

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

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Dedicated to Hansjörg Sinn on the occasion of his 90th birthday.

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 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 theoretical pathway analysis, we can suggest a comprehensive explanation for this non-intuitive behavior. These results are of interest for molecular spintronics, as naphthalene-linked cobaltocenes can form wires on surfaces for potential spin-only information transfer.

Introduction

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 (for example, removing two units from each other decreases through-space interactions,^[15] and going from π to σ bridges removes 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.

A class of compounds which combine competing spin-coupling pathways and the potential for building spin wires, 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 cobaltocenes 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 motif is chemically versatile: It has been realized with different metal cen-

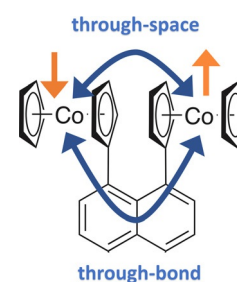


Figure 1. Schematic representation of a system with competing through-bond (TB) and through-space (TS) interactions.

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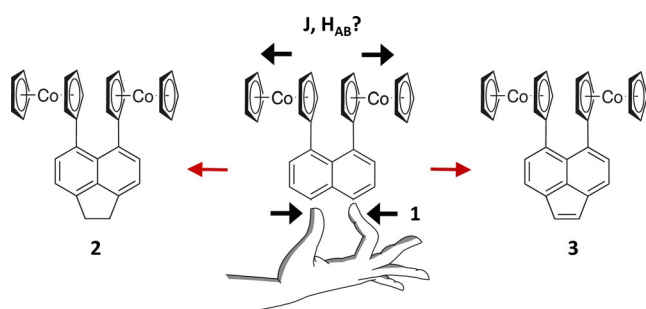


Figure 2. Illustration of chemical pinching and its possible consequences: Introducing chemical clamps should lead to structural compression of the bottom part of the molecules, while the upper part should widen. Additionally, the structural and electronic modifications resulting from pinching could indirectly lead 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 C_2H_4 unit, resulting in an acenaphthene bridge (structure 2), or by adding a shorter $sp^2 C_2H_2$ unit (structure 3) with a suspectedly stronger pinching effect, resulting in an acenaphthylene bridge.

ters,^[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.^[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]

To tune 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).^[11–16] 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 interactions.

This suggests that a chemical “pinching” of the bridge on the side opposite to the cobaltocene substituents should increase the distance between the spin centers, 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 1,8-bis(cobaltocenyl)naphthalene **1**,^[20,21] resulting in the acenaphthene structure **2** and in the acenaphthylene structure **3** (see Figure 2).^[40] 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 analy-

sis,^[41] 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.

Results and Discussion

Synthesis

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 of acenaphthene and acenaphthylene were transformed into the corresponding organolithium compounds, followed by nucleophilic addition to cobaltocenium iodide and oxidation by *endo*-hydride abstraction (Figure 3). The resulting diamagnetic Co^{III} derivatives were then readily reduced to the desired paramagnetic, neutral bis-cobaltocene complexes (see Section S1 in the Supporting Information for details). The advantage of this synthetic strategy is the reasonable stability and the diamagnetism of all intermediates.

Molecular Structures

The attachment to the naphthalene bridge in 1,8-position implies that the two cobaltocene substituents are at a shorter distance to each other than a typical van-der-Waals distance would indicate: for example, 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 (Figure 4): 1) outward tilting (left), 2) sideways torsional twisting of the naphthalene (center), and 3) twisting of the rigid Cp rings with respect to the naphthalene plane (right). 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/substitu-

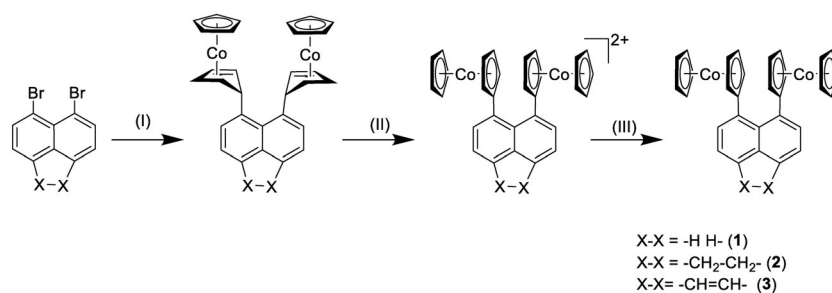


Figure 3. Synthesis of **1–3**. Reaction conditions: i) $nBuLi/Et_2O$, $[CoCp_2]I/Et_2O$; ii) $Ph_3C^+BF_4^- /$ dichloromethane; iii) $Cp_2^*Co/tetrahydrofuran$.

X-X = -H-H- (**1**)
X-X = -CH₂-CH₂- (**2**)
X-X = -CH=CH- (**3**)

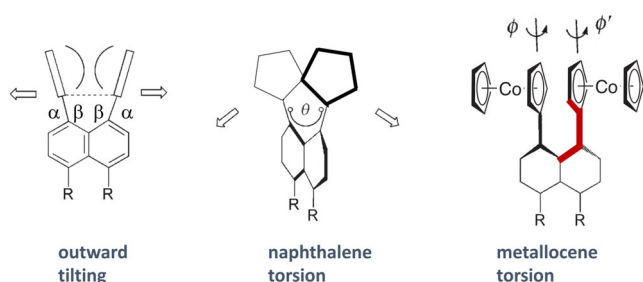


Figure 4. Structural parameters which can be affected by chemical pinching of the naphthalene bridge, that is, by replacing the two R groups by a connecting C_2H_4 or C_2H_2 unit (see Figure 2). One of the dihedral angles used for defining metallocene torsion is highlighted in red. Figure adapted from Ref. [33].

ent 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.^[42] Repulsive electronic interactions correlate with an increase of electron density on the substituents.^[20]

Comparing **1–3** (Table 1; see Figure 5 for nomenclature),^[43] adding chemical clamps (**1**) increases outward tilting, as expected. For example, the distance between carbon atoms C6 and C21 increases by 5.5 pm when going from **1** to **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 in total, compared with **1**). These non-bonding distances are quite short but in line with previous work on other 1,8-substituted naphthalenes (2.94–3.00 Å), 5,6-diarylacenaphthenes (3.08–3.12 Å), and 5,6-diarylacenaphthylene (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).

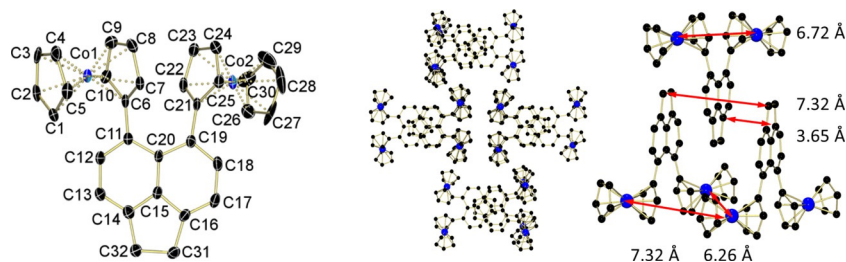


Figure 5. Left: Molecular structure of **2**. Right: Crystal structure of **2** with selected intra- and intermolecular distances. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probability.

Table 1: Representative interplanar and torsion angles [$^\circ$] and distances [Å] of biscobaltocene complexes **1**,^[20] **2**, and **3**, obtained from X-ray structure analysis and from the structure optimization of the Broken-symmetry (BS) determinants using 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
$d(C8-C24)$	exp.	3.848(2)	3.711(4)	–
	DFT	3.950	4.088	4.228
$d(Co1-Co2)$		6.739(4)	6.7236(6)	–
		6.820	6.750	6.800
$d(C6-C21)$		2.940(2)	3.010(3)	–
		3.006	3.063	3.119
$d(C11-C19)$		2.559(2)	2.590(3)	–
		2.556	2.591	2.604
$d(C14-C16)$		2.464(2)	2.334(3)	–
		2.452	2.328	2.305
$\alpha(C12-C11-C10)$	exp.	118.8(1)	119.1(2)	–
	DFT	117.8	117.9	118.0
$\beta(C20-C11-C10)$		122.2(1)	122.7(2)	–
		123.0	123.3	123.4
$\theta(C25-C19-C11-C6)$		29.65(6)	22.3(2)	–
		28.37	21.75	26.21
$\phi(C7-C6-C11-C20)$		43.58(5)	47.2(4)	–
		41.17	43.03	36.91
$\phi'(C22-C21-C19-C20)$		41.86(5)	48.4(4)	–
		41.17	43.32	36.95

In biphenyls, the rings are twisted by 30.3° ,^[44] and a similar value may be expected for ϕ in **1–3** (see Figure 4) if only one cobaltocene substituent were present. Owing to the interaction between the two substituents, the actual angles are between about 43° (**1**) and 48° (**2**). The larger metallocene torsion angle ϕ in structure **2** is likely due to its more rigid naphthalene bridge leading to smaller naphthalene torsion θ (see Figure 4), so that the resulting repulsive interaction between the cobaltocenes is taken care of by the increasing ϕ . DFT calculations underestimate ϕ values somewhat, but since the trend, again, agrees with the experiment, the DFT-derived conclusion that **3** is less twisted with respect to ϕ than the other two is likely reliable. This may be attributed to the fact 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] (Figure 6, left), 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 metallocenyl compounds.^[12,13,39]

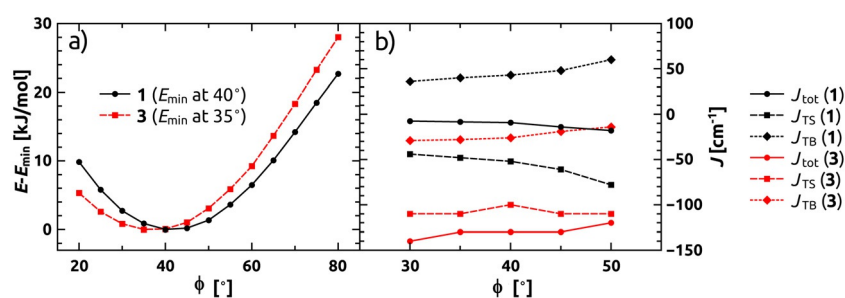


Figure 6. a) Total energies of the broken-symmetry (BS) structures of **1** and **3** as a function of the dihedral angle ϕ (for **1**: minimum at 40° ; for **3**: minimum at 35°). b) Coupling constants (in cm^{-1}) obtained from the Green's function approach (J_{TOT}) as well as the through-bond (J_{TB}) and through-space contributions (J_{TS}) obtained from the atomic contributions. All calculations were performed using 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 true minima without this restriction.

Magnetic Communication

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]trovacenyl)naphthalene.^[39] Our recently developed local decomposition allows for analyzing through-space and through-bridge contributions to J in more detail,^[41] based on an alternative to the popular Broken-Symmetry approach.^[45] This alternative requires only the electronic structure of the ferromagnetically coupled high-spin state as input^[46] and can thus provide J in a form that is suitable for decomposition into atomic contributions. The information on energy differences between the two spin arrangements is extracted from the curvature of the energy as a function of the angle between the two local spin vectors, under the assumption that this function follows a cosine behavior (see Refs. [46,47] and also compare Refs. [48–50] for a different, yet conceptually related approach).

We find that even though 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 π -systems of the Cp rings and the bridge.

Adding an aliphatic clamp to the bridge will only marginally affect the π 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 inter-cobaltocene distance and decreasing naphthalene torsion should decrease $|J_{\text{TS}}|$, while stronger metallocene torsion should increase it (and decrease $|J_{\text{TB}}|$; see Figure 6,

right). 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 nearly constant J (resulting from a slight increase in both $|J_{\text{TS}}|$ and $|J_{\text{TB}}|$, which have opposite sign). This may be attributed to the underestimation of the metallocene torsion by DFT, which can result from neglecting crystal-packing effects in combination with the ease of rotation around ϕ . If J is evaluated on the X-ray crystallographic structure instead of the DFT-optimized structure, J indeed becomes more antiferromagnetic, which is 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

Table 2: Exchange coupling constants (in cm^{-1}) obtained from experiment (J_{exp}), from DFT via a Green's function approach (J_{Green}), and the atomic contributions from the bridge, J_{TB} , and cobaltocene moieties, J_{TS} , evaluated according to Equations (S3) and (S4) in Section S2.2 of the Supporting Information, using TPSSH-D3/def2-TZVP.

system	J_{exp}	J_{Green}	J_{TB}	J_{TS}
1	-28.1	-9.2	+42.5	-51.8
2	-42.3	-8.8 ^[a]	+58.0	-66.8
3	-125.2	-133.0	-26.5	-106.5

[a] The coupling constant for a biscobaltocene cut out of the crystal structure was -15.8 cm^{-1} , with 35.6 cm^{-1} resulting from through-bond and -51.4 cm^{-1} resulting from through-space contributions. The relatively larger through-space contribution compared with the DFT structure is consistent with the larger metallocene torsion in the crystal structure, also compare Figure 6b.

interpret these data. For **2**, a short distance between the cobalt centers of neighboring molecules was observed (see Figure 5). In **1**, a similarly short intermolecular cobalt–cobalt distance was found, but intermolecular exchange interactions could be excluded based on diamagnetic dilution experiments in the solid state.^[20] Still, we cannot exclude that intermolecular exchange interactions play a role for the magnetic behavior of **2** (further discussion is provided in Section S4.4 in the Supporting Information).

When adding a conjugated ethylene clamp to **1**, which results in **3**, the topology of the π -system of the bridge is strongly modified. This can be understood by considering closed-shell resonance structures (Figure 7). In contrast to **1**, this becomes possible in **3**. Alternatively, one can assume that the addition of the clamp results in a second coupling pathway via the bridge, which, according to starring rules,^[51–53] would be antiferromagnetic rather than ferromagnetic (see Supporting Information, Section S6). 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, the through-space contribution to J also becomes consider-

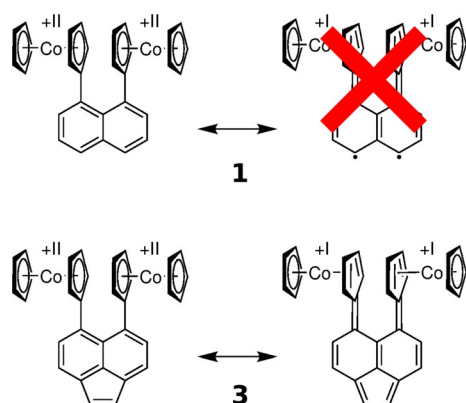


Figure 7. Resonance forms of **1** and **3**. For **1**, only one relevant resonance structure can be drawn, while for **3**, an open-shell and a closed-shell resonance structure can be formulated.

ably more antiferromagnetic, which may result from the two highest-energy majority-spin molecular orbitals, whose energetic splitting is related to antiferromagnetic coupling,^[54] 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 can also make through-space coupling more antiferromagnetic (see Figure S12). 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 the twisting of the cobaltocenes.

To experimentally probe intermolecular effects, we evaluated exchange spin coupling based on variable-temperature (VT) ¹H NMR measurements in solution. The data for both **1** and **2** could be fitted to an expression featuring J close to zero, which should be interpreted as a small rather than zero coupling given the error margin of these experiments, compatible with the solid-state data. This error margin also implies that the experiment does not exclude J being larger for **2** than for **1**, as it was found in the solid state. For **3**, the VT-NMR J in solution, $J = -127 \text{ cm}^{-1}$, agrees almost perfectly with the solid-state value, suggesting that intermolecular interactions play a negligible role (for a detailed discussion of the VT-NMR data, see Section S4.1 in the Supporting Information).

Redox Properties

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 $\Delta E(1/2) = 0.200 \text{ V}$ (**1**(BF₄)₂), 0.179 V (**2**(BF₄)₂), and 0.184 V (**3**(BF₄)₂) in acetonitrile. This would suggest an overall small electronic communication between the cobaltocenes, which slightly decreases when adding chemical clamps to the bridge, in contrast to the exchange spin coupling. This is consistent not only with $\Delta E(1/2)$ being a measure of electronic properties, but also from entropy and delocalization factors.^[55] In contrast to exchange spin coupling. In related compounds, it has been found that electrostatic interactions between the redox centers are dominant for $\Delta E(1/2)$.^[56] 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.

Conclusions

To summarize, two new biscobaltocenes were synthesized and characterized with the intention of decreasing the antiferromagnetic exchange spin coupling by adding chemical clamps to a naphthalene bridge, which causes the metal centers to move away from each other. It turns out that the bridge plays a larger role in mediating spin coupling than assumed, 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 dominates over weaker ferromagnetic through-bridge coupling, bridge and space act in the same direction in **3**, resulting in much stronger overall coupling. Thus, despite the overall dominance of through-space coupling in the parent compound **1**, control of spin coupling is not achieved via purely spatial control in these compounds. Instead, changing the electronic structure and the rigidity of the bridge strongly affects both through-space and through-bond coupling, which can result in the latter dominating chemical control.

The bridge topology also controls whether antiferromagnetic coupling grows weaker (**3**) or stronger (**1**) when the cobaltocenes are twisted out of the plane 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 cobaltocene 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 contrary, 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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Conflict of interest

The authors declare no conflict of interest.

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