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Stereoselective Coordination of C_5-Symmetric Corannulene Derivatives with an Enantiomerically Pure [Rh$^{\mathrm{I}}$(nbd*)] Metal Complex**

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Dedicated to Professor Franco Cozzi on the occasion of his 60th birthday

Numerous stereoselective catalytic processes rely on the differentiation of internally enantiotopic faces of planar π-systems by metal complexation.[1] Chiral bowl-shaped molecules like 1,3,5,7,9-pentasubstituted corannulene, which invert rapidly on the reaction timescale, present themselves as achiral due to tautomeric equilibration of enantiomers,[2] and thereby display externally enantiotopic π-faces.[3] Stereoselective complexation of one such π-face shifts the tautomeric equilibrium and offers the possiblity to effect a complete dynamic resolution.[4] Thus, such systems provide a special platform for studying chiral ligand–metal molecular recognition and metal–arene complex dynamics.

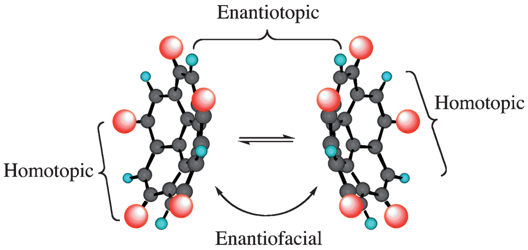
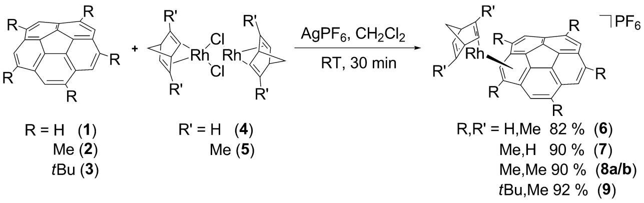


Figure 1. Equilibrating enantiomers (*P* and *M*) of C_5-symmetric corannulene derivatives.

The hydrogens in one bowl form of corannulene (**1**) are chirotopic and segregate into two internally enantiotopic sets of five homotopic hydrogens; the *endo* and *exo* faces of the bowl are diastereotopic. Bowl inversion renders all hydrogens, and the two faces, respectively homotopic. Under conditions of bowl inversion, simple metal coordination to either face of corannulene is not an event wherein stereoselection can occur (the products are homomeric). In contrast, *sym*-pentasubstituted corannulenes, such as 1,3,5,7,9-pentamethylcorannulene (**2**), oscillate between enantiomeric C_5-symmetric bowl conformations (Figure 1). The hydrogens of these conformers are internally homotopic but externally enantiotopic; the faces are diastereotopic in the static bowl, and rendered enantiotopic by inversion. Simple metal complexation of **2** yields enantiomeric products, whereby enantioselection becomes possible.[5]

From this stereochemical analysis, 1) complexation of **1** with a racemic metal fragment should yield two enantiomeric products with diastereotopic hydrogen NMR signals from corannulene, 2) complexation of **2** with a metal bearing enantiotopic hydrogens should yield enantiomeric products with diastereotopic hydrogen NMR signals coming from the metal fragment, and 3) complexation of **2** with an enantiomerically pure metal fragment should lead to diastereoselective chiral complex formation that effectively resolves the bowl forms of **2** into 100% of a single chiral diastereomer. Each of these complexes provides an unambiguous way to follow the dynamics of metal–arene rotation, migration, and transfer from a single complex.[6]

The corannulene partners in this study include **1**, **2**,[7] and 1,3,5,7,9-penta-*tert*-butylcorannulene (**3**).[8] On the metal side, the fragments include {Rh(nbd)}$^+$ (nbd = bicyclo[2.2.1]hepta-2,5-diene), in reagent form as [{(nbd)RhCl}$_2$] (**4**), and {Rh(nbd*)}$^+$ (nbd* = C_2-symmetric (*R*,*R*)-2,5-dimethyl-bicyclo[2.2.1]hepta-2,5-diene), in reagent form as [{(nbd*)RhCl}$_2$] (**5**).[9] Reaction of a corannulene and a [{(nbd)RhCl}$_2$] derivative activated by silver(I) in dichloromethane at room temperature produces the expected complexes **6–9** (Scheme 1).



Scheme 1. Synthesis of compounds **6–9**.

Complexation of **1** with **5** to yield **6** exemplifies the first case from the above stereochemical analysis. At the static limit, the {Rh(nbd*)} fragment is located over one ring and is not rotating. The molecular symmetry is C_1 and all protons of the corannulene and the nbd* are evident as unique signals. Rotation of the metal fragment without migration increases

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the symmetry to effectively dynamic C_2 for the nbd*, but leaves the corannulene in site symmetry C_1. Migration of the metal fragment creates a dynamic C_5 symmetry for the corannulene fragment but leaves it chirotopic. Under such conditions, two diastereotopic sets of five exchanging hydrogens are observed either by 2D EXSY[10] directly on the distinguished hydrogens (Figure 2) or by line-shape coalescence. The symmetry argument excludes external metal–arene exchange and supports a dynamic character where the metal wanders the aromatic surface without dissociation.

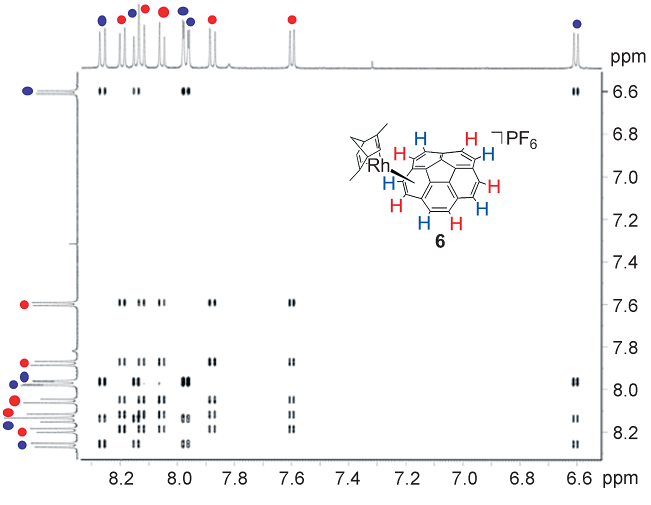

Figure 2. ^1H EXSY NMR spectrum for **6** (273 K in CD_2Cl_2 at $\tau_m = 1.2$ s).

Complexation of **2** with **4** to yield **7** exemplifies the second case from the above stereochemical analysis. Here also the static limiting symmetry is C_1 with all signals uniquely present in the NMR spectrum. Rotation of the metal fragment effects only a C_2 symmetry for the nbd fragment, and as such, A and B signals remain after coalescence of A/C and B/D pairs. Migration again creates a dynamic C_5 symmetry for the corannulene fragment, but does not change the chirotopic character for the nbd unit, and A and B signals persist (Figure 3).

In the case of **7**, crystals suitable for X-ray crystallographic analysis revealed a structure of the static complex (Figure 4).[11] The structure showed the four different stereoelectronic environments of the nbd vinyl hydrogens. From this structure one sees that replacement of homotopic protons by methyl groups could create a significant steric interaction such that matched and mismatched diastereomers would result. This hypothesis was modeled quantum mechanically to get a quantitative prediction of the effect.

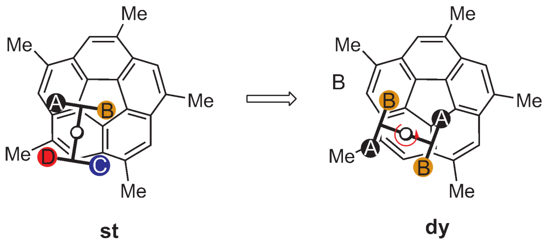

Figure 3. Dynamic symmetry due to rotation of the {M(nbd)} fragment. st: static, all diastereotopic; dy: dynamic, two homotopic pairs.

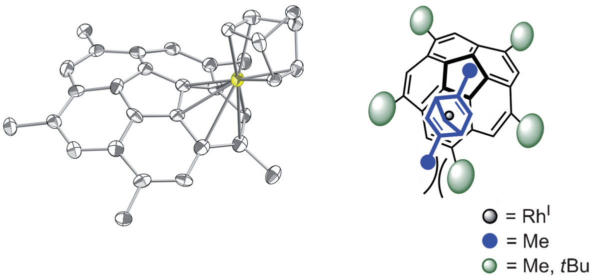

Figure 4. Left: X-ray molecular structure of **7**; right: schematic representation of the steric differentiation hypothesis.

M06/cc-pVDZ + (SDD + f) density functional theory calculations on **7** reproduced the X-ray structure well, and further showed that it would be possible to predict the diastereoselectivity of the complexation of **2** with **5** to yield **8a/b** or of **3** with **5** to yield **9a/b**. Further computations carried out on **8a/b** and **9a/b** predicted a difference of 1.88 kcal mol^{-1} and 3.54 kcal mol^{-1}, respectively. These predicted energy differences in the product isomers would correspond to a product ratio of 25:1 for the former and 400:1 for the latter, were the full energy difference expressed in the transition state to complexation.

Reaction of **2** with **5** yields **8a/b** (2.5:1) and reaction of **3** with **5** produces **9a** with an undetectable amount of **9b**. Compared to the computations, one can see that the product path is locked in before the full energy difference is felt. Such a result is reasonable given that transition state structures are sterically looser than the product structures. The molecular recognition on the basis of the computational results matches the *P* configuration at corannulene with the *R*,*R* configuration of nbd*.

Additional experimental evidence for the chiral nature of these compounds exists in the Cotton effects observed in the circular dichroism (CD) spectra (Figure 5). In the case of nbd*, a negative Cotton effect is observed at 255 nm and only a part of the curve is measurable, as previously observed for non-conjugated norbornadienes.[12] Compound **6** displays a positive Cotton effect at 355 nm, whereas **9** has a maximum at 347 nm. The shifted Cotton effects towards longer wave-

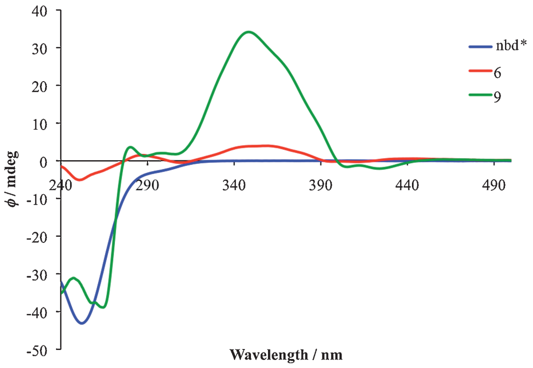

Figure 5. CD spectra of (*R*,*R*)-2,5-dimethyl-bicyclo[2.2.1]hepta-2,5-diene, **6**, and **9** ([nbd*] = 5 × 10^{-4} M; [**6**] and [**9**] = 1 × 10^{-4} M).

lengths for **6** and **9**, compared to the free diene ligand nbd*, point to a probable electron density transfer from the ligand to the corannulene core.[13]

In conclusion, a dynamic resolution of the equilibrating enantiomers of *sym*-pentasubstituted corannulenes by complexation with a chiral, enantiomerically pure metal–NBD* reagent is understood from a matched–mismatched analysis of the stereoelectronic environment of the product diastereomers.[14] Because the bowl forms are equilibrating faster than the time scale for complexation, it is possible to drive the reaction completely to one isomer in the case of **9**, where differences in the energy of the diastereomeric transition states is high. Quantum mechanical computations predict this selectivity well. CD analysis of the various derivatives gives a first glimpse into the possible CD of *sym*-pentasubstituted corannulenes frozen into one bowl form. These complexes also presage stereochemical ways to study the structure and dynamics of a future family of metal complexes of "imperfect" graphenes.[15]

Experimental/Computational Section

9: A solution of $AgPF_6$ (10.1 mg, 0.04 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise to a vial containing 1,3,5,7,9-penta(*tert*-butyl)corannulene (21.2 mg, 0.04 mmol) and $[\{Rh(nbd^*)Cl\}_2]$ (10.0 mg, 0.02 mmol) in CH_2Cl_2 (0.4 mL) and the mixture (yellow) was stirred in the dark for 30 min. The resulting suspension was filtered through a pad of cotton/celite to eliminate the AgCl and the filtrate was evaporated to dryness. The resulting yellow solid was washed with pentane (3 × 2 mL) and dried in vacuo, yielding 33.6 mg (92 %) of the desired compound.

^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): $\delta = 8.58$ (s, 1H), 8.48 (s, 1H), 8.28 (s, 1H), 8.17 (s, 1H), 8.08 (s, 1H), 7.00 (s, 1H), 3.85–3.80 (br, 2H), 3.18–3.14 (m, 2H), 1.92 (s, 9H), 1.77 (s, 9H), 1.73 (s, 18H), 1.63 (s, 9H), 1.51–1.47 (br, 6H), 1.24–1.22 ppm (t, $J = 1.4$ Hz, 2H).

^{13}C NMR (125 MHz, CD_2Cl_2, 215 K): $\delta = 157.2$, 151.8, 150.0, 144.8, 136.9, 135.3, 134.4, 130.4, 129.9, 129.2, 128.7, 128.5, 124.7, 124.0, 121.7, 116.8, 116.1, 112.5, 101.0, 88.7, 78.6 (d, $J_{\text{Rh-C}} = 5.1$ Hz), 74.3, 59.6, 53.7 (DEPT 135), 53.3 (DEPT 135), 49.0 (d, $J_{\text{Rh-C}} = 7.88$ Hz), 46.4 (d, $J_{\text{Rh-C}} = 7.9$ Hz), 37.9, 37.3, 37.19, 37.16, 36.9, 32.0, 31.9. 31.6 (2C), 31.5, 23.1, 18.2 ppm. MS-ESI: *m*/*z* 753.6 $[RhC_{49}H_{62}]^+$ in chloroform. HRMS-ESI: calcd for $RhC_{49}H_6$: 753.3907; found: 753.3902.

The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements and other property calculations, were carried out using Truhlar's module revision D.01 of Gaussian03[16] running on the Minnesota supercomputers (MSI), and the GAMESS[17] software packages. The M06 density functional of Truhlar and Zhao,[18] was used together with a basis set consisting of the relativistic effective Stuttgart/Dresden-double-ζ (6d, 10f) (SDD)[19] core potential for the transition metals with state-averaged optimum f exponents (0.567;1.989) of Martin and Sundermann,[20] and the Dunning correlation consistent basis set,[21] cc-pVDZ, a [3s2p1d] contraction of a (9s4p1d) primitive set for all other atoms. Full geometry optimizations were performed and uniquely characterized via second derivatives (Hessian) analysis to determine the number of imaginary frequencies (0 = minima; 1 = transition state), and zero point contributions. Molecular orbital contour plots, used as an aid in the analysis of results, were generated and depicted using WEBMO,[22] and QMView.[23]

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