Optically Active Transition-metal Compounds.[†],[*] Stereochemistry and Crystal Structure Determination of $[(\eta^5\text{-}C_5H_5)CoI\text{-}NC_5H_4\text{-}C(R)=N\text{-}CH(CH_3)(C_6H_5)]^+I^-$, R = CH_3

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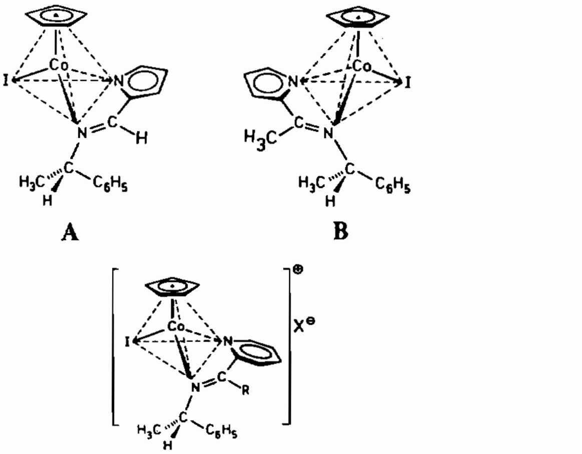
Abstract

The crystal structure and absolute configuration of the title compound has been determined by single-crystal X-ray diffraction. The crystals are orthorhombic with a = 11.837(6), b = 12.206(6) and c = 14.523(7) Å, space group $P2_12_12_1$ and d(calc., Z = 4) = 1.91 gm cm^{-3}. The structure was refined to the final agreement factors of $R(F)$ = 0.061 and $Rw(F)$ = 0.059. The Co–I bond is 2.584(2) Å which is significantly shorter than that observed in related complexes where the metal is bonded to pyrrole instead of pyridine. The two Co–N bonds are quite different; the Co–N (imine) bond being longer (1.99(1) Å) than the Co–N (pyridine) one (1.91(1) Å). The configuration around the chiral carbon and the Co atom has been determined using the Bijvoet method. The conformation of the $CH(CH_3)(C_6H_5)$ substituent with respect to the plane of the chelate ring is in accord with the concept of minimal steric hindrance simultaneously allowing for phenyl/C_5H_5 attraction.

Introduction

From the reaction of $(C_5H_5)Co(CO)I_2$ with the Schiff bases NN*, derived from 2-pyridine-carbaldehyde, 2-acetylpyridine, 2-benzoylpyridine, 2-pyrrole-carbaldehyde, 2-acetylpyrrole, (–)-1-phenylethylamine, and (–)-3-aminomethylpinane, a number of new complexes has been prepared and characterized [1]. The compounds derived from pyrrole Schiff bases NN* are neutral molecules $C_5H_5Co(NN^*)I$ because the chelate ligands NN* are incorporated as anions, whereas the complexes derived from pyridine Schiff bases NN* are salts $[C_5H_5Co(NN^*)I]^+X^-$ with X = I^- or PF_6^- as counterions. Recently, we have determined the X-ray structures and absolute configurations of two neutral complexes **A** and **B** derived from the pyrrole Schiff bases differing only in the substituent at the imine carbon of the chelate ring (Scheme 1), and compared their conformations with those found in solution [2]. We now report the crystal structure and absolute configuration of the ionic complex **III** obtained by the reaction between $C_5H_5Co(CO)I_2$ with the Schiff base, derived from 2-acetylpyridine and (S)-(–)-1-phenylethylamine, having I^- as counterion. Compound **III** is one out of a set of six compounds differing



	I	II	III	IV	V	VI
R	H	H	CH_3	CH_3	C_6H_5	C_6H_5
X	I	PF_6	I	PF_6	I	PF_6

Scheme 1.

[†] Part 23 of Ivan Bernal's series. For part 22 see ref. 4.

[*] Simultaneously part 89 of Henri Brunner's series. For part 88 see ref. 4.

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in R and X (Scheme 1). **III** was crystallized from methanol/THF/petrol ether to give crystals suitable for an X-ray structure determination. The results obtained are compared with the solution stereochemistry of compounds **I–VI** described before [2].

Experimental

Intensity measurements were carried out on a Philips PW 1100/20 four-circle computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing is given in Table I. Lorentz and polarization factors were applied in converting intensities to structure factor amplitudes, $|F_o|$; no absorption corrections were made. All data processing and calculations were carried out using the SHELX-76 [3] system of programs. The structure was solved by the Patterson technique which gave the positions of the iodine atoms. All the remaining non-hydrogen atoms, as well as the hydrogens of the pyridine ring and of the chiral carbon, C(7), were found from successive difference-Fourier maps. Since there was no reason to expect any distortions in the geometry of the phenyl ring, it was refined as rigid-body (with the C–C bonds of 1.395 Å and idealized hydrogens at C–H = 1.00 Å). The η^5-C_5H_5 ring was treated in a similar manner. The hydrogens belonging to the phenyl, η^5-C_5H_5 and the methyl groups were refined using a single isotropic temperature factor for each unit. The hydrogens of the pyridine ring and of the chiral carbon were introduced in the final cycle of least-squares, but were not refined. Full matrix least-squares refinement (anisotropic refinement of all the non-hydrogen atoms except of the phenyl and the η^5-C_5H_5 carbons and hydrogens which were isotropically refined) lead to the final agreement factors listed in Table I. Final positional and thermal parameters are listed in Table II. Bond lengths, angles, least-squares planes are presented in Tables III–V. The atomic labelling scheme employed is shown in Fig. 1. The labelling system used for the hydrogens is such that their numbers are identical to those of the carbons they are attached to. A packing diagram is presented in Fig. 2. The stereodrawings were obtained using Johnson's ORTEP 2 [4].

TABLE I. Summary of Data Collection and Processing Parameters.

Space Group	$P2_12_12_1$
Cell Constants	a = 11.837(6) Å b = 12.206(6) c = 14.523(7)
Cell Volume	2098.3 Å^3
Molecular Formula	$C_{20}N_2CoI_2H_2$
Molecular Weight	602.1 g mol^{-1}
Density (calc., Z = 4)	1.91 g cm^{-3}
Radiation	MoK_α (λ = 0.71075 Å)
Absorption Coefficient	35.36 cm^{-1}
Data Collection Range	$5° \leq \theta \leq 50°$
Scan Width	1.15° ω
Scan Speed	1.5° ω min^{-1}
Total Data Collected	2092
Reflections with $F_o > 1.50\sigma(F_o)$	1913
Total Variables	158
$R(F)$	0.061
$R_w(F)$	0.059
Weighting Scheme	$1.505/\sigma^2(F_o)$

TABLE II. Atomic Positional Parameters (X10^5 for the Iodine Atoms. 10^4 for all Others) and Thermal Parameters (10^4 for Iodine and Cobalt Atoms, 10^3 for all Others).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	41099(9)	84753(9)	89665(8)	580(6)	532(6)	597(6)	–108(6)	21(6)	–150(5)
I(2)	2566(10)	57789(10)	59672(8)	633(7)	786(8)	493(6)	57(7)	–37(6)	3(6)
Co(1)	2561(2)	7176(2)	6351(1)	372(10)	436(11)	357(10)	5(9)	71(9)	–27(10)
N(1)	2298(10)	8124(10)	7324(8)	34(6)	47(7)	40(7)	0(6)	5(6)	6(6)
N(2)	3563(10)	6435(10)	7440(8)	43(6)	36(7)	41(7)	0(6)	8(6)	–3(6)
C(1)	1701(15)	9069(15)	7339(13)	52(10)	60(11)	73(11)	–8(10)	10(10)	26(10)
C(2)	1579(17)	9733(16)	6546(18)	75(13)	50(11)	124(18)	14(12)	–27(13)	16(10)
C(3)	2049(17)	9416(15)	5783(13)	104(13)	53(11)	68(13)	17(10)	–8(10)	3(10)
C(4)	2752(15)	8468(11)	5739(10)	66(12)	38(6)	54(10)	15(7)	–14(9)	–14(8)
C(5)	2818(11)	7830(13)	6555(11)	41(8)	44(9)	51(9)	–1(8)	–17(7)	–5(7)
C(6)	3494(12)	6852(12)	6624(10)	40(8)	33(8)	43(8)	3(7)	–5(7)	–5(7)
C(7)	4305(13)	5479(12)	7509(10)	47(9)	39(6)	50(8)	5(7)	–5(7)	9(7)

(continued on facing page)

TABLE II. *(continued)*

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(8)	5147(13)	5738(14)	8368(12)	48(9)	51(10)	96(12)	18(10)	−20(9)	2(8)
C(9)	4077(15)	6425(12)	5771(9)	104(12)	59(8)	44(7)	−8(6)	9(8)	−16(10)
C(10)	3590(9)	4435(7)	7732(7)	46(4)					
C(11)	2741(9)	4202(7)	7096(7)	62(5)					
C(12)	2126(9)	3231(7)	7168(7)	74(6)					
C(13)	2360(9)	2493(7)	7877(7)	84(5)					
C(14)	3209(9)	2727(7)	8513(7)	77(5)					
C(15)	3824(9)	3698(7)	8441(7)	57(5)					
C(16)	1454(11)	5857(8)	8568(8)	61(4)					
C(17)	2205(11)	5958(8)	9346(8)	73(5)					
C(18)	2068(11)	7021(8)	9726(8)	75(5)					
C(19)	1233(11)	7576(8)	9203(8)	73(6)					
C(20)	353(11)	6858(8)	8500(3)	63(5)					
H(1)	1222(0)	9364(0)	7959(0)	80(0)					
H(2)	1062(0)	10475(0)	6539(0)	80(0)					
H(3)	2042(0)	9886(0)	5118(0)	80(0)					
H(4)	3183(0)	8187(0)	5116(0)	80(0)					
H(7)	4126(0)	4844(0)	7097(0)	60(0)					
H(8A)	4968(13)	6469(14)	8644(12)	22(4)					
H(8B)	5934(13)	5747(14)	8118(12)	22(4)					
H(8C)	5084(13)	5159(14)	8853(12)	22(4)					
H(9A)	3888(15)	6903(12)	5233(9)	14(4)					
H(9B)	3526(15)	5658(12)	5643(9)	14(4)					
H(9C)	4912(15)	6435(12)	5876(9)	14(4)					
H(11)	2573(9)	4730(7)	6588(7)	11(2)					
H(12)	1517(9)	3063(7)	6712(7)	11(2)					
H(13)	1919(9)	1797(7)	7928(7)	11(2)					
H(14)	3377(9)	2198(7)	9021(7)	11(2)					
H(15)	4433(9)	3865(7)	8897(7)	11(2)					
H(16)	1364(11)	5197(3)	8187(8)	17(3)					
H(17)	2737(11)	5381(8)	9572(8)	17(3)					
H(18)	2487(11)	7325(8)	10267(8)	17(3)					
H(19)	960(11)	3342(8)	9311(8)	17(3)					
H(20)	265(11)	7027(8)	8026(8)	17(3)					

TABLE III. Intramolecular Bond Distances (Å).

Co–I	2.584(2)	C2–C3	1.30(3)
Co–N1	1.91(1)	C3–C4	1.43(2)
Co–N2	1.99(1)	C4–C5	1.42(2)
Co–C16	2.10(1)	N1–C5	1.32(2)
Co–C17	2.11(1)	C5–C6	1.44(2)
Co–C18	2.09(1)	C6–C9	1.51(2)
Co–C19	2.06(1)	C6–N2	1.29(2)
Co–C20	2.07(1)	N2–C7	1.48(2)
Co–Cent[a]	1.69(1)	C7–C8	1.52(2)
N1–C1	1.35(2)	C7–C10	1.54(2)
C1–C2	1.41(3)		

[a] Cent: centroid of (η^5-C_5H_5) ring.

TABLE IV. Intramolecular Bond Angles (°).

Cent–Co–I	120.4(1)	N1–C5–C6	115(1)
Cent–Co–N1	126.7(1)	C4–C5–C6	123(1)
Cent–Co–N2	130.6(1)	N2–C6–C5	115(1)
N1–Co–I	90.8(3)	N2–C6–C9	126(1)
N1–Co–N2	81.6(5)	C5–C6–C9	119(1)
N2–Co–I	94.9(3)	Co–N2–C6	113.1(9)
Co–N1–C1	126(1)	Co–N2–C7	126.9(8)
Co–N1–C5	114.6(9)	C6–N2–C7	120(1)
C1–N1–C5	119(1)	N2–C7–C8	110(1)
N1–C1–C2	121(2)	C8–C7–C10	117(1)
C1–C2–C3	119(2)	N2–C7–C10	110(1)
C2–C3–C4	122(1)	C7–C10–C11	119.2(6)
C3–C4–C5	116(1)	C7–C10–C15	120.7(6)
N1–C5–C4	122(1)		

TABLE V. Least-Squares Planes Through Selected Groups of Atoms.

(a) Coefficients of $Ax + By + Cz - D = 0$

		A	B	C	D
Plane 1:	pyridine N1, C1, C2, C3, C4, C5	−0.8118	−0.5201	−0.2655	−10.208
Plane 2:	chelate ring Co, N1, N2, C4, C5	−0.7773	−0.5749	−0.2556	−10.517
Plane 3:	(η^5-C_5H_5) C15–C19	0.7097	0.3488	−0.6122	−3.921
Plane 4:	phenyl C9–C14	0.6678	−0.4619	−0.5837	−6.218

(b) Dihedral Angles (°)

1/2	2/3	3/4
3.75	126.56	47.92

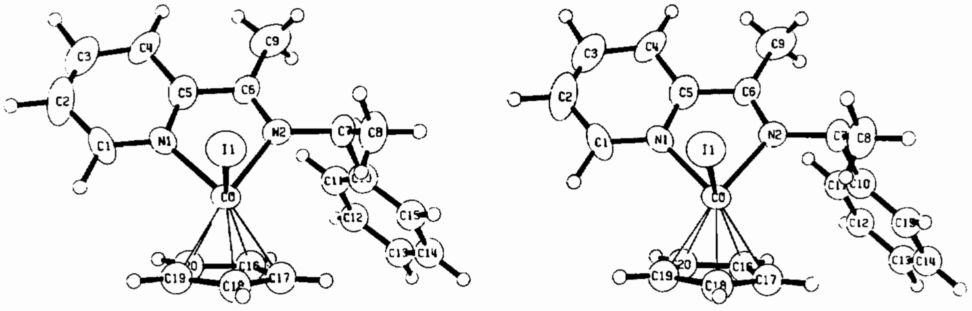


Fig. 1. Stereoscopic view of the cation of III showing the atomic labelling scheme. The thermal ellipsoids are 50% equiprobability envelopes with hydrogens of arbitrary size.

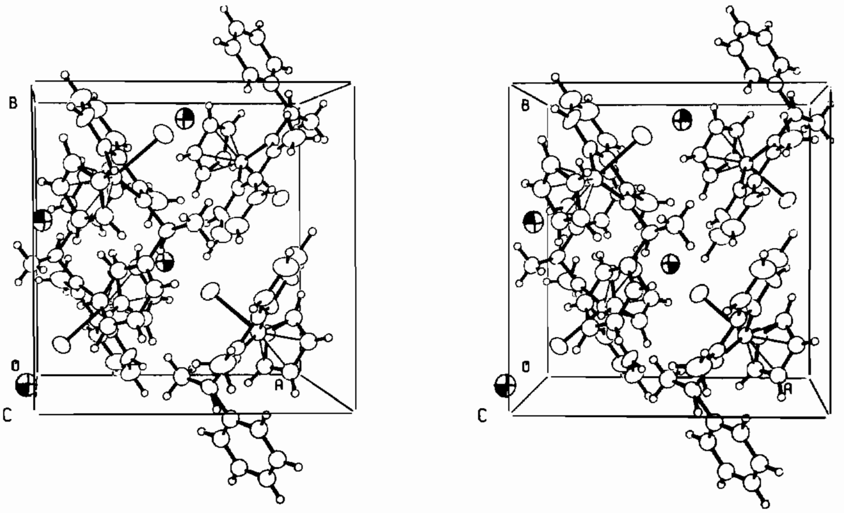


Fig. 2. Stereoscopic view of the packing of III.

Determination of Absolute Configuration

The absolute configuration was determined by the Bijvoet method [5]. After refinement convergence, twelve reflections showed marked differences between *Fc*(*hkl*) and *Fc*($\overline{h}\overline{k}\overline{l}$) (Table VI). These reflections were measured and the results clearly show that the coordinates initially chosen correspond to those of the correct enantiomer.

Applying the extension of the RS system [6] to polyhapto ligands in organometallic complexes

TABLE VI. Determination of Absolute Configuration.

Indices	$F_c(hkl)$	$F_c(\bar{h}\bar{k}\bar{l})$	$F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})$	$F_{obs}(hkl)/F_{obs}(\bar{h}\bar{k}\bar{l})$
2,1,1	48	42	1.14	1.17
6,3,1	37	34	1.09	1.08
4,4,1	99	95	1.04	1.04
2,6,1	39	42	0.93	0.91
3,2,2	34	37	0.92	0.94
1,5,2	27	25	1.08	1.06
8,5,2	39	42	0.93	0.94
7,3,4	24	26	0.92	0.86
5,2,6	29	27	1.07	1.05
2,3,6	28	30	0.93	0.97
1,2,7	82	79	1.04	1.06
2,8,7	87	84	1.04	1.02

[7], the priority sequence of the ligands at the Co atom is I > (η^5-C_5H_5) > N(imine) > N(pyridine). Consequently, the configuration around the metal atom is R. The configuration around C(7), the chiral carbon derived from the optically active amine is also R (the priority sequence of the ligands around C(7) being N(imine) > C(phenyl) > C(methyl) > H).

A recent study of the crystal structure and absolute configuration of the related neutral complex derived from the pyrrole Schiff base NN* (prepared by using (S)-phenylethylamine) and having a methyl substituent at the imine carbon of the chelate ring (compound **B**) showed the configuration about the Co atom to be S [2]. An internal check on the results from **B** was that the Bijvoet test correctly predicted the configuration around the chiral carbon (derived from the optically active (S)-phenylethylamine) as being S. In order to more easily compare the stereochemistry of two compounds during the discussion, the coordinates of the present complex were inverted (Table II). Also, Figs. 1 and 2 represent the compound in its inverted, mirror image configuration.

For the purpose of documenting the effects of absorption on the Bijvoet test, we have also solved the crystal structure and determined the absolute configuration of another crystal from the same sample and refined it to $R(F) = 0.065$. The configuration around the central Co atom was found to be S and the chiral carbon atom also S (as expected). The compound is isomorphous and isostructural (except for the absolute configuration) with the first one.

Results and Discussion

Figure 1 gives a convenient stereoview of the cation of **III** as well as the numbering system employed in the crystallographic study. The cation consists of a central cobalt atom surrounded by iodine, pyridine and imine nitrogens and a (η^5-C_5H_5) group. Its geometry is very close (except for some small details) to that observed for compound **B**. The main difference between the two complexes is due to the fact that in compound **B** the central Co atom is bonded to the nitrogen of a pyrrole anion, whereas in the present case it is bonded to a neutral pyridine nitrogen. The bonding of the Co atom to different ligands leads to slightly different Co–N distances. Thus, the Co–N (pyrrole) distance of 1.885(9) Å observed for complex **B** is shorter than the Co–N (pyridine) bond of 1.91(1) Å found for complex **III**. A similar trend was observed also for related molybdenum complexes where the Mo–N (pyrrole) and Mo–N (pyridine) distances are 2.150(3) and 2.258(11) Å respectively [8, 9].

The reason for the shortening of the metal to pyrrole bond when compared to that of metal to pyridine is that the pyrrole nitrogen, once deprotonated, can not only bond the metal as effectively in the π sense as pyridine nitrogen but, bearing a negative charge, binds more strongly in the σ sense the charged Mo or Co. This difference in the Co–N bonds is probably the reason for the small, but significant shortening of the Co–I distance when changing from pyrrole to pyridine (2.607(2) *vs.* 2.58(2) Å). The shortening of the Co–I distance in the present compound is thus attributed to electronic effects.

The two Co–N bonds observed for complex **III** are quite different; the Co–N (imine) bond being significantly longer (1.99(1) Å) than the Co–N (pyridine) distance (1.91(1) Å). The same behavior was observed for complexes **A** and **B** where the Co–N (imine) bonds (1.971(8) and 2.003(9) Å) are significantly longer than the Co–N (pyrrole) bonds (1.905(9) and 1.885(8) Å). The same pattern was observed also by Bernal for the preferred diastereoisomer of $[(\eta^5\text{-}C_5H_5)Mo(CO_2)NN^*]PF_6$ with NN* = Schiff base derived from pyridine-2-carbaldehyde and

(S)-phenylethylamine where the Mo–N (imine) and Mo–N (pyridine) distances are 2.201(2) and 2.182(2), respectively [10]. Korp and Bernal reported the same trend for a different Mo complex in which the metal atom is bonded to pyrrole [8]. However, we note that the lengthening of the Mo–N (pyridine) distance (when compared to Mo–N (pyrrole) and steric hindrance (between pyridine and the (η^5-C_5H_5) ligand) lead to an inverted relationship in another related complex, with the Mo–N (pyridine) distance being longer (2.258(11) Å) than the Mo–N (imine) bond (2.182(10) Å) [9].

An additional difference between compound **B** and the present complex is, of course, in the angles around the nitrogen atom N(1), the biggest difference being in the Co–N(1)–C(1) angle (137(1)° for the pyrrole substituent and 126(1)° in the present case). All the remaining geometrical features found for **III** closely resemble those observed for compound **B** and are thus not discussed here.

Solution Stereochemistry of Compounds I–VI

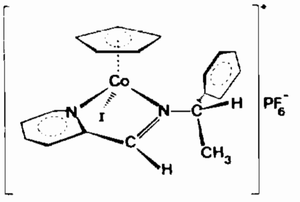
For the synthesis of complex **III** (S)-(–)-1-phenylethylamine, a product of BASF AG, was used. Therefore, the compound only should contain ligands with (S)-configurated carbon atoms. However, as described in the Experimental, the first crystal used for the X-ray structure determination unequivocally was shown to have (R)-configuration at the asymmetric carbon atom. This observation can only be explained by assuming that the (S)-(–)-1-phenylethylamine, used in the synthesis, contains some (R)-(+)-1-phenylethylamine and that the first crystal chosen derives from this impurity of (R)-(+)-1-phenylethylamine. The second crystal picked from the same batch has the expected (S)-configuration at the asymmetric carbon atom as does the bulk material according to the chiroptical measurements reported [1]. So, the following discussion is based on the results obtained with the second crystal containing the (S)-configurated carbon atom in the ligand.

In solution each of the complexes **I–VI** consists of two diastereomers differing only in the Co configuration, R and S, having the same ligand configuration S, if it is agreed upon that the synthesis starts with optically pure (S)-(–)-1-phenylethylamine. The diastereomer ratios in $CDCl_3$ solution, easily determined by ^1H NMR integration, for compounds **I–VI** at room temperature are in the range between 99:1 and 61:29 [1]. For compound **III**, specifically, the diastereomer ratio is 70:30.

For all six complexes **I–VI** there was no diastereomer separation or enrichment by fractional crystallization or chromatography. Solutions obtained from crystalline material, even solutions at low temperatures contained only the equilibrium mixtures [1]. Consequently, if there is isomer separation on crystallization, a fast change of the metal configuration in solution must take place. For **A** this fast isomerization at the Co atom has been demonstrated by the magnetization transfer due to chemical exchange [1].

The labile Co configuration probably originates from the dissociation tendency of the Co–I bond leading to configurationally labile solvates [1]. This hypothesis is supported by the easy substitution of the I^--ligands and by the high conductivities of solutions of complexes of the type **I–VI** [1].

For complex **VI**, 400 MHz ^1H NMR NOE difference spectra were obtained in acetone solution at 270 K [1]. On this basis, the (R)-configuration was assigned to the thermodynamically more stable diastereomer of **VI** (70% of $R_{Co}S_C$ at equilibrium), the thermodynamically less stable diastereomer being the ($S_{Co}S_C$)-form (30% at equilibrium). C*–H and C*–C(methyl) of the asymmetric center stagger the C–C(phenyl) bond at the adjacent imine carbon atom; the methyl substituent is between the ligand plane of NN* and η^5-C_5H_5.



Scheme 2.

The solution structure of compound **III** has not been studied by the NOE technique. However, the conformational analysis of analogous complexes revealed that for compounds containing the substituent R = CH_3 (**III, IV**) instead of R = C_6H_5 (**V, VI**), the assignment of the metal configuration to thermodynamically more stable and less stable diastereomers is the same because both substituents are large substituents [1, 2]. Thus, for **III** the thermodynamically more stable diastereomer in solution has ($R_{Co}S_C$)-configuration (70% at equilibrium) and the thermodynamically less stable diastereomer has ($S_{Co}S_C$)-configuration (30% at equilibrium). However, for compounds **I** and **II**, carrying the small substituent R = H at the imine carbon atom, it is the other way round, the ($S_{Co}S_C$)-isomer (Scheme 2) being the thermodynamically more stable and the ($R_{Co}S_C$)-isomer the less stable [1, 2]. So, the formula in Scheme 1, bottom, represents the thermodynamically more stable ($R_{Co}S_C$)-isomer for **I** and **II** and the thermodynamically more stable ($R_{Co}S_C$)-isomer for **III–VI**.

Comparison of Solid State and Solution Stereochemistry

The present X-ray structure determination shows that the crystal of **III** contains the ($S_{Co}S_C$)-isomer which is the thermodynamically less favored isomer in solution. Therefore, on crystallization, it must be assumed that the isomer present in the equilibrium mixture with only 30%, crystallizes first. Due to the labile Co configuration during crystallization at 243 K, a complete transformation into the (S_{Co}-S_C)-form takes place. Such a behavior, surprising in view of the share at equilibrium, has been observed before for similar compounds [1, 2].

For **III**, the conformation found in the solid state is completely in accord with the set of rules developed earlier to explain the intramolecular interactions [11–20]. For a compound like **III** with a methyl substituent at the adjacent imine carbon atom in the chelate ring only the conformation of the optically active group having the C*–H bond in the ligand plane avoids severe steric hindrance which C*–C(methyl) or C*–C(phenyl) would suffer in the ligand plane. Furthermore, in the conformation found in the X-ray structure analysis the molecule gains the phenyl/C_5H_5 attraction, called the β-phenyl effect [11–20].

It has been pointed out before that for compounds of type **III** the conformations found in the solid state reflect the intramolecular interactions better than the solution conformation, because the solution conformation may be largely influenced by ion pairing, absent in the solid state [1, 2].

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References

1 H. Brunner, G. Riepl, R. Benn and A. Rufinksa, *J. Organomet. Chem., 235,* 93 (1983).
2 I. Bernal, G. M. Reisner, H. Brunner and G. Riepl, *J. Organomet. Chem.,* submitted.
3 G. Sheldrick, 'SHELX-76'. Program for Crystal Structure Determination, University of Cambridge, 1976.
4 C. K. Johnson, 'ORTEP 2' A Fortran Ellipsoid Plot Program for Crystal Structure Illustration, ORNL-5138, Oak Ridge National Laboratory, Tenn., 1972.
5 J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature (London), 168,* 271 (1951).
6 R. S. Cahn, C. Ingold and V. Prelog, *Angew. Chem., Int. Ed. Engl., 5,* 385 (1966).
7 K. Stanley and M. C. Baird, *J. Am. Chem. Soc., 97,* 6598 (1975).
8 J. Korp and I. Bernal, *Polyhedron, 1,* 617 (1982).
9 I. Bernal, S. J. LaPlaca, Y. Korp, H. Brunner and W. Herrmann, *Inorg. Chem., 17,* 382 (1978).
10 I. Bernal, private communication.
11 H. Brunner, G. Agrifoglio, I. Bernal and M. W. Creswick, *Angew. Chem., Int. Ed. Engl., 19,* 641 (1980).
12 I. Bernal, M. W. Creswick, H. Brunner and G. Agrifoglio, *J. Organomet. Chem., 198,* C4 (1980).
13 H. Brunner, J. Lukassek and G. Agrifoglio, *J. Organomet. Chem., 195,* 63 (1980).
14 H. Brunner and G. Agrifoglio, *J. Organomet. Chem., 202,* C43 (1980).
15 H. Brunner, G. Agrifoglio, R. Benn and A. Rufińska, *J. Organomet. Chem., 217,* 365 (1981).
16 H. Brunner, in A. Müller and E. Diemann (eds.), 'Transition Metal Chemistry', Verlag Chemie, Weinheim, Deerfield Beach, Basle, 1981, p. 265.
17 H. Brunner and D. K. Rastogi, *Inorg. Chem., 19,* 891 (1980).
18 H. Brunner and B. Schönhammer, *Z. Naturforsch., Teil B:, 38,* 852 (1983).
19 M. Creswick and I. Bernal, *Inorg. Chim Acta, 57,* 171 (1982).
20 H. Brunner, *Angew. Chem. Int. Ed. Engl., 22,* 897 (1983).