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Naphthalene-Bridged *ansa*-Nickelocene: Synthesis, Structure, Electrochemical, and Magnetic Measurements

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Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

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The reaction of naphthalene-1,8-diylbis(cyclopentadienylsodium) (1) with the nickel triple-decker compound $[Ni_2Cp_3]$ -BF₄ affords the paramagnetic *ansa*-nickelocene 1,1'-(naphthalene-1'',8''-diyl)nickelocene (2). Alternatively, 2 can directly be obtained by a salt metathesis reaction of the disodium salt 1 with hexaammine nickel(II) dichloride $[Ni(NH_3)_6]$ -Cl₂. For magnetic dilution experiments, the corresponding but diamagnetic *ansa*-ruthenocene 3 was synthesized by reaction of the disodium salt 1 with dichloridotetrakis(dimethylsulfoxide)ruthenium(II). The solid-state molecular structures of 2 and 3 were determined by single-crystal X-ray diffraction analysis and revealed bent sandwich complexes. Cyclic voltammetry studies of 2 indicate three oxidation states.

Introduction

Nickelocene is a very prominent example of paramagnetic metallocenes because it contains 20 valence electrons, but is stable under inert-gas conditions. The lowest antibonding orbitals in nickelocene are twofold-degenerated and occupied by two electrons to result in a triplet ground state.^[1] Since its discovery in 1953,^[2] many groups have investigated the magnetic properties and discussed the lack of an EPR signal that results from a strong zero-field splitting in the triplet ground state.^[3] Magnetic susceptibility measurements on nickelocene revealed a deviation from normal Curie–Weiss behavior below 70 K.^[4] The origin of this deviation was interpreted by Prins et al., who attributed it to the zero-field splitting,^[5] whereas Baltzer et al. ascribed it to a predominantly ferromagnetic coupling of the nickelocene molecules to its nearest neighbors in the crystalline state.^[6]

Whereas nickelocene and substituted derivatives have

The electronic structure of complex **2** has been investigated by variable-temperature ¹H NMR spectroscopy, magnetic measurements, and DFT calculations. Superconducting quantum interference device (SQUID) magnetometry has been performed for the neat and diluted samples of **2**. The neat crystalline material of **2** displays antiferromagnetic behavior, whereas the susceptibility of the magnetically diluted sample runs into saturation at T < 4 K. This property is in agreement with an intermolecular antiferromagnetic interaction in the bulk material of compound **2** and the triplet ground state calculated by broken-symmetry (BS)-DFT calculations.

been investigated extensively, studies on ansa-nickelocenes with a linker between the Cp rings are still rare, although ansa-metallocenes have received great attention over the last 20 years due to their markedly different structural and electronic properties and their particular reactivity relative to nonbridged metallocenes.^[7] Mainly ferrocene complexes with different bridging functions were reported. Most commonly, these complexes are synthesized by salt elimination reactions from dimetallated metallocenes and suitable dihalides. This synthetic route is obstructed for nickelocene due to the reactivity of nickelocene toward organolithium compounds.^[8a] However, in very special cases, deprotonation reactions in the distant ligand sphere of nickelocene derivatives are possible.^[8b] With respect to these difficulties in synthesis, only very few nickelocenophanes were known. The first nickelocenophane synthesized in 1976 exhibits a 3-oxopentamethylene bridge.^[9] Recently, two [n]carbanickelocenophanes (n = 4, 6) were synthesized by ring-closing metathesis of 1,1'-bis(alkenyl)-substituted nickelocenes.^[10] A peculiar type of nickelocenophane is the dinuclear nickel complex bis(fulvalene)dinickel,[11a] which displays a reduced paramagnetism, although it is composed of two nickelocenes.^[11b] These complexes have a relatively nonstrained structure due to their long handle between the two cyclopentadienyl (Cp) ligands. Recently, the first

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strained [2]nickelocenophane was prepared with a tetramethyldisilane bridge.^[12]

Here we report the synthesis of the first *ansa*-nickelocene with a rigid bridge and a strained structure in which the two Cp units are linked by a naphthalene molecule. We describe the structural parameters and redox as well as magnetic properties.

Results and Discussion

Synthesis

In our ongoing research on stacked nickelocene complexes, we attempted to synthesize the unmethylated derivative of 1,8-bis(pentamethylnickelocenyl)naphthalene.^[13] As starting materials, naphthalene-1,8-diylbis(cyclopentadienylsodium) (1) and $[Cp_3Ni_2]^+$ triple-decker as CpNi transfer reagent^[14] were used. But instead of the desired unmethylated 1,8-bis(nickelocenyl)naphthalene (Scheme 1), nickelocenophane complex **2** and nickelocene were obtained.



Scheme 1. Synthesis of ansa-nickelocene 2 and ansa-ruthenocene 3.

The mechanism for the reaction depicted in Scheme 1 is still unknown. However, this reaction very much resembles the formation of the corresponding Co complex by the reduction of 1,8-bis(cobaltocenyl)naphthalene.^[15] The intermediately formed bis(cyclopentadienyl)cobaltate is isoelectronic to nickelocene. Presumably, a naphthalene-bound nickelocene intermediate was achieved, but cleavage of the unsubstituted Cp ligand and subsequent intramolecular rearrangement might precede formation of the ansa-nickelocene compound 2. The driving force of this reaction might be the chelating effect of the naphthalene-1,8-diylbis(cyclopentadienyl) ligand. A related dismutation reaction was reported by Köhler and co-workers from fulvalene-bridged binickelocene to form bis(fulvalene)dinickel and nickelocene.^[16] Eilbracht found a ligand exchange from the di-µcarbonyl-µ-[3-oxopentamethylenebis(n⁵-cyclopentadiene1,1'-diyl)]dinickel(Ni-Ni) to the [5]nickelocenophan-8-one in the presence of triphenylphosphane.^[9]

In a more straightforward synthesis of compound **2**, an equimolar amount of hexaammine nickel(II) chloride was subjected to reaction with the disodium salt **1** (Scheme 1). In the same manner, the corresponding Ru complex **3** was synthesized with dichloridotetrakis(dimethyl sulfoxide)ruthenium(II) (Scheme 1). Complex **3** was taken as a diamagnetic host material for compound **2** in doping experiments.

Molecular Structure

Suitable crystals of the complex 2 and 3 for X-ray structure analysis were obtained by crystallization from *n*-pentane solution, with data listed in Table 1. Compound 2 crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, and compound 3 crystallizes in the monoclinic space group $P2_1/c$ with four independent molecules in the asymmetric unit.

Table 1. Selected interatomic distances [pm] and angles [°] of **2** and **3** obtained from X-ray structure analysis and DFT calculations.

	2 : X-ray $M = Ni^{II}$	2 : DFT M = Ni ^{II}	3: X-ray M = Ru
C1C11	149.4(5)	148.9	149.5(4)
C8–C16	149.9(5)	148.9	148.5(4)
C1–C8	259.6(5)	258.7	261.7(7)
C11–C16	309.1(10)	311.0	311.9(9)
C13-C18	387.0(12)	404.1	388.4(9)
C14-C19	387.0(12)	404.1	388.2(10)
M1-C11	210.6(5)	213.6	209.4(4)
M1-C16	211.0(5)	213.6	210.3(4)
M1-C12	216.4(7)	218.7	216.0(6)
M1-C15	213.4(5)	218.8	215.6(5)
M1-C17	212.3(5)	218.8	215.4(4)
M1-C20	216.2(6)	218.7	216.2(6)
M1-C13	219.4(6)	224.9	221.8(6)
M1-C14	217.1(5)	224.8	220.0(4)
M1-C18	217.1(5)	224.8	221.1(4)
M1-C19	219.4(7)	224.9	221.3(6)
M1-X _{Cp1}	178.3(5)	184.0	178.9(5)
M1-X _{Cp2}	178.2(5)	184.0	179.2(5)
$X_{Cp1} - X_{Cp2}$	353.2(11)	363.9	356.0(1)
C11-C1-C2	114.5(19)	113.8	114.5(17)
C16-C8-C7	114.3(19)	113.8	114.1(17)
C11-C1-C9	125.3(18)	126.6	125.8(16)
C16-C8-C9	126.0(18)	126.6	126.2(16)
C2C1C9	120.1(19)	119.6	119.7(15)
C7–C8–C9	119.8(18)	119.6	119.7(15)
C1–C9–C8	127.3(16)	127.0	127.2(15)
$\delta (X_{Cp1} - M1 - X_{Cp2})^{[a]}$	164.4(14)	162.9	167.6(12)
a(plane Cp1–plane Cp2)	20.2(6)	26.7	19.4(8)
Plane(Cp)-plane(naph)	80.6(4)/81.4	89.5/89.5	83.5/83.2
C11-C1-C8-C16; ring	7.9(2); 7.8/8.8	7.0;	5.4(15);
slippage [pm]			10.7/12.7

[a] $X_{\rm Cp}$: Centroid of the corresponding 5 carbon atoms of the Cp ligand.

The *ansa*-metallocene entities demonstrate a slightly distorted structure caused by bridging of the two Cp units with the rigid naphthalene linker (Figure 1). Naphthalene-Bridged ansa-Nickelocene

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Figure 1. Left: Molecular structure of compound 2. Right: Projection of the molecule of complex 2 along the C11–C17 axis (hydrogen atoms are omitted for clarity; anisotropic displacement ellipsoids are depicted at the 50% probability level). The molecular structure of the Ru complex 3 looks very much the same.

The dihedral angle C1–C11–C8–C16 amounts to 7.9 and 5.4° for **2** and **3**, respectively (Figure 1, Table 1). The angle between the best planes of the Cp ligands and the naphth-

alene is about 81° for **2** and 83° for **3**, respectively. The distances between the metal and the bridgehead carbon atoms are significantly shorter (Ni1–C11 210.6 pm, Ni1–C16 211.0 pm, Ru1–C11 209.4 pm, and Ru1–C16 210.3 pm, respectively) than the other metal–carbon(Cp) distances, which range between 217.1 and 219.6 pm for **2** and between 215.4 and 221.3 pm for **3** (Table 1). The most significant structural features for strained metallocenophanes are the tilt angle *a* between the best planes of the Cp ligands and the angle δ between the two axes defined by the metal center and the centroid X_{Cp}, which describe the extent of the distortion from a perfect sandwich structure (Figure 2).^[17]



Figure 2. Geometric parameters of the ring slippage in *ansa*-metallocenes.

Angles of a = 20.2 and 19.4°, and of $\delta = 164.4$ and 167.6° for **2** and **3**, respectively, are indicative of a considerably bent metallocene structure. Complex **2** exhibits a somewhat larger distortion than the tetramethyldisilane bridged com-



Figure 3. Plot of the crystal structure of 2 (a), intermolecular Ni–Ni distances (b) and shortest intermolecular C–Ni distances (c).

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pound ($a = 9.37^{\circ}$, $\delta = 171.4^{\circ}$).^[12] The fixation of the Cp fragments by the nonflexible naphthalene clamp appeared to be the reason. Due to the distortion of the metallocene units, the metal atoms are shifted away from the naphthalene bridge (Figure 1, right). On the whole, the geometric parameters of the molecular structure of the *ansa*-nickelocene **2** very much resemble those of the corresponding *ansa*-ruthenocene **3**, which makes **3** an ideal diamagnetic host for the paramagnetic guest **2**.^[6]

A distinctive feature of the crystal packing is the antiparallel alignment of the nickelocenophane complexes depicted in Figure 3. The shortest intermolecular nickel–nickel distance amounts to 521.1 pm.

DFT Calculations

To investigate the influence of the X_{Cp}-Ni-X_{Cp} bend angle and the naphthyl substitution on the electronic structure in the ansa-nickelocene complex 2, quantum chemical calculations were performed using the density functional theory (DFT) method, which has been successfully employed on calculations of related complexes.^[13] Initial optimization of complex 2 revealed a nearly $C_{2\nu}$ -symmetric structure. Calculated bond lengths and angles are in good agreement with the structural parameters obtained by means of X-ray structure analysis (Table 1). The main difference between the calculated and X-ray structure is observed in the distance of the β -carbon atoms (C13/C14 to C18/C19) of the Cp ligands, which indicates a less deformed metallocene unit in the experimental structure. The stronger deviation of the structure from the ideal $C_{2\nu}$ symmetry and a twist of the Cp rings might be caused by packing forces and does not affect other structural parameters such as the X_{Cp} -Ni- X_{Cp} bend angle.

Calculations on the electronic ground state revealed a triplet state to be most energetically favorable. Higher singlet states calculated by broken symmetry and an unrestricted (U)-DFT approach were calculated to be $+34 \text{ kJ mol}^{-1}$ for an open-shell singlet and $+69 \text{ kJ mol}^{-1}$ for a closed-shell singlet state above the triplet ground state.

The frontier molecular orbitals of the triplet ground state are depicted in Figure 4. The splitting of the two (in nickelocene) degenerate orbitals was calculated to be 15 kJ mol⁻¹.^[18] The influence of the naphthyl bridge on the splitting can be deduced from the SOMOs. The SOMO that is higher in energy (SOMO1) exhibits an antibonding interaction between the naphthyl σ orbitals with the π system of the Cp rings, which causes an increase in energy. In addition, due to the bending of the nickelocene fragment, the antibonding overlap between the π system of the Cp ring and the nickel $3d_{\nu z}$ orbital increases, which also destabilizes the SOMO1. Due to the nonbonding interaction between the π system of the Cp ring and the naphthyl ring and lower increase in the antibonding contribution between the π system of the Cp ring and the $3d_{xz}$ orbital at the Ni center, the SOMO2 (Figure 4) is less destabilized. In total, this resulted in a splitting of SOMO1 and SOMO2.^[18]



Figure 4. Frontier molecular orbitals of complex 2: LUMO (top), SOMO1 (center, left), SOMO2 (center, right), and HOMO (bottom) obtained from DFT calculations.

Magnetic Measurements

The magnetic behavior of complex 2 was investigated in solution by variable-temperature (VT) ¹H NMR spectroscopy in toluene in the range of 203 to 343 K (see Figures 5 and 6). The assignment of the proton NMR spectroscopy signals have been performed following the spin densities of the different carbon atoms obtained from DFT calculations. They result in two sets of Fermi contact terms: two large and negative values for the Cp rings and three of an order of magnitude smaller, assigned to the naphthalene protons. Hence, the signals for the Cp protons of compound **2** are shifted to high field ($\delta_{para}^{293 \text{ K}} = -248.8, -280.1 \text{ ppm}$; Figure 5) as a consequence of the two unpaired electrons delocalized on the Ni atom and the Cp rings (compare Figure 4). The dispersion for the mean chemical shift of the Cp protons of compound 2 ($\delta_{para}^{293 \text{ K}} = -265 \text{ ppm}$) is even larger than found for the unsubstituted nickelocene ($\delta_{para}^{293 \text{ K}}$ = -255.2 ppm). The assignment of the resonance signals to the Cp protons H-12/15 and H-13/14 occurred in accord with Köhler et al.[16]



Figure 5. ¹H NMR spectrum of compound **2** in toluene at 293 K. The solvent signals are marked with an S. The sample contains minor impurities, most likely due to solvent traces from the synthesis.

The proton signals of the naphthalene bridge were shifted to low field in the range $10 < \delta < 15$ ppm. This slight low-field shift proves a subtle spin density in the naphthalene scaffold, which is in harmony with the DFT calculation.

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Figure 6. Curie plot of the chemical shift (δ) versus reciprocal temperature.

The highest SOMO (SOMO1; Figure 4) displays a certain spin density on the carbon atoms of the naphthalene bridge (+0.008 e at C2, +0.0001 e at C3, and +0.001 e at C4) that is predominantly due to small σ -spin delocalization effects. This order implies the proximal protons H-2/7 to be most low-field-shifted. Nevertheless, when the relaxation is affected by the dipolar interaction, the line width of the signal should distinctly increase as the distance between the paramagnetic center and the related proton decreases. Therefore, the signal at $\delta = 10$ ppm is assigned to H-2/7.

The VT ¹H NMR spectra demonstrate a linear correlation between the chemical shifts of the proton-resonance signals of **2** and the reciprocal temperature (Figure 6). The linear slope proves a Curie behavior in the temperature range of 203 < T < 343 K. The large temperature-dependent shift difference in the Cp signals exhibits a large spin density as is suggested by the frontier molecular orbitals in Figure 4.

To obtain more information about the magnetic behavior of 2, the susceptibility of a microcrystalline sample was determined by superconducting quantum interference device (SQUID) measurements in the temperature range 2–300 K. From the magnetic susceptibility of compound 2 depicted in Figure 7, a paramagnetic behavior above approximately 30 K can be deduced. Below 30 K a deviation from the Curie-Weiss law is observed. Complex 2 (Figure 7) exhibits antiferromagnetic behavior with a maximum of the susceptibility $\chi_{\rm m}$ at about $T \approx 25$ K. The magnetic behavior of 2 can be rationalized by magnetic interaction between two molecules arranged in pairs. The susceptibility data could be simulated satisfactory (Figure 7, solid line) by using the spin Hamiltonian $\hat{H} = -2J_{12}\Sigma \hat{S}_1 \cdot \hat{S}_2$, in which $\hat{S}_1 = \hat{S}_2 = 1$, $J_{12} = -10.07 \text{ cm}^{-1}$, $\Theta = -0.2 \text{ K}$ and g = 2.029, and considering pairs of complexes as the paramagnetic unit. An additional paramagnetic "impurity" of 9.9% with a spin S =1 has to be taken in account, which may be due to ansanickelocene species without a coupling counterpart.

The magnetic moment μ_{eff} calculated from χ_m data of the neat sample is equal to 2.92 at room temperature, which fits



Figure 7. The molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) of pure *ansa*-nickelocene complex **2**.

the theoretical value quite well for $S_{\rm Ni} = 1$ ($\mu_{\rm eff} = 2.83$ at room temperature for g = 2, using the spin-only approximation).

The antiferromagnetic behavior was unexpected for a mononuclear nickelocene complex and can be explained by an intramolecular singlet-triplet change, or alternatively, by an intermolecular coupling through space. However, our DFT calculations for an isolated molecule reveal a triplet ground state as was found for nickelocene itself. The antiferromagnetic coupling through an intermolecular magnetic interaction between two molecules is corroborated by the crystal structure determination, which demonstrates a pairwise packing order of the molecules in the crystal. The closest distance between two molecules amounts to 393.3 pm, which is calculated between a hydrogen-bearing carbon atom of the Cp ligands of one molecule and the Ni center of the second molecule and vice versa (Figure 3, c).

To prove the intermolecular magnetic interaction attributed to crystal packing, diluted samples of 2 in a diamagnetic host were investigated by SQUID measurements. The molecular structure of ruthenocene very much resembles the geometry of the molecular structure of nickelocene and, hence, allows the application of the ansa-ruthenocene 3 as a diamagnetic host for the corresponding nickelocene 2 in magnetic measurements.^[6] Crystals of diluted samples of complex 2 in the diamagnetic ansa-ruthenocene 3 with different doping rates could be obtained from toluene solutions. The exact doping rates were determined by flame atomic absorption spectroscopy. The doped samples show paramagnetic behavior above approximately 10 K (Figure 8). Below T = 10 K, a deviation from the Curie–Weiss law was obtained and the susceptibility runs into saturation below T = 4 K (Figure 8).

The lack of the maximum in the χ_m versus *T* curve at 25 K, which was observed from the neat complex **2** (Figure 7), indicate an intermolecular antiferromagnetic interaction between the nickelocene units, and from X-ray structure determination it is clear that the interaction occurs pairwise, which is in agreement with the fitting procedure.



Figure 8. The molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) of the *ansa*-nickelocene complex **2** doped into **3**. The χ_m values take into account the dilution of **2** of about 26 mol-% of the diamagnetic ruthenium congener **3**.

Redox Properties

The redox chemistry of *ansa*-nickelocene **2** was investigated by means of cyclic voltammetry (Figure 9). The cyclic voltammogram of **2** in acetonitrile displays two redox couples with a separation of about 1 V and an additional irreversible reduction in the range of the archetype nickelocene.^[19] All redox couples correspond to a one-electron transfer that results in three different oxidation states of complex **2** (0, +1, +2; Scheme 2). In contrast to the redox properties of the parent nickelocenes, only the first oxidation step at $E_{1/2} = -0.522$ V is electrochemically reversible, whereas the second oxidation step at $E_{1/2} = 0.487$ V is only partially reversible, and the reduction to the anion at $E_{pc} = -2.294$ V is electrochemically irreversible (Table 2).



Figure 9. Cyclic voltammogram of **2**: overview (solid line); 0/+1 (dotted line).

$$\left[\mathsf{Ni}(\mathsf{II})\right]^{0} \underset{\mathsf{E}_{1/2}(2)}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{$$

Scheme 2. Redox cascade of compound 2.

Table 2. Cyclic voltammetry data^[a] of 2.

Redox couples	E _{1/2} ^[b]	Epa	$E_{\rm pc}$	$\Delta E_{\rm p}^{\rm [c]}$		
-1/0	_	_	-2.294	_		
0/+1	-0.522	-0.485	-0.558	0.073	$\Delta E_{\rm pc}(2-1)^{[d]}$	1.736
+1/+2	0.487	0.523	0.450	0.073	$\Delta E_{1/2}(3-2)^{[e]}$	1.009

[a] In acetonitrile at room temperature, $[nBu_4N]PF_6$ (0.2 M) as the supporting electrolyte, Pt as the standard electrode referenced versus $E_{1/2}(FcH/FcH^+) = 0$ V, scan rate 200 mV s⁻¹. Potentials *E* in volts (±0.005 V). [b] $E_{1/2} = (E_{pa} + E_{pc})/2$. [c] $\Delta E_p = |E_{pc} - E_{pa}|$. [d] $\Delta E_{pc}(2-1) = |E_{pc}(0/+1) - E_{pc}(-1/0)|$. [e] $\Delta E_{1/2}(3-2) = |E_{1/2}(+1/+2) - E_{1/2}(0/+1)|$.

The small reduction wave at -0.960 V (Figure 9, solid line) only appears in connection with the oxidation of complex **2** to the dication beyond 0.485 V, which is confirmed by the additional cyclic voltammogram from the first redox couple (Figure 9, dotted line).

Conclusion

The synthesis of new *ansa*-metallocenes of nickel (2) and ruthenium (3) has been shown. Complex 2 and 3 have been characterized by single-crystal structure determination and established a very similar molecular structure for both complexes.

VT ¹H NMR spectroscopy revealed a Curie behavior in the temperature range for the paramagnetic nickel compound 2 that has been additionally investigated by SOUID measurements in the solid state. The neat sample exhibits antiferromagnetic coupling with a maximum of the molar magnetic susceptibility at about $T \approx 25$ K. SQUID measurements of diluted samples of 2 in the diamagnetic ruthenium host prove it as an intermolecular coupling. The intermolecular coupling can be rationalized by a pairwise magnetic interaction as shown by the fitting procedure of the molar susceptibility and the result of the X-ray structure analysis. Cyclic voltammetry presented a close electronic relationship to nickelocene, although the structural distortion caused by the 1,1'-disubstitution yields a considerably bent metallocene, in which the twofold degeneracy of the former e_{1g} orbitals is broken. DFT calculations revealed a triplet ground state with a SOMO1–SOMO2 gap of 15 kJ mol⁻¹ for complex 2.

Experimental Section

General: Unless otherwise noted, the reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were saturated with nitrogen. THF and *n*-hexane were dried by sodium potassium alloy. Naphthalene-1,8-diylbis(cyclopentadienylsodium) (1)^[13] and hexaamminenickel(II) dichloride [Ni-(NH₃)₆]Cl₂^[20] were synthesized according to literature procedures. Dichloridotetrakis(dimethyl sulfoxide)ruthenium(II) was purchased and used without further purification. NMR spectroscopy was carried out with a Bruker AVANCE 400 instrument; variable-temperature ¹H NMR spectra of the paramagnetic compound **2** were measured in an NMR Young tube. MS: Finnigan MAT 311 A (FAB). Elemental analysis: CHN-O-Rapid, F. Heraeus, Zentrale Elementaranalytik, Fachbereich Chemie, Universität Hamburg. Naphthalene-Bridged ansa-Nickelocene

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Cyclic Voltammetry: Measurements were performed in acetonitrile with 0.2 M [*n*Bu₄N]PF₆ as supporting electrolyte. A Metrohm Autolab PGSTAT-101 system was used with a Pt disk as working electrode, Pt wire as reference electrode, and Pt rod as counter electrode. The potentials were referenced to $E_{1/2}$ (ferrocene/ferrocenium) = 0 V.

Magnetic Measurements: The magnetic susceptibility data of compound 2 were collected in a temperature range of 2-300 K under an applied field of 10 kG on powdered microcrystalline samples with a SQUID magnetometer (MPMS-XL, Quantum Design). The samples were sealed in quartz tubes under vacuum or were measured in gelatin capsules. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants.^[21] The temperature-dependent magnetic contribution of the holder was experimentally determined and subtracted from the measured susceptibility data. The resulting molar susceptibility data were plotted in $\chi_{\rm M}$ versus T and $\mu_{\rm eff}$ versus T. The program julx31 was used for spin-Hamiltonian simulations of the data (E. Bill, Max-Planck Institute for Bioinorganic Chemistry, Mülheim, http:// www.mpi-muelheim.mpg.de/bac/logins/bill/julX_en.php). The susceptibility data could be simulated using the spin Hamiltonian $\hat{H} = -2J_{12}\Sigma\hat{S}_1\cdot\hat{S}_2$, with $\hat{S}_1 = \hat{S}_2 = 1$, $J_{12} = -10.07 \text{ cm}^{-1}$, $\Theta = -0.2 \text{ K}$ and g = 2.029, and considering pairs of complexes as the paramagnetic unit.

X-ray Structure Determination: The data were collected with a Bruker AXS Smart APEX CCD, Mo- K_{α} , $\lambda = 0.71073$ Å (for crystallographic data of **2** and **3**, see Table 3). The structures were solved by direct methods (SHELXS-86)^[22] and the refinements on F^2 were carried out by full-matrix least-squares techniques (SHELXL-97).^[23] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic parameter of their carrier atoms. Weights were optimized in the final refinement cycles.

Table 3. Crystallographic data of the dinuclear complex 2 and 3.

	2	3
Empirical formula	C ₂₀ H ₁₄ Ni	C ₂₀ H ₁₄ Ru
$M_{\rm r}$ [g mol ⁻¹]	313.02	355.40
<i>T</i> [K]	100(2)	100(2)
λ [pm]	71.073	71.073
Crystal system	triclinic	monoclinic
Space group	PĪ	$P2_1/c$
<i>a</i> [pm]	777.5(3)	771.8(2)
<i>b</i> [pm]	963.6(3)	1882.5(6)
<i>c</i> [pm]	990.7(3)	966.4(3)
a [°]	107.100(1)	
β [°]	75.097(4)	106.246(3)
γ [°]	76.607(4)	
$V [10^6 \text{ pm}^3]$	670.8(4)	1347.9(7)
Ζ	2	4
$\rho_{\rm calcd.} [{\rm Mg m^{-3}}]$	1.550	1.751
$\mu \text{ [mm^{-1}]}$	1.434	1.151
<i>F</i> (000)	324	712
Crystal size [mm]	$0.31 \times 0.07 \times 0.03$	$0.24 \times 0.07 \times 0.02$
2θ [°]	4.34–50	4.32-53.98
Total reflections	3141	10155
R _{int}	0.0490	0.0723
Independent reflections	2145	2872
Parameters	190	206
GOF	1.100	1.094
$R_1/WR_2 [I > 2\sigma(I)]$	0.0543/0.1367	0.0492/0.0910
R_1/wR_2 (all data)	0.0633/0.1429	0.0852/0.1045

CCDC-844818 (for **2**) and -844819 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,1'-(Naphthalene-1'',8''-diyl)nickelocene (2) from [Cp₃Ni₂]BF₄: Naphthalene-1,8-diylbis(cyclopentadienylsodium) THF (1) (182 mg, 0.49 mmol) was dissolved in THF (30 mL) and cooled to -78 °C. The triple-decker complex tris(cyclopentadienyl)dinickel tetrafluoridoborate [Cp₃Ni₂]BF₄ (395 mg, 0.99 mmol) was added and stirred for one hour. The volatiles were removed under reduced pressure, and the solid residue was extracted with hexane. The solvent was removed and a part of nickelocene was sublimated from the residue. The separation was not quantitative and efforts led to a mixture of nickelocene and *ansa***-nickelocene 2**. Hence, no exact yield could be determined.

1,1'-(Naphthalene-1'',8''-diyl)nickelocene (2) from Hexaamminenickel(II) Dichloride: Naphthalene-1,8-diylbis(cyclopentadienylsodium)·THF (1) (641 mg, 1.73 mmol) and hexaamminenickel(II) dichloride (401 mg, 1.73 mmol) were dissolved in THF (60 mL). The resulting solution was heated at reflux overnight. The volatiles were removed under reduced pressure, and the solid residue was extracted with pentane. The extract was reduced in volume and crystallization at -20 °C afforded green crystalline needles (403 mg, 74%). ¹H NMR (400 MHz, C₆D₆, 293 K): $\delta = 17.6$ (s, 2 H, 3-H, 6-H), 14.3 (s, 2 H, 4-H, 5-H), 10.5 (s, 2 H, 2-H, 7-H), -248.8(s, 2 H, 13-H, 14-H), -280.1 (s, 2 H, 12-H, 15-H) ppm. MS (FAB): *m*/*z* [%]: 312.1 (100), 314.1 (46), 313.01 (31). HRMS (FAB): *m*/*z*: calcd. for C₁₀H₁₄Ni [M]⁺: 312.04623; found: 312.04489. Elemental analysis calcd. C 76.74, H 4.51; found C 76.30, H 4.57.

1,1'-(Naphthalene-1'',8''-diyl)ruthenocene (3): Naphthalene-1,8diylbis(cyclopentadienylsodium)·THF (1) (207 mg, 0.559 mmol) was dissolved in THF (15 mL) and cooled to -78 °C. Dichloridotetrakis(dimethyl sulfoxide)ruthenium(II) (240 mg, 0.495 mmol) was added in five portions, and the solution was additionally stirred at ambient temperature for two days. A white precipitate formed, and to complete the reaction the mixture was heated at reflux overnight. The solvent was removed under reduced pressure, and the crude product was subjected to chromatography [toluene, alumina (5% water)] to give the ansa-ruthenocene 3 in pale yellow crystals (156 mg, 0.438 mmol, 89%). ¹H NMR (400 MHz, CD₂Cl₂) [the assignment of the Cp signals has been performed by assuming an anisotropy of the aromatic ring current of the naphthalene inducing a stronger shielding effect at the protons in position 12 and 15 compared to H-13 and H-14 (Figure 10); multiplicities of highorder signals were described as first-order and marked with the prefix m~]: δ = 7.92 (m~dd, J = 1.4, 8.3 Hz, 2 H, H-2, H-7 or H4, H-5), 7.80 (m~dd, J = 1.5, 7.0 Hz, 2 H, H-4, H-5 or H-2, H-7), 7.46 (m~dd, J = 7.0, 8.1 Hz, 2 H, H-3, H-6), 4.90 (m~dd, J = 1.7, 1.7 Hz, 2 H, H-13, H-14), 4.66 (m~dd, J = 1.7, 1.7 Hz, 2 H, H-12, H-15) ppm. ¹³C NMR (200 MHz, CD₂Cl₂): δ = 132.53 (C-2, C-7) or C-4, C-5), 130.13 (C-4, C-5 or C-2, C-7), 124.39 (C-3, C-6),



Figure 10. Atom labeling for NMR spectroscopy.

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86.63 (C-11), 73.62 (C-13, C-4), 73.10 (C-12, C-15) ppm. MS (FAB): m/z (%): 356.1 (100), 355.1 (68), 358.1 (55), 354.1 (51), 357.1 (44), 353.1 (41), 359.1 (28), 350.1 (22), 360.2 (4). HRMS (FAB): m/z: calcd. for C₁₀H₁₄Ru [M]⁺: 356.01390; found 356.01459.

Computational Details: All calculations on complexes were performed at the DFT level of theory and by employing the B3LYP hybrid functional.^[24] For all atoms the def2-TZVP basis set was used.^[25] The ground state of the complex was calculated to be an open-shell singlet state in which the geometry optimization was performed in the frame of broken-symmetry formalism. The broken-symmetry solution was obtained by using the solution for the triplet state, and adjustment of the spin orbitals as a guess for the singlet-state. For all calculations the Gaussian 09 program suite was used.^[26]

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Naphthalene-Bridged ansa-Nickelocene

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A paramagnetic naphthalene-bridged *ansa*nickelocene has been synthesized. Although DFT calculations indicate a triplet ground state for the isolated single molecules, SQUID measurements with the neat compound reveal an antiferromagnetic interaction due to an intermolecular coupling between two molecules arranged in pairs.



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Naphthalene-Bridged *ansa*-Nickelocene: Synthesis, Structure, Electrochemical, and Magnetic Measurements

Keywords: Metallocenes / Sandwich complexes / Nickel / Magnetic properties