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

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Complexes $[CpMo(CO)_2NN']X$ (**1a–d/2a–d**; Cp = η^5-C_5H_5; X = Cl, PF_6; NN' = Schiff bases **a–d**), derived from 2-pyridinecarbaldehyde and four optically active primary amines, were reacted with Na/Hg to give the anionic intermediates **3** with an uncoordinated pyridine substituent. The rearrangement of the σ-coordinated imine in **3** to the π-coordinated imine in **4** and **5** fixed the configuration of the asymmetric carbon atom in the three-membered MoNC ring. Protonation from the pyridine side gave rise to the new metallaaziridine complexes **6a–d** to **9a–d**. Typical for the structures of the more stable isomers of **6a–d/9a–d** is the cis arrangement of Cp, H, and py substituents with an H bridge between the amine N and the pyridine N. In the less stable isomers, observed in the low-temperature ^1H NMR spectra, the NC unit is rotated by 180°. For complexes **6c** and **8d** the absolute configurations have been determined by X-ray crystallography. Complexes **6a–d/9a–d** reacted with $[Rh(norbornadiene)Cl]_2$, when deprotonated at the amine N, to give the corresponding Rh complexes. In the more stable isomers of the rhodium series the N–Rh–py chelate is on the CO side of the three-membered MoNC ring due to the formation of the Rh–C bond to a semibridging carbonyl group. The absolute configuration of complex **11d** was determined by X-ray crystallography.

Introduction

In the reaction of $CpMo(CO)_3Cl$ with Schiff bases NN', derived from 2-pyridinecarbaldehyde and primary amines, the compounds $[CpMo(CO)_2NN']Cl$ are obtained in high yield; they can be transformed to the corresponding PF_6 salts.[2] In this reaction the molybdenum atom, located in the center of a square pyramid, becomes a new asymmetric center. Therefore, the derivatives of (*S*)-(−)-1-phenylethylamine form a pair of diastereomers $R_{Mo}S_C/S_{Mo}S_C$, 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, PF_6) of type **1/2** react with LiMe to give a ring contraction, yielding complexes of type **6/9** with three-membered MoNC rings[11,12] 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-phenylethylamine, **b** from (*S*)-(+)-1-cyclohexylethylamine, **c** from (1*S*,2*S*,3*S*)-(+)-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 PF_6, were prepared from $CpMo(CO)_3Cl$ and pyridine imines **a–d**. The two diastereomers were separated in system **a** by fractional crystallization to give pure **1a** and **2a** (X = PF_6). 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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Table I. Details of Crystal Structure Determinations

	6c	8d	11d
formula	$C_{24}H_{30}MoN_2O_2$	$C_{18}H_{22}MoN_2O_2$	$C_{25}H_{29}MoN_2O_2Rh$
M_r	474.46	394.33	588.36
cryst habit	orange prism	orange prism	opaque rectangular prism
cryst size, mm	0.6 × 0.25 × 0.1	0.6 × 0.3 × 0.3	0.5 × 0.35 × 0.3
cell const, Å			
a	6.876 (2)	12.933 (2)	12.615 (2)
b	11.726 (2)	12.933 (2)	12.619 (2)
c	28.487 (5)	10.858 (2)	14.785 (2)
space group	$P2_12_12_1$	$P4_1$	$P2_12_12_1$
U, Å^3	2297	1816	2354
Z	4	4	4
D_{calcd}, g cm^{-3}	1.37	1.44	1.66
μ, mm^{-1}	0.6	0.7	1.2
absorptn correctn (transmissn factors)	none	none	ψ scans; 0.61–0.69
$2\theta_{max}$, deg	55	60	55
octants measd	±(*hkl*)	±(*hkl*)	±(*hkl*)
reflctns measd	5338	4772	5645
unique reflctns	4701	4206	4743
R_{int}	0.044	0.037	0.028
obsd reflctns ($> 4\sigma(F)$)	3646	3670	4312
R	0.044	0.037	0.028
R'	0.036	0.033	0.027
g	0.0002	0.00025	0.0002
no. of parameters	277	215	286
η	−1.19 (9)	+1.11 (9)	−1.10 (7)

perature. 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 ^{1}H 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 ^{1}H NMR of the material in the single band showed only one set of signals and the low-temperature ^{1}H 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

Table II. Atom Coordinates (×10^4) and Isotropic Temperature Factors (Å^2 × 10^3) for Complex 6c

	x	*y*	*z*	U^a
Mo	4440 (1)	5713.2 (0.3)	583.5 (0.1)	45 (1)
N(1)	5897 (5)	5187 (2)	1223 (1)	38 (1)
C(1)	4050 (6)	4661 (3)	1216 (1)	39 (1)
C(2)	6471 (6)	5936 (3)	1612 (1)	43 (1)
C(4)	4904 (7)	7282 (3)	762 (1)	59 (2)
O(4)	5168 (6)	8241 (2)	851 (1)	91 (2)
C(5)	1839 (7)	6203 (4)	755 (1)	68 (2)
O(5)	291 (6)	6488 (4)	864 (1)	121 (2)
C(1′)	9257 (7)	5802 (3)	2739 (1)	53 (1)
C(2′)	7538 (6)	6206 (3)	2444 (1)	44 (1)
C(3′)	6961 (6)	5317 (3)	2069 (1)	39 (1)
C(4′)	8439 (6)	4345 (4)	1999 (1)	54 (1)
C(5′)	10030 (6)	4326 (4)	2373 (1)	69 (2)
C(6′)	9197 (8)	4511 (3)	2874 (1)	63 (2)
C(7′)	10929 (7)	5512 (5)	2403 (2)	82 (2)
C(8′)	7332 (9)	3938 (3)	3013 (2)	83 (2)
C(9′)	10746 (10)	4257 (5)	3259 (2)	116 (3)
C(10′)	5847 (7)	6630 (4)	2735 (1)	61 (2)
C(21)	4038 (6)	3399 (3)	1134 (1)	41 (1)
N(22)	5777 (6)	2915 (3)	1088 (1)	56 (1)
C(23)	5791 (9)	1783 (3)	1002 (1)	71 (2)
C(24)	4148 (10)	1138 (4)	950 (1)	76 (2)
C(25)	2382 (10)	1656 (4)	995 (1)	69 (2)
C(26)	2323 (7)	2798 (3)	1090 (1)	54 (2)
C(31)	4631 (10)	4178 (4)	43 (1)	94 (2)
C(32)	6467 (9)	4579 (5)	104 (1)	98 (2)
C(33)	6523 (9)	5699 (5)	−61 (1)	99 (2)
C(34)	4677 (10)	5965 (4)	−218 (1)	99 (3)
C(35)	3525 (10)	5024 (4)	−148 (1)	97 (3)

[a] Equivalent isotropic *U* calculated from anisotropic *U*.

Table III. Atom Coordinates (×10^4) and Isotropic Temperature Factors (Å^2 × 10^3) for Complex 8d

	x	*y*	*z*	*U*
Mo	−580.4 (0.2)	3294.8 (0.2)	5000	36 (1)[a]
N(1)	799 (2)	4101 (2)	5642 (3)	36 (1)[a]
C(1)	878 (3)	3058 (3)	6001 (3)	38 (1)[a]
C(4)	−229 (3)	3663 (3)	3325 (3)	45 (1)[a]
O(4)	−35 (2)	3842 (2)	2300 (2)	62 (1)[a]
C(5)	−197 (3)	1959 (3)	4332 (4)	49 (1)[a]
O(5)	39 (3)	1165 (3)	3921 (3)	73 (1)[a]
C(11)	1599 (3)	4532 (3)	4811 (4)	44 (1)[a]
C(12)	2648 (3)	4701 (3)	5436 (4)	57 (1)[a]
C(13)	3471 (4)	4855 (4)	4447 (5)	69 (2)[a]
C(14)	2500 (12)	5885 (12)	5960 (16)	70 (5)
C(15)	3449 (11)	6264 (12)	6670 (15)	70 (5)
C(14′)	2673 (6)	5467 (5)	6498 (7)	61 (2)
C(15′)	2496 (7)	6557 (7)	6015 (9)	82 (3)
C(21)	817 (2)	2818 (2)	7337 (3)	37 (1)[a]
N(22)	657 (2)	3603 (2)	8113 (3)	45 (1)[a]
C(23)	579 (3)	3381 (3)	9314 (3)	50 (1)[a]
C(24)	660 (3)	2399 (3)	9782 (4)	56 (1)[a]
C(25)	826 (4)	1583 (4)	8968 (4)	65 (2)[a]
C(26)	898 (3)	1799 (3)	7734 (4)	53 (1)[a]
C(31)	−1708 (3)	4247 (4)	6326 (5)	67 (2)[a]
C(32)	−2119 (3)	4234 (4)	5114 (6)	70 (2)[a]
C(33)	−2363 (3)	3229 (4)	4812 (4)	63 (2)[a]
C(34)	−2089 (3)	2594 (4)	5822 (5)	63 (2)[a]
C(35)	−1693 (3)	3229 (4)	6748 (4)	65 (2)[a]

[a] Equivalent isotropic *U* calculated from anisotropic *U*.

50:50: for the **a** series 55:45, for the **b** series 51:49, and for the **c** series 34:66. In system **a** the isomer ratio was 55:45, irrespective of whether pure **1a**, **2a**, or a mixture **1a/2a** was used for the Na/Hg reaction.

The absolute configurations of **6c** and **8d** were determined (Tables I–III, V, VI) by using single crystals obtained from ether/pentane solutions of **6c/7c** and **8d/9d** at −20 °C (Figures 1 and 2).[17] Similar to **6a** and **8a**,[1] in

(17) Rogers, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 734.

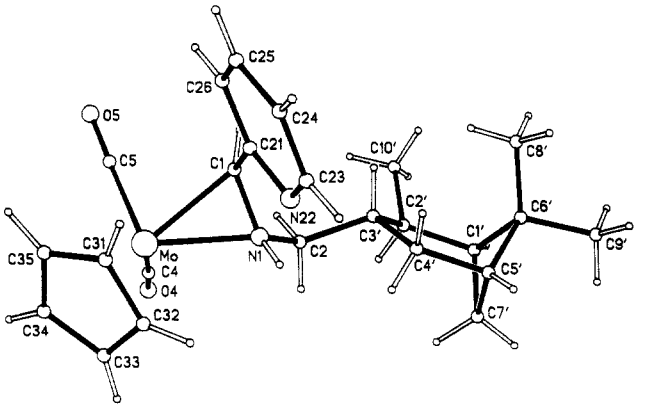

Figure 1. Molecular geometry and absolute configuration of complex **6c** in the crystal. Selected bond lengths (Å) and angles (deg): Mo–N1 = 2.168 (4), Mo–C1 = 2.200 (4), C1–N1 = 1.412 (6), Mo–C4 = 1.936 (5), Mo–C5 = 1.942 (6), C4–O4 = 1.167 (6), C5–O5 = 1.157 (7), Mo–Cp = 2.308 (5)–2.372 (6), C1–C21 = 1.498 (6), N1–C2 = 1.469 (5), C2–C3′ = 1.530 (6), C–C(pyridyl) = 1.364 (10)–1.379 (7), C–N(pyridyl) = 1.331 (7) and 1.349 (6), C–C(pinanyl) = 1.524 (8)–1.563 (7); N1–Mo–C1 = 37.7 (2), Mo–N1–C1 = 72.4 (3), Mo–C1–N1 = 69.9 (3), N1–Mo–C5 = 107.3 (3), N1–Mo–C4 = 88.5 (2), C1–Mo–C4 109.8 (3), C4–Mo–C5 = 78.7 (3), C1–Mo–C5 = 81.2 (3), Mo–N1–C2 = 120.9 (4), Mo–C1–C21 = 115.3 (3).

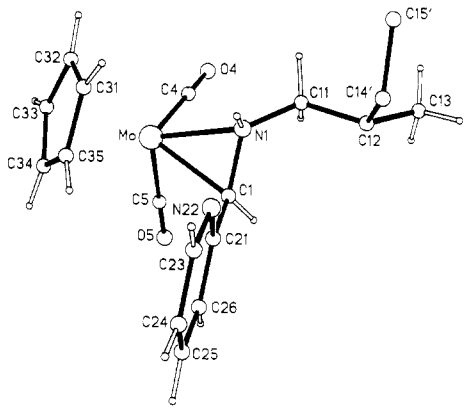

Figure 2. Molecular geometry and absolute configuration of complex **8d** in the crystal. Selected bond lengths (Å) and angles (deg): Mo–N1 = 2.181 (4), Mo–C1 = 2.198 (5), C1–N1 = 1.407 (6), Mo–C4 = 1.934 (5), Mo–C5 = 1.938 (5), C4–O4 = 1.164 (6), C5–O5 = 1.160 (6), Mo–Cp = 2.316 (5)–2.391 (6), C1–C21 = 1.486 (6), N1–C11 = 1.481 (6), C11–C12 = 1.532 (6), C12–C13 = 1.525 (8), C12–C14 = 1.521 (10), C–C(pyridyl) = 1.372 (7)–1.393 (7), N22–C21 = 1.336 (6), N22–C23 = 1.339 (6); N1–Mo–C1 = 37.5 (2), Mo–N1–C1 = 71.9 (3), Mo–C1–N1 = 70.6 (3), N1–Mo–C5 = 109.7 (2), N1–Mo–C4 = 89.5 (2), C1–Mo–C4 = 107.3 (2), C4–Mo–C5 = 78.9 (3), C1–Mo–C5 = 80.9 (3), Mo–N1–C11 = 127.8 (3), Mo–C1–C21 = 117.8 (3).

6c and **8d** substituents Cp on Mo, H on N, and py on C are located at the same side 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 $S_{Mo}S_NS_C$ for **6c** and $R_{Mo}R_NR_C$ 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[18,19] nor their extension to organometallic compounds[20,21] would allow the specification of the configuration of the asymmetric Mo atoms in compounds of type **6/9** without arbitrary assumptions, e.g.,

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Table IV. Atom Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for Complex 11d

	x	*y*	*z*	*U*[a]
Rh(1)	5967.9 (0.2)	3819.8 (0.2)	7314.5 (0.2)	34 (1)
Mo(1)	8141.8 (0.2)	4920.8 (0.2)	7264.7 (0.2)	43 (1)
C(11)	9242 (5)	6370 (5)	7356 (4)	100 (2)
C(12)	8331 (6)	6652 (4)	7768 (6)	112 (3)
C(13)	8236 (6)	6041 (6)	8543 (5)	105 (3)
C(14)	9104 (6)	5394 (4)	8582 (4)	89 (2)
C(15)	9717 (4)	5604 (5)	7850 (6)	102 (3)
N(21)	6639 (3)	2803 (2)	6352 (2)	41 (1)
C(22)	7687 (3)	2627 (3)	6485 (3)	47 (1)
C(23)	8273 (4)	2012 (3)	5877 (3)	64 (2)
C(24)	7750 (4)	1592 (3)	5128 (3)	79 (2)
C(25)	6701 (5)	1765 (3)	5009 (3)	72 (2)
C(26)	6171 (4)	2380 (3)	5624 (2)	55 (1)
C(10)	6948 (3)	5366 (3)	6514 (3)	54 (1)
O(10)	6419 (3)	5825 (3)	6001 (3)	86 (1)
C(20)	8661 (4)	4599 (4)	6069 (4)	73 (2)
O(20)	8983 (4)	4410 (3)	5348 (3)	125 (2)
N(1)	7408 (2)	3536 (2)	7898 (2)	38 (1)
C(2)	8142 (3)	3124 (3)	7286 (3)	47 (1)
C(3)	7561 (3)	3344 (3)	8872 (2)	48 (1)
C(4)	7118 (3)	2270 (3)	9174 (2)	49 (1)
C(5)	6780 (4)	2318 (4)	10179 (3)	71 (2)
C(6)	6121 (4)	1423 (4)	10489 (4)	87 (2)
C(7)	7849 (4)	1367 (4)	8975 (4)	83 (2)
C(31)	3951 (3)	3584 (3)	8026 (3)	63 (1)
C(32)	4972 (3)	3951 (4)	8475 (3)	56 (1)
C(33)	5178 (3)	4954 (3)	8145 (3)	53 (1)
C(34)	4292 (3)	5196 (3)	7477 (3)	63 (2)
C(35)	4564 (3)	4435 (3)	6721 (3)	56 (1)
C(36)	4366 (3)	3412 (3)	7073 (3)	56 (1)
C(37)	3346 (3)	4633 (4)	7936 (4)	78 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

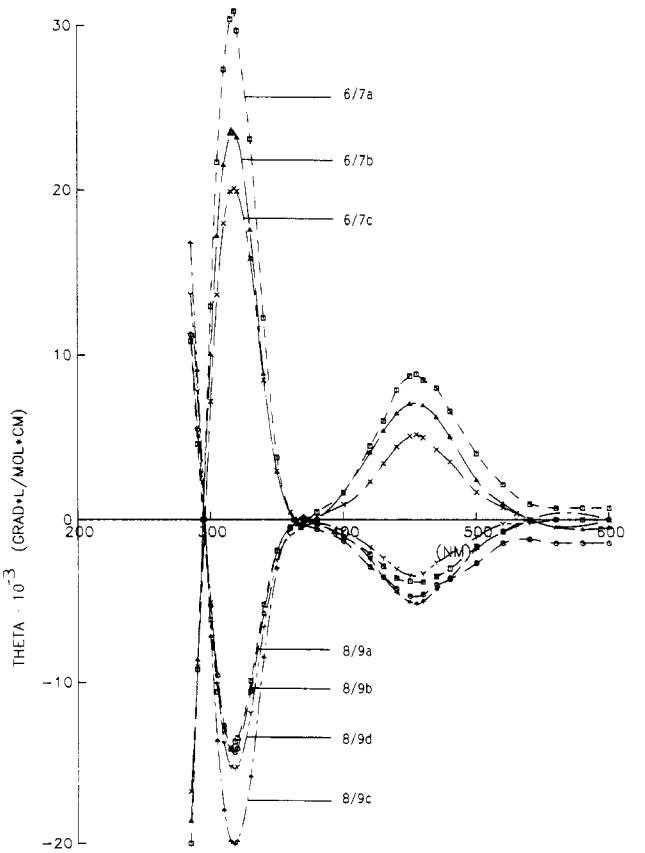
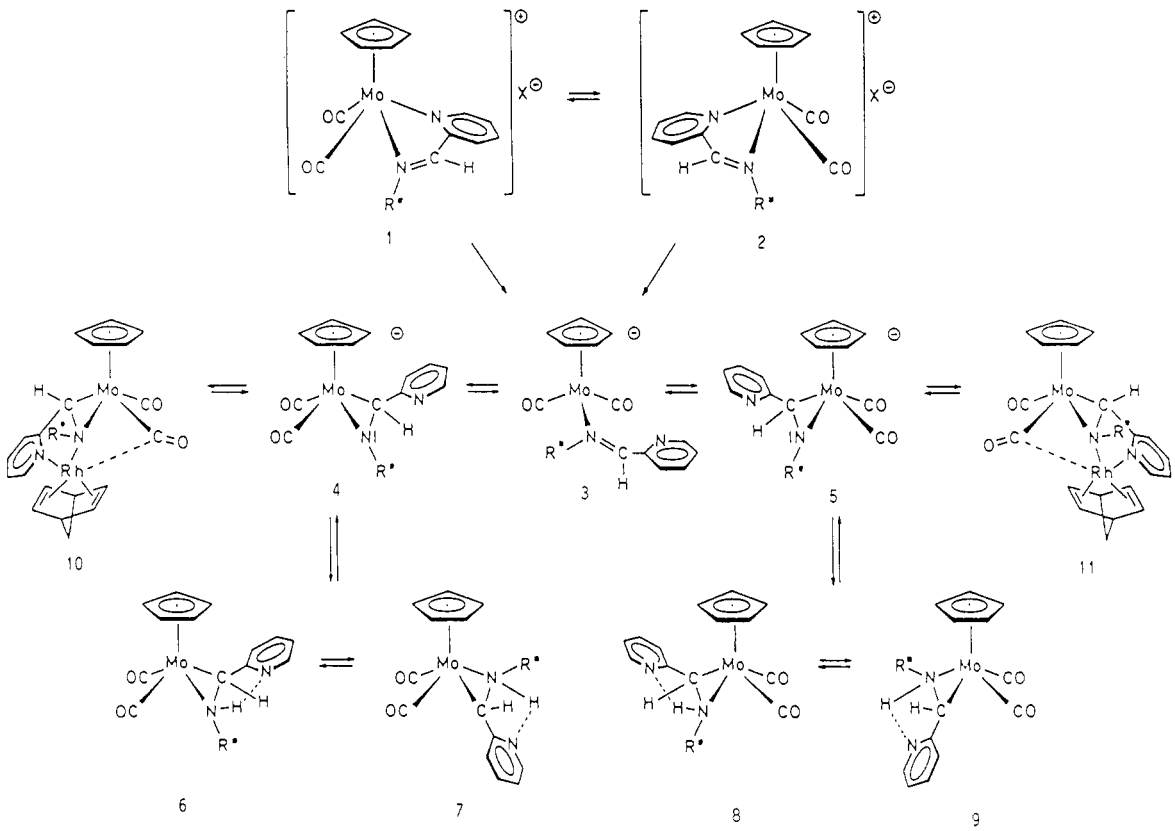


Figure 3. CD spectra of complexes **6a–d/9a–d** (ca. 5 × 10⁻⁴ M in toluene).

Scheme I



R*				
	a	b	c	d

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 ^{1}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 $S_{Mo}S_NS_C$ and $R_{Mo}R_NR_C$ 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 **1d/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/NBu_4HSO_4 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 ^{1}H NMR spectroscopy at high and low temperatures.

In series **a** the ^{1}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 ^{1}H NMR spectrum two pairs of major/

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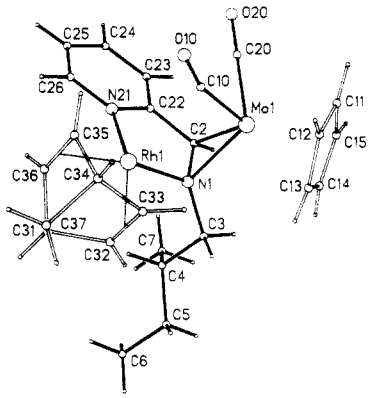

Figure 4. Molecular geometry and absolute configuration of complex **11d** in the crystal. Selected bond lengths (Å) and angles (deg): Mo–N1 = 2.188 (3), Mo–C2 = 2.268 (3), N1–C2 1.395 (5), Mo–C10 1.953 (4), Mo–C20 = 1.928 (5), C10–O10 = 1.164 (5), C20–O20 = 1.165 (7), Mo–Cp = 2.299 (6)–2.363 (7), C2–C22 = 1.458 (5), N1–C3 = 1.474 (4), C–N(pyridyl) = 1.354 (5) and 1.339 (5), Rh–N21 = 2.095 (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 = 36.4 (1), Mo–C2–N1 = 68.7 (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–C22–C2 = 115.6 (3).

minor isomers could be observed in ratios **10b**:**10b′** = 97:3 and **11b**:**11b′** = 87:13. At higher temperatures they coalesce 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 coalesced 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**/**9c**.

In the **d** series the Mo compounds **8d**/**9d** give only one pair of isomers **11d**/**11d′**, visible in the low-temperature ^{1}H NMR spectrum with a ratio of 70:30. At 80 °C there is coalescence 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 analysis[17,24] (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**,[1] 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 hydrogen 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 $S_{Mo}S_NR_C$, compared to **8d** (configuration $R_{Mo}R_NR_C$) which contains the same ligand. The inversion of configuration at the Mo atom in going from **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).

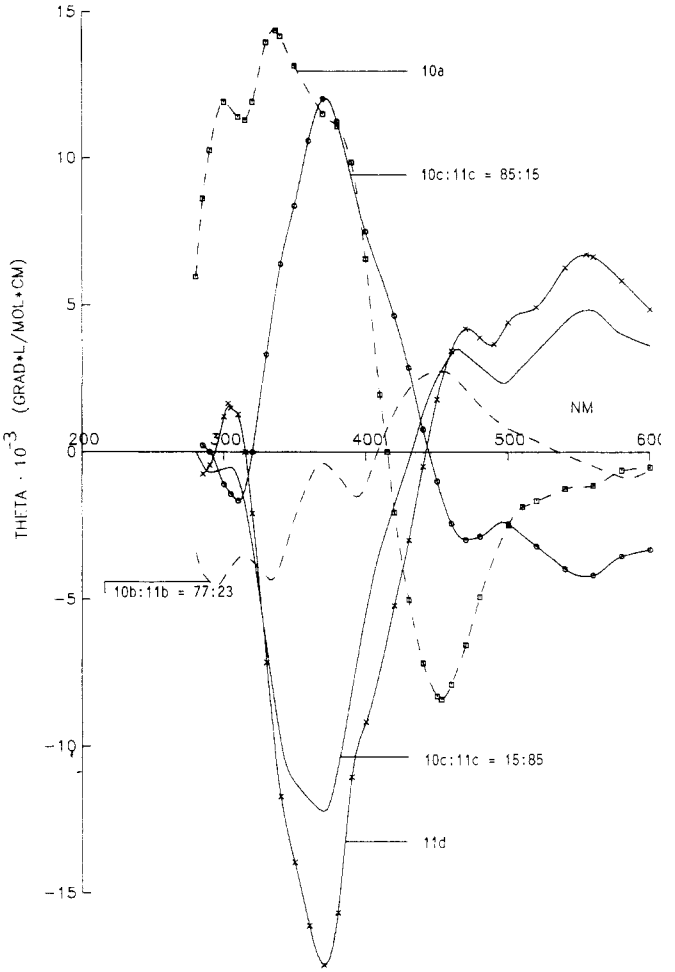

Figure 5. CD spectra of complexes **10a–d**/**11a–d** (ca. 5 × 10^{-4} M in toluene).

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 **c** 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

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intermediate **3** is formed (Scheme I); because of this bond cleavage the chirality of the Mo atom disappears. This explains why complexes **1a** or **2a** with opposite Mo configurations, and also mixtures of **1a** and **2a**, give the identical products **6a/9a**. The σ-bonded imine ligand in **3** adopts a π-bonded structure in **4** and **5**. In the transformation of **3** to **4** and **5** the configuration at the C atom of the three-membered ring is determined, S_C in **4** and R_C in **5**. If it is assumed that the protonation of **4** and **5** occurs from the side of the pyridine substituent via a preformed hydrogen bridge, the cis position of substituents H and py in all the complexes **6a–d/9a–d** can be understood. There is no experimental evidence for a trans orientation of H and py in compounds **6–9**. To isomers **7a–d**, present in the equilibrium mixtures with **6a–d** ($S_{Mo}S_NS_C$) in amounts between 4% and 13% at −70 °C, is assigned the opposite Mo configuration ($R_{Mo}S_NS_C$). The rapid isomerization **6a–d** $\rightleftarrows$ **7a–d** can be viewed as an intramolecular 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 $R_{Mo}R_NR_C$ and $S_{Mo}R_NR_C$, 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 metallaaziridine 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 equilibrations **6/7** $\rightleftarrows$ **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 **a** 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 π-coordinated intermediates **4c** and **5c** react with $[Rh(nbd)Cl]_2$, 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 metallaaziridine complexes **6a–d/9a–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), **10c/11c** (15:85), and **11d** were used as catalysts for the hydrosilylation of 2 mL of acetophenone with 3.4 mL of diphenylsilane in 5 mL of toluene, according to procedures given before.[25,26] 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 **10c/11c** (85:15) with $R_{Mo}R_NS_C$ configuration thus favor (*S*)-1-phenylethanol, and complexes **10c/11c** (15:85) and **11d** with $S_{Mo}S_NR_C$ 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; ^{1}H NMR, Varian T 60 and Bruker WM 250; ^{13}C 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-(aminomethyl)pinane 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 93%; oil (bp 108 °C (10^{-3} mm)); ^{1}H NMR ($CDCl_3$) δ 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, $[\alpha]^{20}_{578}$ −47°, $[\alpha]^{20}_{546}$ −55°, $[\alpha]^{20}_{436}$ −116°, $[\alpha]^{20}_{365}$ −224° (*c* 1, acetone).

Pyridine imine **b**: yield 87%; oil (bp 110 °C (10^{-3} mm)); ^{1}H NMR ($CDCl_3$) δ 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, $[\alpha]^{20}_{578}$ +82°, $[\alpha]^{20}_{546}$ +97°, $[\alpha]^{20}_{436}$ +195°, $[\alpha]^{20}_{365}$ +409° (*c* 1, acetone).

Pyridine imine **c**: yield 89%; oil (bp 165 °C (10^{-3} mm)); ^{1}H NMR ($CDCl_3$) δ 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, $[\alpha]^{20}_{578}$ +30°, $[\alpha]^{20}_{546}$ +34°, $[\alpha]^{20}_{436}$ +55°, $[\alpha]^{20}_{365}$ +80° (*c* 1, acetone).

Pyridine imine **d**: yield 83%; oil (bp 105 °C (7×10^{-2} mm)); ^{1}H NMR ($CDCl_3$) δ 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 = 7.4 Hz, 3 H); optical rotation, $[\alpha]^{20}_{578}$ +6°, $[\alpha]^{20}_{546}$ +7°, $[\alpha]^{20}_{436}$ +14°, $[\alpha]^{20}_{365}$ +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 (1*S*,2*S*,3*S*)-(+)-3-(aminomethyl)pinane were gifts of BASF AG. (*S*)-(+)-2-Methylbutylamine was prepared according to the following procedure, analogous to ref 23.

(*S*)-(+)-2-Methylbutylamine. PBr_3 (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% H_2SO_4, and water. After the solution was dried with $CaCl_2$ and the solvent evaporated, the product (*S*)-(+)-2-methylbutyl bromide was distilled at 120 °C: yield 66%; colorless oil; $[\alpha]^{20}_{578}$ +5.81° (*c* 4.8, chloroform).[23]

(*S*)-(+)-2-Methylbutyl bromide (10.6 g, 70 mmol), 10.3 g (70 mmol) of phthalimide, and 4.84 g (35 mmol) of K_2CO_3 were refluxed in DMF for 15 h. KBr and phthalimide were filtered

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(26) Brunner, H.; Reiter, B.; Riepl, G. *Chem. Ber.* **1984**, *117*, 1330.

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, 165 °C): yield 52%; 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-methylbutylamine: yield 72%; white solid.

Treatment of the hydrochloride of (*S*)-2-methylbutylamine with 200 mL of triethylamine in 100 mL of ethanol gave (*S*)-(+)-2-methylbutylamine. On concentration of the solution $NHEt_3Cl$ precipitated and was filtered off. After evaporation of the volatile products (*S*)-(+)-2-methylbutylamine was purified by a Kugelrohr distillation (high vacuum, 105 °C): yield 83%; yellow oil; ^1H NMR ($CDCl_3$) δ 8.55 (s, 1 H), 8.5–6.6 (m, 4 H), 3.36 (m, 2 H), 1.75 (m, 1 H), 1.31 (m, 2 H), 0.92 (d, 3 H), 0.86 (t, 3 H); optical rotation, $[\alpha]^{20}_{578}$ +6°, $[\alpha]^{20}_{546}$ +7°, $[\alpha]^{20}_{436}$ +14°, $[\alpha]^{20}_{365}$ +25° (*c* 1, acetone).

Pyridine Imine Complexes 1 and 2. $C_5H_5Mo(CO)_3Cl$ (2.79 g, 10 mmol) and 13 mmol of the corresponding Schiff bases **a–d**, dissolved in 300 mL of benzene, were treated as follows: for the preparation of **1a/2a**, 15 h of reflux, for **1b–d/2b–d**, 5 h at room temperature. Red crystals of **1a–d/2a–d** (X = Cl) separated. They were washed with benzene and ether and dried.

The chlorides were dissolved in 10 mL of hot ethanol. After filtration 90 mL of water was added. Addition of 2.12 g (13 mmol) of NH_4PF_6 caused the precipitation of the red complexes **1a–d/2a–d** (X = PF_6). They were washed with water and ether and dried in high vacuum.

A 3-g sample of the mixture of the diastereomers **1a/2a** (X = PF_6) was dissolved in boiling acetone (30 mL)/CH_2Cl_2 (4.5 mL)/ethanol (1.5 mL). For the success of the diastereomer separation it was important that crystals formed on slow cooling to room temperature. After 10 h at −25 °C the system was cooled to −78 °C for 2 h. Five repetitions of this operation with reduced solvent quantities gave the less soluble diastereomer **1a** in optically pure form.

For the enrichment of the more soluble diastereomer **2a** the solid obtained from the solution of the first crystallization was used. It was crystallized analogously to the procedure given above, with the material contained in the solution as the starting material for the next separation. After five steps an enrichment of **1a**:**1b** = 9:91 was achieved.

1a/2a: red solid; yield 80%; mp 166 °C dec; diastereomer ratio after isolation (X = PF_6) **1a**:**2a** = 49:51; IR (KBr) 1915, 1885 (ν_{CO}), 1615 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{21}H_{19}F_6MoN_2O_2P$: C, 44.07; H, 3.45; M_r, 572.31. Found: C, 43.98; H, 3.40.

1a: ^1H NMR ($(CD_3)_2CO$) δ 9.30 (s, 1 H), 9.36 (d, J = 5.8 Hz, 1 H), 7.5–8.6 (m, 8 H), 5.65 (s, 5 H), 5.87 (q, 1 H), 2.01 (d, J = 6.8 Hz, 3 H); optical rotation, $[\alpha]^{20}_{578}$ +900°, $[\alpha]^{20}_{546}$ +1510°, $[\alpha]^{20}_{436}$ −2325°, $[\alpha]^{20}_{365}$ −4150° (*c* 0.007, acetone).

2a: ^1H NMR ($(CD_3)_2CO$) δ 9.21 (s, 1 H), 9.40 (d, J = 5.7 Hz, 1 H), 7.4–8.6 (m, 8 H), 6.02 (s, 5 H), 5.89 (q, 1 H), 1.93 (d, J = 6.5 Hz, 3 H); optical rotation, $[\alpha]^{20}_{578}$ −810°, $[\alpha]^{20}_{546}$ −1180°, $[\alpha]^{20}_{436}$ +1870°, $[\alpha]^{20}_{365}$ +3040° (*c* 0.007, acetone), for a **1a**:**2a** = 9:91 mixture.

1b/2b: red solid; yield 76%; mp 180 °C dec; diastereomer ratio after isolation 62:38; IR (KBr) 1965, 1900 (ν_{CO}), 1605 cm^{-1} (ν_{CN}); ^1H NMR ($(CD_3)_2CO$) δ 8.97/8.94 (s/s, 1 H), 9.38 (m, 1 H), 7.6–8.5 (m, 3 H), 6.03/6.02 (s/s, 5 H), 1.7–1.2 (m, 11 H), 4.42 (m, 1 H), 1.52/1.58 (d/d, J = 6.7 Hz, 3 H). Anal. Calcd for $C_{21}H_{25}F_6MoN_2O_2P$: C, 43.61; H, 4.36; M_r, 578.36. Found: C, 43.63; H, 4.29.

1c/2c: red solid; yield 78%; mp 98 °C dec; diastereomer ratio after isolation 52:48; IR (KBr) 1990, 1910 (ν_{CO}), 1620 cm^{-1} (ν_{CN}); ^1H NMR ($(CD_3)_2CO$) δ 8.54 (s, 1 H), 9.05 (m, 1 H), 8.4–7.4 (m, 3 H), 5.65/5.66 (s/s, 5 H), 4.25 (m, 2 H), 2.6–0.8 (m, 17 H). Anal. Calcd for $C_{24}H_{29}F_6MoN_2O_2P$: C, 46.41; H, 4.73; M_r, 618.42. Found: C, 46.35; H, 4.71.

1d/2d: red solid; yield 72%; mp 61 °C dec; diastereomer ratio after isolation 52:48; IR (KBr) 1990, 1910 (ν_{CO}), 1620 cm^{-1} (ν_{CN}); ^1H NMR ($(CD_3)_2CO$) δ 8.87 (m, 1 H), 9.40 (d, J = 5.1 Hz, 1 H), 8.5–7.6 (m, 3 H), 6.01/6.00 (s/s, 5 H), 4.25/4.45 (m/m, 2 H), 2.30 (m, 1 H), 1.35/1.55 (m/m, 2 H), 1.02 (d, 3 H), 1.00 (t, 3 H). Anal. Calcd for $C_{18}H_{21}F_6MoN_2O_2P$: C, 40.16; H, 3.56; M_r, 538.29. Found: C, 40.20; H, 3.59.

Metallaaziridine Complexes 6a–d/9a–d. A 10-mmol sample of the complexes **1a–d/2a–d** was added to Na/Hg in 100 mL of THF. After being stirred for some hours (**a**, 15 h; **b–d**, 4 h) at room temperature, the black solution was decanted from excess Na/Hg. The residue obtained on evaporation of the solvent was dissolved in 10 mL of toluene. In the chromatography at SiO_2 (40 × 3.5 cm) 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.

A 400-mg sample of complexes **6a–d/9a–d** were chromatographed on two connected Merck-Lobar columns (type B (310/25 mm); LiChroprep Si60 (40–63 μm)) with exclusion of light in toluene/ether (50:1).[15,16] There was complete separation in two zones for complexes **6a–c/9a–c**; only for compound **6d/9d** was there no separation into two zones. The first red zone contained the complexes **6a/7a**, **8b/9b**, and **6c/7c** and the second red zone the complexes **8a/9a**, **6b/7b**, and **8c/9c**. All the complexes obtained from the two chromatographic zones were recrystallized from ether/pentane at −20 °C. The ^1H NMR spectra, the optical rotations, and the absolute configurations are given below.

6a/9a: orange prisms; yield 46%; mp 123–124 °C; diastereomer ratio 45:55; IR (KBr) 1865, 1785 (ν_{CO}), 1600 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{21}H_{20}MoN_2O_2$: C, 58.88; H, 4.71; M_r, 428.38. Found: C, 58.72; H, 4.53.

6a/7a: $S_{Mo}S_NS_C/R_{Mo}S_NS_C$; ^1H NMR see ref 1; optical rotation, $[\alpha]^{20}_{578}$ +1267°, $[\alpha]^{20}_{546}$ +1933°, $[\alpha]^{20}_{436}$ −2467°, $[\alpha]^{20}_{365}$ +2178° (*c* 0.05, toluene), for a **6a/7a**:**8a/9a** = 95:5 mixture.

8a/9a: $R_{Mo}R_NR_C/S_{Mo}R_NR_C$; ^1H NMR see ref 1; optical rotation, $[\alpha]^{20}_{578}$ −1190°, $[\alpha]^{20}_{546}$ −1685°, $[\alpha]^{20}_{436}$ +1910°, $[\alpha]^{20}_{365}$ −2003° (*c* 0.05, toluene), for a **8a/9a**:**6a/7a** = 96:4 mixture.

6b/9b: orange oil; yield 41%; diastereomer ratio 51:49; IR (KBr) 1910, 1810 (ν_{CO}), 1590 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{21}H_{26}MoN_2O_2$: C, 58.06; H, 6.03; M_r, 434.30. Found: C, 58.11; H, 6.12.

8b/9b: $R_{Mo}R_NR_C/S_{Mo}R_NR_C$; ^1H NMR (toluene-d_8, Bruker WM 250, 100 °C) δ 7.93 (d, J = 4.50 Hz, 1 H), 7.1–6.4 (m, 3 H), 4.90 (s, 1 H), 4.86 (m, 5 H), 3.77 (d, J = 7.27 Hz, 1 H), 1.88 (m, 1 H), 1.19 (d, J = 6.71 Hz, 3 H), 1.8–0.8 (m, 10 H); ^1H NMR (toluene-d_8, Bruker WM 250, −70°C) δ 7.83/8.15 (d/d, 1 H), 7.2–6.2 (m, 3 H), 5.05 (m, 1 H), 4.73/4.86 (s/s, 5 H), 3.83/3.51 (d/d, 1 H), 1.86 (m, 1 H), 1.26 (d, 3 H), 1.7–0.6 (m, 10 H), ratio **8b**:**9b** = 87:13 at −70°C; optical rotation, $[\alpha]^{20}_{578}$ +812°, $[\alpha]^{20}_{546}$ +1345°, $[\alpha]^{20}_{436}$ −2100°, $[\alpha]^{20}_{365}$ +2280° (*c* 0.05, toluene).

6b/7b: $S_{Mo}S_NS_C/R_{Mo}S_NS_C$; ^1H NMR (toluene-d_8, Bruker WM 250, 100 °C) δ 7.95 (d, J = 4.62 Hz, 1 H), 7.1–6.4 (m, 3 H), 5.10 (m, 1 H), 4.87 (s, 5 H), 3.65 (d, J = 7.16 Hz, 1 H), 2.11 (m, 1 H), 0.89 (d, J = 6.61 Hz, 3 H), 1.7–0.9 (m, 11 H); ^1H NMR (toluene-d_8, Bruker WM 250, −70 °C) δ 7.92/8.12 (d/d, 1 H), 7.2–6.3 (m, 3 H), 5.13 (m, 1 H), 4.79/4.92 (s/s, 5 H), 3.53 (d, 1 H), 2.34 (m, 1 H), 1.9–0.8 (m, 11 H), 0.70 (d, 3 H), ratio **6b**:**7b** = 87:13 at −70 °C; optical rotation $[\alpha]^{20}_{578}$ −970°, $[\alpha]^{20}_{546}$ −1483°, $[\alpha]^{20}_{436}$ +2300°, $[\alpha]^{20}_{365}$ −2440° (*c* 0.05, toluene).

6c/9c: red prisms; yield 46%; mp 165–167 °C; diastereomer ratio 34:66; IR (KBr) 1910, 1800 (ν_{CO}), 1590 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{24}H_{30}MoN_2O_2$: C, 60.76; H, 6.37; M_r, 474.46. Found: C, 60.71; H, 6.15.

6c/7c: $S_{Mo}S_NS_C/R_{Mo}S_NS_C$; ^1H NMR (toluene-d_8, Bruker WM 250, 90 °C) δ 7.92 (d, J = 4.93 Hz, 1 H), 7.0–6.3 (m, 3 H), 5.18 (m, 1 H), 4.80 (s, 5 H), 3.65 (d, J = 6.95 Hz, 1 H), 2.7–0.5 (m, 19 H); ^1H NMR (toluene-d_8, Bruker WM 250, −70 °C) δ 7.87 (d, 1 H), 7.1–6.2 (m, 3 H), 5.32 (m, 1 H), 4.76/4.95 (s/s, 5 H), 3.72 (d, 1 H), 2.6–0.4 (m, 19 H), ratio **6c**:**7c** = 97:3 at −70 °C; optical rotation, $[\alpha]^{20}_{578}$ +760°, $[\alpha]^{20}_{546}$ +1140°, $[\alpha]^{20}_{436}$ −1400°, $[\alpha]^{20}_{365}$ +2500° (*c* 0.05, toluene).

8c/9c: $R_{Mo}R_NR_C/S_{Mo}R_NR_C$; ^1H NMR (toluene-d_8, Bruker WM 250, 90 °C) δ 7.91 (d, J = 5.01, 1 H), 7.1–6.3 (m, 3 H), 5.09 (m, 1 H), 4.81 (s, 5 H), 3.63 (d, J = 6.79 Hz, 1 H), 2.7–0.5 (m, 19 H); ^1H NMR (toluene-d_8, Bruker WM 250, δ 7.87/8.11 (d/d, 1 H), 7.1-6.2 (m, 3 H), 5.17/4.98 (m, 1 H), 4.73/4.88 (s/s, 5 H), 3.54/3.36

(d/d, 1 H), 2.4–0.4 (m, 19 H); ratio **8c:9c** = 94:6 at −70 °C; optical rotation, $[\alpha]^{20}_{578}$ −830°, $[\alpha]^{20}_{546}$ −1215°, $[\alpha]^{20}_{436}$ +1508°, $[\alpha]^{20}_{365}$ −2595° (*c* 0.05, toluene).

8d/9d: orange needles; yield 43%; mp 100–101 °C; IR (KBr) 1910, 1800 (ν_{CO}), 1590 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{18}H_{22}MoN_2O_2$: C, 54.83; H, 5.62; M_r, 394.33. Found: C, 54.90; H, 5.65.

8d/9d: $R_{Mo}R_NR_C/S_{Mo}R_NR_C$; ^{1}H NMR (toluene-$d_8$, Bruker WM 250, 90 °C) δ 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); ^{1}H NMR (toluene-d_8, Bruker WM 250, −70 °C) δ 7.83 (d, 1 H), 7.1–6.2 (m, 3 H), 4.99 (m, 1 H), 4.71/4.84 (s/s, 5 H), 3.55 (d, 1 H), 2.6–1.4 (m, 3 H), 1.2–0.8 (m, 2 H), 0.66 (t, 3 H), 0.53 (d, 3 H); ratio 96:4 at −70 °C; optical rotation, $[\alpha]^{20}_{578}$ −1138°, $[\alpha]^{20}_{546}$ −1672°, $[\alpha]^{20}_{436}$ +2086°, $[\alpha]^{20}_{365}$ −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/9a–d. A 0.2-mmol sample of complexes **6a,c,d/9a,c,d**, 0.12 mmol of $[Rh(nbd)Cl]_2$, 100 mg of pulverized KOH, and 20 mg of [18]crown-6 were stirred in 5 mL of toluene at room temperature. The orange suspension turned black. After 2 h the filtered solution was concentrated to 1 mL and chromatographed on Al_2O_3 (neutral, without addition of water) in toluene/ether (6:1) (column 20 × 1.5 cm). Black decomposition products remained adsorbed. The red zone contained the product **10a,c,d/11a,c,d**, respectively, which was crystallized from ether/pentane at −20 °C.

As the procedure given did not work for **10b/11b** this complex was prepared in 3 mL of CH_2Cl_2 by using 100 mg of KOH and 20 mg of *n*-tetrabutylammonium/hydrogen sulfate in 2 mL of water. Workup was as described above.

10a/10a′: black-brown crystals; yield 61%; mp 196 °C dec; IR (KBr) 1865, 1785 (ν_{CO}), 1600 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{28}H_{27}MoN_2O_2Rh$: C, 54.04; H, 4.37, M_r, 622.38. Found: C, 53.95; H, 4.29.

10a/10a′: $R_{Mo}R_NS_C$ (**10a**); ^{1}H NMR see ref 1; optical rotation, $[\alpha]^{20}_{578}$ −72°, $[\alpha]^{20}_{546}$ −576°, $[\alpha]^{20}_{436}$ +1340°, $[\alpha]^{20}_{365}$ −162° (*c* 0.02, toluene).

10a: ^{13}C{^{1}H} NMR (C_6D_6, Bruker WH 90, 25 °C) δ 208.7, 204.8 (CO), 148.4, 130.5-127.0 (Ph), 176.7, 146.2, 134.5, 116.8, 116.1 (py), 91.4 (Cp), 75.0 (MoCN), 62.3, 24.5 ($CHCH_3$), 60.5–48.8 (nbd).

10b/11b: dark brown oil; yield 60%; IR (KBr) 1890, 1780 (ν_{CO}) 1590 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{28}H_{33}N_2O_2Rh$: C, 53.52; H, 5.29; M_r, 628.43. Found: C, 53.61; H, 5.35.

10b/11b: ^{1}H NMR (toluene-d_8, Bruker WM 250, 90 °C) δ 7.2–5.9 (m, 4 H), 4.94/5.09 (s/s, 5 H), 3.7–3.4 (m, 9 H), 2.00 (m, 1 H), 1.6–1.0 (m, 11 H), 0.80 (d, *J* = 6.37 Hz, 3 H); ratio **10b/10b′:11b/11b′** = 77:23, when pure **6b/7b** was used as starting material; ^{1}H NMR (toluene-d_8, Bruker WM 250, −70 °C) δ 7.2–5.8 (m, 4 H), 4.84/5.05/5.20/5.45 (s/s/s/s, 5 H), 3.9–3.4 (m, 9 H), 2.25 (m, 1 H), 2.1–0.9 (m, 11 H), 0.68 (d, 3 H); ratio **10:10′** = 97:3, **11b:11b′** = 87:13 at −70 °C; optical rotation, $[\alpha]^{20}_{578}$ −205°, $[\alpha]^{20}_{546}$ −480°, $[\alpha]^{20}_{436}$ +1520°, $[\alpha]^{20}_{365}$ −360° (*c* 0.02, toluene), for a **10b/10b′:11/11b′** = 77:23 mixture.

10c/11c: black-brown needles; yield 67%; mp 161 °C dec; IR (KBr) 1900, 1790 (ν_{CO}), 1610 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{31}H_{37}MoN_2O_2Rh$: C, 55.70; H, 5.58; M_r, 668.48. Found: C, 55.72; H, 5.51.

10c/11c: ^{1}H NMR (toluene-d_8, Bruker WM 250, 90 °C) δ 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), 3.1–2.5 (m, 2 H), 2.3–0.5 (m, 17 H); ratio **10c/10c′:11c/11c′** = 85:15, when pure **6c/7c** was used as starting material; ratio **10c/10c′:11c/11c′** = 15:85, when pure **8c/9c** was used as starting material; ^{1}H NMR (toluene-d_8, Bruker WM 250, −70 °C) δ 7.3–6.1 (m, 3 H), 5.73/5.59/5.71/5.57 (t/t/t/t, 1 H), 4.86/5.19/4.88/5.19 (s/s/s/s, 5 H), 4.1–3.0 (m, 8 H), 4.20/4.58/4.18/4.60 (s/s/s/s, 1 H), 2.7–0.6 (m, 19 H); ratio **10c:10c′** = 65:35, **11c:11c′** = 72:28 at −70 °C; optical rotation, $[\alpha]^{20}_{578}$ −200°, $[\alpha]^{20}_{546}$ +1050°, $[\alpha]^{20}_{436}$ +4650°, $[\alpha]^{20}_{365}$ −2400° (*c* 0.02, toluene), for a **10c/10c′:11c/11c′** = 85:15 mixture, $[\alpha]^{20}_{578}$ +272°, $[\alpha]^{20}_{546}$ −909°, $[\alpha]^{20}_{436}$ −4090°, for a **10c/10c′:11c/11c′** = 15:85 mixture.

11d/11d′: black-brown crystals; yield 59%; mp 174 °C dec; IR (KBr) 1875, 1760 (ν_{CO}), 1600 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{25}H_{29}MoN_2O_2Rh$: C, 51.04; H, 4.97; M_r, 588.36. Found: C, 51.01; H, 4.95.

11d/11d′: $S_{Mo}S_NR_C$ (**11d**); ^{1}H NMR (toluene-d_8, Bruker WM 250, 80 °C) δ 7.2–5.9 (m, 4 H), 5.12 (s, 5 H), 3.7–3.1 (m, 8 H), 4.20 (d, *J* = 2.23 Hz, 1 H), 2.9–1.1 (m, 5 H), 0.89 (d, 3 H), 0.88 (t, 3 H); ^{1}H NMR (toluene-d_8, Bruker WM 250, −60 °C) δ 7.1–5.6 (m, 4 H), 4.86/5.24 (s/s, 5 H), 4.1–3.0 (m, 8 H), 4.02/4.33 (s/s, 1 H), 3.1–1.2 (m, 5 H), 0.89 (m, 6 H); ratio **11d:11d′** = 70:30 at −60 °C; optical rotation, $[\alpha]^{20}_{578}$ +160°, $[\alpha]^{20}_{546}$ −520°, $[\alpha]^{20}_{436}$ −2280°, $[\alpha]^{20}_{365}$ +500° (*c* 0.02, toluene).

Complexes **10a,c** and **11b,d** showed the molecular ions in the mass spectra, when the field desorption technique was applied (solvent toluene).

Crystal Structure Determinations. Data were collected on a Stoe-Siemens four-circle diffractometer at 293 K in profile-fitting mode[24] using monochromated Mo Kα radiation (λ = 0.710 69 Å). Cell constants were refined from 2θ values of selected strong reflections in the range 20–23°. The structures were solved by the heavy-atom method and refined anisotropically on |*F*|. Hydrogen atoms were included in the refinement using a riding model. (The disordered terminal ethyl group of compound **8d** furnished an exception; the alternative C sites were refined isotropically, and the H atoms were not included.) Weighting schemes were of the form $w^{-1} = \sigma^2(F) + gF^2$. Absolute configurations were determined by Rogers' η method[17] (negative η, obtained for compounds **6c** and **11d**, indicated a wrong absolute configuration, and the coordinates were thus inverted for the final cycles of refinement). The program system was SHELXTL (written by G.M.S.), which incorporates atomic scattering factors from ref 27. Further details are given in Table I. Tables II–IV contain the atomic coordinates of complexes **6c**, **8d**, and **11d**.

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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 **6c**, **8d**, and **11d** (11 pages); a listing of structure factors for complexes **6c**, **8d**, and **11d** (81 pages). Ordering information is given on any current masthead page.

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.