possible first intermediates a neutral borane, 2-$CH_3$py·$BHBr_2$, obtained by amine loss, or a cation, $(CH_3)_3N$(2-$CH_3$py)-$BHBr^+$, obtained by bromide loss. The preparation of the adduct 2-$CH_3$py·$BHI_2$ as an intermediate, and the final isolation of stable (2-$CH_3$py)$_3BH^{2+}$ shows that sterically even more encumbered structures are capable of existence.

The reactivity order with trimethylamine–dibromoborane established in Table I, 4-methylpyridine > pyridine ≫ 2-methylpyridine > 2,6-dimethylpyridine > 2-fluoropyridine, thus is to be interpreted as reflecting decreasing nucleophilicity in the attacking amine, caused by progressively greater electron withdrawal away from the nitrogen atom or by steric inhibition of the attack on boron by substituents in the 2-position of the pyridine ring.

The observed enhanced reactivity of diiodoboranes when compared to dibromoboranes would then be a consequence of iodide being a much better leaving group than bromide, while the accelerations of cation formation when pyridine boranes are used as starting materials, rather than trimethylamine borane, are reminiscent of similar reactivity enhancement when the organic isosteric benzyl and neopentyl systems are compared.

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**Registry No.** $(C_5H_5N)_3BHBr_2$, 25397-28-8; $(C_5H_5N)_3BH(PF_6)_2$, 25447-31-8; (4-$CH_3C_5H_4N)_3BH(PF_6)_2$, 25338-40-3; (3-$CH_3C_5H_4N)_3BHBr_2$, 72541-38-9; (3-$CH_3C_5H_4N)_3BH(PF_6)_2$, 72541-40-3; [3,5-$(CH_3)_2C_5H_3N]_3BHBr_2$, 72541-41-4; [3,5-$(CH_3)_2C_5H_3N]_3BH(PF_6)_2$, 72541-43-6; (4-$CH_3C_5H_4N)_3BHI_2$, 25397-29-9; (2-$CH_3C_5H_4N)_3BHI_2$, 72541-44-7; (2-$CH_3C_5H_9N)_3BH(PF_6)_2$, 72541-46-9; (4-$CH_3C_5H_4N)_3BHBr_2$, 72541-47-0; $(CH_3)_3N$·$BHBr_2$, 32805-31-5; $C_5H_5N$·$BH_2Br$, 60228-77-5; $C_5H_5N$·$BHBr_2$, 72541-88-9; $(CH_3)_3N$·$BH_3$, 75-22-9; 4-$CH_3C_5H_4N$·$BH_3$, 3999-39-1; 2-$CH_3C_5H_4N$·$BH_3$, 3999-38-0; 4-$CH_3C_5H_4N$, 1003-67-4; $C_5H_5N$, 110-86-1; 2,6-$(CH_3)_2C_5H_3N$, 108-48-5; 2-$CH_3C_5H_4N$, 109-06-8; 3-$CH_3C_5H_4N$, 108-99-6; 3,5-$(CH_3)_2C_5H_3N$, 591-22-0.

Contribution from the Institut für Chemie der Universität Regensburg, D-8400 Regensburg, Germany

# Optically Active Transition-Metal Complexes. 65.[1] Conformational Analysis in Diastereoisomer Equilibria of Square-Pyramidal Dicarbonylcyclopentadienylmolybdenum–Pyridine-2-carbaldimine Complexes Using the Ruch/Ugi Rules

HENRI BRUNNER* and DEVENDRA K. RASTOGI

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Ten chiral amines and amino acids $H_2NCH(R^1)(R^2)$ were used to prepare the corresponding pyridine-2-carbaldimines, abbreviated NN*. The unsymmetrical chelate ligands NN* were introduced into the complexes $[C_5H_5Mo(CO)_2NN^*]PF_6$, chiral at the Mo atom. Because racemic amines were used and the optically active amino acids racemized during the reaction, mixtures of two diastereoisomeric pairs of enantiomers were obtained. The diastereoisomers differ in their $^1H$ NMR spectra and were separated by fractional crystallization. On heating in acetone-$d_6$ at 80 °C the diastereoisomers interconvert. In this epimerization the labile Mo configuration changes under the influence of the stable asymmetric carbon atom in the ligand NN*. A gauge for the asymmetric induction in this equilibration is the equilibrium ratio of the diastereoisomers, obtained by $^1H$ NMR integration. The asymmetric inductions, ranging from 8 to 62%, can be interpreted on the basis of the stereochemical model of Ruch and Ugi, by using λ values distinctly different from those found for organic systems. The negative phenyl value indicates a weak attraction between the phenyl substituent at the asymmetric carbon atom and the $MC_5H_5$ group which accounts for the high optical inductions observed and the high chemical shift differences of the diastereoisomers.

## Introduction

One of the challenging problems in conformational analysis is to find the preferred conformations which a substituent can adopt with respect to a ring system. Since the work of Corey and Bailar,[2] chelate rings in coordination chemistry also have been taken into consideration. The effects change with ring size, ring type, and ring structure (planar or not) and with nature, number, and position of the substituents.[3] In the present paper a conformational analysis for chiral substituents at the nitrogen atom in a planar five-membered ring is carried out. The chelate ligands used are the Schiff bases NN* derived from pyridine-2-carbaldehyde and chiral primary amines $H_2NCH(R^1)(R^2)$. The chelate ring includes the Mo atom of a $C_5H_5(CO)_2Mo$ group in the square-pyramidal complexes $[C_5H_5Mo(CO)_2NN^*]PF_6$. Chelate ligands with optically active substituents are frequently used in asymmetric catalysis.[4-7] As the orientation of the substituents at the asymmetric center affects the various other coordination positions of the metal atom, it controls the addition of a prochiral substrate with either its *re* or its *si* face which may determine the stereochemistry of its conversion to optically active products.[8,9] Thus, an understanding of the preferred conformations of a chiral substituent with respect to a chelate ring and a neighboring metal atom should provide a basis for the estimation

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Table I. $^1$H NMR Spectra of Complexes $[C_5H_5Mo(CO)_2NN^*]PF_6$ (I-X) in Acetone-$d_6$: Assignments, Multiplicities,[a] and $\tau$ Values in Ppm (Internal $Me_4Si$)

| compd | $CH_2CH_3$ [b] | $CH(CH_3)_2$ | $CH_3$ | $^mCH_2CH_3$ | $CH_2C_6H_5$ | $COOCH_3$ | $^1C_5H_5$ | $^mC_6H_5$ | $^mH^3$ | $^mH^4$ | $^mH^5$ | $^mH^6$ | $H^\alpha$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | | | $^2$8.04<br>$^2$7.95 | | | | 4.34<br>3.97 | 2.57 | 1.36 | 1.71 | 2.40 | 0.26 | 0.78 |
| II | $^3$9.01<br>$^3$8.99 | | | 7.60 | | | 4.37<br>3.98 | 3.54 | 1.33 | 1.69 | 2.39 | 0.58 | 0.67 |
| III | | $^2$8.89<br>$^2$8.82 | | | | | 4.44<br>4.06 | 2.49 | 1.30 | 1.70 | 2.36 | 0.64 | 0.49 |
| IV | $^3$8.96<br>$^3$8.94 | | $^2$8.42<br>$^2$8.36 | | | | 3.95 | | 1.50 | 1.76 | 2.49 | 0.60 | 1.00 |
| V | | | $^2$8.18<br>$^2$8.09 | | | 6.16<br>6.14 | 3.97<br>3.90 | | 1.40 | 1.75 | 2.35 | 0.56 | 0.98 |
| VI | $^3$8.90<br>$^3$8.88 | | | 7.66 | | 6.16<br>6.12 | 4.00<br>3.91 | | 1.35 | 1.71 | 2.35 | 0.56 | 0.96 |
| VII | | $^2$8.94<br>$^2$8.86 | | | | 6.13<br>6.02 | 4.02<br>3.90 | | 1.28 | 1.66 | 2.33 | 0.55 | 0.85 |
| VIII | | | | | 6.41[c]<br>6.34[c] | 6.21<br>6.16 | 4.45<br>4.00 | 2.63 | 1.31 | 1.70 | 2.36 | 0.60 | 0.91 |
| IX | | | | | | 6.23<br>6.11 | 4.65<br>4.02 | *e* | *e* | *e* | *e* | *e* | *e* |
| X | | | | | 6.34[d]<br>6.33[d] | | 4.41<br>4.06 | 2.65 | 1.30 | 1.68 | 2.35 | 0.59 | 0.85 |

[a] Multiplicity is shown as superscript. [b] $J$ = 7 Hz. [c] $J$ = 1.6 Hz. [d] $J$ = 1.0 Hz. [e] Could not be resolved due to the presence of the tryptophan substituent $CH_2C_8NH_6$.

whether a given ligand system will be effective in asymmetric catalysis and the prediction of the configuration of the preferred product.[10]

## The Analytical Model

Square-pyramidal compounds $C_5H_5Mo(CO)_2LL'$ with an unsymmetrical chelate ligand LL′ form pairs of enantiomers with Mo configurations $R$ and $S$ in which the $C_5H_5$ ligand occupies the top of the pyramid.[11] The first unsymmetrical chelate ligands used were Schiff bases of pyridine-2-carbaldehyde and primary amines,[12] but other ligands LL′, mainly thioamides, were also investigated.[13-15] If the unsymmetrical ligand LL′ contains an optically active center of $S'$ configuration, a pair of diastereoisomers $RS'$ and $SS'$ arises, differing only in the metal configuration $R,S$. The diastereoisomers $RS'$ and $SS'$ usually exhibit different chemical shifts in their $^1$H NMR spectra and can be separated.[13-15]

The diastereoisomers $RS'$ and $SS'$ interconvert by a first-order metal-centered rearrangement, considered to be an intramolecular pseudorotation.[16-19] In this epimerization the labile Mo configuration changes under the influence of the stable optically active center in the ligand LL′. Thus, the asymmetric center at the carbon atom controls the interconversion of the two opposite configurations $R$ and $S$ at the Mo atom on equilibration. A measure for the optical induction from the ligand LL′ to the metal atom is the diastereoisomer ratio $RS'$:$SS'$ at equilibrium, identical with the equilibrium constant.[18-21] These diastereoisomer equilibria can be studied as a function of the substituents in the chelate ligand LL′. For the thioamidato ligand system LL′ = SC(R)N(R*) the equilibrium values $RS'$:$SS'$ could be rationalized[15] on the basis of the stereochemical model of Ruch/Ugi (eq 1)[22,23] where

$$\delta \ln \frac{[RS']}{[SS']} = \zeta(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)(\lambda_3 - \lambda_1) \qquad (1)$$

$\delta = +1$ or $-1$, depending on the configuration of the inducing center, $[RS']$ and $[SS']$ are the equilibrium concentrations of the diastereoisomers, $\zeta$ is a reaction constant, and $\lambda_i$ is the substituent constant of the $i$th substituent at the asymmetric center. This factorization in terms of substituent constants leads to an excellent internal agreement, although $\lambda$ parameters distinctly different from organic values have to be used.[15]

As far as $C_5H_5Mo(CO)_2$ complexes of pyridine-2-carbaldimines NN* are concerned, only (*S*)-(−)-1-phenylethylamine has been applied as amine component.[12,16-19] In this paper we describe the use of 10 different chiral primary amines and amino acids as amino components in the Schiff bases NN* derived from pyridine-2-carbaldehyde and the determination of the asymmetric induction from the ligand NN* to the metal atom in $[C_5H_5Mo(CO)_2NN^*]PF_6$ after equilibration. With the diastereoisomer ratios at equilibrium it should be checked whether additivity in terms of the Ruch/Ugi theory also holds for pyridine-2-carbaldimine derivatives and whether the same substituent parameters $\lambda_i$ as for the thioamidato complexes[15] can be used. If so, the general applicability of the $\lambda$ parameters to asymmetric centers at a planar chelate ring in $\beta$ position to the metal atom would be apparent.

## Results and Discussion

In the reaction of $C_5H_5Mo(CO)_3Cl$ with the pyridine-2-carbaldimines NN* 1 mol of CO is liberated and the Cl ligand, covalently bonded to Mo, is displaced as $Cl^-$. These two coordination positions are occupied by the chelate ligand NN* with formation of the salts $[C_5H_5Mo(CO)_2NN^*]Cl$ which in water by treatment with $NH_4PF_6$ can be converted into the sparingly soluble salts $[C_5H_5Mo(CO)_2NN^*]PF_6$.

If a Schiff base ligand NN* derived from an optically pure amine of stable configuration $S'$ is used, only two isomers, the diastereomers $RS'$ and $SS'$, are formed (Scheme I). However,

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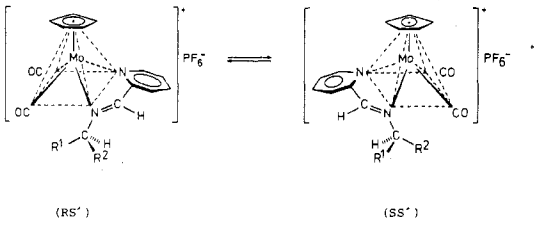
Table II. Equilibrium Ratios of the Diastereomers for the Complexes I–X

| | I | II | III | IV | V | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|---|---|---|---|
| found[a] | 59:41 | 75:25 | 81:19 | 54:46 | 54:46 | 58:42 | 66:34 | 57:43 | 63:37 | 55:45 |
| calcd[b] | | 72.8:27.2 | 79.2:20.8 | 52.2:47.8 | | 60.4:39.6 | 64.5:35.5 | | | |

[a] Obtained by $^1$H NMR integration after epimerization at 80 °C in acetone-$d_6$. [b] Calculated by using eq 1 and the parameters discussed in the text.

Scheme I




| | I | II | III | IV | V | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $CH_3$ | $C_2H_5$ | $i\text{-}C_3H_7$ | $CH_3$ | $CH_3$ | $C_2H_5$ | $i\text{-}C_3H_7$ | $CH_2C_6H_5$ | $CH_2C_8NH_6$ *) | $CH_2C_6H_5$ |
| $R^2$ | $C_6H_5$ | $C_6H_5$ | $C_6H_5$ | $C_2H_5$ | $COOCH_3$ | $COOCH_3$ | $COOCH_3$ | $COOCH_3$ | $COOCH_3$ | $COOCH_2C_6H_5$ |

*) Substituent of the amino acid tryptophan.

a Schiff base NN* containing a chiral amine component in its racemic form *R'/S'* results in the formation of four isomers, the two diastereomeric pairs of enantiomers *RS'/SR'* and *SS'/RR'*. Then, to the two diastereoisomers *RS'* and *SS'* in the scheme must be added the corresponding mirror image isomers *SR'* and *RR'*. The configuration at the metal atom is specified as *R* or *S* as discussed previously.[14,24]

For the synthesis of the compounds II–IV racemic amines *R'/S'* were used, whereas the compounds V–X were prepared with optically pure (*S*)-amino acid esters. Nevertheless, compounds V–X do not show optical activity after fractional crystallization, probably due to a racemization initiated by deprotonation of the enolizable H atom at the asymmetric center during the synthesis.

The IR spectra (KBr) of all the complexes show two characteristic strong $\nu$(C≡O) absorptions in the regions 1985–2000 and 1915–1925 cm$^{-1}$ as well as a band of medium intensity due to the $\nu$(C=N) vibration between 1615 and 1625 cm$^{-1}$. Additionally, the spectra of complexes V–X contain a medium-intensity band due to the $\nu$(C=O) stretching vibration of the ester group at 1740–1750 cm$^{-1}$.

For all ten complexes both diastereoisomers differ appreciably in the chemical shifts of most of their $^1$H NMR signals (Table I). As enantiomers under achiral conditions have identical $^1$H NMR spectra, mixtures of two diastereoisomers *RS'/SS'* as well as two diastereomeric pairs of enantiomers *RS'/SR'/SS'/RR'* give the same $^1$H NMR spectra. In the $^1$H NMR spectra of all the complexes containing a phenyl or an ester group at the asymmetric carbon atom, two sharp singlets between $\tau$ = 3.90–4.65 due to the the $C_5H_5$ protons of the two diastereoisomers have been observed, suitable for the determination of the equilibrium ratio by integration. The $^1$H NMR spectrum of complex IV in $CD_3COCD_3$ shows only one sharp singlet at $\tau$ = 3.95 due to the $C_5H_5$ protons of both diastereoisomers, but in this case the chemical shift differences of the $CH_3$ signals were sufficient to estimate the diastereomer ratio at equilibrium.

The diastereoisomers of the complexes I–X were separated on the basis of their different solubilities. In some cases pure compounds were obtained, and in some only enrichments of the less soluble isomer in the crystallized fraction and of the more soluble isomer in the mother liquor were achieved. The equilibration with respect to the Mo configuration was brought about by heating the complexes I–X in acetone-$d_6$ in sealed tubes at 80 °C. It was ascertained that from both sides, i.e., enrichment in the more soluble and in the less soluble diastereoisomers, the same equilibrium composition was obtained. The diastereoisomer ratios at equilibrium are shown in Table II.

It is evident from the above table that the equilibrium ratio of the diastereoisomers of the square-pyramidal complexes $[C_5H_5Mo(CO)_2NN^*]PF_6$ depends strongly on the substituents at the chiral C atom. Within the series of primary amine derivatives I–III the asymmetric induction increases considerably by increasing the alkyl substituent in the alkyl aryl derivatives with the ratios 59:41, 75:25, and 81:19 for $(R^1)(R^2)$ = $(CH_3)(C_6H_5)$, $(C_2H_5)(C_6H_5)$, and $(i\text{-}C_3H_7)(C_6H_5)$, respectively, and it drops in the dialkyl derivative IV with $(R^1)(R^2)$ = $(CH_3)(C_2H_5)$ to 54:46. The same trend as for I–III is observed for the methyl ester derivatives V–VII in the series $(R^1)(R^2)$ = $(CH_3)(COOCH_3)$, $(C_2H_5)(COOCH_3)$, $(i\text{-}C_3H_7)(COOCH_3)$, although all the values are lower. Also, the diastereoisomer ratios for all the amino acid derivatives V–X are quite low compared to the corresponding thioamidato complexes $C_5H_5(CO)_2MoSC(R)NR^*$.[13,15]

The equilibration with respect to the Mo configuration is a corresponding reaction according to the stereochemical model of Ruch and Ugi.[22,23] Equation 1 relates the diastereoisomer ratio to the chirality product which expresses the ability of the stereostable unit to induce chirality, while the reaction constant $\zeta$ is a measure for the sensitivity of the stereolabile unit to induction. The scale for the ligand parameters $\lambda$ is defined by setting $\lambda(H) = 0$ and $\lambda(CH_3) = 1$.

For the present system, the reaction constant $\zeta$ has been evaluated to be 0.05 by using the diastereoisomer ratio of complex I. But, the experimental diastereoisomer ratios for the complexes II–X cannot be rationalized on the basis of the $\lambda$ parameters from organic systems[25,26] in agreement with recent observations that $\lambda$ values, though constant within one system, may vary from system to system.[15,27-31] However, with the $\lambda$ values recently derived from the diastereoisomer equilibria of $C_5H_5Mo(CO)_2$ thioamidato complexes,[15] i.e., $\lambda(C_2H_5) = 1.90$, $\lambda(CH(CH_3)_2) = 2.35$, and $\lambda(C_6H_5) = -2.40$, the calculated diastereoisomer ratios for the amine derivatives II–IV are in agreement with the experimental values within the limits of error for $^1$H NMR integration. With the experimental diastereoisomer ratio for complex V, eq 1 yields two values of $\lambda(COOCH_3)$, −1.36 and 2.36. Taking $\lambda(COOCH_3) = -1.36$ and the values for $\lambda(C_2H_5)$ and $\lambda(CH(CH_3)_2)$ given above, the calculated ratios of diastereoisomers of the amino acid derivatives VI and VII are in agreement with the experimental values. For the complexes VIII, IX, and X

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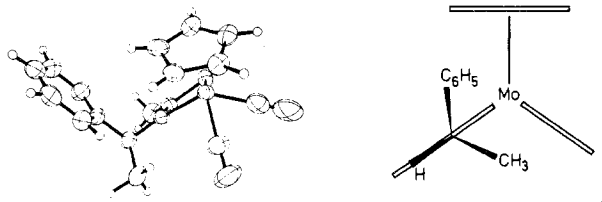


**Figure 1.** ORTEP diagram and projection of (*SS'*)-(−)$_{578}$-$C_5H_5(CO)_2MoSC(CH_3)NCH(CH_3)(C_6H_5)$,[14] the diastereoisomer preferred at equilibrium (conformation 1).

the following λ values were calculated from the experimental diastereoisomer ratio: $\lambda(CH_2C_6H_5) = 1.46$; $\lambda(CH_2CCHNHC_6H_4) = 2.2$; $\lambda(COOCH_2C_6H_5) = -1.08$.

Thus, the asymmetric induction at equilibrium in the complexes I–X can only be rationalized by the stereochemical model of Ruch/Ugi, if the λ parameters derived from the series of thioamidato complexes $C_5H_5(CO)_2MoSC(R)NCH(R^1)(R^2)$[15] are used which are quite different from those found for organic systems.[25-31] Thus, for ethyl, isopropyl, benzyl, and the tryptophan substituent large positive values have to be chosen and similar to the $\lambda(C_6H_5)$ value in the series of the thioamidato complexes $\lambda(COOCH_3)$ and $\lambda(COOCH_2C_6H_5)$ turn out to be strongly negative which literally would mean that all these groups are "smaller" than hydrogen ($\lambda(H) = 0$). An explanation for these negative λ parameters is a weak intramolecular attraction between the unsaturated substituents $C_6H_5$ and COOR and the $MC_5H_5$ group which in terms of the Ruch/Ugi model must show up in negative λ values[15] and which is revealed by X-ray crystallographic and $^1H$ NMR spectroscopic evidence.

For the thioamidato complex $C_5H_5(CO)_2MoSC(CH_3)NCH(CH_3)(C_6H_5)$ an X-ray determination of the structure of the isomer preferred at equilibrium was carried out.[14] In Figure 1 an ORTEP diagram and a projection are given which show the arrangement of the substituents at the asymmetric carbon atom in this molecule with respect to the ligand plane and the other ligands at the Mo atom. Interestingly, four other molecules containing different chiral substituents at the nitrogen atom were also found by X-ray examination in the solid state to have the same conformation, called conformation 1 (Figure 1),[32] in which the H substituent at the asymmetric center is in the ligand plane close to the methyl group at the carbon atom of the four-membered ring.

As larger substituents like phenyl or alkyl in the ligand plane would cause severe steric crowding with the adjacent methyl group, the tendency of the hydrogen atom to be in the ligand plane seems to be the most important conformation-determining factor. The second important factor appears to be a weak attraction of the phenyl ring with the $MC_5H_5$ group. Both these favorable arrangements, H in the ligand plane and phenyl close to $MC_5H_5$, are possible for the isomer, preferred at equilibrium, shown in Figure 1, but not for the disfavored isomer, for which the phenyl ring cannot be close to the $MC_5H_5$ group if the H substituent is in the ligand plane and vice versa. In the series of the pyridinecarbaldimine complexes only one X-ray analysis for compound I (*SS'*), the isomer not preferred at equilibrium, is available.[23,33] The conformation found in the crystal is that given in Figure 2a, in which the bond $CH_3$–C* makes an angle of about 30° with the ligand plane and the phenyl substituent is pointing away from the $C_5H_5$ ring. Arguments why this conformation, called conformation 2a, is better than others have been given.[33]

Nevertheless, it is surprising that I (*SS'*) adopts conformation 2a (Figure 2) and not conformation 1 (Figure 1) be-

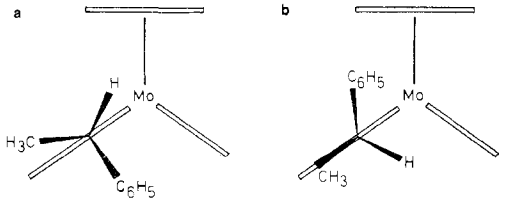


**Figure 2.** Projections of different conformations of $[C_5H_5(CO)_2MoNC_5H_4CH{=}NCH(CH_3)(C_6H_5)]PF_6$ (I). a is the conformation found in the crystalline *SS'*-(+)$_{578}$ isomer of I,[24] disfavored at equilibrium, and b is the conformation assumed for the *RS'* isomer of I, dominating at equilibrium.

cause by a counterclockwise rotation of the asymmetric carbon atom by 150° around the C–N bond 2a would be transformed into 1. Obviously, conformation 1, the favorable rotamer for the isomers of the thioamidato complexes preferred at equilibrium, is not a good conformation for the pyridinecarbaldimine compound I, not even for the isomer I (*SS'*) disfavored at equilibrium. Apparently, for the pyridine imine complexes, methyl in the ligand plane is a much better arrangement than hydrogen in the ligand plane. This situation parallels that of organic systems in which frequently methyl rather than hydrogen eclipses double bonds like C=O, C=N, or C=C.[34-43] Thus, it is assumed that the best conformation for isomers (*RS'*) of the pyridinecarbaldimine complexes dominating at equilibrium is conformation 2b (Figure 2) with methyl eclipsing the C=N bond in the chelate ring and phenyl close to the $C_5H_5$ group, as the conformation-determining effects. This assumption is corroborated by the $^1H$ NMR spectroscopic results, discussed in the next section.

The dominating feature of the $^1H$ NMR spectra of the thioamidato complexes $C_5H_5(CO)_2MoSC(X)NCH(R)(R')$ is the upfield chemical shift of the isomer favored at equilibrium.[13,15] This upfield shift is small for R = R' = alkyl but is 0.5 ppm and more for R = alkyl and R' = aryl. For the pyridine-2-carbaldimine complexes $[C_5H_5(CO)_2MoNC_5H_4CH{=}NCH(R)(R')]PF_6$ chemical shift differences of the diastereoisomers are very similar. For complex IV with R = R' = alkyl the $C_5H_5$ signals are isochronous. However, the alkyl and phenyl containing complexes I–III exhibit chemical shift differences for the $C_5H_5$ signals of 0.3–0.4 ppm. For the ester derivatives V–VII which do not contain aryl groups the $C_5H_5$ chemical shift differences are about 0.1 ppm, whereas for the ester derivatives VIII–X containing aryl groups they rise to 0.35–0.63 ppm. In the case of the thioamidato complexes this upfield shift has been interpreted on the basis of the "β-phenyl effect", the tendency of the phenyl substituent at the asymmetric center β to the metal atom to stay in the preferred isomer in the proximity of the $MC_5H_5$ moiety (conformation 1). Thus, the $C_5H_5$ ring is exactly in the anisotropy "beam" of the phenyl ring.[15] On the basis of the β-phenyl effect the $^1H$ NMR spectra of complexes I–IV and also those of complexes V–VII in which the β phenyl is replaced by the less effective ester substituent can be rationalized. The complexes VIII–X show that aryl groups in positions other than β also induce big chemical shift differences in the $C_5H_5$

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**Table III.** Analytical Data and Physical Properties of $[C_5H_5Mo(CO)_2NN^*]PF_6$ Complexes (II-X)

| compd | formula (mol wt) | %C calcd | %C found | %H calcd | %H found | %N calcd | %N found | % yield | color | mp or dec pt, °C |
|---|---|---|---|---|---|---|---|---|---|---|
| II | $(C_{17}H_{19}N_2O_2Mo)PF_6$ (524.2) | 38.94 | 38.90 | 3.65 | 3.85 | 5.34 | 5.35 | 87 | carmine | 170-172[a] |
| III | $(C_{22}H_{21}N_2O_2Mo)PF_6$ (586.3) | 45.06 | 45.04 | 3.61 | 3.29 | 4.77 | 4.77 | 95 | deep red | 195-197[a] |
| IV | $(C_{23}H_{23}N_2O_2Mo)PF_6$ (600.3) | 46.01 | 45.46 | 3.86 | 3.87 | 4.66 | 4.50 | 63 | brownish red | 230-231[b] |
| V | $(C_{17}H_{17}N_2O_4Mo)PF_6$ (554.2) | 36.84 | 37.09 | 3.09 | 3.09 | 5.05 | 4.85 | 81 | red | 138-140[a] |
| VI | $(C_{18}H_{19}N_2O_4Mo)PF_6$ (568.3) | 38.05 | 37.84 | 3.37 | 3.30 | 4.93 | 5.02 | 85 | red | 168[b] |
| VII | $(C_{19}H_{21}N_2O_4Mo)PF_6$ (582.3) | 39.19 | 39.03 | 3.63 | 3.57 | 4.81 | 4.43 | 85 | brownish red | 185[b] |
| VIII | $(C_{23}H_{21}N_2O_4Mo)PF_6$ (630.3) | 43.82 | 43.74 | 3.35 | 3.16 | 4.44 | 4.44 | 85 | carmine | 176-178[a] |
| IX | $(C_{25}H_{22}N_3O_4Mo)PF_6$ (669.4) | 44.86 | 45.49 | 3.31 | 3.84 | 6.27 | 6.27 | 90 | brownish red | 107-110[a] |
| X | $(C_{29}H_{25}N_2O_4Mo)PF_6$ (706.3) | 49.31 | 49.12 | 3.55 | 3.48 | 3.97 | 4.22 | 82 | brownish red | 88[b] |

[a] Decomposition point. [b] Melting point.

signals of the diastereoisomers *RS'/SR'* and *RR'/SS'*. Obviously, the arrangement of the phenyl substituent at the asymmetric center $\beta$ to the metal atom close to the $MC_5H_5$ moiety in conformation 1 for the thioamidato complexes and in conformation 2b for the pyridinecarbaldimine complexes persists in solution and accounts for the $^1H$ NMR spectra and the optical inductions observed.

## Experimental Section

The experiments were carried out under nitrogen by using freshly distilled solvents. The amino acid ester hydrochlorides were converted into the free-ester bases by the literature method.[44]

**Synthesis of $[C_5H_5Mo(CO)_2NN^*]PF_6$ Complexes II-X.** A solution of 5 mmol of $C_5H_5Mo(CO)_3Cl$ and 7 mmol of Schiff base NN* in 100 mL of benzene was refluxed until the theoretical quantity of CO was liberated. The dark red crystals of dicarbonylcyclopentadienyl(pyridine-2-carbaldimine)molybdenum chloride separated out. They were filtered off and dissolved in the minimum quantity of ethanol. After filtration, about 100 mL of water was added to this solution. Addition of 7 mmol of ammonium hexafluorophosphate to the stirred solution resulted in the precipitation of the hexafluorophosphate salt, which was filtered, washed with water and ether, and then dried. The analytical data are given in Table III. Compounds II-X are readily soluble in acetone, alcohols, $CH_2Cl_2$, chloroform, and THF, sparingly soluble in benzene, and almost insoluble in ether and pentane.

The Schiff bases NN* used to prepare compounds II-X were derived from pyridine-2-carbaldehyde and the primary amines $H_2NCH(R^1)(R^2)$, with $(R^1)(R^2) = (CH_3)(C_6H_5)$ (I),[12] $(C_2H_5)(C_6H_5)$ (II), $(C_6H_5)(i\text{-}C_3H_7)$ (III), and $(CH_3)(C_2H_5)$ (IV), the amino acid methyl esters $H_2NCH(COOCH_3)(R_3)$, with $R^3 = CH_3$ (V), $C_2H_5$ (VI), $i\text{-}C_3H_7$ (VII), $CH_2C_6H_5$ (VIII), and $CH_2CCHNHC_6H_4$ (the substituent of tryptophan) (IX), and the phenylalanine benzyl ester $H_2NCH(COOCH_2C_6H_5)(CH_2C_6H_5)$ (X).

Compounds II-IV were prepared from racemic amines, while compounds V-X were prepared from optically pure amino acid esters.

**Diastereoisomer Separation.** Compound II was heated in the minimum quantity of a mixture of acetone-$CH_2Cl_2$-ethanol (20:3:1) needed for dissolution. On cooling the system to -25 °C for 15 h, we obtained a solid fraction enriched in the less soluble diastereoisomers. The separation can be monitored by $^1H$ NMR spectroscopy as the diastereoisomers differ in the chemical shifts of their signals. Fractionation of compound IV was carried out by the same procedure whereas for compounds III and V-IX the minimum quantity of acetone-$CH_2Cl_2$-ether (1:4:2) necessary for dissolution was used. Fractionation of compounds III and V gave diastereoisomerically pure samples after one crystallization. With compound X only a pure sample of the less soluble fraction could be obtained. These diastereoisomer separation experiments revealed the following general relationship: the less soluble diastereoisomers in the $^1H$ NMR spectrum show the high-field $C_5H_5$ signal and the more soluble diastereoisomers the low-field $C_5H_5$ signal.

**Diastereoisomer Equilibration.** The fractions enriched in the more soluble and less soluble diastereoisomers, respectively, were dissolved in acetone-$d_6$ and sealed in NMR tubes. The diastereoisomer equilibria were approached from both sides except for compound X, for which only a sample enriched in the less soluble diastereoisomers was available. To fully equilibrate the samples, we heated them at 80 °C for 15 h. After freezing out the isomer interconversion by cooling, we recorded the room-temperature $^1H$ NMR spectra on an expanded scale with a Bruker WH 90 spectrometer.

The diastereoisomer ratio at equilibrium was determined from the $C_5H_5$ signals (compounds II, III, V, IX, and X), the $CH_3$ signals (compound IV), and both the $C_5H_5$ and the $COOH_3$ signals (compounds VI-VIII), by using a planimeter. The reproducibility within a series of spectra was found to be better than 1.5%.

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**Registry No.** I (*RS'/SR'*), 72377-37-8; I (*SS'/RR'*), 72377-39-0; II (*RS'/SR'*), 72347-16-1; II (*SS'/RR'*), 72377-41-4; III (*RS'/SR'*), 72347-18-3; III (*SS'/RR'*), 72377-43-6; IV (*RS'/SR'*), 72347-20-7; IV (*SS'/RR'*), 72377-45-8; V (*RS'/SR'*), 72347-22-9; V (*SS'/RR'*), 72377-47-0; VI (*RS'/SR'*), 72347-24-1; VI (*SS'/RR'*), 72377-49-2; VII (*RS'/SR'*), 72347-26-3; VII (*SS'/RR'*), 72377-51-6; VIII (*RS'/SR'*), 72347-28-5; VIII (*SS'/RR'*), 72377-53-8; IX (*RS'/SR'*), 72347-30-9; IX (*SS'/RR'*), 72377-55-0; X (*RS'/SR'*), 72347-32-1; X (*SS'/RR'*), 72401-46-8; $C_5H_5Mo(CO)_3Cl$, 12128-23-3.

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