Synthesis, Epimerization, *X*-Ray Structure, and Absolute Configuration of an Optically Active Molybdenum Complex Having Five Independent Ligands

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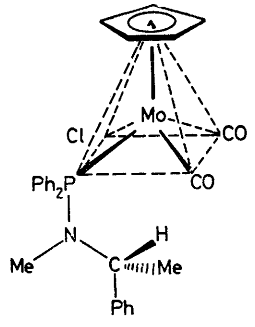
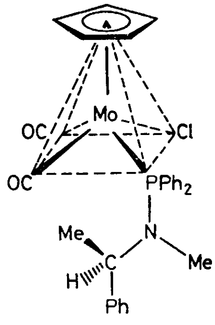
Summary Synthesis and epimerization of $[C_5H_5Mo(CO)_2\{(S)\text{-PN*}\}Cl]$ [(*S*)-PN* = (*S*)-(+)-$Ph_2PN(Me)CH(Me)(Ph)$], the first optically active square-pyramidal molecule containing 5 independent ligands, are reported; the absolute configuration at the Mo atom is determined by *X*-ray crystallography to be (*S*).

In square-pyramidal complexes $[C_5H_5Mo(CO)_2LX]$, the C_5H_5 group always occupies the top of the pyramid.[1] Depending on the arrangement of the remaining 4 ligands at the square base, there are *cis* and *trans* isomers, the *cis*-isomers forming enantiomeric pairs. If L and X are combined into one chelate ligand, only *cis*-isomers are possible, the separation of which has been carried out for several derivatives.[2] Recently, the separation of *cis* and *trans* isomers for monodentate ligands L and X was reported.[3] We describe here for the first time the synthesis, absolute configuration, and interconversion by epimerization at the metal atom of optically active *cis*-isomers $[C_5H_5Mo(CO)_2LX]$ with 5 independent ligands which differ only in the configuration at the Mo atom.

In the reaction of $[C_5H_5Mo(CO)_3Cl]$ with (*S*)-(+)-$Ph_2PN(Me)CH(Me)(Ph)$ [(*S*)-PN*] only the two *cis*-isomers, (+)-(**1a**) and (−)-(**1b**) with opposite Mo-configurations, are formed. The mixture can be purified by column chromatography on silica gel using CH_2Cl_2 (yield 70%). The isomers (+)-(**1a**) and (−)-(**1b**) exhibit different chemical shifts (measured on Bruker WH90 spectrometer in $CDCl_3$) for the *N*-methyl [τ 7·55 and 7·59 (d, J_{Me-CH} 8·5 Hz)] and the *C*-methyl [τ 8·41 and 8·58 (d,J_{Me-CH} 7 Hz)] groups but the same chemical shifts for the C_5H_5 signals (τ 4·63) and the same CO stretching frequencies (1970 and 1885 cm^{-1}, KBr). The compounds decomposed during attempts to record their mass spectra.



(-)-(1a)



(+)-(1b)

When the mixture of (+)-(**1a**) and (−)-(**1b**) is crystallised from pentane–methylene chloride (3:1) at −20 °C, the proportion of the less soluble diastereoisomer (+)-(**1a**) increases (90:10) as determined by integration of the low temperature ^1H n.m.r. spectrum ([α]$^{-30}_{436}$ 2100°, 2 mg ml^{-1}, toluene). The high-field Me-signals in the spectrum are assigned to (+)-(**1a**). In solution at room temperature, (+)-(**1a**) is rapidly converted into an equilibrium mixture {(+)-(**1a**):(−)-(**1b**) 55:45; [α]$^{25}_{436}$ 75°}. The reaction in toluene was followed polarimetrically in the temperature range −10 to 0 to 10 °C. For the first-order approach to equilibrium, the half-lives $t_{1/2}$ = 109·5, 27·0, and 7·5 min were found (E_A = 20·2 ± 0·4 kcal mol^{-1}). Neither the addition of (*S*)-PN* nor variations in concentration of (+)-(**1a**) change the rate of epimerization. There is no phosphine exchange during epimerization, as demonstrated by ^{1}H n.m.r. measurements, on addition of (*S*)-(+)-$Ph_2PNHCH(Me)(Ph)$. Even at −20 °C, the rate of equilibration is rapid compared to the rate of crystallization. Keeping the isomers in pentane–methylene chloride solution at −20 °C can be used to disturb the equilibrium and results in the isolation of a crystalline material which is predominantly the less soluble diastereoisomer (+)-(**1a**). If the crystallization is carried out at −60 °C, the isomer ratio of the crystalline product is identical to that of the equilibrium mixture.

When the aminophosphine with opposite configuration, (*R*)-(−)-$Ph_2PN(Me)CH(Me)(Ph)$ [(*R*)-PN*], was used in the above experiments, the respective diastereoisomers (−)-(**1a**) and (+)-(**1b**) were formed, the properties of which, including the composition at equilibrium and the rate of epimerization, are identical with those of the (*S*)-PN* complexes (+)-(**1a**) and (−)-(**1b**), except for the sign of the chiroptical parameters. The structure of (−)-(**1a**) has been determined by *X*-ray crystallography.

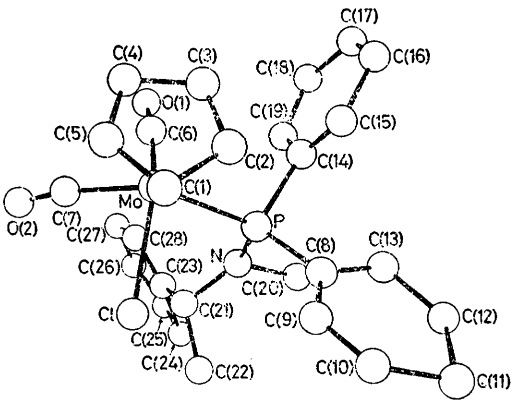


FIGURE. *X*-Ray crystal structure of [$C_5H_5Mo(CO)_2$\{(*R*)-PN*\}Cl] (−)-(**1a**). All distances and angles within the ligands agree with standard values. The Mo atom is located 0·90 Å above the plane defined by Cl, P, C(6), and C(7). The metal–ligand bond lengths and angles are as follows: Mo–Cl, 2·49(2); Mo–P, 2·58(1); Mo–CO, 1·89(6); Mo–C(Cp), in the range 2·29(7)—2·44(6); and Mo–Cp (ring centroid), 1·99 Å; ∠Cl–Mo–P, 85·2(5); ∠Cl—Mo—C(6), 136·3(1·8); ∠Cl–Mo–C(7), 81·1(2·6); ∠P–Mo–C(6), 80·7(1·4); ∠P–Mo–C(7), 125·9(2·0); and C(6)–Mo–C(7), 74·5(2·6)°.

Crystal data: orthorhombic, space group $P2_12_12_1$, a = 9·172(3), b = 16·265(7), c = 22·470(7) Å; U = 3352·1 Å^3 D_c = 1·13 g cm^{-3}, μ(Mo-K_α) = 5·30 cm^{-1}, Z = 4. 1265 reflexions were measured in the range 4·0° $\leqslant 2\theta \leqslant$ 35·0°, of which 942 were used in the solution and least-squares refinement [$R(F)$ = 0·11]. To test the absolute configuration, the reflections 2,3,4; 1,1,1; 1,2,4; 1,3,1, and their Friedel pairs were measured, four times each, and the ratios of the averaged values, $F(hkl):F(\bar{h}\bar{k}\bar{l})$, were compared with their respective calculated ratios. The results clearly indicate that the absolute configuration at the Mo atom is (*S*),[4] provided the priority sequence $C_5H_5 > Cl > P$ is used, and at the C atom, C(21), is (*R*) (Figure). The data were measured with a computer-controlled diffractometer.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] K. W. Barnett and D. W. Slocum, *J. Organometallic Chem.*, 1972, **44**, 1.

[2] D. L. Beach and K. W. Barnett, *J. Organometallic Chem.*, 1975, **97**, C27; R. B. King, R. H. Reimann, and D. J. Darensbourg, *ibid.*, 1975, **93**, C23; R. B. King and R. H. Reimann, *Inorg. Chem.*, 1976, **15**, 179.

[3] H. Brunner, *Ann. New York Acad. Sci.*, 1974, **239**, 213; *Topics Current Chem.*, 1975, **56**, 67; *Chemie in unserer Zeit.*, 1977, **11**, 157.

[4] I. Bernal, S. J. LaPlaca, J. Korp, H. Brunner, and W. A. Herrmann, *Inorg. Chem.*, 1978, **17**, 382; M. G. Reisner, I. Bernal, H. Brunner, and J. Wachter, *J. Organometallic Chem.*, 1977, **137**, 329.