Controlling Through-Space and Through-Bond Exchange Pathways in Bis-Cobaltocenes for Molecular Spintronics

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Abstract

Pinching molecules via chemical strain suggests intuitive consequences, such as compression at the pinched site, and clothespin-like opening of other parts of the structure. If this opening affects two spin centers, it should result in reduced communication between them. We show that for a naphthalene-bridged biscobaltocenes with competing through-space and through-bond pathways, the consequences of pinching are far less intuitive: despite the known dominance of through-space interactions, the bridge plays a much larger role for exchange spin coupling than previously assumed. Based on a combination of chemical synthesis, structural, magnetic and redox characterization, and a newly developed first-principles theoretical pathways analysis, we can suggest a comprehensive explanation for this nonintuitive behavior. These results are of interest for molecular spintronics, as naphthalene-linked cobaltocenes can form wires on surfaces for potential spin-only information transfer.

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Information transfer at the nanoscale is a basic requirement for nanoelectronics and -spintronics. In nanoscale electronics, a major problem is heating and the resulting decomposition of wires under charge flow [1]. As an alternative, a sequence of spin flips along a chain of exchange-coupled spins incorporated in such wires allows for information transfer without any charge flow, suggesting reduced heating [2]. Molecular chains provide an elegant way of assembling such spin wires by self-assembly on surfaces [3–5] or via intermolecular interactions in the solid state [6–8]. Operating them at reasonably high temperatures requires a sufficiently strong coupling between adjacent spins. To control this coupling, it is crucial to understand structure–property relationships for these molecules and how they are affected by environments such as metal surfaces.

Tuning molecular spin interactions is particularly intriguing when two competing pathways play an important role. This allows for more chemical control than just a single mechanism would offer, in particular when one pathway favors ferromagnetic and the other antiferromagnetic spin coupling (see Figure 1), and when both can be controlled independently or respond differently to a given control parameter. For competing pathways studied in the context of exchange spin coupling [9,10], mixed-valence compounds [11–17] or electron transfer [18], structure–property relationships often follow chemical intuition (e.g., removing two units from each other decreases through-space interactions [15], and going from $\pi$ to $\sigma$ bridges kills through-bond contributions [17]). In some cases, chemical control is more challenging to achieve, and it is important to understand these cases to (1) reliably design molecules for molecular spintronics and to (2) reap the benefits that result from their subtle structure–property relationships.
Figure 1: Schematic representation of a system with competing through-bond (TB) and through-space (TS) interactions.

A class of compounds which combine competing spin coupling pathways and the potential for building spin wires, and which have successfully been brought onto metal surfaces and shown spin-related features in the scanning tunneling microscope [19], are cobaltocenes linked by 1,8-substituted naphthalene bridges [20] (see Figure 1). Two of their cyclopentadienyl rings are stacked roughly face-to-face, and increasing the distance between the rings will reduce through-space coupling (which is antiferromagnetic [20]). Rotating the metallocenes around the bonds that connect them to the π-conjugated bridge (Figure 2) will also affect this through-space pathway: The more the cyclopentadienyl (Cp) rings are rotated out of the bridge plane, the more they will face each other, favoring through-space interactions. At the same time, this rotation out of the bridge plane will diminish the overlap between the π-systems of the Cp rings and the bridge, thus reducing through-bridge coupling (which is ferromagnetic for the 1,8-naphthalene bridge, see below). The general motive is chemically versatile: It has been realized with different metal centers [20–26], with phosphine and other group 15 and 16 substituents [27–30] or thiophenes [31], and the naphthalene bridge has been structurally modified in related compounds [26, 32–36]. 1,8-naphthalene-bridged cobaltocene wires have been
constructed with up to four cobaltocene units [19,37], and polymers have been synthesized based on ferrocene, nickelocene, mixtures of the two, and as ferrocene-cobaltocene copolymers [24,25].

For tuning exchange spin coupling via competing pathways, we need to know how the pathways contribute to coupling, and to what extent they can be controlled. In 1,8-substituted naphthalenes, it was found that through-space contributions to electron transfer play an important role (possibly in addition to through-bond terms) [11–14,16,38]. Previous experimental studies on 1,8-naphthalene-bridged bis-cobaltocene [20] and on 1,8-di([5]trovacenyl)naphthalene [39] have suggested that exchange spin coupling is antiferromagnetic, and that through-space interactions dominate over through-bridge ones.

This suggests that “pinching” the bridge chemically on the side opposite to the cobaltocene substituents should remove the spin centers from each other, and thus decrease their antiferromagnetic coupling. We achieved this pinching by adding chemical “clamps” of decreasing length, similar to previous work on naphthalenes with organic substituents in 1,8 positions [32–36], on a 1,8bis(cobaltocenyl)naphthalene 1 [20,21], resulting in the acenaphthene structure 2 and in the acenaphthylene structure 3 (see Figure 2). Contrary to what one would expect, we find that the antiferromagnetic coupling increases as the clamp is tightened.

We elucidate this unexpected behavior by measuring exchange spin coupling in solution and in the solid state, comparing with electronic coupling, and tying these data to a structural analysis. Owing to a new quantum chemical pathway analysis [40], we can evaluate the through-space and through-bond pathways separately. These data shed new light on the chemical control of exchange spin coupling in candidate structures for spin wires, in particular on the importance of seemingly negligible through-bridge coupling.
Red single crystals suitable for X-ray structure analysis could be obtained for both Co(I) complexes 2 and 5 in the triclinic space group \( \text{P} \). Complexes 3 and 6 were obtained using decamethylcobaltocene. The advantage of this synthetic strategy is the reasonable stability and the diamagnetism of all isolated intermediates.

Figure 2: Illustration of “chemical pinching” and its possible consequences: Introducing chemical clamps should lead to structural compression of the “bottom” part of the molecules, while the “upper” part should open up. In addition, the structural and electronic modifications resulting from pinching could lead indirectly to rotations of the cobaltocene substituents. These changes could result in modifications of exchange spin couplings \( (J) \) and electronic couplings \( (H_{AB}) \). Pinching the naphthalene bridge (structure 1) was achieved by adding either an aliphatic \( \text{C}_2\text{H}_4 \) unit, resulting in an acenaphthene bridge (structure 2), or by adding a shorter \( sp^2 \) \( \text{C}_2\text{H}_2 \) unit (structure 3) with a suspected stronger pinching effect, resulting in an acenaphthylene bridge.

Compounds 2 and 3 featuring the “pinched” bridges had not been synthesized previously. They were obtained using the strategy that had proven successful for the parent naphthalene-bridged structure 1 [20,21]: Dibromo-functionalized derivatives ofacenaphthene and acenaphthylene were transformed into the corresponding organolithium compounds, followed by nucleophilic addition to cobaltocene iodide and oxidation by endo-hydride abstraction (Figure 3). The resulting diamagnetic Co(III) derivatives were then readily reduced to the desired paramagnetic, neutral biscobaltocene complexes (see Supporting Information, SI, Section S1 for details). The advantage of this synthetic strategy is the reasonable stability and the diamagnetism of all intermediates.
The attachment to the naphthalene bridge in 1,8 position implies that the two metallocene substituents are closer together than a typical van der Waals distance would indicate: e.g., in the parent compound 1, the two Cp carbon atoms directly attached to the bridge are 2.94 Å apart (compare the interlayer distance of 3.35 Å in graphite). The structure has several options for dealing with the resulting repulsion between the substituents: (1) outward tilting (left-hand side of Figure 4), (2) side-ways torsional twisting of the naphthalene (middle of Figure 4), and (3) twisting of the rigid Cp rings with respect to the naphthalene plane (right-hand side of Figure 4). In related compounds, depending on the nature of the substituents, these strategies are combined to different extents [12,13,33,34,39]. Factors controlling this choice of strategies are (a) the electronic structure of the bridge, where a stronger tendency towards π-conjugation would favor less metallocene/substituent torsion, (b) the rigidity of the bridge, which disfavors naphthalene torsion, and (c) electronic and steric interactions between the substituents, which encourage all of the above\(^1\). Repulsive electronic interactions are correlated with an increase of electron density on the substituents [20].

Comparing 1-3\(^2\) (see Table 1), adding chemical clamps 1 increases outward tilting, as expected. E.g., the distance between carbon atoms C6 and C21 increases by 5.5 pm when going from 1 to

\(^1\)A nonbonding interaction between the α hydrogen atoms on naphthalene and the ones on the unsubstituted Cp rings was excluded experimentally [13].

\(^2\)CCDC 1811721 (2), 1811719 (2(BF\(_4\))\(_2\)), 1811720 (3(BF\(_4\))\(_2\)), 1811717 (synthetic intermediate 5, see Supporting
2. Even though absolute distances are slightly overestimated, this trend is very well reproduced by Kohn–Sham density functional theory (KS-DFT) (5.7 pm). This suggests that for 3, for which no reliable X-Ray structural data were available, the DFT data can be trusted with respect to trends, suggesting an additional increase of 5.6 pm (or 11.3 pm total compared with 1). These data are on the short side, but in line with previous work on other 1,8-substituted naphthalenes (2.94-3.00 Å), 5,6-diarylanapthenes (3.08-3.12 Å), and 5,6-diarylanaphthylene (3.095 Å) [33]. Interestingly, the distances between the cobalt atoms decrease slightly when going from 1 to 2. An analysis of intra-metallocenyl bond distances suggests that this is not due to the cobalt atoms moving closer to the Cp rings attached to the bridge, but rather results from the differences in torsional angles discussed in the following (see Supporting Information Figure S16).

In biphenyls, the rings are twisted by 30.3° [41], and a similar value may be expected for φ in 1-3 if only one metallocene substituent was present. Owing to the interaction between the two substituents, the actual angles are between about 43° for 1 and 48° for 2. The larger metalocene torsion φ in structure 2 is likely due to its more rigid naphthalene bridge leading to smaller naphthalene torsion θ, so that the resulting repulsive interaction between the cobaltocenes is taken care of by increasing φ. DFT underestimates these angles φ somewhat, but since the trend, again, agrees with the experiment, the DFT conclusion that 3 is less twisted w.r.t. φ than the other two is likely reliable. This may be attributed to the fact the the bridge in 3 has stronger π-conjugation, encouraging a more coplanar arrangement. The resulting increase in repulsive interaction between the Cp rings is mitigated by a stronger torsion around the naphthalene-like bridge (θ) compared with 2. This nearly overcompensates the fact that compared with 1 and 2, the bridge in 3 is even more rigid, opposing naphthalene torsion. Also, given the relatively flat potential energy surface for substituent torsion [34] (see left-hand side of Figure 7), intermolecular interactions in the crystal may affect φ. Overall, the torsional angles do not vary too much as a function of the bridge and are similar to related metalloccenyl compounds [12,13,39].

Information), and 1811718 (synthetic intermediate 7, see SI) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
Figure 4: Structural parameters which can be affected by chemical pinching the naphthalene bridge, i.e., by replacing the two R groups by a connecting C$_2$H$_4$ or C$_2$H$_4$ unit (see Figure 2). Figure adapted from Ref. [33].

Figure 5: Molecular structure of 2 (left); Crystal structure of 2 with selected intra- and intermolecular distances (right). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50 % probability.
Table 1: Representative interplanar and torsion angles [°] and distances [Å] of biscobaltocene complexes 1 [20], 2 and 3 obtained from X-ray structure analysis and from the structure optimization of the BS determinants with TPSSh-D3/def2-TZVP. For 3, it was not possible to obtain crystal data with sufficient quality. The good agreement between TPSSh and X-ray structures suggests that the available TPSSh data are reliable enough for our purposes. Experimental data for 1 were taken from Ref. [20].

|                  | 1   | 2   | 3  |
|------------------|-----|-----|----|
| d(C8–C24)        | 3.848 | 3.711 | –  |
| DFT              | 3.950 | 4.088 | 4.228 |
| d(Co1–Co2)       | 6.739(4) | 6.720(1) | –  |
| DFT              | 6.820 | 6.750 | 6.800 |
| d(C6–C21)        | 2.940(2) | 2.995(6) | –  |
| DFT              | 3.006 | 3.063 | 3.119 |
| d(C11–C19)       | 2.559(2) | 2.585(9) | –  |
| DFT              | 2.556 | 2.591 | 2.604 |
| d(C14–C16)       | 2.464 | 2.333 | –  |
| DFT              | 2.452 | 2.328 | 2.305 |
| α = ζ(C12–C11–C10) | 118.8 | 119.0 | –  |
| DFT              | 117.8 | 117.9 | 118.0 |
| β = ζ(C20–C11–C10) | 122.2 | 122.7 | –  |
| DFT              | 123.0 | 123.3 | 123.4 |
| θ = C25–C19–C11–C6 | 29.65(6) | 22.42(2) | –  |
| DFT              | 28.37 | 21.75 | 26.21 |
| φ = C7–C6–C11–C20 | 43.58(5) | 47.21 | –  |
| DFT              | 41.17 | 43.03 | 36.91 |
| φ’ = C22–C21–C19–C20 | 41.86(5) | 48.40 | –  |
| DFT              | 41.17 | 43.32 | 36.95 |
In the parent compound 1, the overall exchange spin coupling is antiferromagnetic, with a Heisenberg coupling constant of \( J = -28.1 \text{ cm}^{-1} \) in the solid state. This was previously assigned to predominantly through-space interactions between the cobaltocenyl substituents [20], in line with the topology of the bridge suggesting ferromagnetic rather than antiferromagnetic coupling, and with previous work on 1,8-di([5]triovacyenyl)naphthalene [39]. Our recently developed local decomposition allows for analyzing through-space and through-bridge contributions to \( J \) in more detail [40]. We find that even through-space contributions are indeed dominant, the overall coupling results from a partial compensation of antiferromagnetic through-space and ferromagnetic through-bridge interactions (\( J_{TS} \) and \( J_{TB} \) in Table 2). This is in line with the dihedral angle of about 43° discussed above, which allows for non-negligible overlap between the \( \pi \) systems of the Cp rings and the bridge.

Adding an aliphatic clamp to the bridge will only marginally affect the \( \pi \) system of the bridge, suggesting that mostly the structural changes affecting through-space coupling should be important. These are a subtle combination of the three parameters discussed above (Figure 4), which each influence through-space interactions differently: Increasing the intermetalocene distance and decreasing naphthalene torsion should reduce \( |J_{TS}| \), and stronger metallocene torsion should increase it (and decrease \( |J_{TB}| \), see right-hand side of Figure 7). In 2, this interplay results in an overall more antiferromagnetic coupling (\( J = -42.3 \text{ cm}^{-1} \)) compared with 1. DFT does not describe this trend correctly, rather suggesting a near-constant \( J \) (resulting from a slight increase in both \( |J_{TS}| \) and \( |J_{TB}| \)). This may be attributed to the underestimation of the metallocene dihedral angle by DFT, which can result from neglecting crystal packing effects in combination with the ease of rotation around \( \phi \). If \( J \) is evaluated on the X-Ray crystallographic structure rather than on the DFT-optimized one, \( J \) indeed becomes more antiferromagnetic, in line with the experimental trend. For both 1 and 2, DFT underestimates \( J \) in absolute terms, but given the small values, the agreement is sufficient to trust these data. Intermolecular interactions are unlikely to play a role based on both computational and experimental data (see Supporting Information Section S3).

When adding a conjugated ethylene clamp to 1, resulting in 3, the topology of the bridge’s \( \pi \) system is strongly modified. This can be understood from considering the possibility of drawing closed-shell resonance structures (Figure 6). In contrast to 1, this becomes possible in 3. Alternatively,
one can think of the addition of the clamp resulting in a second coupling pathway via the bridge, which according to starring rules [42–44] would be antiferromagnetic rather than ferromagnetic (see Supporting Information, Section S5). This is reflected both in the overall coupling, which becomes strongly antiferromagnetic ($J = -125.2 \text{ cm}^{-1}$), and in the bridge contribution becoming overall antiferromagnetic, in contrast to 1 and 2. Interestingly, also the through-space contribution to $J$ becomes considerably more antiferromagnetic, which may result from the two highest-energy majority spin molecular orbitals, whose energetic splitting is related to antiferromagnetic coupling [45], becoming partially localized on the bridge and partially on the cyclopentadienyl rings in 3. Therefore, the larger splitting between these orbitals resulting from the changed topology of the bridge not only results in an antiferromagnetic bridge contribution, but also can make through-space coupling more antiferromagnetic (see Figure S10 in the Supporting Information). Accordingly, when the Cp rings are twisted more strongly out of the bridge plane, the overall coupling becomes less antiferromagnetic, a trend which is caused by the decrease of antiferromagnetic bridge contributions. In contrast, $J$ in 1 becomes more antiferromagnetic, which is dominated by the through-space contributions. This suggests that the topology of the bridge is not only important for absolute values of $J$, but also for its qualitative dependence on twisting of the cobaltocenes.
Figure 6: Resonance forms of 1 and 3. For 1 only one relevant resonance structure can be drawn, while for 3 an open-shell and a closed-shell resonance structure can be formulated.

Table 2: Exchange coupling constants in cm\(^{-1}\) obtained from experiment, \(J_{\text{exp.}}\), from DFT via a Green’s-function approach \(J_{\text{Green}}\), and the atomic contributions evaluated according to Equation (8) in the SI from the bridge, \(J_{\text{TB}}\), and cobaltocene moieties, \(J_{\text{TS}}\), using TPSSH-D3 / def2-TZVP.

| system | \(J_{\text{exp.}}\) | \(J_{\text{Green}}\) | \(J_{\text{TB}}\) | \(J_{\text{TS}}\) |
|--------|----------------------|----------------------|----------------|----------------|
| 1      | −28.1                | −9.2                 | +42.5          | −51.8          |
| 2      | −42.3                | −8.8*                | +58.0          | −66.8          |
| 3      | −125.2               | −133.0               | −26.5          | −106.5         |

* Coupling constant for a biscobaltocene cut out of the crystal structure was −15.8 cm\(^{-1}\). (more details in the SI).
Figure 7: a) Total energies of the BS structures of 1 and 3 as a function of the dihedral angle $\phi$ with the global, energetic minima set to zero (for 1 minimum at 40°; for 3 minimum at 35°). b) Coupling constants in cm$^{-1}$ obtained from the Green’s-function approach ($J_{\text{tot}}$) and the TB ($J_{\text{TB}}$) and TS contributions ($J_{\text{TS}}$) obtained from the atomic contributions (right panel). All calculations were performed with TPSSH-D3 / def2-TZVP in the high-spin state on the optimized structures of the BS determinants. Note that the location of the “minima” deviates slightly from the values reported in Table 1, because here scans of a fixed series of angles spaced by 5 degrees were done for the sake of comparability, whereas Table 1 reports the overall minima without this restriction.

When bringing spin-polarized molecules onto metal surfaces, charge transfer can lead to a loss of spin polarization. Therefore, and as an additional means of learning about communication through molecular bridges in these compounds, it is important to study the redox properties of the three biscobaltocenes 1-3. Based on cyclovoltammetry, the half-wave potential splittings were determined as $\Delta E(1/2) = 0.200$ V (1(BF$_4$)$_2$), 0.179 V (2(BF$_4$)$_2$), and 0.184 V (3(BF$_4$)$_2$) in acetonitrile solvent. This would suggest an overall small electronic communication between the metallocenes, which is slightly reduced when adding chemical clamps to the bridge, in contrast to the exchange spin coupling. This is consistent with $\Delta E(1/2)$ being not only a measure of electronic properties [46], in contrast to exchange spin coupling. In related compounds, it has been found that electrostatic interactions between the redox centers are dominant for $\Delta E(1/2)$ [47]. It is likely that this is also the case here, which is also a possible explanation for why $\Delta E(1/2)$ is quite similar for all three compounds under study. This finding is consistent with Ref. [39], which suggests that exchange spin coupling is more sensitive to structural changes than electronic coupling in these types of compounds. These data
indicate that what has been found for 1 on gold surfaces (the spin is preserved in many cases, resulting in a measurable Kondo resonance) may translate to 2 and 3 (provided the adsorption structures are not largely different from 1). This is an important consideration for constructing spin chains on surfaces.

To summarize, two new biscobaltocenes were synthesized and characterized, with the intention of reducing the antiferromagnetic exchange spin coupling by adding chemical clamps to a naphthalene bridge, such that the metal centers move away from each other. It turns out that the bridge plays a larger role than assumed in mediating spin coupling, resulting in an increase rather than decrease in spin coupling as the clamp is tightened. Based on our structural and first-principles theoretical analysis, this could be attributed to a subtle interplay between torsional degrees of freedom and the rigidity of the bridge for the structure with the aliphatic clamp (2), while for 3 with its π-conjugated clamp, the change of bridge topology led to a new coupling pathway via the bridge, switching its contribution from ferromagnetic to antiferromagnetic. In contrast to 1 and 2, where antiferromagnetic through-space coupling wins over weaker ferromagnetic through-bridge coupling, bridge and space act in the same direction in 3, resulting in much stronger overall coupling.

The bridge topology also controls whether antiferromagnetic coupling grows weaker (3) or stronger (1) when the metallocenes are twisted out of the naphthalene bridge. This is important for spin wires on substrates: Scanning tunneling microscopy data indicate that bridged biscobaltocenes on gold surfaces are forced flat such that the two metallocene units are maximally twisted [19], suggesting that their spin coupling may differ from what is measured in solution or in the solid state, where twisting is less pronounced. On the other hand, the sensitivity provided by competing through-space / through-bond interactions suggests a powerful design principle when twisting can be controlled, potentially allowing for controlling spin states mechanically or via pressure. It would be interesting for future studies to test the limits of the suggested design considerations when changing the metal atoms / ligands or for organic molecules (see Ref. [16] for a recent example), aiming at spin wires for molecular spintronics.

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Chemical pinching removes spin centers from each other. This should result in reduced through-space exchange spin coupling. In naphthalene-bridged biscobaltocenes, the bridge turns out to play a larger role than anticipated, leading to an increase of spin coupling. This is important for tuning interactions in spin wires for information transfer.

**Keywords:** Density functional calculations, magnetic properties, metallocenes, molecular spintronics, pathways