$(CO)_{42}]^{n-}$: A. Ceriotti, A. Fait, G. Longoni, G. Piro, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Am. Chem. Soc.* **1986**, *108*, 8091; c) $[H_{6-n}Ni_{34}C_4(CO)_{38}]^{n-}$: A. Ceriotti, A. Fait, G. Longoni, G. Piro, L. Resconi, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Am. Chem. Soc.* **1986**, *108*, 5370; d)$[Ni_{32}C_6(CO)_{36}]^{6-}$: F. Calderoni, F. Demartin, M. C. Iapalucci, G. Longoni, *Angew. Chem.* **1996**, *108*, 2393; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2225; e) $[Pd_{38}(CO)_{28}(PEt_3)_{12}]$: E. G. Mednikov, N. K. Eremenko, Yu. L. Slovakhotov, Yu. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1987**, 218; f) $[Pd_{34}(CO)_{24}(PEt_3)_{12}]$: E. G. Mednikov, N. I. Kanteeva, *Russ. Chem. Bull.* **1995**, *44*, 163; g) $[Ni_9Pd_{33}(CO)_{41}(PPh_3)_6]^{4-}$: M. Kawano, J. W. Bacon, C. F. Campana, L. F. Dahl, *J. Am. Chem. Soc.* **1996**, *118*, 7869; h) $[H_{12}Pd_{28}Pt_{13}(CO)_{27}(PMe_3)(PPh_3)_{12}]$: J. M. Bemis, L. F. Dahl, *J. Am. Chem. Soc.* **1997**, *119*, 4545.

[4] J. M. van Ruitenbeek, D. A. van Leeuwen, L. J. de Jongh in *Physics and Chemistry of Metal Cluster Compounds, Vol. 18* (Ed.: L. J. de Jongh), Kluwer Academic, Dordrecht, **1994**, p. 277.

[5] N. Rösch, G. Pacchioni in *Clusters and Colloids: From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**, p. 5.

[6] P. Zanello in *Stereochemistry of Organometallic and Inorganic Compounds, Vol. 5* (Ed.: P. Zanello), Elsevier, Amsterdam, **1994**, p. 163.

[7] F. Calderoni, F. Demartin, F. Fabrizi De Biani, C. Femoni, M. C. Iapalucci, G. Longoni, P. Zanello, *Inorg. Chem.*, submitted.

[8] D. A. Nagaki, L. D. Lower, G. Longoni, P. Chini, L. F. Dahl, *Organometallics* **1986**, *5*, 1764.

[9] A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, G. Piva, G. Piro, M. Sansoni, B. T. Heaton, *J. Organomet. Chem.* **1986**, *301*, C5.

[10] B. K. Teo, H. Zhang, *J. Cluster Sci.* **1990**, *1*, 155.

[11] Crystal data for $0.5[NMe_3CH_2Ph]_6[Ni_{36}Pt_4(CO)_{45}]/0.5[NMe_3CH_2Ph]_6[Ni_{37}Pt_4(CO)_{46}] \cdot C_3H_8O$: hexagonal, space group $P6_3$ (no. 173), $a = 17.853(9)$, $c = 27.127(13)$ Å, $V = 7488(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.29$ g cm^{-3}, graphite-monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 82.5$ cm^{-1}. A total of 86976 reflections with $3 < \theta < 29°$ were measured on a Siemens CCD area-detector SMART diffractometer at 210 K on a crystal of approximate dimensions 0.10 × 0.15 × 0.08 mm, mounted in air but protected by the cooling N_2 stream during data collection. Data were corrected for Lorentzian polarization and absorption effects (empirical absorption correction with SADABS;[12] transmission factors in the range 0.61 – 1.00). The structure was solved by direct methods (SIR97[13]) and refined with full-matrix least-squares (SHELX93[14]) on 9209 independent reflections with $I > 3\sigma(I)$. Anisotropic displacement parameters were assigned to all atoms of the anions. The final R value was 0.057 ($R_w = 0.128$). Maximum $\Delta\rho = 2.2$ e Å^{-3} close to the Pt atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102917. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] G. M. Sheldrick, SADABS, Universität Göttingen, Germany, unpublished results.

[13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *24*, 435.

[14] G. M. Sheldrick, SHELX93, program for the refinement of crystal structures, Universität Göttingen, Germany, **1993**.

[15] a) A. Ceriotti, G. Longoni, M. Manassero, M. Perego, M. Sansoni, *Inorg. Chem.* **1985**, *24*, 117; b) A. Ceriotti, G. Longoni, M. Manassero, L. Resconi, M. Sansoni *J. Chem. Soc. Chem. Commun.* **1985**, 181; c) A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, G. Piro, L. Resconi, M. Sansoni *J. Chem. Soc. Chem. Commun.* **1985**, 1402; d) A. Ceriotti, G. Longoni, G. Piro, M. Manassero, N. Masciocchi, M. Sansoni, *New J. Chem.* **1988**, *12*, 501.

A Chelate with Conformational Memory?**

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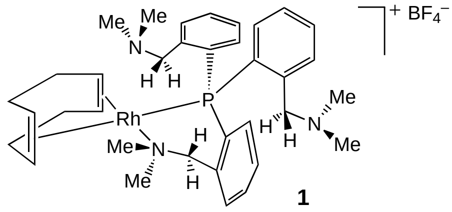
and Katerina Soulantica

Advances in NMR techniques have enabled detailed observation of some dynamic phenomena at the molecular level. One problem that has attracted attention is restricted rotation around single bonds,[1] particularly in chiral molecules. Because of their movements, some molecular systems have been referred to as molecular motors, brakes, ratchets, etc.[2–5] The possible selective directionality of these restricted rotations is governed by the principle of microscopic reversibility: Rotations that interconvert degenerate states cannot have a preferred sense.[3, 6] An illustrative case of this and other related basic aspects is presented here.

The complexes $[Rh(diene)\{P(bzN)_3\}]BF_4$ (**1**: diene = 1,5-cyclooctadiene (cod), **2**: diene = tetrafluorobenzobarrelene (tfb); bzN = 2-(dimethylaminomethyl)phenyl) are square planar in solution, and the $P(bzN)_3$ ligand acts as a P,N chelate with two pendant amino group arms. The chelate ring has a boat conformation, which makes the complexes chiral (racemic).[7] Racemization by inversion of the boat is slow on the NMR time scale at room temperature, as can be seen in the ^1H COSY spectrum of **1** (Figure 1). The four olefinic hydrogen atoms are inequivalent, the CH_2 groups give rise to three AB systems, and the methyl groups give four singlets (3:3:6:6); hence, the two methyl groups on the coordinated N center are inequivalent, and those at each pendant N atom are equivalent owing to fast inversion of the amino group, although the two pendant arms are inequivalent.[8] The coordination plane clearly defines two half-spaces, one concave and one convex,[9] which contain the two possible positions for nucleophilic attack by an entering ligand (Scheme 1).



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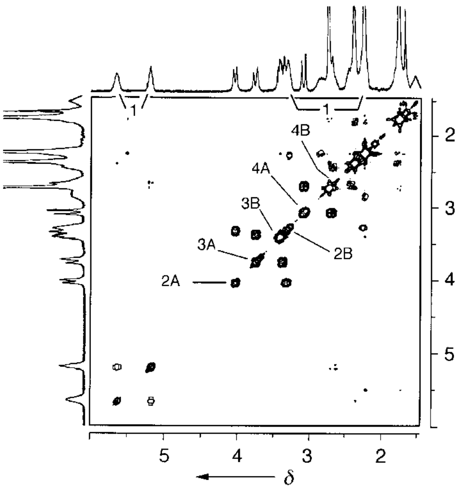
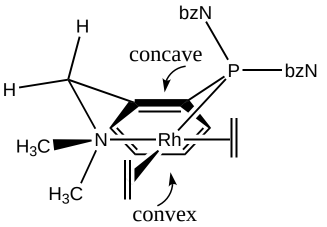


Figure 1. ^{1}H COSY spectrum (300 MHz, $CDCl_3$, 20 °C) of **1**. 2A/2B, 3A/3B, and 4A/4B are the three methylene groups, each of which constitutes an AB spin system. Label 1 denotes the olefinic protons: *cis* to the coordinated N atom to the left, and *cis* to the coordinated P atom to the right; note the pronounced upfield shift of the olefinic proton at $\delta \approx 2.1$, probably due to anisotropic shielding by the aromatic rings of the pendant arms.



Scheme 1. Two possible positions for nucleophilic attack by an entering nucleophile.

The striking behavior of **1** and **2** is that they undergo exchange between the coordinated and pendant amino groups with complete retention of the conformation of the ring. It can be said that the molecule remembers the conformation of the ring during the exchange process. This is clearly seen in the ^{1}H EXSY spectrum of **1** at room temperature (Figure 2):[10] 1) All the methyl groups exchange with each other; 2) the olefinic protons do not exchange; and 3) all the methylene groups undergo selective exchange, in which the inequivalence of their two protons is conserved. This is consistent only with an associative substitution mechanism, in which the incoming ligand adopts the same configuration as the leaving group. A dissociative mechanism or a fast inversion of the boat can be discounted, as both should lead to exchange of the olefinic protons on the same double bond and of all methylene protons; that is, racemization would occur simultaneously with exchange of the N centers. (A three-coordinate intermediate would have a symmetry plane, and fast inversion of the boat would generate a time-averaged plane of symmetry in the square-planar complex or in the trigonal bipyramidal pentacoordinate intermediate.) These observations are further supported by magnetization transfer experiments,[11] which clearly show that the selective inversion of a given methylene proton leads to magnetization transfer to only two other methylene protons, each on a different methylene group; moreover, the magnitude of the magnetization transfer to these is, within the experimental error, the same. Hence, the two pendant arms exchange at the same rate with a coordinated arm, that is, attack at the concave and the convex positions occurs at the same rate, and both produce the conformation of the ring that is already present in the molecule.

The two processes were investigated independently for **2**. The rate of ligand exchange was measured by line-shape analysis of the singlets of the methyl groups,[12] which afforded $\Delta G^{\ddagger}_{298} = 55.7\ \mathrm{kJ\,mol^{-1}}$ ($\Delta H^{\ddagger} = 51.5 \pm 2.7\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger} = -14 \pm 10\ \mathrm{J\,K^{-1}mol^{-1}}$). The inversion of the boat conformation was studied by magnetization transfer on the F atoms of the tfb ligand, which gave $\Delta G^{\ddagger}_{298} = 66.9\ \mathrm{kJ\,mol^{-1}}$ ($\Delta H^{\ddagger} = 49.6 \pm 2.7\ \mathrm{kJ\,mol^{-1}}$; $\Delta S^{\ddagger} = -58 \pm 10\ \mathrm{J\,K^{-1}mol^{-1}}$). At 298 K the rate of exchange of pendant and coordinated amino groups in **2** is about 100 times faster than the inversion of the boat.

The associative substitution mechanism is shown in Scheme 2, starting from one of the two enantiomers. It deserves several comments on the concept of chirality:

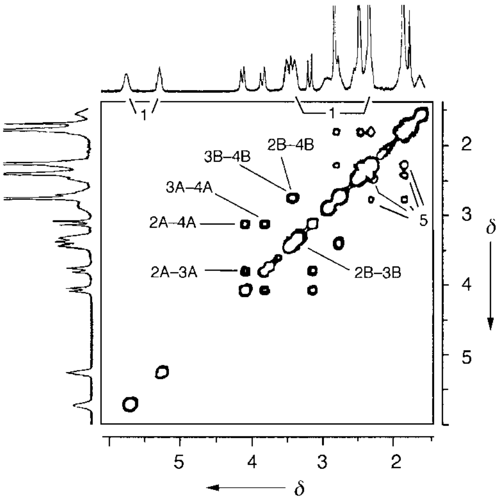
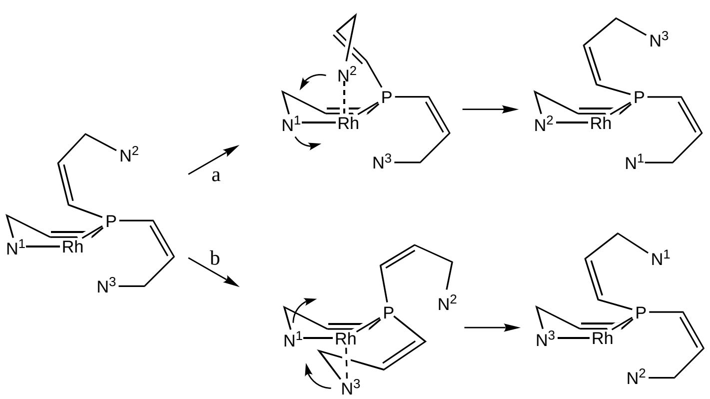


Figure 2. ^{1}H EXSY spectrum (300 MHz, $CDCl_3$, 20 °C) of **1**. Label 5 indicates cross-peaks of the methyl groups, and the others are cross-peaks of the methylene protons, numbered as in the COSY spectrum of Figure 1.



Scheme 2. a) Nucleophilic attack at the concave site. b) Nucleophilic attack at the convex site. For clarity the aromatic ring is represented by a double bond, and the olefin bound to Rh has been omitted.

1) The two pendant arms are disposed in such a way that N^2 can attack the concave position, and N^3 the convex position.

Although steric hindrance at the two sites appears to be very different, attack occur at the same rate at both. Otherwise there would be a preferred sense for rotation, but this cannot occur if both rotations give rise to identical molecules, that is, the motion interconverts degenerate states. This problem was discussed in detail for the rotation of triptycenes[4] and an aryl ring.[3] Although the approach to one of the two sites is initially less hindered, the rate of substitution is controlled only by the energy of the transition state, which is the same regardless of the initial position of attack.

2) The pendant arms are not chiral, but they are "prochiral" in the sense that chirality is produced upon coordination and adoption of a particular conformation. Thus, in the substitution reaction chirality is efficiently induced in the "prochiral" entering arm by the chiral leaving arm. It can be said that the system exhibits "strong chirality towards the entering arm,[13] the origin of which is clearly geometric: The pentacoordinate intermediate has severe steric constraints which can be minimized only if the two nonplanar rings are stacked concave/concave (or convex/convex), but not concave/convex. The incoming ligand adopts the conformation with the best "steric complementarity" to the coordinated ligand.[14]

3) The system is an example of the principle of self-regeneration of stereocenters.[15] Here the "stereocenter" is the conformation of the chelating ring, which, for a given arm, is lost and regenerated during the exchange process.

4) Racemization of the complex requires inversion of the boat conformation, which takes place ($k_{298} = 11.7\ \text{s}^{-1}$) without any bond scission. Thus the system possesses what has been called "dynamic chirality", and consequently the exchange process is an example of a reaction with "memory of chirality".[16] Clearly, its "good memory" is also associated with the large difference in rate between the exchange and the racemization processes: On the time scale of the exchange process ($k_{298} = 1054.7\ \text{s}^{-1}$) the conformation of the boat is static.

In summary, there is no need for coining a new term, as the "conformational memory" of these molecules can be analyzed on the basis of well-known concepts: The induction of chirality, the effect of differences in the rates of "simultaneous" processes, and the principle of microscopic reversibility.

Experimental Section

Compounds **1** and **2** were prepared from their corresponding precursors[17] as follows: A solution of [{Rh(diene)(μ-Cl)}$_2$] and P(bzN)$_3$ in acetone was treated with $AgBF_4$ (for **1**) or $TlBF_4$ (for **2**). After 1 h insoluble MCl (M = Ag, Tl) was filtered off, and the complex was crystallized by concentration to a small volume, addition of ethanol, and cooling to $-20\,^{\circ}C$. **1**: Yield: 78 %; elemental analysis calcd for $C_{35}H_{48}BF_4N_3PRh$: C 57.47, N 5.75, H 6.61; found: C 57.19, N 5.88, H 6.31; ^1H NMR ($CDCl_3$, 300 MHz, 20 °C): δ = 10.08 (m, 1 H), 8.06 (m, 1 H), 7.93 (m, 1 H), 7.85 (m, 3 H), 7.63 (m, 2 H), 7.50 (m, 1 H), 7.40–7.10 (m, 3 H), 5.60 (m, 1 H), 5.25 (m, 1 H), 4.08 (d, 1 H), 3.81 (d, 1 H), 3.45 (d, 1 H), 3.39 (m, 2 H), 3.12 (d, 1 H), 2.88 (m, 1 H), 2.80 (s, 3 H), 2.72 (m, 2 H), 2.50 (m, 2 H), 2.43 (s, 3 H), 2.31 (m, 8 H), 1.82 (s, 6 H), 1.78 (m, 2 H), 1.57 (m, 1 H); ^{31}P NMR ($CDCl_3$, 121.4 MHz, 20 °C): $\delta = 21.4$ (d, $J_{\text{Rh,P}} = 153$ Hz). **2**: Yield: 71 %; elemental analysis calcd for $C_{39}H_{42}BF_8N_3PRh$: C 55.14, N 4.94, H 4.98; found: C 54.59, N 4.53, H 5.10; ^1H NMR ($CDCl_3$, 300 MHz, 213 K): δ = 10.25 (m, 1 H), 7.93 (m, 2 H), 7.79 (m, 1 H), 7.70 (m, 1 H), 7.55 (m, 2 H), 7.45 (m, 1 H), 7.35 (m, 2 H), 7.17 (m, 1 H), 6.97 (m, 1 H), 6.03 (m, 1 H), 5.88 (m, 1 H), 5.45 (m, 1 H), 5.33 (m, 1 H), 4.01 (m, 1 H), 3.82 (m, 1 H), 3.38 (m, 2 H), 3.21 (m, 1 H), 3.16 (m, 1 H), 2.89 (m, 1 H), 2.79 (s, 3 H), 2.43 (s, 6 H), 2.39 (s, 3 H), 2.15 (m, 1 H), 1.84 (s, 6 H); ^{31}P (NMR, 121.4 MHz, $CDCl_3$, 213 K): $\delta = 26.3$ (d, $J_{\text{Rh,P}} = 172$ Hz). ^{19}F NMR ($CDCl_3$, 20 °C): δ = −145.6 (m, 1 F), −146.7 (m, 1 F), −152.07 (s, 4 F, BF_4^-), −158.7 (m, 2 F).

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[1] See, for instance, M. Oki, *The Chemistry of Rotational Isomers*, Springer, Heidelberg, **1993**.

[2] T. R. Kelly, I. Tellitu, J. Pérez-Sestelo, *Angew. Chem.* **1997**, *109*, 1966; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1866.

[3] J. A. Casares, S. Coco, P. Espinet, Y.-S. Lin, *Organometallics* **1995**, *14*, 3058.

[4] T. R. Kelly, M. C. Bowyer, K. V. Bhasakar, D. Bebbington, A. García, F. Lang, M. H. Kim, M. P. Jette, *J. Am. Chem. Soc.* **1994**, *116*, 3657.

[5] F. P. Fanizzi, M. Lanfranchi, G. Natile, A. Tiripicchio, *Inorg. Chem.* **1994**, *33*, 3331.

[6] A. P. Davis, *Angew. Chem.* **1998**, *110*, 953; *Angew. Chem. Int. Ed.* **1998**, *37*, 909, and references therein.

[7] This boat conformation has been found for Pd and Pt complexes with the same chelate ring: a) W. de Graaf, S. Harder, J. Boersma, G. van Koten, J. A. Kanters, *J. Organomet. Chem.* **1988**, *358*, 545; b) N. C. Payne, G. R. Tobin, *Acta Crystallogr. Sect. C* **1992**, *48*, 45; c) G. M. Kapteijn, M. P. R. Spee, D. M. Grove, H. Kooijman, A. L. Spek, G. van Koten, *Organometallics* **1996**, *15*, 1405.

[8] Related complexes with the less sterically hindered ligand P(bzN)Ph$_2$ show a somewhat faster inversion of the boat, with $\Delta G^{\neq} = 36.6\ \text{kJ mol}^{-1}$ for Rh$^{\text{I}}$ (T. B.Rauchfuss, F. T. Patino, D. M. Roudhill, *Inorg. Chem.* **1975**, *14*, 652) and 46 kJ mol^{-1} for Pd$^{\text{II}}$ complexes.[7c]

[9] G. Helmchen, R. Schmierer, *Angew. Chem.* **1981**, *93*, 208; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 205, and references therein.

[10] The EXSY experiments were carried out with a standard NOESY program in phase-sensitive mode with a 5 % random variation of the evolution time to avoid COSY cross-peaks and a mixing time of 0.6 s.

[11] The magnetization transfer experiments were carried out by using a 180° Gaussian shaped soft pulse for the selective excitation of the desired signal, followed by a variable delay (ten values were used: 10^{-4}, 0.005, 0.01, 0.015, 0.02, 0.03, 0.04, 0.06, 0.08, and 10.0 s) and a 90° nonselective pulse. The data were analyzed as described in M. L. H. Green, A. Sella, L.-L. Wong, *Organometallics* **1992**, *11*, 2650.

[12] Line-shape analysis was carried out using the standard DNMR6 program: DNMR6, Quantum Chemical Program Exchange (QCPE 633), Indiana University, Bloomington, IN, **1995**.

[13] For a discussion on the quantification of chirality, see A. B. Buda, T. Auf der Heyde, K. Mislow, *Angew. Chem.* **1992**, *104*, 1012; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 989.

[14] J.-M Lehn *Supramolecular Chemistry*, VCH, Weinheim, **1995**.

[15] D. Seebach, A. R. Sting, M. Hoffmann, *Angew. Chem.* **1996**, *108*, 2880; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2708.

[16] K. Fuji, T. Kawabata, *Chem. Eur. J.* **1998**, *4*, 373.

[17] a) [Rh$_2$(μ-Cl)$_2$(1,5-cod)$_2$]: G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1990**, *28*, 84; b) [Rh$_2$(μ-Cl)$_2$(tfb)$_2$]: R. Usón, L. A. Oro, M. Valderrama, C. Claver, *Synth. React. Inorg. Met. Org. Chem.* **1979**, *9*, 577; c) P(bzN)$_3$: C. Chuit, R. J. P. Corriu, P. Monforte, C. Reyé, J.-P. Declerq, A. Dubourg, *Angew. Chem.* **1993**, *105*, 1529; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1430.