.139 mmol) were added to a Schlenk flask. The flask was taken out of the glove box, and freshly distilled degassed benzene (15 mL) was added under N_2. The mixture was heated to 70 °C in an oil bath for 23 h and then cooled to r.t. The solvent was removed in vacuo, furnishing a black residue that was filtered rapidly through a plug of neutral alumina (activity III; 2.5 × 3.5 cm), eluting with hexanes–THF (100:1) under N_2. The solvents were again removed in vacuo, and the ensuing black residue was crystallized from acetone–EtOAc (100:1) at −78 °C to give reddish-black crystals; yield: 57 mg (56%). ^{1}H NMR (400 MHz, acetone-d_6): δ = 7.36 (s, 4 H), 4.89 (m, 4 H), 4.81 (s, 2 H), 0.39 (s, 36 H). ^{13}C NMR (100 MHz, acetone-d_6): δ = 150.5, 145.4, 125.9, 82.8, 57.1, 53.7, 2.66. MS (FAB): *m/z* = 762 ([M$^+$]). HRMS (EI, 70 eV): *m/z* [M$^+$] calcd for $C_{40}H_{52}Co_2Si_4$: 762.1810; found: 762.1791. UV/Vis (hexane): λ_{max} (log ε) = 221 (3.36, sh), 244 (3.44), 286 (3.63), 386 (2.79, sh), 439 nm (2.58).