Optically Active Transition Metal Complexes. 129.[1] Novel Cycloheptatrienyl−Molybdenum and Cyclopentadienyl−Ruthenium Complexes with Chiral Pyridinecarbaldiminato Chelate Ligands: Syntheses, Molecular Structures, Properties, and Stereochemistry at the Metal Atom

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Received July 2, 2002

The reaction of $[(\eta^7\text{-}C_7H_7)Mo(\eta^6\text{-}C_6H_5CH_3)]BF_4$ with the optically active Schiff base ligands LL^1−LL^3 (LL^1 = pyridine-2-carbald-(*S*)-1-phenylethylimine, LL^2 = 6-methylpyridine-2-carbald-(*S*)-1-phenylethylimine, LL^3 = pyridine-2-carbald-(*S*)-1-cyclohexylethylimine) in acetonitrile afforded the diastereomers (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^{1-3})(NCMe)]BF_4$ (**1a**,**b**, **3a**,**b**, and **5a**,**b**). Reaction with carbon monoxide resulted in a mixture of the diastereomers (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^{1-3})(CO)]BF_4$ (**2a**,**b**, **4a**,**b**, and **6a**,**b**). The ligand LL^4 = (*S*)-2-(4,5-dihydro-4-isopropyloxazol-2-yl)pyridine gave the pure diastereomer **9b**. In both series **a** and **b** the diastereomers only differed in the configuration of the metal atom. Complex **1a**,**b** reacted with CN^tBu and PPh_3 to give (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^1)(CN^tBu)]BF_4$ (**7a**,**b**) and (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^1)(PPh_3)]BF_4$ (**8a**,**b**). Substitution experiments of **8a**,**b** with $PPhMe_2$ revealed a significantly different reactivity of the two diastereomers. The neutral complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^1)I]$ (**10a**,**b**) were obtained by refluxing $[(\eta^7\text{-}C_7H_7)Mo(CO)_2I]$ with LL^1 in toluene. The isoelectronic ruthenium diastereomers (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^5\text{-}C_5R_5)Ru(LL^{1,4})(L')]PF_6$ (R = H, Me, L′ = CO, PPh_3) (**11a**,**b**−**14a**,**b**) were prepared analogously to their $(\eta^7\text{-}C_7H_7)Mo$ counterparts by starting from $[(\eta^5\text{-}C_5R_5)Ru(NCMe)_3]PF_6$. The diastereomers were separated by fractional crystallization. X-ray structure analyses established the conspicuously similar molecular structures of the isoelectronic molybdenum and ruthenium complexes and the absolute configurations of **2a**, **7b**, **8b**, **9b**, **10a**, **12a**, and **13b**. In the diastereomers (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^1)(CO)]BF_4$ (**2a**,**b**), the molybdenum configuration was configurationally labile at room temperature. The epimerization **2a** ⇆ **2b** was a clean first-order reaction in acetone-d_6 solution ($\tau_{1/2}$ = 335 min at 21.8 °C; $\Delta H^{\ddagger} = 93 \pm 14$ kJ mol^{-1} and $\Delta S^{\ddagger} = -20 \pm 20$ J K^{-1} mol^{-1}). Additional experiments with the sterically more hindered 6-methylpyridine complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^2)(CO)]BF_4$ (**4a**,**b**) indicated that the mechanism of the epimerization involved a chelate ring opening at the imine side of LL^1 and LL^2. For the carbonyl complexes **2a**,**b** the diastereomer ratio at equilibrium was **2a**:**2b** = 76:24, whereas for the corresponding triphenylphosphane complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^1)(PPh_3)]BF_4$ (**8a**,**b**) it was **8a**:**8b** = 4:96. These diastereomer ratios reflected the thermodynamic chiral induction from the stable ligand configuration to the labile metal configuration. In contrast to the molybdenum complexes **2a**,**b** and **8a**,**b**, which were configurationally labile at room temperature in acetone solution, the related ruthenium complexes (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^5\text{-}C_5Me_5)Ru(LL^{1,4})(CO)]PF_6$ (**12a**,**b** and **14a**,**b**) turned out to be configurationally stable.

Introduction

Optically active transition metal complexes have proven their usefulness in stoichiometric stereoselective synthesis and, in particular, in enantioselective catalysis. Cyclopentadienyl ($\eta^5\text{-}C_5H_5$) and benzene ($\eta^6\text{-}C_6H_6$) are among the most common ligands encountered in organotransition metal chemistry. Although transition metal complexes of the cycloheptatrienyl ligand $\eta^7\text{-}C_7H_7$ have been known for a long time, the chemistry of this ligand has been studied little in comparison.[2] Until now, there has only been one example of a chiral-at-metal cycloheptatrienyl complex.[3]

Whereas the neutral $\eta^5\text{-}C_5H_5$ ligand contributes five electrons to a metal center, the ($\eta^7\text{-}C_7H_7$) ligand is a

(1) Part 128: Brunner, H.; Klankermayer, J.; Zabel, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2264.
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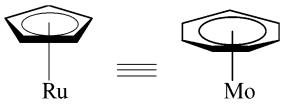
Publication on Web 11/19/2002

Chart 1



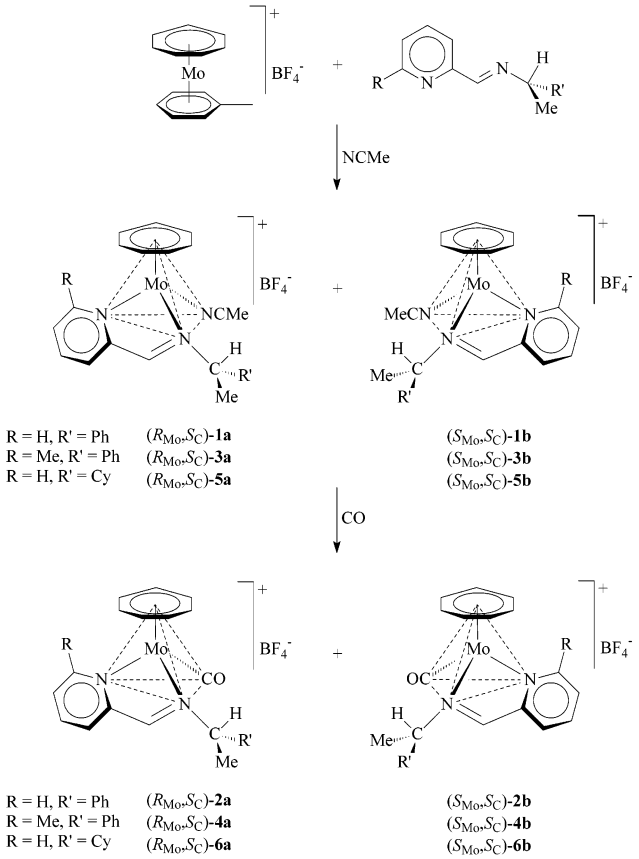
seven-electron ligand. As ruthenium has two electrons more than molybdenum, the isoelectronic fragments (η^5-C_5H_5)Ru and (η^7-C_7H_7)Mo should be closely related (Chart 1). This was demonstrated in a comparison of the stereochemistry of the new [(η^7-C_7H_7)Mo(prophos)X] (X = Cl, I, CN, H, Me) complexes with their known counterparts [(η^5-C_5H_5)Ru(prophos)X].[4] On the other hand, with ∼154° the cone angle of the η^7-C_7H_7 ligand is much larger than the cone angle of the η^5-C_5H_5 ligand (∼110°).[5] As the cone angle of the η^5-C_5Me_5 ligand (∼142°) is similar to that of the η^7-C_7H_7 ligand, the (η^5-C_5Me_5)Ru derivatives have been included in the present study.

"Three-legged piano stool" complexes of the type [(η^n-C_nH_n)MLL′L″] are chiral at the metal atom.[6−9] Provided one of the ligands, e.g. an unsymmetrical chelate ligand LL′, is enantiomerically pure, a pair of diastereomers arises, differing only in the metal configuration. Usually, such diastereomers can be distinguished on the basis of their NMR spectra. Thus, the diastereomer ratio and enrichment can be determined by the integration of suitable signals.

In solution such chiral-at-metal complexes may be configurationally stable even at higher temperatures or labile with respect to the metal configuration.[6−9] As a rule, changes of the metal configuration are initiated by ligand dissociation, which converts an 18-electron species into an unsaturated 16-electron intermediate. Theoretical studies for isoelectronic 16-electron fragments [(η^n-C_nH_n)M(CO)$_2$] claim that the ring size of the polyenyl ligand and the position of the metal atom in the periodic table have a decisive influence on the barrier of the pyramidal inversion at the metal center.[10,11] The calculations showed that [(η^5-C_5H_5)Mn(CO)$_2$] and [(η^6-C_6H_6)Cr(CO)$_2$] have a pyramidal ground state and high inversion barriers. However, for [(η^4-C_4H_4)Fe(CO)$_2$] and [(η^7-C_7H_7)V(CO)$_2$] extremely shallow, only weakly pyramidal minima were found. Consequently, [(η^5-C_5H_5)RuLL′L″] and [(η^7-C_7H_7)MoLL′L″] complexes should differ in their configurational stabilities, provided a ligand dissociation is involved in the change of the metal configuration.

In the present paper we compare the stereochemistry of the ruthenium complexes [(η^5-C_5H_5)Ru(LL′)X] and [(η^5-C_5Me_5)Ru(LL′)X] with the corresponding molybdenum compounds [(η^7-C_7H_7)Mo(LL′)X] (X = NCMe, CO, CN^{t}Bu, PPh$_3$), in which LL′ = pyridine-2-carbald-(*S*)-1-phenylethylimine (LL^1), 6-methylpyridine-2-carbald-(*S*)-1-phenylethylimine (LL^2), pyridine-2-carbald-(*S*)-1-cyclohexylethylimine (LL^3), and (*S*)-2-(4,5-dihydro-4-isopropyloxazol-2-yl)pyridine (LL^4).[12]

Scheme 1. Preparation of the Diastereomeric Molybdenum Complexes [(η^7-C_7H_7)Mo(LL$^{1-3}$)(CO)]BF$_4$ (2a,b, 4a,b, and 6a,b)[a]



[a] Note that the priority sequence of the ligands in compounds **1**, **3**, and **5** is η^7-C_7H_7 > NCMe > imine > pyridine, whereas in compounds **2**, **4**, and **6** it is η^7-C_7H_7 > imine > pyridine > CO.

Results and Discussion

The Complexes [(η^7-C_7H_7)Mo(LL^1)(CO)]BF$_4$ (2a,b). Pyridine-2-carbald-(*S*)-1-phenylethylimine (LL^1) was prepared from pyridine-2-carbaldehyde and (*S*)-1-phenylethylamine.[13] Treatment of the reactive complex [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF$_4$[14] with the chiral pyridinecarbaldimine LL^1 in CH_3CN resulted in the formation of a diastereomeric mixture of [(η^7-C_7H_7)Mo(LL^1)(NCMe)]BF$_4$ (**1a**,**b**) (Scheme 1). The diastereomer ratio in acetone-d_6 was 62:38. It remained unchanged after 1 day in acetone solution. The acetonitrile ligand in the labile complex **1** undergoes substitution reactions on addition of other ligands.[15,16]

Reaction of [(η^7-C_7H_7)Mo(LL^1)(NCMe)]BF$_4$ (**1a**,**b**) with carbon monoxide in acetone afforded the diastereomeric carbonyl complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)-

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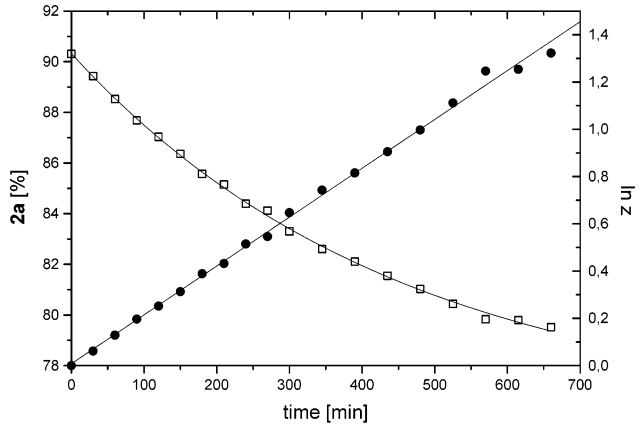

Figure 1. Epimerization of complex **2a** in acetone-d_6 at 21.8 °C (equilibrium ratio **2a**:**2b** = 76:24) and interpretation according to a first-order rate law. $z = ([\mathbf{2a}_0] - [\mathbf{2a}_\infty])/([\mathbf{2a}] - [\mathbf{2a}_\infty])$.

Table 1. Kinetic Data of the Approach to the Epimerization Equilibrium 2a ⇆ 2b at Various Temperatures ϑ in Acetone-d_6 Solution

ϑ (°C)	10^3k (min^{-1})	$\tau_{1/2}$ (min)	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$[A_\infty]$ (%)
21.8	2.07	334.9	97.4	75.6
31.0	5.63	123.1	98.0	74.0
39.4	18.13	38.2	97.7	72.8

Mo(LL^1)(CO)]BF$_4$ (**2a**,**b**) (Scheme 1). The mixture of diastereomers was precipitated from CH_2Cl_2 solution by addition of hexane. Integration of the singlet signals of the η^7-C_7H_7 protons at 5.57 and 5.61 ppm in the ^{1}H NMR spectrum of the diastereomer mixture in acetone-d_6 gave the ratio **2a**:**2b** = 76:24 at this stage of the purification procedure. It remained unchanged after 1 day in acetone solution.

Crystallization of the diastereomer mixture **2a**,**b** from CH_2Cl_2/hexane at −30 °C gave small blue plates. With the mixture **2a**:**2b** = 76:24 as a starting point, it was possible to increase the diastereomer ratio to 92:8 by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. The major isomer was the $(-)_{589}$ diastereomer **2a**.

The conversion of **2a** (de = 84%) into the equilibrium mixture **2a** ⇆ **2b** was followed in acetone-d_6 solution by ^{1}H NMR spectroscopy. To determine the ratio **2a**:**2b**, the methyl doublets were integrated. The epimerization **2a** ⇆ **2b** turned out to be first order, and no decomposition products could be detected. The equilibrium ratio at 21.8 °C was **2a**:**2b** = 75.6:24.4. The epimerization (Scheme 1) was measured at different temperatures. The analysis was performed with the function $\ln\{([A_0] - [A_\infty])/([A] - [A_\infty])\} = (\ln 2/k)t = \tau_{1/2}t$. The equilibrium ratios were determined after 10 half-lives. A typical plot is shown in Figure 1. At 21.8 °C the half-life of the approach to the equilibrium **2a** ⇆ **2b** in acetone-d_6 was 334.9 min. At 39.4 °C it was reduced to 38.2 min (Table 1). The activation parameters of the epimerization **2a** ⇆ **2b** were derived from the temperature dependence of the rate constants, using the Eyring equation. The enthalpy of activation was 93 ± 14 kJ mol^{-1} and the entropy of activation −20 ± 20 J K^{-1} mol^{-1}.

The absolute configuration of **2a** was determined by a single-crystal X-ray diffraction analysis.[17] In Figure 2 an ORTEP[18] plot of the molecular structure of one of the cations of the complex **2a** is shown. In the unit cell of diastereomer **2a** there are four independent cations. The chiral carbon atoms of the chelate ligands all have the expected S_C configuration, and the stereogenic molybdenum centers have an R_{Mo} configuration, specified with the priority sequence η^7-C_7H_7 > N2 > N1 > C1.[19−21] In the molecular structure of **2a**, the hydrogen atom of the 1-phenylethyl group (the smallest substituent at C2) is pointing toward the η^7-C_7H_7 ring. As a consequence, the phenyl ring is face-on oriented toward the carbonyl ligand. The distances between the carbonyl oxygen and the phenyl center in the four independent cations are in the range 3.14−3.67 Å, indicating an unconventional attractive intramolecular CO···π(arene) interaction.[22]

The Complexes [(η^7-C_7H_7)Mo(LL^2)(CO)]BF$_4$ (4a,b). 6-Methylpyridine-2-carbald-(*S*)-1-phenylethylimine (LL^2) was prepared from 6-methylpyridine-2-carbaldehyde and (*S*)-1-phenylethylamine.[13] Treatment of [(η^7-C_7H_7)-Mo(η^6-$C_6H_5CH_3$)]BF$_4$ with LL^2 in CH_3CN resulted in the formation of a diastereomeric mixture of [(η^7-C_7H_7)Mo-(LL^2)(NCMe)]BF$_4$ (**3a**,**b**) (Scheme 1). The diastereomer ratio in acetone-d_6 was 75:25. Reaction of [(η^7-C_7H_7)-Mo(LL^2)(NCMe)]BF$_4$ (**3**) with carbon monoxide in acetone afforded the diastereomeric carbonyl complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^2)(CO)]BF$_4$ (**4a**,**b**) (Scheme 1). Integration of the η^7-C_7H_7 singlets at 5.62 and 5.71 ppm in acetone-d_6 gave the ratio **4a**:**4b** = 78:22. It remained unchanged after 1 day in acetone solution.

With the mixture **4a**:**4b** = 78:22 as a starting point, it was possible to increase the diastereomer ratio to 98:2 by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Similar to the case for (R_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(CO)]BF$_4$ (**2a**) the signal of the η^7-C_7H_7 protons in the major isomer **4a** was shifted to higher field and, more importantly, the optical rotations at the Hg lines 589 and 546 nm in both compounds have the same signs and similar magnitudes (compounds **2a** and **4a** contain the same chromophore); the absolute configuration of **4a** was assigned as $R_{Mo}S_C$.

Complex **4**, containing the ligand 6-methylpyridine-2-carbald-(*S*)-1-phenylethylimine (LL^2), is configurationally more stable than the related complex **2** containing the ligand pyridine-2-carbald-(*S*)-1-phenylethylimine (LL^1). Compound **4a** (de > 96%) showed no sign of epimerization at room temperature within 18 h in

(17) The X-ray structure determination suffered from poor crystal quality, leading to a low precision data set. However, the structure solution is significant as far as the constitution and configuration of the complex are concerned. The assumption that the crystal submittted to the X-ray diffraction analysis belonged to the major diastereomer **2a** was based on the facts (i) that X-ray structure determinations of another two different crystals gave the same molybdenum configuration and (ii) that the three crystals investigated corresponded in habitus with the majority of the crystalline material.

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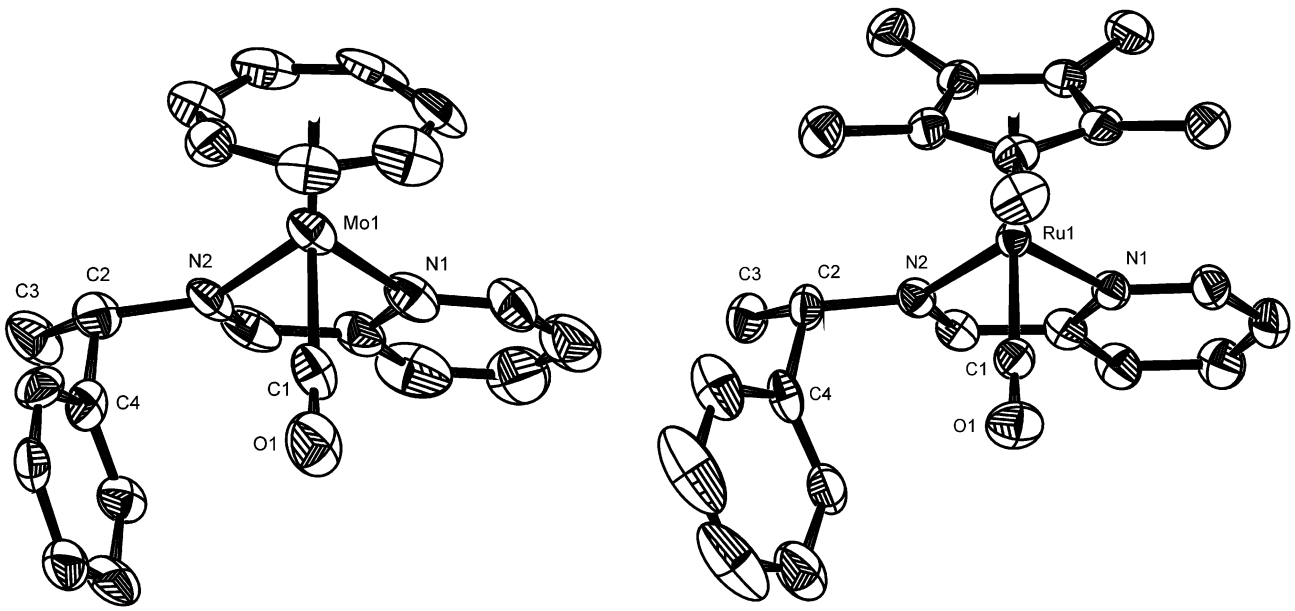
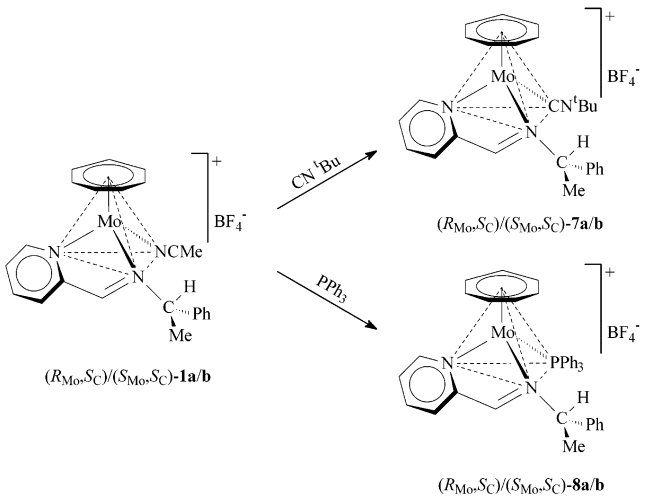


Figure 2. Structures of one of the independent cations of (R_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(CO)]BF_4 (**2a**) and the cation of (R_{Ru},S_C)-[η^5-C_5Me_5)Ru(LL^1)(CO)]PF_6 (**12a**) (hydrogen atoms omitted for clarity).

acetone solution. However, at temperatures >45 °C epimerization took place. Starting from de = 96%, the diastereomeric excess decreased at 50 °C to 86% after 150 min and to 66% after 360 min. For complex **2** containing ligand LL^1 a half-life of 13 min at 50 °C can be extrapolated for the approach to equilibrium. This shows that a methyl group in the 6-position of the pyridine ring in the chelate ligand LL^2 distinctly slows down the epimerization process. If the epimerization started with a rate-determining dissociation of the carbonyl ligand or a chelate ring opening on the pyridine side, the increased steric hindrance of the 6-methyl group should favor both of them. However, the opposite trend is observed experimentally, in accord with a mechanism in which the chelate ring opens on the imine side. In the chelate ring of **2a** the ring tension is indicated by a Mo−N(py)−C(para) angle of ∼171°. On dissociation of the imine group the Mo−N(py)−C(para) angle in the intermediate should tend to become 180°, increasing the steric hindrance in **4** with respect to **2**.

The Complexes [(η^7-C_7H_7)Mo(LL^3)(CO)]BF_4 (6a,b). With [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 as the starting material, the complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^3)(CO)]BF_4 (**6a**,**b**) were prepared via [(η^7-C_7H_7)Mo(LL^3)(NCMe)]BF_4 (**5a**,**b**), which was not isolated (Scheme 1). After precipitation from CH_2Cl_2 with hexane the diastereomer ratio was **6a**:**6b** = 76:24, close to the ratio obtained for **2a**,**b**. This shows, that the chiral carbon centers in ligands LL^1 and LL^3 with phenyl and cyclohexyl substituents, respectively, displayed almost the same chiral induction at the metal atom. The diastereomer ratio **6a**:**6b** remained unchanged after 1 day in acetone solution. In the samples (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(CO)]BF_4 (**2a**:**2b** = 92:8) and (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^2)(CO)]BF_4 (**4a**:**4b** > 98:2) the high enrichment of the R_{Mo},S_C diastereomers resulted in the positive optical rotations $[\alpha]_{546}$ = +930° and $[\alpha]_{546}$ = +590°, respectively. As the 76:24 diastereomer mixture of [(η^7-C_7H_7)Mo(LL^3)(CO)]BF_4 also showed a positive optical rotation at 546 nm ($[\alpha]_{546}$ = +380°), the major diastereomer **6a** was assigned the $R_{Mo}S_C$ configuration.

Scheme 2. Preparation of the Complexes [(η^7-C_7H_7)Mo(LL^1)(CN^tBu)]BF_4 (7a,b) and [(η^7-C_7H_7)Mo(LL^1)(PPh_3)]BF_4 (8a,b)[a]



[a] Only the diastereomers with the R_{Mo},S_C configuration are shown.

The Complexes [(η^7-C_7H_7)Mo(LL^1)(CN^tBu)]BF_4 (7a,b). Treatment of the reactive complex [(η^7-C_7H_7)-Mo(LL^1)(NCMe)]BF_4 (**1**) with CN^tBu in CH_2Cl_2 afforded the diastereomeric complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(CN^tBu)]BF_4 (**7a**,**b**) (Scheme 2). After precipitation from a CH_2Cl_2 solution with hexane, integration of the η^7-C_7H_7 singlets in acetone-d_6 gave the ratio **7a**:**7b** = 50:50. It remained unchanged after 1 day in acetone solution.

By repeated fractional crystallization from CH_2Cl_2/hexane solution at −30 °C it was possible to isolate the diastereomerically pure complex (S_{Mo},S_C)-[(η^7-C_7H_7)-Mo(LL^1)(CN^tBu)]BF_4 (**7b**). Complex **7** is configurationally more stable than the carbonyl complex **2**. **7b** showed no sign of epimerization at room temperature within 24

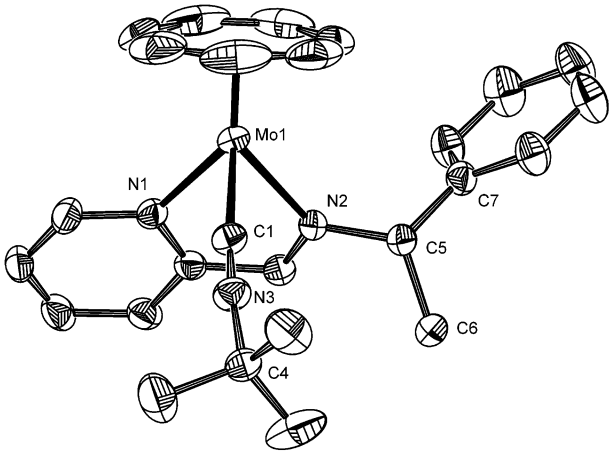


Figure 3. Structure of the cation of (S_{Mo},S_C)-[(η^7-C_7H_7)-Mo(LL^1)(CN^{t}Bu)]BF_4 (**7b**) (hydrogen atoms omitted for clarity).

h in acetone solution. However, at higher temperatures (>45 °C) epimerization took place.

The molecular structure of diastereomerically pure **7b** was determined using a green prism. In Figure 3 an ORTEP plot of the structure of the cation of complex **7b** is shown. In **7b**, the chiral carbon atom of the chelate ligand has the expected S_C configuration and the stereogenic molybdenum center has the S_{Mo} configuration specified with the priority sequence η^7-C_7H_7 > N2 > N1 > C1. The hydrogen atom of the 1-phenylethyl group (the smallest substituent at C2) is pointing toward the sterically demanding CN^{t}Bu ligand. The phenyl group at the chiral carbon atom is face-on oriented with respect to the η^7-C_7H_7 ring. In the thermodynamically more stable isomers of many transition metal half-sandwich complexes the phenyl substituents adopt a similar orientation relative to the π-bonded ligand in the solid state and in solution, called the β-phenyl effect.[23] The distance between the two ring centers in **7b** is 5.151 Å, which is relatively long for an attractive CH/π-interaction.[24]

The Complexes [(η^7-C_7H_7)Mo(LL^1)(PPh_3)]BF_4 (8a,b). Treatment of [(η^7-C_7H_7)Mo(LL^1)(NCMe)]BF_4 (**1**) with PPh_3 in CH_2Cl_2 afforded the diastereomeric complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(PPh_3)]-BF_4 (**8a**,**b**) (Scheme 2). The mixture of diastereomers was purified by precipitation from CH_2Cl_2 solution with hexane. Integration of the η^7-C_7H_7 doublets at 5.33 and 4.97 ppm in acetone-d_6 gave the ratio **8a**:**8b** = 4:96. It remained unchanged after 1 day in acetone solution.

The diastereomerically pure complex **8b** was separated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Its configurational stability at the metal center was investigated by epimerization experiments and by substitution reactions with $PPhMe_2$ using ^{1}H NMR (Figure 4) and ^{31}P NMR spectroscopy. The diastereomerically pure complex **8b** was dissolved in acetone-d_6 at room temperature. Keeping the solution for 180 min at 21 °C, the signals of the diastereomeric complex **8a** showed up in the NMR spectra. After 20 h at 21 °C the thermodynamic equilibrium in acetone-d_6 was determined to be **8a**:**8b** = 4:96. To this solution was added a 10-fold excess of $PPhMe_2$. After 5 min the substitution products (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)-Mo(LL^1)($PPhMe_2$)]BF_4 could be detected. Interestingly, after 175 min the signal for complex **8a** had disappeared, indicating that the PPh_3 ligand in **8a** was completely replaced by $PPhMe_2$. In contrast, after the same time period only 25% of complex **8b** had been converted to the substitution product. Even 24 h after the addition of $PPhMe_2$ 15% of the complex **8b** had remained. This shows that the substitution of PPh_3 by $PPhMe_2$ in **8a** is significantly faster than the epimerization **8a** ⇆ **8b**. Furthermore, the results exclude that the substitution is initiated by a PPh_3 dissociation assumed for the epimerization of **8**. The diastereomer ratio in the substitution product changed during the experiment from 66:34 after 175 min to 83:14 after 24 h.

The crystal structure of diastereomerically pure **8b** was determined using a green prism. In Figure 5 an ORTEP plot of the structure of the cation of **8b** is shown. The molybdenum configuration in the cation of **8b** is S_{Mo}, as specified with the priority sequence η^7-C_7H_7 > PPh_3 > N2 > N1. The phenyl substituent of the 1-phenylethyl group adopts a face-on orientation with respect to the η^7-C_7H_7 ligand. Assuming that the structure found in the solid state also represents an energy minimum in solution as far as the conformation of the 1-phenylethyl group is concerned,[23] the high-field shift of the ^{1}H NMR signal at 4.97 ppm of the η^7-C_7H_7 ligand in **8b** can be explained by an attractive β-phenyl effect. In addition to the S_C and S_{Mo} centers of chirality the cation of diastereomer **8b** contains another element of chirality, the triphenylphosphane helicity, which is found to be *M*. Therefore, **8b** has to be formulated as (S_{Mo},S_C,M_{PPh_3})-[(η^7-C_7H_7)Mo(LL^1)(PPh_3)]BF_4.

The Complex [(η^7-C_7H_7)Mo(LL^4)(CO)]BF_4 (9b). Reaction of [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 with (*S*)-2-(4,5-dihydro-4-isopropyloxazol-2-yl)pyridine (LL^4)[25] in CH_3CN and treatment with carbon monoxide resulted in the formation of [(η^7-C_7H_7)Mo(LL^4)(CO)]BF_4 (**9b**) (Scheme 3). The ^{1}H NMR spectrum showed only the signals of one diastereomer (**9b**). Even after 24 h in acetone solution at temperatures up to 50 °C the signals of the second diastereomer **9a** could not be detected. By crystallization from CH_2Cl_2/hexane at −30 °C crystals of **9b** were obtained, which were submitted to a single-crystal X-ray diffraction study. In Figure 6 an ORTEP plot of **9b** is shown. The stereogenic ruthenium center has an S_{Mo} configuration specified with the priority sequence η^7-C_7H_7 > N2 > N1 > C1.

In the series of the square-pyramidal chiral-at-metal complexes [(η^5-C_5H_5)Mo(LL′)($CO)_2$] the equilibrium induction from the stable chiral center in the LL′ ligands to the chiral metal atom, which was configurationally labile at higher temperatures, had been investigated.[23,26,27] The LL′ ligands were the thioamidato anions RC(S)NCH(Alkyl)Ph$^-$, derived from formic acid (R = H), acetic acid (R = CH_3), and benzoic acid (R = C_6H_5). When the alkyl substituent was varied at the chiral carbon atom, the diastereomer ratio at equilib-

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(25) Brunner, H.; Obermann, U. *Chem. Ber.* **1989**, *122*, 499.
(26) Brunner, H.; Lukas, R. *Chem. Ber.* **1979**, *112*, 2528.
(27) Brunner, H. *Acc. Chem. Res.* **1979**, *12*, 250.

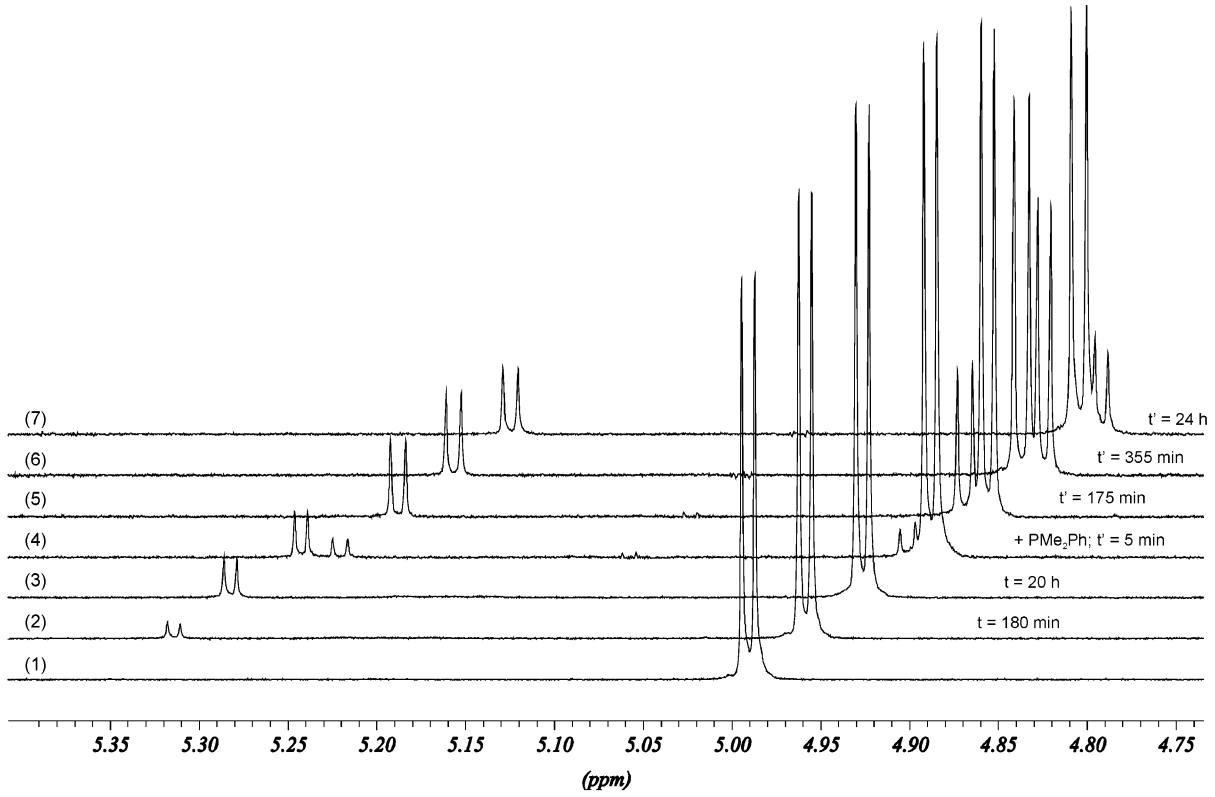


Figure 4. ^{1}H NMR spectra between 5.40 and 4.75 ppm (η^7-C_7H_7 doublet region) for the epimerization of (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(PPh_3)]BF_4 (**8b**) to give the equilibrium mixture **8a**:**8b** = 4:96 (spectra 1−3) and the substitution of PPh_3 by $PPhMe_2$ in [(η^7-C_7H_7)Mo(LL^1)(PPh_3)]BF_4 (**8a**,**b**) as a function of time (spectra 4−7).

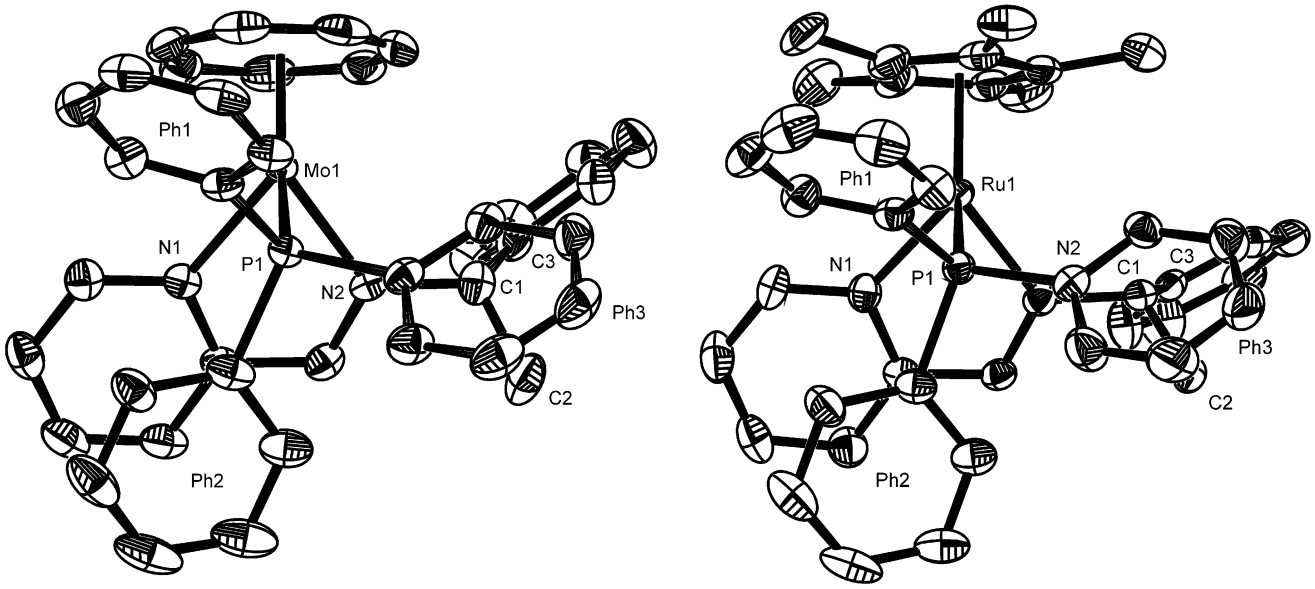
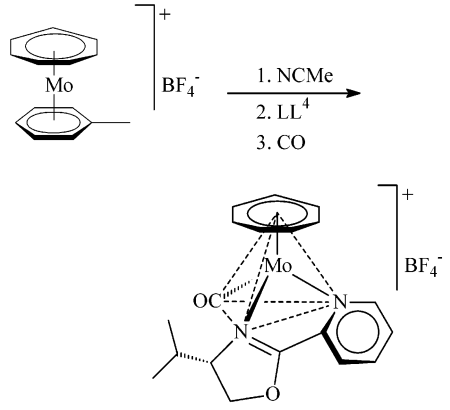


Figure 5. Structures of the cations of (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)(PPh_3)]BF_4 (**8b**) and (S_{Ru},S_C)-[(η^5-C_5Me_5)Ru(LL^1)(PPh_3)]-PF_6 (**13b**) (hydrogen atoms omitted for clarity).

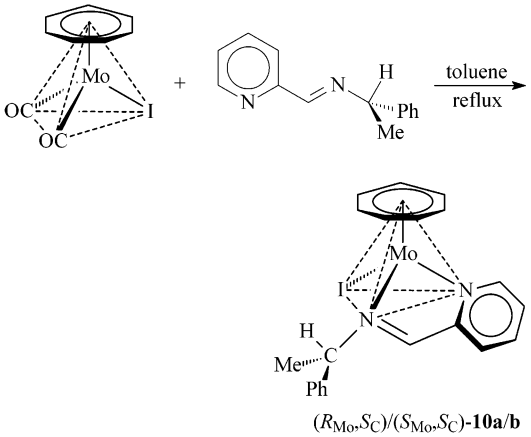
rium changed from 50:50 all the way up to 99:1. This diastereomer ratio is a measure for the thermodynamic chiral induction from the stable ligand configuration to the labile metal configuration. Rules were established indicating that the smallest substituent H at the chiral carbon atom tended to arrange in the ligand plane to avoid strongly negative eclipsed 1,3-interactions of large substituents with the methyl or the phenyl groups of the thioamidato ligands. As a consequence the other two substituents of the chiral carbon atom had to orient toward the cyclopentadienyl and the carbonyl ligands. Whereas the arrangement face-oriented phenyl/cyclopentadienyl gave an attractive CH/π interaction (the β-phenyl effect mentioned above), the interaction alkyl/cyclopentadienyl was a strong steric repulsion contributing to the 99:1 diastereomer ratio in the benzoic acid derivative with alkyl = isopropyl. In line with this reasoning the isopropyl substituent of the oxazoline ring in [(η^7-C_7H_7)Mo(LL^4)(CO)]BF_4 (**9b**) is oriented toward the small carbonyl ligand, avoiding the severe steric hindrance with the C_7H_7 ring which would occur in the other diastereomer **9a**.

Scheme 3. Preparation of the Complex (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^4)(CO)]BF_4 (9b)



(S_{Mo},S_C)-**9b**

Scheme 4. Preparation of the Complexes [(η^7-C_7H_7)Mo(LL^1)I] (10a,b)[a]



(R_{Mo},S_C)/(S_{Mo},S_C)-**10a/b**

[a] Only the diastereomer with the R_{Mo},S_C configuration is shown.

The Complexes [(η^7-C_7H_7)Mo(LL^1)I] (10a,b). Treatment of [(η^7-C_7H_7)Mo(CO)$_2$I] in refluxing toluene with 1 equiv of LL^1 caused displacement of the two carbonyl ligands (Scheme 4). The complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^1)I] (**10a**,**b**) initially failed to give satisfactory ^{1}H NMR spectra, probably due to trace oxidation. However, good NMR data for **10a**,**b** were obtained on addition of a small quantity of $CoCp_2$ to the sample.[16] The diastereomer ratio could be determined as **10a**:**10b** = 95:5 in C_6D_6. It remained unchanged after 1 day in benzene solution.

By crystallization from toluene/hexane at −30 °C crystals of **10a** were obtained, which were submitted to a single-crystal X-ray diffraction study. In Figure 7 an ORTEP plot of **10a** is shown. The stereogenic ruthenium center has an R_{Mo} configuration specified with the priority sequence I > η^7-C_7H_7 > N2 > N1.

The Complexes [(η^5-C_5H_5)Ru(LL^1)(CO)]PF_6 (11a,b) and [(η^5-C_5Me_5)Ru(LL^1)(CO)]PF_6 (12a,b). With the tris(acetonitrile) complexes [(η^5-C_5H_5)Ru(NCMe)$_3$]PF_6 and [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF_6 as starting materials, the ruthenium complexes [(η^5-C_5H_5)Ru(LL^1)(CO)]PF_6 (**11a**,**b**) and [(η^5-C_5Me_5)Ru(LL^1)(CO)]PF_6 (**12a**,**b**) (Schemes 5 and 6) were prepared. The mixtures of diastereomers were purified by precipitation from CH_2Cl_2 solution with hexane. The diastereomeric mixtures

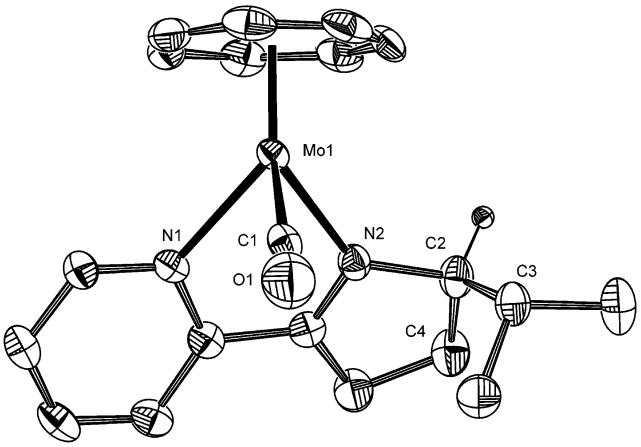


Figure 6. Structure of the cation of (S_{Mo},S_C)-[(η^7-C_7H_7)-Mo(LL^4)(CO)] (**9b**).

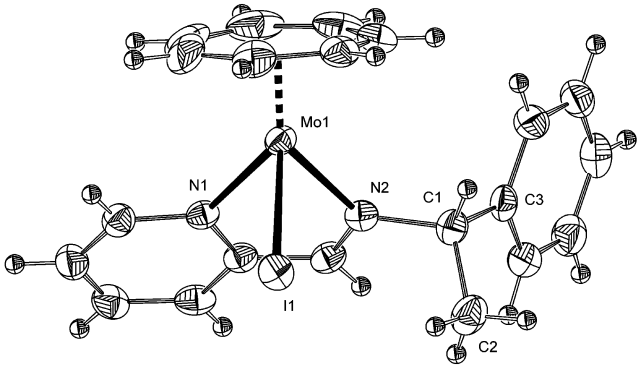
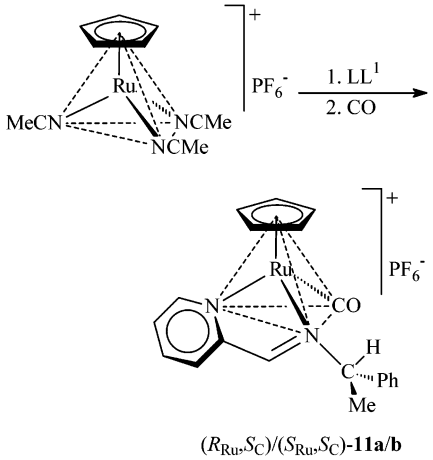


Figure 7. Structure of (R_{Mo},S_C)-[(η^7-C_7H_7)Mo(LL^4)I] (**10a**).

Scheme 5. Preparation of the Complexes [(η^5-C_5H_5)Ru(LL^1)(CO)]PF_6 (11a,b)[a]



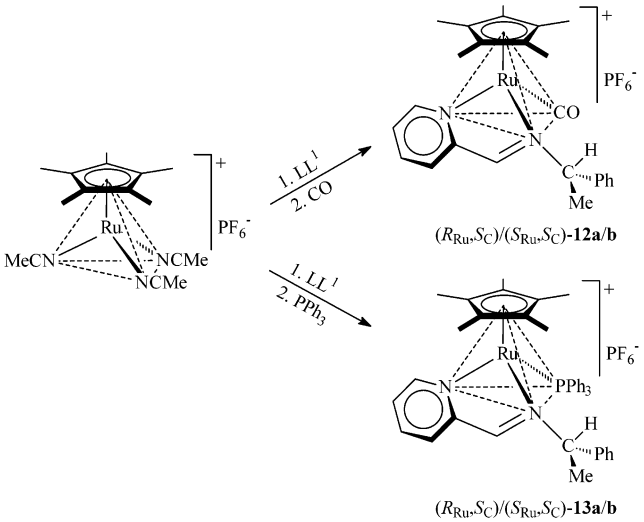
(R_{Ru},S_C)/(S_{Ru},S_C)-**11a/b**

[a] Only the diastereomer with the R_{Ru},S_C configuration is shown.

in acetone-d_6 gave the ratios **11a**:**11b** = 56:44 and **12a**:**12b** = 71:29. With the mixture **12a**:**12b** = 71:29 as a starting point, it was possible to increase the diastereomer ratio to >99:1 by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. The diastereomerically pure complex **12a** is configurationally stable for 18 h in acetone solution at 45 °C.

The molecular structure of **12a** was determined using an orange plate. In Figure 2 an ORTEP plot of the structure of the cation of **12a** is shown. In **12a**, the chiral carbon atom of the chelate ligand has an S_C configuration and the stereogenic ruthenium center has an R_{Ru}

Scheme 6. Preparation of the Complexes $[(\eta^5\text{-}C_5Me_5)Ru(LL^1)(CO)]PF_6$ (12a,b) and $[(\eta^5\text{-}C_5Me_5)Ru(LL^1)(PPh_3)]PF_6$ (13a,b)[a]



[a] Only the diastereomers with the R_{Ru},S_C configuration are shown.

configuration specified with the priority sequence η^5-C_5Me_5 > N2 > N1 > C1. Thus, in the analogous molybdenum and ruthenium complexes **2a** and **12a** the same configuration at the chiral metal atom is favored. Moreover, in both complexes the 1-phenylethyl group adopts the same conformation (Figure 2). The distance between the carbonyl oxygen and the phenyl center in the ruthenium complex **12a** is 3.715 Å, slightly longer than in **2a**.

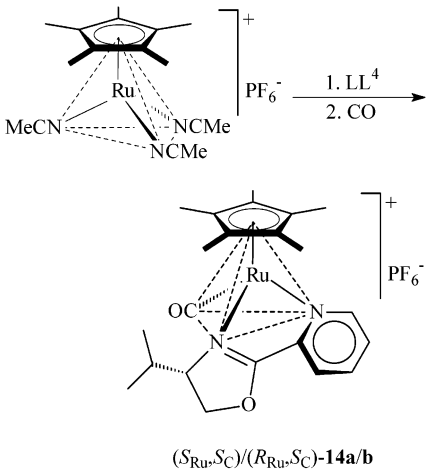
The Complexes $[(\eta^5\text{-}C_5Me_5)Ru(LL^1)(PPh_3)]PF_6$ (13a,b). Addition of LL^1 and PPh_3 to a solution of $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ in CH_3CN afforded (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^5\text{-}C_5Me_5)Ru(LL^1)(PPh_3)]PF_6$ (**13a**,**b**) (Scheme 6). The integration of the η^5-C_5Me_5 singlets of the two diastereomers in CD_2Cl_2 and acetone-d_6 gave the ratio 50:50. This ratio significantly differed from the ratio obtained for the related molybdenum complexes (R_{Mo},S_C)- and (S_{Mo},S_C)-$[(\eta^7\text{-}C_7H_7)Mo(LL^1)(PPh_3)]BF_4$ (**8a**,**b**), in which the diastereomer **8b** was strongly favored.

13 could also be prepared by starting from the diastereomerically pure complex $[(\eta^5\text{-}C_5Me_5)Ru(LL^1)(CO)]PF_6$ (**12a**). After **12a** was dissolved in 1 mL of CD_2Cl_2 and a 1.5-fold excess of PPh_3 was added, the solution was irradiated. The substitution reaction was monitored by ^1H and ^{31}P NMR spectroscopy. During the reaction the ratio **13a**:**13b** was constantly 50:50.

By crystallization from CH_2Cl_2/hexane at −30 °C brown-red crystals of **13b** were obtained, which were submitted to a single-crystal X-ray diffraction study. In Figure 6 an ORTEP plot of the cation of **13b** is shown. The stereogenic ruthenium center has an S_{Ru} configuration specified with the priority sequence η^5-C_5Me_5 > P > N2 > N1. The similarity of the analogous molybdenum and ruthenium complexes **8b** and **13b** is conspicuous. Both have not only the same S_M configuration at the chiral metal atoms and the same triphenylphosphane helicity M_{PPh_3} but 1-phenylethyl substituent and triphenylphosphane ligand adopt strikingly similar conformations (Figure 5).

The Complexes $[(\eta^5\text{-}C_5Me_5)Ru(LL^4)(CO)]PF_6$ (14a,b). The ruthenium complexes (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^5\text{-}C_5Me_5)Ru(LL^4)(CO)]PF_6$ (**14a**,**b**) were prepared by adding LL^4 and passing carbon monoxide through a solution of $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ in CH_2Cl_2 (Scheme 7). After precipitation from CH_2Cl_2 with hexane, the integration of the η^5-C_5Me_5 singlets in acetone-d_6 gave the diastereomer ratio 77:23. By fractional crystallization it was possible to increase the ratio to 98:2. It did not change after 20 h at 45 °C in acetone solution, indicating a configurationally stable ruthenium center. As (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^5\text{-}C_5Me_5)Ru(LL^4)(CO)]PF_6$ (**14a**,**b**) were prepared by passing carbon monoxide for 20 min through a solution of the corresponding acetonitrile derivative at room temperature, the diastereomer ratio of 77:23 obtained in the synthesis definitively was in the regime of kinetic control.

Scheme 7. Preparation of the Complexes $[(\eta^5\text{-}C_5Me_5)Ru(LL^4)(CO)]PF_6$ (14a,b)[a]



[a] Only the diastereomer with the S_{Ru},S_C configuration is shown.

Conclusion

The new $(\eta^7\text{-}C_7H_7)Mo$ complexes described in this paper are isolobal with the corresponding $(\eta^5\text{-}C_5R_5)Ru$ complexes (R = H, Me). Whereas $[(\eta^7\text{-}C_7H_7)Mo(LL^1)(CO)]BF_4$ (**2a**,**b**) undergoes epimerization in solution at room temperature, initiated by an opening of the chelate ring LL^1 on the imine side, $[(\eta^5\text{-}C_5H_5)Ru(LL^1)(CO)]PF_6$ (**12a**,**b**) is configurationally stable under these conditions. This can be generalized: the $(\eta^7\text{-}C_7H_7)Mo$ complexes are configurationally more labile at the metal center than their $(\eta^5\text{-}C_5R_5)Ru$ counterparts. Interestingly, in both series of complexes the same configuration at the metal atom is favored. The equilibrium ratios of the complexes $[(\eta^7\text{-}C_7H_7)Mo(LL^1)X]BF_4$ (**2**, **7**, and **8)** with the ligands X = CO, CN^tBu, PPh_3 are changing from 76:24 in **2a**,**b** via 50:50 in **7a**,**b** to 4:96 in **8a**,**b**, indicating that the equilibrium ratio is strongly dependent on the monodentate ligand bound to the $(\eta^7\text{-}C_7H_7)Mo(LL^1)$ fragment. Finally, we have been able to show that the substitution of PPh_3 by $PPhMe_2$ in $[(\eta^7\text{-}C_7H_7)Mo(LL^1)(PPh_3)]BF_4$ (**8a**,**b**) does not proceed by way of the epimerization equilibrium, because the two diastereomers **8a** and **8b** have significantly different reactivities.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Most of

the commercially available reagents were used without further purification. Solvents were dried by standard methods and distilled prior to use. Melting points: Büchi SMP 20, not corrected. IR spectra: BioRad FT-IR (KBr pellets). Mass spectra: Finnigan Mat 311 A, Finnigan Mat 95, and ThermoQuest TSQ 7000 (the most intense peak of the isotope cluster is specified). Optical rotations: Perkin-Elmer 241 polarimeter at room temperature. ^{1}H NMR (reference TMS), ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR spectra: Bruker ARX 400 spectrometer. Elemental analyses: Heraeus Elementar Vario EL III. The chelate ligands pyridine-2-carbald-(*S*)-1-phenylethylimine (LL^1),[13] 6-methylpyridine-2-carbald-(*S*)-1-phenylethylimine (LL^2),[13] pyridine-2-carbald-(*S*)-1-cyclohexylethylimine (LL^3),[13] and (*S*)-2-(4,5-dihydro-4-isopropyloxazol-2-yl)pyridine (LL^4)[25] and the complexes [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4,[14] [(η^5-C_5H_5)-Ru(NCMe)$_3$]PF_6,[28] and [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF_6[29] were prepared according to the literature.

[(η^7-C_7H_7)Mo(LL^1)(NCMe)]BF_4 (1). A solution of [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 (0.685 g, 1.87 mmol) was stirred in CH_3CN (45 mL) for 45 min at 70 °C. The red solution was cooled to 0 °C and stirred with LL^1 (0.420 g, 2.00 mmol) for 3 h at room temperature. The resulting green solution was filtered, and the volume was reduced to ca. 10 mL. Addition of hexane precipitated **1** as a green solid.

Yield: 0.620 g (62%) of a mixture of two diastereomers in a ratio of 62:38. Mp: >70 °C dec. Anal. Calcd for $C_{23}H_{24}BF_4MoN_3$ (525.2): C, 52.60; H, 4.61; N, 8.00. Found: C, 52.40; H, 4.62; N, 6.98. MS (ESI, CH_3CN): *m*/*z* 440 (cation, 60), 399 (cation − NCMe, 100). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.43 (9.56) (d, $^3J_{HH}$ = 5.8 Hz, 1H, py-*H*$_6$), 8.41 (s, 1H, N=C*H*), 8.03 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 1.0 Hz, 1H, py-*H*$_3$), 7.99−6.86 (m, 7H, py-*H* + Ph-*H*), 7.14 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-*H*$_5$), 6.77 (6.35) (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*CH$_3$), 5.27 (5.25) (s, 7H, η^7-C_7H_7), 1.91 (2.37) (s, 3H, NCC*H*$_3$), 1.97 (1.70) (d, $^3J_{HH}$ = 6.8 Hz, 3H, CHC*H*$_3$).

[(η^7-C_7H_7)Mo(LL^1)(CO)]BF_4 (2). [(η^7-C_7H_7)Mo(LL^1)(NCMe)]-BF_4 (0.600 g, 1.14 mmol) was dissolved in acetone (40 mL). A slow stream of carbon monoxide was passed through the solution for 2 h, in which the reaction temperature was increased in stages from room temperature to 55 °C. The resulting deep blue solution was filtered and reduced in volume. Hexane was added to precipitate **2** as a blue solid.

Yield: 0.345 g (59%) of a mixture of two diastereomers in a ratio of 76:24. Mp: 111−114 °C dec. Anal. Calcd for $C_{22}H_{21}BF_4MoN_2O{\cdot}0.5CH_2Cl_2$ (554.7): C, 48.72; H, 4.55; N, 5.05. Found: C, 48.57; H, 4.32; N, 5.18. MS (ESI, acetone): *m*/*z* 457 (cation − CO + acetone, 12), 399 (cation − CO, 100). IR (KBr, cm^{-1}): 1974 (C≡O). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.33 (9.41) (d, $^3J_{HH}$ = 5.7 Hz, 1H, py-*H*$_6$), 8.93 (8.27) (s, 1H, N=C*H*), 8.32 (8.15) (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, py-*H*$_3$), 8.02 (7.97) (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-*H*$_4$), 7.65−7.27 (m, 5H, Ph-*H*), 7.51 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-*H*$_5$), 6.11 (5.95) (q, $^3J_{HH}$ = 6.7 Hz, 1H, C*H*CH$_3$), 5.57 (5.61) (s, 7H, η^7-C_7H_7), 1.93 (1.72) (d, $^3J_{HH}$ = 6.7 Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (δ, acetone-d_6): 222.6 (s, 1C, *C*O), 157.3 (s, 1C, *C*HN), 153.5 (s, 1C, py-*C*$_6$), 153.0 (s, 1C, *C*$_q$), 142.3 (s, 1C, *C*$_q$), 137.4 (s, 1C, py-*C*$_4$), 130.3 (s, 1C, py-*C*$_3$), 129.6 (s, 2C, Ph-*C*), 128.9 (s, 1C, Ph-*C*), 128.2 (s, 2C, Ph-*C*), 125.4 (s, 1C, py-*C*$_5$), 93.7 (s, 7C, *C*$_7$H$_7$), 73.1 (s, 1C, *C*HMe), 22.3 (s, 1C, *C*H$_3$).

With the mixture **2a**:**2b** = 76:24 as a starting point, complex **2a** (de = 84%) was isolated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Mp: 125−127 °C dec. [α]$_{589}$ = −460°, [α]$_{546}$ = +930°, [α]$_{436}$ = +190° (*c* = 0.54, CH_2Cl_2).

[(η^7-C_7H_7)Mo(LL^2)(NCMe)]BF_4 (3). A solution of [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 (0.500 g, 1.37 mmol) was stirred in CH_3CN (45 mL) for 45 min at 70 °C. The red solution was cooled to 0 °C and stirred with LL^2 (0.306 g, 1.37 mmol) for 3 h at room temperature. The resulting green solution was filtered, and the volume was reduced to ca. 10 mL. Addition of hexane precipitated **3** as a green solid.

Yield: 0.620 g (84%) of a mixture of two diastereomers in a ratio of 75:25. Mp: >75 °C dec. Anal. Calcd for $C_{24}H_{26}BF_4MoN_3$ (539.2): C, 53.46; H, 4.86; N, 7.79. Found: C, 54.01; H, 5.11; N, 7.40. MS (ESI, CH_2Cl_2): *m*/*z* 413 (cation − NCMe, 100). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 8.22 (s, 1H, N=C*H*), 8.02−6.94 (m, 8H, py-*H* + Ph-*H*), 6.59 (6.30) (q, $^3J_{HH}$ = 6.7 Hz, 1H, C*H*CH$_3$), 5.29 (5.30) (s, 7H, η^7-C_7H_7), 3.10 (3.23) (s, 3H, py-C*H*$_3$), 1.97 (1.70) (d, $^3J_{HH}$ = 6.7 Hz, 3H, CHC*H*$_3$), 1.96 (s, 3H, NCC*H*$_3$).

[(η^7-C_7H_7)Mo(LL^2)(CO)]BF_4 (4). [(η^7-C_7H_7)Mo(LL^2)(NCMe)]-BF_4 (0.540 g, 1.00 mmol) was dissolved in acetone (40 mL). A slow stream of carbon monoxide was passed through the solution for 3.5 h, in which the reaction temperature was increased in stages from room temperature to 55 °C. The resulting deep blue solution was filtered and reduced in volume. Hexane was added to precipitate **4** as a blue solid.

Yield: 0.450 g (86%) of a mixture of two diastereomers in a ratio of 78:22. Mp: >156 °C dec. Anal. Calcd for $C_{23}H_{23}BF_4MoN_2O{\cdot}CH_2Cl_2$ (611.2): C, 47.17; H, 4.12; N, 4.58. Found: C, 47.25; H, 4.09; N, 4.53. MS (ESI, acetone): *m*/*z* 457 (cation − CO + acetone, 12), 427 (cation, 62), 399 (cation − CO, 100). IR (KBr, cm^{-1}): 1963 (C≡O). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 8.78 (7.92) (d, $^4J_{HH}$ = 1.1 Hz, 1H, N=C*H*), 8.24−7.22 (m, 8H, py-*H* + Ph-*H*), 6.05 (5.89) (dq, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, C*H*CH$_3$), 5.62 (5.71) (s, 7H, η^7-C_7H_7), 2.88 (3.00) (s, 3H, py-C*H*$_3$), 1.94 (1.69) (d, $^3J_{HH}$ = 6.6 Hz, 3H, CHC*H*$_3$).

With the mixture **4a**:**4b** = 78:22 as a starting point, complex **4a** (de > 96%) was isolated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Mp: >168 °C dec. [α]$_{589}$ = −660°, [α]$_{546}$ = +590°, [α]$_{436}$ = −530° (*c* = 0.08, CH_2Cl_2).

[(η^7-C_7H_7)Mo(LL^3)(CO)]BF_4 (6). A solution of [(η^7-C_7H_7)-Mo(η^6-$C_6H_5CH_3$)]BF_4 (0.730 g, 2.00 mmol) was stirred in CH_3CN (45 mL) for 45 min at 70 °C. The red solution was cooled to 0 °C and stirred with LL^3 (0.420 g, 2.00 mmol) for 3 h at room temperature. The resulting green solution was filtered, and the volume was reduced to ca. 10 mL. Addition of hexane precipitated a green solid. The solid was dissolved in acetone (40 mL). A slow stream of carbon monoxide was passed through the solution for 3 h, in which the reaction temperature was increased in stages from room temperature to 55 °C. The resulting deep blue solution was filtered and reduced in volume. Hexane was added to precipitate **6** as a blue solid.

Yield: 0.390 g (68%) of a mixture of two diastereomers in a ratio of 76:24. Mp: >71 °C dec. $C_{22}H_{27}BF_4MoN_2O$ (518.2). MS (ESI, CH_3CN): *m*/*z* 446 (cation − CO + NCMe, 95), 433 (cation, 100). IR (KBr, cm^{-1}): 1964 (C≡O). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.40 (d, $^3J_{HH}$ = 5.7 Hz, 1H, py-*H*$_6$), 8.58 (s, 1H, N=C*H*), 8.24 (ddd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, py-*H*$_3$), 8.03 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-*H*$_4$), 7.55 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, py-*H*$_5$), 5.69 (5.70) (s, 7H, η^7-C_7H_7), 4.77−4.63 (m, 1H, C*H*CH$_3$), 1.60 (1.25) (d, $^3J_{HH}$ = 6.6 Hz, 3H, CHC*H*$_3$), 1.91−1.04 (m, 11H, Cy-*H*). [α]$_{546}$ = +380° (*c* = 0.22, CH_2Cl_2).

[(η^7-C_7H_7)Mo(LL^1)(CN^{t}Bu)]BF_4 (7). [(η^7-C_7H_7)Mo(LL^1)-(NCMe)]BF_4 (0.430 g, 0.82 mmol) was dissolved in CH_2Cl_2 (35 mL). The green solution was cooled to 0 °C and treated with CN^{t}Bu (0.095 g, 1.15 mmol), and the reaction temperature was increased to the boiling point for 3 h. The resulting solution was filtered and reduced in volume. Hexane was added to precipitate the product **7** as a green solid.

Yield: 0.428 g (92%) of a mixture of two diastereomers in a ratio of 50:50. Mp: 138−142 °C. Anal. Calcd for $C_{26}H_{30}BF_4MoN_3$ (567.3): C, 55.05; H, 5.33; N, 7.41. Found: C, 55.31; H, 5.24; N, 7.40. MS (ESI, CH_2Cl_2): *m*/*z* 482 (cation, 15), 399

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(cation − CN^{t}Bu, 100). IR (KBr, cm^{-1}): 2148 (C≡N). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.38 (9.30) (ddd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.9 Hz, 1H, py-H_6), 8.01 (8.60) (s, 1H, N=CH), 7.98 (8.10) (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{HH}$ = 0.9 Hz, 1H, py-H_3), 7.60−7.43 (m, 5H, Ph-H), 7.65 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-H_4), 7.23 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, py-H_5), 6.10 (q, $^3J_{HH}$ = 7.0 Hz, 1H, CHCH$_3$), 5.34 (5.33) (s, 7H, η^7-C$_7H_7$), 1.71 (1.95) (d, $^3J_{HH}$ = 7.0 Hz, 3H, CHCH_3), 1.35 (1.12) (s, 9H, CN^t*Bu*).

With the mixture **7a**:**7b** = 50:50 as a starting point, complex **7b** (de > 98%) was isolated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Mp: 156−158 °C. $[\alpha]_{589}$ = +430°, $[\alpha]_{546}$ = +1160° (*c* = 0.20, CH_2Cl_2).

[(η^7-C$_7$H$_7$)Mo(LL^1)(PPh$_3$)]BF$_4$ (8). [(η^7-C$_7$H$_7$)Mo(LL^1)(NCMe)]BF$_4$ (0.380 g, 0.72 mmol) was dissolved in CH_2Cl_2 (45 mL). The green solution was cooled to 0 °C and treated with PPh_3 (0.190 g, 0.72 mmol), and the reaction temperature was increased to the boiling point for 1.5 h. The resulting solution was filtered and reduced in volume. Hexane was added to precipitate the product **8** as a green solid.

Yield: 0.439 g (89%) of a mixture of two diastereomers in a ratio of 96:4. Mp: >195 °C dec. Anal. Calcd for $C_{39}H_{36}BF_4MoN_2P$ (746.5): C, 62.75; H, 4.86; N, 3.75. Found: C, 61.95; H, 4.62; N, 3.66. MS (ESI, CH_3CN): *m*/*z* 661 (cation, 100). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.28 (d, $^3J_{HH}$ = 5.9 Hz, 1H, py-H_6), 8.47 (s, 1H, N=CH), 8.06 (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 1.1 Hz, 1H, py-H_3), 7.62−7.02 (m, 20H, py-H_4 + Ph-H), 6.84 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-H_5), 5.81 (q, $^3J_{HH}$ = 7.0 Hz, 1H, CHCH$_3$), 4.97 (5.33) (d, J_{HP} = 2.9 Hz, 7H, η^7-C$_7H_7$), 0.91 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CHCH_3). ^{31}P{^{1}H} NMR (acetone-d_6): δ 35.4 (s).

With the mixture **8a**:**8b** = 4:96 as a starting point, complex **8b** (de > 98%) was isolated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Mp: >195 °C dec. $[\alpha]_{589}$ = +790°, $[\alpha]_{546}$ = +670°, $[\alpha]_{436}$ = −6520° (*c* = 0.08, CH_2Cl_2).

[(η^7-C$_7$H$_7$)Mo(LL^4)(CO)]BF$_4$ (9). A solution of [(η^7-C$_7$H$_7$)Mo(η^6-C$_6$H$_5$CH$_3$)]BF$_4$ (0.864 g, 2.36 mmol) was stirred in CH_3CN (45 mL) for 45 min at 70 °C. The red solution was cooled to 0 °C and stirred with LL^4 (0.440 g, 2.36 mmol) for 3 h at room temperature. The resulting green solution was filtered, and the volume was reduced to ca. 10 mL. Addition of hexane precipitated a green solid. The solid was dissolved in acetone (40 mL). A slow stream of carbon monoxide was passed through the solution for 2 h, in which the reaction temperature was increased in stages from room temperature to 55 °C. The resulting deep blue solution was filtered and reduced in volume. Hexane was added to precipitate **9** as a blue solid.

Yield: 0.650 g (83%) of a single diastereomer. Mp: >167 °C dec. Anal. Calcd for $C_{19}H_{21}BF_4MoN_2O_2$ (492.1): C, 46.37; H, 4.30; N, 5.69. Found: C, 45.96; H, 3.75; N, 5.57. MS (ESI, CH_2Cl_2): *m*/*z* 407 (cation, 100), 379 (cation − CO, 60). ^{1}H NMR (acetone-d_6): δ 9.42 (ddd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.9 Hz, 1H, py-H_6), 8.10 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, py-H_4), 8.05 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.9 Hz, 1H, py-H_3), 7.72 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, py-H_5), 5.70 (s, 7H, η^7-C$_7H_7$), 5.2−4.9 (m, 3H, CH_2 + CH), 2.18 (m, 1H, CH), 1.05 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 0.57 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). $[\alpha]_{589}$ = −710°, $[\alpha]_{546}$ = −280°, $[\alpha]_{436}$ = −520° (*c* = 0.11, CH_2Cl_2).

[(η^7-C$_7$H$_7$)Mo(LL^1)I] (10). LL^1 (0.600 g, 2.85 mmol) and [(η^7-C$_7$H$_7$)Mo(CO)$_2$I] (1.00 g, 2.70 mmol) were dissolved in toluene (55 mL) and gently refluxed for 3 h, the solution turning from green to deep blue. The resulting solution was filtered, and the solvent was removed. The residue was recrystallized from toluene/hexane at −30 °C to give a deep blue solid.

Yield: 1.110 g (79%) of a mixture of two diastereomers in a ratio of 95:5. Anal. Calcd. for $C_{21}H_{21}IMoN_2$ (524.3): C, 48.11; H, 4.04; N, 5.34. Found: C, 48.70; H, 4.13; N, 5.28. MS (ESI, CH_2Cl_2): *m*/*z* 526 (MH$^+$, 25), 399 (MH$^+$ − I, 100). ^{1}H NMR (C_6D_6, signals of the minor diastereomer in parentheses): δ 8.93 (8.14) (ddd, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.9 Hz, 1H, py-H_6), 7.28 (s, 1H, N=CH), 7.23−7.10 (m, 3H, Ph-H), 7.08−7.04 (m, 2H, Ph-H), 6.88 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.9 Hz, 1H, py-H_3), 6.50 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, py-H_4), 6.10 (ddd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-H_5), 6.08 (q, $^3J_{HH}$ = 7.0 Hz, 1H, CHCH$_3$), 4.78 (4.84) (s, 7H, η^7-C$_7H_7$), 1.56 (1.45) (d, $^3J_{HH}$ = 7.0 Hz, 3H, CHCH_3). $[\alpha]_{589}$ = +430°, $[\alpha]_{546}$ = +1160° (*c* = 0.20, CH_2Cl_2).

[(η^5-C$_5$H$_5$)Ru(LL^1)(CO)]PF$_6$ (11). A solution of [(η^5-C$_5$H$_5$)Ru(NCMe)$_3$]PF$_6$ (0.140 g, 0.32 mmol) was dissolved in CH_2Cl_2 (20 mL). The solution was cooled to 0 °C and stirred with LL^1 (0.068 g, 0.32 mmol) for 2 h at room temperature. A slow stream of carbon monoxide was passed through the solution for 10 min at room temperature. The resulting solution was filtered and reduced in volume. Hexane was added to precipitate **11** as an orange solid.

Yield: 0.137 g (78%) of a mixture of two diastereomers in a ratio of 56:44. Mp: >65 °C dec. Anal. Calcd for $C_{20}H_{19}F_6N_2OPRu$ (549.4): C, 43.72; H, 3.49; N, 5.10. Found: C, 44.10; H, 4.04; N, 5.28. MS (ESI, CH_2Cl_2): *m*/*z* 405 (cation, 14), 377 (cation − CO, 100). IR (KBr, cm^{-1}): 1978 (C≡O). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.34 (8.95) (d, J_{HH} = 1.2 Hz, 1H, N=CH), 9.31−7.64 (m, 4H, py-H), 7.58−7.41 (m, 5H, Ph-H), 5.69−5.54 (m, 1H, CHCH$_3$), 5.10 (5.29) (s, 5H, η^5-C$_5H_5$), 1.93 (1.94) (d, J_{HH} = 6.7 Hz, 3H, CHCH_3).

[(η^5-C$_5$Me$_5$)Ru(LL^1)(CO)]PF$_6$ (12). A solution of [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]PF$_6$ (0.360 g, 0.71 mmol) was dissolved in CH_2Cl_2 (30 mL). The solution was cooled to 0 °C and stirred with LL^1 (0.150 g, 0.71 mmol) for 8 h at room temperature. A slow stream of carbon monoxide was passed through the solution for 10 min at room temperature. The resulting solution was filtered and reduced in volume. Hexane was added to precipitate **12** as an orange solid.

Yield: 0.308 g (70%) of a mixture of two diastereomers in a ratio of 71:29. Mp: 195−109 °C dec. Anal. Calcd for $C_{25}H_{29}F_6N_2OPRu$ (619.6): C, 48.47; H, 4.72; N, 4.52. Found: C, 47.93; H, 4.64; N, 4.56. MS (ESI, CH_2Cl_2): *m*/*z* 475 (cation, 33), 447 (cation − CO, 100). IR (KBr, cm^{-1}): 1950 (C≡O). ^{1}H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.34 (8.91) (d, $^4J_{HH}$ = 1.2 Hz, 1H, N=CH), 8.95 (ddd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, py-H_6), 8.43 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, py-H_3), 8.31 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-H_4), 7.83 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, py-H_5), 7.40−7.30 (m, 5H, Ph-H), 5.53 (5.36) (qd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, CHCH$_3$), 1.95 (1.87) (d, $^3J_{HH}$ = 6.8 Hz, 3H, CHCH_3), 1.79 (1.91) (s, 15H, η^5-C$_5Me_5$).

Starting from the mixture **12a**:**12b** = 71:29, complex **12a** (de > 98%) was isolated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C. Mp: 202−204 °C dec. $[\alpha]_{589}$ = +420°, $[\alpha]_{546}$ = +500°, $[\alpha]_{436}$ = +520° (*c* = 0.09, CH_2Cl_2).

[(η^5-C$_5$Me$_5$)Ru(LL^1)(PPh$_3$)]PF$_6$ (13). A solution of [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]PF$_6$ (0.300 g, 0.60 mmol) was dissolved in CH_2Cl_2 (20 mL). The solution was cooled to 0 °C and stirred with LL^1 (0.125 g, 0.60 mmol) for 12 h at room temperature. To this solution was added PPh_3 (0.125 g, 0.60 mmol), and stirring was continued for 4 h. The resulting solution was filtered over Celite and reduced in volume. Hexane was added to precipitate **13** as a reddish solid.

Yield: 0.435 g (80%) of a mixture of two diastereomers in a ratio of 50:50. Mp: >108 °C dec. Anal. Calcd for $C_{42}H_{44}F_6N_2P_2Ru$ (853.8): C, 59.08; H, 5.19; N, 3.28. Found: C, 58.84; H, 4.83; N, 3.19. MS (ESI, CH_2Cl_2): *m*/*z* 709 (cation, 75), 447 (cation − CO, 100). ^{1}H NMR (CD_2Cl_2; signals of the second diastereomer in parentheses): δ 8.81 (m, 1H, py-H), 8.52/8.21 (d, J = 2.9/3.4 Hz, 1H, N=CH), 7.67−7.04 (m, 23H, py-H + Ph-H), 5.66/5.49 (q, J_{HH} = 7.0/7.1 Hz, 1H, CHMe), 1.87/1.29 (d, J_{HH} = 7.0/7.1 Hz, 3H, CH_3), 1.56/1.30 (d, J_{HP} = 1.5/1.5 Hz,

Table 2. Crystallographic Data for Compounds 2a, 7b, 8b, 9b, 10a, 12a, and 13b

	2a	7b	8b	9b	10a	12a	13b
empirical formula	$C_{22}H_{21}MoN_2O(BF_4)$	$C_{26}H_{30}MoN_3(BF_4)\cdot CH_2Cl_2$	$C_{39}H_{36}MoN_2P(BF_4)$	$C_{19}H_{21}MoN_2O_2(BF_4)$	$C_{21}H_{21}IMoN_2$	$C_{25}H_{29}N_2ORu(PF_6)\cdot CH_2Cl_2$	$C_{42}H_{44}N_2PRu(PF_6)\cdot 2CH_2Cl_2$
fw	512.16	652.21	746.42	492.13	524.4	704.47	1023.65
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic	tetragonal
space group	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P4_1$
Z	8	2	2	4	4	4	4
a, Å	19.3665(15)	10.1951(8)	9.8578(6)	10.3053(8)	8.6726(7)	10.8308(6)	10.9531(3)
b, Å	13.5804(8)	15.3395(9)	19.4208(16)	16.2959(10)	10.7098(9)	15.1121(12)	10.9531(3)
c, Å	20.1149(2)	10.4637(9)	9.8592(7)	11.6062(7)	20.5019(16)	17.9658(10)	38.3369(15)
β, deg	116.610(10)	117.807(9)	116.955(7)	90	90	90	90
V, Å^3	4738.0(8)	1447.4(2)	1682.5(2)	1949.1(2)	1904.3(3)	2940.6(3)	4599.3(3)
d_{calcd}, g/cm^3	1.436	1.497	1.473	1.677	1.829	1.591	1.478
μ, mm^{-1}	0.60	0.69	0.491	0.73	2.32	0.83	0.701
F(000)	2064	664	764	992	1024	1424	2088
cryst dimens, mm	0.64 × 0.38 × 0.04	0.44 × 0.40 × 0.30	0.70 × 0.40 × 0.20	0.70 × 0.40 × 0.16	0.38 × 0.25 × 0.11	0.40 × 0.07 × 0.06	0.30 × 0.20 × 0.20
T, K	173	173	173	173	173	173	173
no. of rflns collected	42 390	20 324	19 369	27 262	25 664	41 386	27 315
no.of indep rflns (R_{int})	17 531 (0.1184)	5436 (0.0505)	6312 (0.0538)	3719 (0.0694)	3579 (0.0372)	5622 (0.0590)	7179 (0.0339)
no. of rflns $I > 2\sigma(I)$	10 149	5320	6135	3588	3286	5385	6923
no. of data/restraints/params	17 531/1/1117	5436/1/343	6312/1/433	3719/0/263	3579/0/226	5622/0/352	7179/1/532
goodness of fit on F^2	0.811	1.070	1.058	1.103	1.046	1.078	1.116
final R indices ($I > 2\sigma(I)$)							
R1	0.0573	0.0244	0.0289	0.0267	0.0187	0.0306	0.0307
wR2	0.1070	0.0632	0.0723	0.0687	0.0463	0.0788	0.0781
R indices (all data)							
R1	0.0969	0.0250	0.0295	0.0277	0.0218	0.0324	0.0323
wR2	0.1193	0.0635	0.0725	0.0691	0.0471	0.0796	0.0793
largest diff peak, hole, e Å^{-3}	0.949, −0.495	0.565, −0.348	0.750, −0.280	1.107, −0.477	0.635, −0.335	1.127, −0.344	0.687, −0.499
CCDC no.	193223	193224	193228	193226	193222	193225	193227

15H, η^5-C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.9/47.1 (s), −143.8 (sept, J_{PF} = 710.6 Hz).

[(η^5-C_5Me_5)Ru(LL^4)CO]PF_6 (14). A solution of [(η^5-C_5Me_5)-Ru(NCMe)$_3$]PF_6 (0.210 g, 0.42 mmol) was dissolved in CH_2Cl_2 (20 mL). The solution was cooled to 0 °C and stirred with LL[1] (0.079 g, 0.42 mmol) for 8 h at room temperature. A slow stream of carbon monoxide was passed through the solution for 20 min at room temperature. The resulting solution was filtered and reduced in volume. Hexane was added to precipitate **14** as a yellow solid.

Yield: 0.214 g (85%) of a mixture of two diastereomers in a ratio of 77:23. Mp: >165 °C dec. $C_{22}H_{29}F_6N_2O_2PRu$ (599.5). MS (ESI, CH_2Cl_2): *m/z* 455 (cation, 20), 427 (cation − CO, 100). IR (KBr, cm^{-1}): 1945 (C≡O). ^1H NMR (acetone-d_6; signals of the minor diastereomer in parentheses): δ 9.03 (9.01) (ddd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.4 Hz, $^5J_{HH}$ = 0.8 Hz 1H, py-H_6), 8.34 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, py-H_4), 8.16 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, py-H_3), 7.93 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, py-H_5), 5.11 (dd, $^2J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, CH), 5.06 (dd, $^2J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, CH), 4.68 (4.46) (ddd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 2.8 Hz, 1H, CH), 2.25 (dsept, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 2.8 Hz, 1H, CH-^{i}Pr), 1.86 (1.90) (s, 15H, η^5-C_5Me_5), 1.09 (1.14) (d, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 0.79 (0.95) (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3).

With the mixture **14a**:**14b** = 77:23 as a starting point, complex **14a** (de > 96%) was isolated by repeated fractional crystallization from CH_2Cl_2/hexane at −30 °C.

X-ray Crystallographic Studies. The data were collected on a STOE-IPDS diffractometer (Mo Kα radiation). The structures were solved by direct methods (SIR97).[30] Refinement was done by full-matrix least squares on F^2 (SHELXL-97).[31] The crystallographic data for compounds **2a**, **7b**, **8b**, **9b**, **10a**, **12a**, and **13b** are summarized in Table 2.

Supporting Information Available: Lists containing tables of atomic coordinates and equivalent isotropic parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen coordinates for the X-ray structure determination of compounds **2a**, **7b**, **8b**, **9b**, **10a**, **12a**, and **13b**. This material is available free of charge via the Internet at http://www.acs.org.

OM020523A

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