Optically Active Transition-Metal Complexes. 90.1
Cp(CO)2Mo[NH(R*)CH(py)] Complexes and Their
Rh(norbornadiene) Derivatives: Stereochemistry and Absolute
Configuration of the Metallaaziridine System

Henri Brunner, * Joachim Wachter, and Johann Schmidbauer
Institut für Anorganische Chemie, Universität Regensburg, D-8400 Regensburg, Germany
George M. Sheldrick and Peter G. Jones
Institut für Anorganische Chemie, Universität Göttingen, D-3400 Göttingen, Germany

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Complexes [CpMo(CO)2NN']X (1a-d/2a-d; Cp = C5H5, X = Cl, PF3; NN' = Schiff bases a-d), derived
from 2-pyridinecarbaldehyde and primary amines, are obtained in high yield; they can be transformed to the corresponding PF3
salts. In this reaction the molybdenum atom, located in
the center of a square pyramid, becomes an asymmetric center. Therefore, the derivatives of (S)-(−)-1-phenyl-
ethylamine form a pair of diastereomers RMo(NC)C1/SMo(NC)C1, which differ only in the configuration at the Mo atom.2,3
The separation of the diastereomers, their absolute configurations, and their interconversion have been investigated.4–10

In a reactivity study it was shown that compounds
[CpMo(CO)2NN']X (X = Cl, PF3) of type 1/2 react with
LiMe to give a ring contraction, yielding complexes of type
6/9 with three-membered MoNC rings11,12 containing a nonligating pyridine substituent.13,14 However, in the
LiMe reaction these compounds were only accessible in
3% yield. In the reduction with Na amalgam, we found a new high-yield synthesis of compounds 6/9. The
mechanism of this reaction and the stereochemistry of the products and also their conversion into the new binuclear
Mo-Rh complexes 10/11 are described in this paper. A
short account of part of this work has been given.1

Metallaaziridine Complexes 6a-d/9a-d
Four different pyridine imines a–d were used as ligands in
the present study: a derives from (R)-(−)-1-phenyl-
ethylamine, b from (S)-(−)-1-cyclohexylethylamine, c from
(1S,2S,3S)-(−)-3-(aminomethyl)pinane, and d from (S)-(−)-2-methylbutylamine. These four Schiff bases define
the four different systems a–d shown in Scheme I.

Complexes 1a–d/2a–d, containing the anions X = Cl and
PF3, were prepared from CpMo(CO)2Cl and pyridine
imines a–d. The two diastereomers were separated in
system a by fractional crystallization to give pure 1a and
2a (X = PF3). Complexes 1b–d/2b–d were used as
diastereomer mixtures (X = Cl) for the reaction with Na
 amalgam.

In the reaction of the salts 1a–d/2a–d with excess
Na/Hg in THF, the neutral complexes 6a–d/9a–d were formed in yields between 41% and 46%. The reaction mixtures were purified by chromatography, the complexes
6a–d/9a–d being eluted as red zones. Isomer separation
was attempted with preparative-liquid chromatography
using a set of two Merck Lobar columns.15,16 Separation
into two bands was achieved for systems a–c; for d only
one band was obtained.

1H NMR spectroscopy revealed the isomer composition of complexes 6a–d/9a–d. For all four systems a–d the
1H NMR signals of compounds 6/9 were broad at room tem-

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The high-temperature-limiting spectra were therefore obtained at 90 or 100 °C and the low-temperature-limiting spectra at −60 or −70 °C.

In the $^1H$ NMR spectrum of the material in the first chromatographic band of system a there was only one set of signals at 100 °C. However, there were two sets of signals in an intensity ratio of 96:4 at −70 °C. Similar results were obtained for the material in the second band of the chromatography of system a with an intensity ratio of 90:10 at −70 °C. The two sets of signals for the compounds in the first band were assigned to isomers 6a and 7a and those for the compounds in the second band to 8a and 9a. This assignment was corroborated by the X-ray structure analyses for the major isomers 6a and 8a, which were described in a preliminary communication.¹

On chromatography the 1-cyclohexylethylamine system b also separated into two bands, each of which gave one high-temperature set of signals and two low-temperature sets of signals assigned to complexes 6b/7b and 8b/9b, both in ratios of 87:13. System c behaved similarly to system b with −70 °C ratios of 6c:7c = 97:3 and 8c:9c = 94:6. In the d series there was no chromatographic separation into two bands. The high-temperature $^1H$ NMR of the material in the single band showed only one set of signals and the low-temperature $^1H$ NMR two sets of signals in a ratio of 96:4, which were assigned to structures 8d and 9d on the basis of the chiroptical evidence and the absolute configurations discussed below.

The low-temperature-limiting spectra thus demonstrated that each of the bands obtained by Merck Lobar chromatography of systems a–d consisted of two isomers, a major isomer, 6 or 8, and a minor isomer, 7 or 9, which were rapidly interconverting, according to Scheme I.

The high-temperature-limiting spectra, on the other hand, allowed a determination of the isomer composition present in the reaction mixtures after Na/Hg reduction of complexes 1a–d/2a–d by integration of corresponding signals. These isomer ratios 6/7/8/9 were not far from temperature.

### Table I. Details of Crystal Structure Determinations

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<th></th>
<th>6c</th>
<th>8d</th>
<th>11d</th>
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<tbody>
<tr>
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<td>394.33</td>
<td>588.36</td>
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<td>12.61</td>
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<td>$b$</td>
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<td>$\mu$, mm⁻¹</td>
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<td>none</td>
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<tr>
<td>(transmision factors)</td>
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<td>(0.61–0.69)</td>
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The absolute configurations of 6a, 7a, 8a, and 9a were determined (Tables 1–111, V, VI) by using single crystals obtained at −70 °C. (Figures 1 and 2).¹ Similar to 6a and 8a,¹ in

### Table II. Atom Coordinates ($x10^4$) and Isotropic Temperature Factors ($\AA^2 \times 10^4$) for Complex 8d

<table>
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<th>x</th>
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¹ Equivalent isotropic U calculated from anisotropic U.
Table IV. Atom Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^6) for Complex 11d

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<td>75 (2)</td>
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*Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensors.

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Figure 3. CD spectra of complexes 6a-d/9a-d (ca. 5 x 10^-4 M in toluene).

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6c and 8d substituents Cp on Mo, H on N, and py on C are located at the same site of the MoNC ring, the NH proton forming a hydrogen bridge to pyridine N. The configurations of the chiral centers in the three-membered ring are S_MoS NC for 6c and R_MoR NC for 8d, provided that the ligand sequence Cp > N(MoNC ring) > C(MoNC ring) is used to specify the absolute configuration at Mo, looking to the molecule from the side opposite to the two carbonyl groups, which arbitrarily are excluded from the configurational assignments. It should be mentioned that neither the Cahn-Ingold-Prelog rules nor their extension to organometallic compounds would allow the specification of the configuration of the asymmetric Mo atoms in compounds of type 6/9 without arbitrary assumptions, e.g.,
the definition given above.22

The CD spectra of complexes 6a-d/9a-d show two characteristic maxima at 450 and 338 nm (Figure 3). It is obvious that the CD spectra are almost mirror images except for intensity differences. These differences arise because the CD spectra are measured in solution at room temperature with isomer mixtures 6 = 7 and 8 = 9. It is true that the equilibrium ratios, varying for series a-d between 97:3 and 87:13, could be measured by 'H NMR at -70 °C. However, the equilibrium ratios at room temperature are not known. In any case the major isomers 6 and 8 should dominate the CD spectra, and the minor isomers 7 and 9 should make only small contributions. For the a series the absolute configurations of the isomers 6a and 8a have been determined previously.1 From the present study the absolute configurations of 6c and 8d are available for the c and d series. In agreement with this the CD spectra of 6c/7c and 8d/9d are almost coincident with the spectra of 6a/7a and 8a/9a. For the b series there is no X-ray structure analysis. However, on the basis of the CD spectra, safe assignments of the configurations SM&+ and R&& to the major isomers 6b and 8b can be made (Figure 3). Conclusions similar to those inferred from the CD spectra of complexes 6a-d/9a-d can be drawn from their optical rotations, given for four different wavelengths in the Experimental Section.

For the a and c series the first band from the chromatographic separation contains compounds 6 and 7 and the second band compounds 8 and 9. For the b system this elution order is reversed. The conclusion that the single band in the d series consists only of compounds 8d and 9d is confirmed by the CD spectrum. Obviously, compounds 6d and 7d are not formed in the Na/Hg reduction of ld/2d.

The Binuclear Mo–Rh Complexes 10 and 11

The Mo-Rh complexes 10 and 11 (Scheme I) were formed in the reaction of [Rh(nbd)Cl]2 (nbd = norbornadiene), with complexes 6a-d/9a-d in yields around 60%. As catalysts KOH/[18]crown-6 and KOH/NBu4HSO4 were used. The red-brown neutral complexes can be purified by chromatography. Similar to compounds 6a-d/9a-d, the isomeric composition is unraveled by 'H NMR spectroscopy at high and low temperatures.

In series a the 'H NMR spectrum of the reaction product shows one set of signals at 90 °C and two sets of signals in a ratio of 98:2 at -70 °C. The major isomer is assigned structure 10a on the basis of a single-crystal X-ray analysis reported earlier.1 The minor isomer 10a' is not depicted in Scheme I because its structure is not clear. Complexes 11a and 11a' could not be detected in series a.

In the 1-cyclohexylethylamine system b the fraction 8b/9b was converted into the rhodium complexes. In the low-temperature 'H NMR spectrum two pairs of major/

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Figure 4. Molecular geometry and absolute configuration of complex 11d in the crystal. Selected bond lengths (Å) and angles (deg): Mo-N1 = 2.188 (3), Mo-C2 = 2.268 (3), N1-C2 1.395 (6), Mo-C10 1.953 (4), Mo-C20 = 1.928 (5), C10-O10 = 1.164 (5), C20-O20 = 1.165 (7), Mo-Cp = 2.299 (6)-2.363 (7), C2-C22 = 1.458 (5), N1-C3 = 1.474 (4), C-N(pypy) = 1.354 (5) and 1.339 (5), Rh-N21 = 2.096 (3), Rh-N1 = 2.043 (3), Rh-C32 = 2.133 (4), Rh-C33 = 2.133 (4), Rh-C35 = 2.124 (4), Rh-C36 = 2.115 (4); N1-Mo-C2 = 104.4 (1), Mo-C2-N1 = 88.7 (2), Mo-N1-C2 = 74.9 (2), C10-Mo-C20 = 78.5 (2), Mo-C10-O10 = 162.7 (3), Mo-C20-O20 = 179.4 (5), N1-Rh-N21 = 79.6 (1), C22-C2-N1 = 115.2 (3), Rh-N1-C2 = 112.4 (2), Rh-N21-C22 = 113.3 (2), N21-C2-C2 = 115.6 (3).

minor isomers could be observed in ratios 10b:10b' = 97:3 and 11b:11b' = 87:13. At higher temperatures they coalesced to two sets of signals with a 10b:10b':11b:11b' = 77:23 ratio.

There are the same four isomers in the c series, two of which coalesce in the high-temperature-limiting spectrum. Interestingly, the overall ratio 10c/10c':11c/11c' was 85:15 if the Mo complexes 6c/7c were used in the synthesis, and it was 15:85 if the preparation started with the Mo complexes 8c/8c.

In the d series the Mo compounds 8d/9d give only one pair of isomers 11d/11d', visible in the low-temperature 1H NMR spectrum with a ratio of 70:30. At 80 °C there is coalesence to one set of signals due to the rapid equilibration 11d = 11d'. The absolute configuration of the major isomer 11d was determined by a single-crystal X-ray analysis17,24 (Figure 4).

A single crystal of 11d was obtained on crystallization of the 11d/11d' mixture at -20 °C from ether/pentane. Similar to 10a, in 11d the chelate ring formed between the rhodium atom and the two nitrogen atoms is on the side opposite to the Cp with respect to the MoNC ring. This is surprising because in the X-ray analyses of 6a, 8a, 6c, and 8d the substituents Cp, H, and py were found on the same side of the MoNC ring. The reason that the N-Rh-py chelate ring (in contrast to the N-H-py hydrocarbon bridge) prefers the side of the CO ligands is the formation of a weak bond between the Rh atom and C10 of the CO group C10-O10 (Figure 4). Although the interaction between Rh and C10 is only weak (Rh-C10 = 2.596 (5) Å), the Mo-CO system deviates from linearity as apparent from the angle Mo-C10-O10 of 162.7°. The formation of the CO bridge in 11d is unusual because semibridging carbonyl groups normally are formed only when there are metal–metal bonds.

In 11d the three asymmetric centers of the MoNC ring have the configurations S_M,S_S,R_C, compared to 8d (configuration R_M,R_S,R_C) which contains the same ligand. The inversion of configuration at the Mo atom in going from

Figure 5. CD spectra of complexes 10a-d/11a-d (ca. 5 x 10⁻⁴ M in toluene).

8d to 11d arises because the N-H-py substituent prefers the Cp side and the N-Rh(nbd)-py substituent the CO side of the MoNC three-membered ring. The change in the configurational symbol for N is a consequence of substitution of H (lowest priority) by Rh(nbd) (highest priority).

The CD spectra of complexes 10 and 11 are depicted in Figure 5. The Rh complex of series a contains only isomers 10a and 10a', whereas the corresponding complex of the series d consists only of isomers 11d and 11d'. Therefore, these two CD spectra are almost mirror images of each other. In the (aminomethyl)pinane series there are two Rh complexes with isomer ratios 10c/10c':11c/11c' of 85:15 and 15:85. Their CD spectra are almost exact mirror images. The similarity to the spectra of 11d/11d' and 10a/10a', respectively, allows the unequivocal assignment of the configurations. The CD spectrum of the Rh complex in the b series corresponds to a 10b/10b':11b/11b' mixture of 77:23.

Discussion

Excluding the chiral centers of the substituents a–d (Scheme I), complexes 6/9 each contain three chiral centers (the Mo, N, and C atoms of the three-membered ring); these give rise to a total of eight possible stereoisomers. Four of these isomers are observed in series a, b, and c whereas only two are found in system d.

In the reduction with Na amalgam of the pyridine imine complexes 1a–d/2a–d to the metallaaziridine complexes 6a–d/9a–d, the cation of 1/2 accepts two electrons. This leads to a cleavage of the Mo–N(py) bond, and the anionic
the ir-coordinated intermediates are dynamically more stable than the rates of formation of the Rh complexes and the rates of rotation of the immonium ligand, comparable to the rotation of an olefin in a π-complex. Similarly, 8a-d and 9a-d are assigned the configurations R,R,R,R and S,S,S,S, respectively. 6a-d and 8a-d, with a cis arrangement of the substituents Cp, H, and py at the MoNC ring, are thermodynamically more stable than 7a-d and 9a-d.

There is rapid equilibration between the metallalazaridine complexes 6 and 7 and between 8 and 9; however, there is no crossing over from system 6/7 into 8/9 and vice versa without deprotonation at the N atoms in complexes 6-9. For the 6/7 equilibrium, deprotonation leads to the anionic π-bonded intermediate 4, whereas deprotonation of 8/9 gives 5. Transition between systems 6/7 and 8/9 requires passage through the σ-coordinated intermediate 3, in which the asymmetry of all the atoms of the former three-membered ring is lost. From this intermediate 3 all the configurations of the compounds on both sides in Scheme I are accessible. Intermediate 3 is thus responsible for the equilibriums 6/7 = 8/9, which take place in strongly alkaline medium; e.g., treatment of both pure 6c/7c and 8c/9c with KOH/[18]crown-6 in toluene for 10 min results in a 6c/7c:8c/9c ≈ 35:65 mixture, whereas without base there is no isomerization.

The formation of the Rh complexes 10/11 from 6/9 also starts with a deprotonation at the NH group. Whether 6/7 can be stereospecifically converted to 10 and 8/9 to 11 depends on the relative rates of the formation of the Rh complexes 4 → 10 and 5 → 11 with respect to the formation of the σ-coordinated intermediate 4 → 3 and 5 → 3. In the 6a series, 6a/7a and 8a/9a are stereospecifically transformed to 10a/10a'. This implies that intermediate 5a, formed by deprotonation of 8/9a, is converted to 3a more rapidly than to 11a/11a'. In series c, however, pure 6c/7c is transformed into 10c/11c = 85:15 and pure 8c/9c to 10c/11c = 15:85. Therefore it must be concluded that the σ-coordinated intermediates 4c and 5c react with [Rh(nbdCl)2], more rapidly than rearranging to the σ-bonded intermediate 3c. A complicated balance of the rates of formation of the Rh complexes and the rates of isomerization via 3 has therefore to be assumed for the different series a/d.

Similar to the metallalazaridine complexes 6a-d/8a-d, the low-temperature-limiting spectra of all the Rh complexes 10a-d/11a-d show two isomers in intensity ratios between 98:2 and 65:35; these interconvert rapidly at higher temperatures. It cannot be decided whether the minor isomers 10' and 11' have structures in which the C=N unit of the three-membered ring is rotated by 180° with respect to 10 or 11 (without Rh–CO interaction) or the rotation of the C=N unit is only such that there is a Rh–C bond to the other carbonyl group.

Enantioselective Catalysis with Complexes 10 and 11

The Rh complexes 10a, 10c/11c (85:15), 10e/11e (15:85), and 11d were used as catalysts for the hydrodsilylation of 2 mL of acetophenone with 3.4 mL of diphenylsilane in 5 mL of toluene, according to procedures given before.29-32 In 4 h at 25°C the conversion ranged between 7% and 9%. The optical inductions were 0.2% ee (s), 0.6% ee (S), 0.5% ee (R), and 0.8% ee (R) for the four catalysts. Complexes 10a and 10e/11e (85:15) with RhMo(RC) configuration thus favor (S)-1-phenylethanol, and complexes 10e/11e (15:85) and 11d with Sm(S,S) configuration favor (R)-1-phenylethanol, but only to a small extent.

Experimental Section

All manipulations were carried out with dry solvents in an atmosphere of purified nitrogen. Apparatus used for spectroscopic measurements: IR, Beckman IR 4240; 'H NMR, Varian T 60 and Bruker WM 250; 13C NMR, Bruker WH 90; MS, Varian 311 A; CD, Jasco J 40 A; optical rotation, Perkin-Elmer polarimeter 241; melting points (in sealed capillaries), Büchi SMP 20 (uncorrected).

Pyridine Imines a-d. The Schiff bases a-d, the ligands in complexes 1 and 2, were prepared by stirring 40-75 mmol of freshly distilled 2-pyridinecarbaldehyde and an equimolar amount of the corresponding optically active amine in 300 mL of benzene for 2 h at 80°C. Instead of (+)-3-aminomethylpine and (+)-2-methylbutylamine the corresponding hydrochlorides and an excess of triethylamine were used. In these two cases the ammonium salts formed were filtered off at the end of the reaction. For all compounds the water formed in the condensation was then removed together with the solvent. The remaining oily products were purified by a high vacuum Kugelrohr distillation.

Pyridine imine a: yield 98%; oil (bp 108°C (10⁻³ mm)); 'H NMR (CDCl₃) 6 8.40 (s, 1 H), 6.9-8.5 (m, 9 H), 4.57 (q, 1 H), 1.58 (d, J = 6.7 Hz, 3 H); optical rotation, [α]20578 = +6.4°, [α]20578 = +24° (c 1, acetone).

Pyridine imine b: yield 87%; oil (bp 110°C (10⁻³ mm)); 'H NMR (CDCl₃) 6 8.43 (s, 1 H), 6.6-8.5 (m, 4 H), 0.9-1.7 (m, 11 H), 2.94 (m, 1 H), 1.16 (d, J = 6.4 Hz, 3 H); optical rotation, [α]20578 = +82°, [α]30464 = +97°, [α]30464 = +195°, [α]30464 = +409° (c 1, acetone).

Pyridine imine c: yield 89%; oil (bp 185°C (10⁻³ mm)); 'H NMR (CDCl₃) 6 8.25 (s, 1 H), 7.1-8.7 (m, 4 H), 3.60 (m, 2 H), 0.8-2.4 (m, 17 H); optical rotation, [α]20578 = +30°, [α]30464 = +34°, [α]30464 = +55°, [α]30464 = +80° (c 1, acetone).

Pyridine imine d: yield 88%; oil (bp 105°C (7 × 10⁻² mm)); 'H NMR (CDCl₃) 6 8.55 (s, 1 H), 6.6-8.5 (m, 4 H), 3.36 (m, 2 H), 1.75 (m, 1 H), 0.92 (d, J = 6.7 Hz, 3 H), 1.31 (m, 2 H), 0.86 (t, J = 7.3 Hz, 3 H); optical rotation, [α]20578 = +64°, [α]30464 = +7°, [α]20468 = +14°, [α]30468 = +25° (c 1, acetone).

The optically active amines, required for the condensations to the Schiff bases a-d, were obtained as follows: (R)-(++)-1-phenylethylamine, (S)-(++)-1-cyclohexylethylamine, and (1S,2S,3S)-(++)-3-aminomethylpine were gifts of BASF AG. (S)-(++)-2-Methylbutylamine was prepared according to the following procedure, analogous to ref 23.

(S)-(++)-2-Methylbutylamine. PBr₃ (18.5 g, 68 mmol) was added dropwise to a mixture of 15.0 g (170 mmol) of (S)-(++)-2-methylbutanol and 4.65 g (59 mmol) of pyridine at 0 °C for 2 h. After the mixture was warmed to room temperature, the residue was distilled. The volatile fraction was dissolved in 50 mL of petroleum ether and washed with 5% NaOH, 10% H₂SO₄, and water. After the solution was dried with CaCl₂ and the solvent evaporated, the product (S)-(++)-2-methylbutyl bromide was distilled at 120°C: yield 86%; colorless oil; [α]2378 = +5.81° (c 4.8, chloroform).32

(S)-(++)-2-Methylbutyl bromide (10.6 g, 70 mmol), 10.3 g (70 mmol) of phthalimide, and 4.84 g (35 mmol) of K₂CO₃ were refluxed in DMF for 15 h. KBr and phthalimide were filtered

off, and the solvent was removed. The newly formed precipitate of phthalimide was separated. The product (S)-(2-methylbutyl)phthalimide was distilled by a Kugelrohr distillation (high vacuum, 105 °C) and yellow oil.

Several combined runs were added to give 28.0 g (128 mmol) of (S)-(2-methylbutyl)phthalimide. Hydrazine hydrate (6.5 g, 128 mmol) and 150 mL of ethanol were added. After the mixture was heated 10 h to reflux, the solvent was evaporated. The yellow residue was heated with 200 mL of concentrated HCl for 4 h. Insoluble material was filtered off. The filtrate was concentrated to give the hydrochloride of (S)-(2-methylbutyl)amine: yield 72%; yellow oil.

Butylphthalimide was distilled by a Kugelrohr distillation (high vacuum, 105 °C): yield 52%; yellow oil.

Treatment of the hydrochloride of (S)-2-methylbutylamine with 200 mL of triethylamine in 100 mL of ethanol gave (S)-(2-methylbutyl)amine. On concentration of the solution the material contained in the solution as the starting material precipitated and was filtered off. After evaporation of the volatile products (S)-(2-methylbutyl)amine was purified by a Kugelrohr distillation (high vacuum, 105 °C) for 10 h to reflux, the solvent was evaporated. The yellow oil was filtered and was yellow.

Pyridine Imine Complexes 1 and 2.

C21H20MoN2O2P C, 43.61; H, 4.36; MR, 518.42. Found: C, 44.07; H, 4.36; MR, 518.42.

Pyrroolidine Imine Complexes 1 and 2.

C21H26MoN2O2 C, 58.06; H, 6.03; MR, 528.84. Found: C, 58.11; H, 6.12.

A 400-mg sample of complexes 6a-d/9a-d was chromatographed on two connected Merck-Lobar columns (type B (310/25 mm); LiChroprep S60 (40-63 μm)) with exclusion of light in toluene/ether (50:1) a black material remained at the top of the column. Complexes 6a-d/9a-d eluted as a red zone in each chromatography. Evaporation of the solvent gave an orange oil in all cases. The oils solidified for a, c, and d on stirring with petroleum ether. The yields, melting points, IR bands, isomer ratios, and elemental analyses, given below, were determined at this stage.

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Butylphthalimide was distilled by a Kugelrohr distillation (high vacuum, 105 °C): yield 52%; yellow oil.

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Optically Active Transition-Metal Complexes

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(d/d, 1 H), 2.4-0.4 (m, 19 H); ratio $\delta$e 9 94:6 at -70 °C; optical rotation, $[\alpha]_{D}^{2578}$ = -83°, $[\alpha]_{D}^{2546}$ -1218°, $[\alpha]_{D}^{2535}$ = +1508°, $[\alpha]_{D}^{2535}$ -2595° (c 0.05, toluene).

8d/9d: orange needles; yield 43%; mp 100-101 °C; IR (KBr) 1910, 1800 (vCO), 1590 cm$^{-1}$ (vCN). Anal. Calcd for C$_{31}$H$_{37}$MoN$_{2}$O$_{2}$Rh: C, 54.90; H, 5.65. Found: C, 54.90; H, 5.65.

$[\alpha]_{D}^{2578}$ -830°, $[\alpha]_{D}^{2546}$ -1215°, $[\alpha]_{D}^{2535}$ -2595° (c 0.05, toluene).

8d/9d: R$_{M}$-R$_{6}$/S$_{M}$-R$_{6}$/R$_{C}$: 1H NMR (toluene-d$_{8}$, Bruker WM 250, 90 °C) $\delta$ 7.96 (d, $J$ = 4.98 Hz, 1 H), 7.1-6.4 (m, 3 H), 5.05 (m, 1 H), 4.86 (s, 5 H), 3.64 (d, $J$ = 6.58 Hz, 1 H), 2.6-1.7 (m, 3 H), 1.3-1.0 (m, 2 H), 0.77 (d, $J$ = 6.71 Hz, 3 H), 0.75 (t, $J$ = 7.44 Hz, 3 H); $[\alpha]_{D}^{2578}$ -1138°, $[\alpha]_{D}^{2546}$ -1672°, $[\alpha]_{D}^{2535}$ -2621° (c 0.05, toluene).

Optically Active Transition-Metal Complexes

Rh(nbd) Derivatives 10a-d/11a-d of the Metallaaziridine Complexes 6a-d/7a-d. A 0.2-mmol sample of complexes 6a-d/7a-d/9a-d/9d was filtered solution was concentrated to 1 mL and chromatographed

and 20 mg of [Rh(nbd)Cl],, 100 mg of pulverized KOH, and 0.12 mmol of [Rh(nbd)Cl], were used

Optically Active Transition-Metal Complexes

$\delta$H NMR (toluene-d$_{8}$, Bruker WM 250, 90 °C) $\delta$ 7.83 (d, $J$ = 7.46 Hz, 1 H), 7.1-5.8 (m, 4 H), 5.05/5.04 (s/s, 5 H), 4.84/5.19/5.20/5.45 (s/s/s/s, 5 H), 3.55 (m, 1 H), 2.6-1.4 (m, 3 H), 1.2-0.8 (m, 2 H), 0.66 (s, 3 H), 0.53 (d, 3 H); ratio 96:4 at -70 °C; optical rotation, $[\alpha]_{D}^{2578}$ -1138°, $[\alpha]_{D}^{2546}$ -1672°, $[\alpha]_{D}^{2535}$ -2621° (c 0.05, toluene).

complexes 6a-c/7a-c and 8d/9d showed the molecular ions in the mass spectra, when the field desorption technique was applied (solvent toluene).

Rh(nbd) Derivatives 10a-d/11a-d of the Metallaaziridine Complexes 6a-d/7a-d/9a-d. A 0.2-mmol sample of complexes 6a-d/7a-d/9a-d/9d was filtered solution was concentrated to 1 mL and chromatographed

As the procedure given did not work for

$\delta$H NMR (toluene-d$_{8}$, Bruker WM 250, 90 °C) $\delta$ 7.2-5.8 (m, 4 H), 5.05/5.04 (s/s, 5 H), 3.7-3.0 (m, 8 H), 4.35/4.29 (d/d, 1 H), 9.1-2.3 (m, 2 H), 2.3-0.5 (m, 17 H); ratio 10c/10c':11c/11c' = 85:15, when pure 8e/9e was used as starting material; ratio 10c/10c':11c/11c' = 18:85, when pure 8d/9d was used as starting material; $[\alpha]_{D}^{2578}$ +20578°, $[\alpha]_{D}^{2546}$ +1508°, $[\alpha]_{D}^{2535}$ -2595° (c 0.05, toluene).

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Supplementary Material Available: Complete tables of bond lengths and bond angles, anisotropic temperature factors, H atom coordinates, and isotropic temperature factors for complexes 6e, 8d, and 11d (11 pages); a listing of structure factors for complexes 6e, 8d, and 11d (81 pages). Ordering information is given on any current masthead page.