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Preliminary communication

CONFORMATIONAL ANALYSIS AND CHIRALITY TRANSMISSION IN ORGANOMETALLIC COMPOUNDS: X-RAY STRUCTURE ANALYSIS OF $C_5H_5(CO)_2MoN(CH_2C_6H_5)C(C_6H_5)N[CH(CH_3)(C_6H_5)]$

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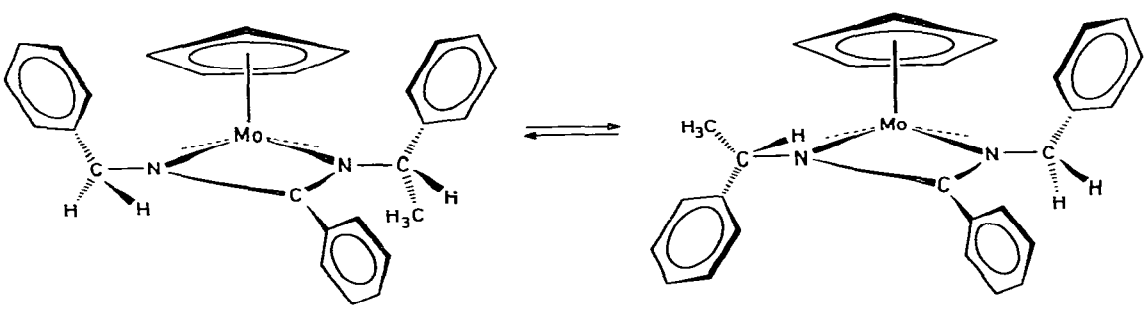
Summary

The structure and absolute configuration of $C_5H_5(CO)_2MoN(CH_2C_6H_5)$-$C(C_6H_5)N[CH(CH_3)(C_6H_5)]$ was determined to establish the rules governing the conformation of chiral substituents on chelate rings.

Complexes like $C_5H_5(CO)_2MoN(R')C(R)N(R^*)$ with asymmetric centers at the Mo atom and in $R^* = CH(CH_3)(C_6H_5)$ exist in diastereoisomeric forms which in solution interconvert in first-order metal-centered rearrangements [1]. We have previously reported the molecular structure of A ($R' = CH_2C_6H_5$, $R = C_6H_5$), the diastereoisomer predominating at equilibrium [2]. Now we present X-ray crystallographic data for the less stable diastereoisomer, B. This constitutes the first example of a structural comparison between optically active transition metal complexes differing only in configuration at the central metal atom. It confirms our rationale for the relative stability of such pairs of dia-



A B

stereoisomers, and provides further insight into the way in which chiral information may be transmitted in asymmetric catalysis.

$(+)_{578}$-$C_5H_5(CO)_2MoN(CH_2C_6H_5)C(C_6H_5)N[(S)$-$CH(CH_3)(C_6H_5)]$: Crystal data: orthorhombic, space group $P2_12_12_1$, a = 9.885(3), b = 11.550(5), c = 22.260(9) Å, V = 2623.7 Å^3, D_c = 1.34 g cm^{-3}, μ(Mo-K_α) = 4.58 cm^{-1}, Z = 4. 3830 reflections were measured with a computer controlled diffractometer in the range $4.0° \leq 2\theta \leq 65.0°$, of which 1893 were used in the solution and refinement [$2\sigma(I)$ cut off]. The structure was solved by Patterson and difference Fourier methods and was refined, with rigid body constraints applied to the Cp and phenyl groups, to the final agreement factor: $R(F)$ = 0.043. The absolute configuration was determined by the Bijvoet method. The results indicate that the absolute configuration at the Mo atom is (*S*) provided the priority sequence η^5-C_5H_5 > $NCH(C_6H_5)(CH_3)$ > $NCH_2C_6H_5$ > CO is used [3]. At C(22) the absolute configuration is also (*S*).

On the basis of X-ray crystallographic evidence and of the diastereoisomer ratios A/B at equilibrium as well as the C_5H_5 chemical shift differences of $C_5H_5(CO)_2Mo$ thioamidato and amidinato complexes, the following rules were formulated concerning the conformation of the N substituents R* and R′ with respect to the $C_5H_5(CO)_2Mo$ chelate fragment which are valid for the solid state and for solution [1,2]:

(1) C—H lies in the ligand plane and points away from the metal to minimize steric hindrance with substituent R at the adjacent carbon atom.
(2) There is a phenyl—Cp attractive interaction (β-phenyl effect).
(3) Alkyl and Cp interactions are sterically undesirable.

As the ORTEP drawing of *B* in Fig. 1 shows, the benzyl substituent strictly adheres to rules (1) and (2) with a C—H bond in the ligand plane and phenyl oriented towards the Cp ring. However, the arrangement of the chiral substituent R* does not exactly follow rules (1) to (3). Looking down the C(22)—N(2) axis, R* is rotated counter-clockwise by 45.6° compared to the conformation expected on the basis of rules (1) to (3), which places the C—H bond approximately midway between the ligand plane and the MC_5H_5 moiety. The reason for this may lie in factor (3), the C_5H_5—alkyl repulsion, which is relieved to some extent by this rotation without bringing the phenyl of R* too close to the ligand plane. Nevertheless, this 45.6° angle of the C—H bond with respect to the ligand plane is the largest deviation observed hitherto, the angles between the C—H bonds and the ligand plane in the other 8 molecules studied being less than 10° [2,4]. As usual, the C—phenyl substituent is perpendicular to the ligand plane.

The results of the spectroscopic studies of about 50 thioamidato [5] and amidinato complexes [1] and the X-ray structural analyses of 7 molecules of the more stable type A isomers [2,4] show that the potential energy curves for rotation around the N—C(R*) bond have high barriers, conformation A representing a deep minimum (effects (1) through (3) cooperative). The two X-ray analyses available for B-type isomers [4] indicate that the potential energy curve for C—N(R*) bond rotation is much shallower (effects (1) through (3) non-cooperative). Whereas the solution chemistry of isomers A and B is completely in accord with rules (1)—(3) [1] the conformation of the less stable B isomer found in this study, unlike that of the type A isomers [2,4,5], may be influenced by packing forces.

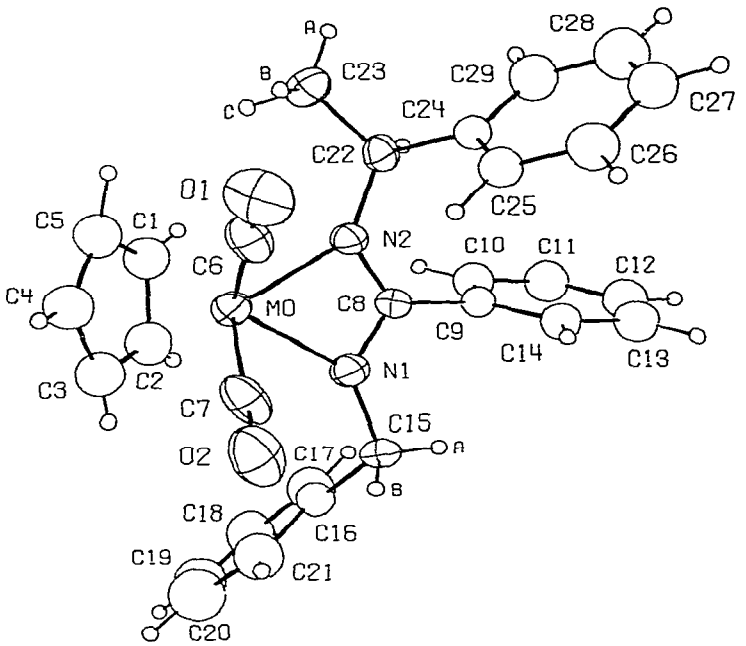


Fig. 1. Absolute configuration of B.
Mo is located 1.02 Å above the plane of C(6), C(7), N(1), and N(2). Some bond lengths and angles: Mo—CO, 1.98 av.; Mo—N, 2.17 av.; Mo—C(Cp) 2.28—2.41; and Mo—Cp (centroid), 2.03 Å; C(6)—Mo—C(7), 75.5; C(6)—Mo—N(1), 118.2; C(7)—Mo—N(2), 121.5, N(1)—Mo—N(2), 58.9; N(1)—C(8)—N(2), 109.5°; selected torsional angles: N(1)—Mo—Cp—C(2), 2.84; N(2)—Mo—Cp—C(1), −2.76; Mo—N(1)—C(15)—C(16), 57.8; Mo—N(1)—C(15)—H(15A), −175.24; Mo—N(2)—C(22)—C(24), 115.9; Mo—N(2)—C(22)—H(22), −134.6; and N(2)—C(8)—C(9)—C(10), −76.7°.

The conformational analysis given bears relevance to asymmetric catalysis because a well-defined orientation of a chiral substituent R* at nitrogen in a chelate ring will control the stereochemistry at adjacent coordination positions in a definite way. In most of the catalysts thus far used in asymmetric catalysis, the chiral information is located in the backbone of an optically active chelate phosphine and transmitted to the catalytically active metal sites mainly by the arrangements of the phenyl rings of $P(C_6H_5)_2$ groups [6]. In a catalyst, the coordination positions occupied in A or B by CO being the sites for a prochiral substrate, a direct transfer of the chiral information from substituent R* to the active site can be envisaged without the need for a chirality transmitter.

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