[CR] 

[1] IR: $\nu = 790, 730, 690$ cm$^{-1}$; MS: m/z 158 (M$, 10\%$), 104 (M$-$ C$_8$H$_8$, 100$); $^1$H-NMR (360 MHz, CDCl$_3$): $\delta = 7.20$ (2H, dd, $^1J = 1.0, ^2J = 0.9$ Hz, H$_1^1, H_2^1$), 7.07 (2H, dd, $^1J = 1.0, ^2J = 0.9$ Hz, H$_1^1, H_2^1$), 4.68 (2H, XX of AA$'BB'XX'$, $^1J = 12.2, ^2J = 11.9, ^3J = -0.8, ^5J = 5$ Hz, H$_1^$), 2.79 (2H, ddd, $^1J = 12.0, ^2J = 3.5, ^3J = 3.5$ Hz, H$_1^, H_2^$), 2.26 (2H, ddd, $^1J = 12.0, ^2J = 12.0, ^3J = 3.0$ Hz, H$_1^, H_2^$), 1.88 (2H, m, H$_1^, H_2^$), 1.01 (2H, m, H$_1^, H_2^$).

Upon irradiation at $\delta = 4.68$, the multiplets at 1.88 and 1.01 changed into ddd with $^1J = 12.0, ^2J = 3.5, ^3J = 3.0$ Hz and $^1J = 12.0, ^2J = 12.0, ^3J = 3.5$ Hz, respectively. $^1$C-NMR (CDCl$_3$): $\delta =$ 142.9 (s), 136.0 (d), 132.1 (d), 132.0 (d), 35.8 (t), 34.2 (t).

[IS] 

[6] Paracyclophane: UV (hexane): $\lambda_{max} =$ 299 (460), 251 (500), and 214 (17000) nm.

[10] Paracyclophane: UV (hexane): $\lambda_{max} =$ 299 (460), 251 (500), and 214 (17000) nm.

[2] Paracyclophane: UV (hexane): $\lambda_{max} =$ 299 (460), 251 (500), and 214 (17000) nm.

[3] Paracyclophane: UV (hexane): $\lambda_{max} =$ 299 (460), 251 (500), and 214 (17000) nm.

[4] Paracyclophane: UV (hexane): $\lambda_{max} =$ 299 (460), 251 (500), and 214 (17000) nm.

[5] Paracyclophane: UV (hexane): $\lambda_{max} =$ 299 (460), 251 (500), and 214 (17000) nm.
The configurations of the chirality centers in the three-membered ring are $S_{Mo}S_{N}S_{C}$ in 3a and $R_{Mo}R_{N}R_{C}$ in 3c. The chirality of the Mo atom disappears, and the imine ligand becomes π-bonded and thereby the configuration at the C atom of the three-membered ring is established ($S_{C}$ in 2b and $R_{C}$ in 2c). The placement of the proton on 2b and 2c on the pyridine side via a preformed H bridge explains the cis orientation of the substituents H and pyridyl in 3a and 3c; there is no experimental evidence for a trans orientation. The isomer 3b, which constitutes about 4% of the mixture with 3a ($S_{Mo}S_{N}S_{C}$), is assigned opposite Mo configuration ($R_{Mo}S_{N}S_{C}$) whereby rapid isomerization 3a $\rightarrow$ 3b might arise by intramolecular rotation of the immonium ligand, comparable with the rotation of an olefin in a π-complex. Correspondingly, 3c and 3d can be assigned the configurations $R_{Mo}R_{N}R_{C}$ and $S_{Mo}R_{N}R_{C}$, respectively. 3a and 3c, with cis oriented Cp, H, pyridyl substituents on the MoNC three-membered ring, are thermodynamically more stable than 3b and 3d.

Reactions of 3a/3b with [Rd(nbd)Cl], (nbd = norbornadiene) afforded the complex 4, which after chromatography was isolated as a reddish-brown powder in 61% yield. The same product is formed on using 3c/3d as starting material. Crystallization from ether/pentane at $-20^\circ$C furnished single crystals of 4a, whose absolute configuration was determined by X-ray crystallography. In 4a the chelate ring formed via the two N atoms and the Rh atom lies on the side of the MoNC three-membered ring opposite to the cyclopentadienyl ring. This is surprising, since the substituents Cp, H, and pyridyl are located on the same side of the MoNC three-membered ring in the complexes 3a and 3c. The reason for the chelate ring in 4a, in contrast to the N–H–N hydrogen bridge in 3a and 3c, preferring that side of the three-membered ring with the CO ligands, may be sought in the formation of a bond between the Rh atom and ClO of the CO group C10–O10 (Fig. 3). This CO group (Mo–C10–O10 166.9°) deviates from linearity: the Rh–ClO distance (2.821 Å), however, points to only a weak interaction of the Rh atom with the C atom. The formation of this CO bridge is unusual, because semibridging CO groups normally only occur when metal–metal bonds are present.

Thus, the following picture emerges: In the reduction of 1, the cation accepts two electrons. The anionic intermediate 2a is formed in which the Mo–N(pyridyl) bond is broken. The chirality of the Mo atom disappears, and 1a and 1b, despite the contrary Mo configurations, give the same products. In the reaction 2a $\rightarrow$ 2b + 2c the σ-bonded imine ligand becomes π-bonded and thereby the configuration at the C atom of the three-membered ring is established.
The 1H-NMR spectra show that 4 forms two diasteromers a and b, which rapidly interconvert in solution at room temperature. The high-temperature limiting spectrum for 4a/4b is observed at 100°C, while the low-temperature limiting spectrum, with separate signals for 4a and 4b in the intensity ratio 98:2, is observed at $-70$°C.10 It is not possible, as yet, to make any statements about the structure of 4b.

The finding that the reactions of 3a/3b and 3c/3d with [Rh(nbd)CL], lead to the same product 4a/4b can only be explained in terms of an intermediate 2a. The intermediate 2a is formed from both 3a/3b as well as from 3c/3d; the asymmetry of all former three-membered ring atoms is removed, leading under the strongly alkaline conditions used in the synthesis,9 to establishment of the equilibrium 3a/3b$\rightleftharpoons$3c/3d, even in the absence of [Rh(nbd)CL],. It therefore follows that epimerization of the intermediates 2b and 2c (with $\pi$-coordinated imine ligand) via 2a (with $\sigma$-coordinated imine ligand) is more rapid than the reaction with [Rh(nbd)CL],: Otherwise, if the complex 4a (RMSR,SMR) is formed from 3a/3b, then 3c/3d would have to yield a Rh-complex 4c with SSMR,SRM configuration, which is not observed.

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[4] Type B (310/25 mm) LiChroprep Si60 (40-63 pm), toluene/ether 50:50.


Fig. 1. Asymmetric unit of the crystal structure of 1-C6H5. Space group P21/n, a = 968.02(2), b = 1583.44(2), c = 2402.96(6) pm, $\beta = 99.46(5)^\circ$. Z = 4, R = 0.115 for 2292 reflections with $F > 3.0 \sigma(F)$. The high R value is due to decomposition of the crystal in the X-ray beam. The H atoms on C(7) and C(7a) were given a fixed C-H distance (96 pm) and a common isotropic temperature factor. All other H atoms were refined according to a riding model with C-H = 96 pm. All calculations were carried out with the SHELXTL (Rev. 5.1) program system (G. M. Sheldrick, Göttingen 1985). Selected bond lengths [pm] and angles [°] (mean values: Li-NTMEDA) 205(4), Li-N(anion) 204(3), C1K7 143(2), C7-C8 138(2), C8-N9 115(3), Lil-Li2 264(5); C1-K7-C8-N9 178.4(1.0), N9-Lil-N9a 98.2(0.5), Lil-N9-Li2 80.9(0.5), C6-C1-C7 179.2(0.7). Because of the small anisotropic vibration of the nitrogen atom, an analysis of the C5-C9 bond length according to a riding model [8] gave only a slight lengthening to 117(2) pm. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-75144 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-511841, the names of the authors, and the full citation of the journal.

1 C6H5 crystallizes as a dimer, in which Li atoms are bonded to the N atoms of the nitride groups and the TMEDA molecules. This solid state structure may correlate...