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EVIDENCE FOR CHIRAL ORGANOMETALLIC INTERMEDIATES IN STEREOSPECIFIC PHOSPHINE EXCHANGE REACTIONS*

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Manganese esters of the type $C_5H_5Mn(COOR)(NO)P(C_6H_5)_3$ with 4 different ligands around the metal atom can be prepared and resolved into the optically active components by established methods [1-3]. These new optically active complexes are configurationally stable in the solid state but configurationally labile in solution [4]. If the methyl esters (+)- and (—)-$C_5H_5Mn(COOCH_3)(NO)P(C_6H_5)_3$ (+I and —I) are dissolved in benzene at 30°C specific rotations of about +2500° and —2500° can be measured [2,3]. These rotations decrease exponentially in a first order reaction with a half life of 2 hours 50 minutes according to Fig. 1. During the racemisation reaction the configuration at the manganese atom changes and a 1/1 equilibrium between the two enantiomers +I and —I of Scheme 1 is approached [2,3].

The positive entropy of activation for the racemisation of +I and —I is consistent with a dissociative pathway [2]. As the cleavage of the bond between the manganese atom and the triphenylphosphine ligand was expected to be responsible for the racemisation, the effect of added triphenylphosphine on the rate of racemisation of +I and —I and the kinetics of the phosphine exchange in I was studied [2-4].

The rate of racemisation of the esters +I and —I is not changed if triphenylphosphine, up to a 10 fold excess with respect to the complex concentration, is added [2]. Deuteration experiments, however, showed that triphenylphosphine exchange takes place. If the racemisation of the manganese ester I is carried out in the presence of $P(C_6D_5)_3$, the deuterated triphenylphosphine is incorporated into the complex with a rate which is exactly equal to the rate of racemisation [3].

These results are in accord with the S_N1 mechanism of Scheme 1. In the rate-determining step k_1 the Mn—P bond in +I is broken with formation of a planar intermediate.

Triphenylphosphine attacks the planar intermediate in a rapid reaction step k_2 with equal probability at the front side or at the back; both enantio-

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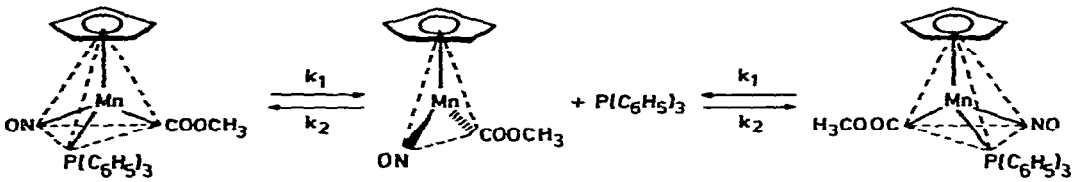
SCHEME 1



(+I) (−I)

mers +I and −I being formed in equimolar amounts. Although phosphine exchange occurs at this stage, triphenylphosphine does not show up in the rate law because it is not involved in the rate-determining step k_1. Therefore the rate

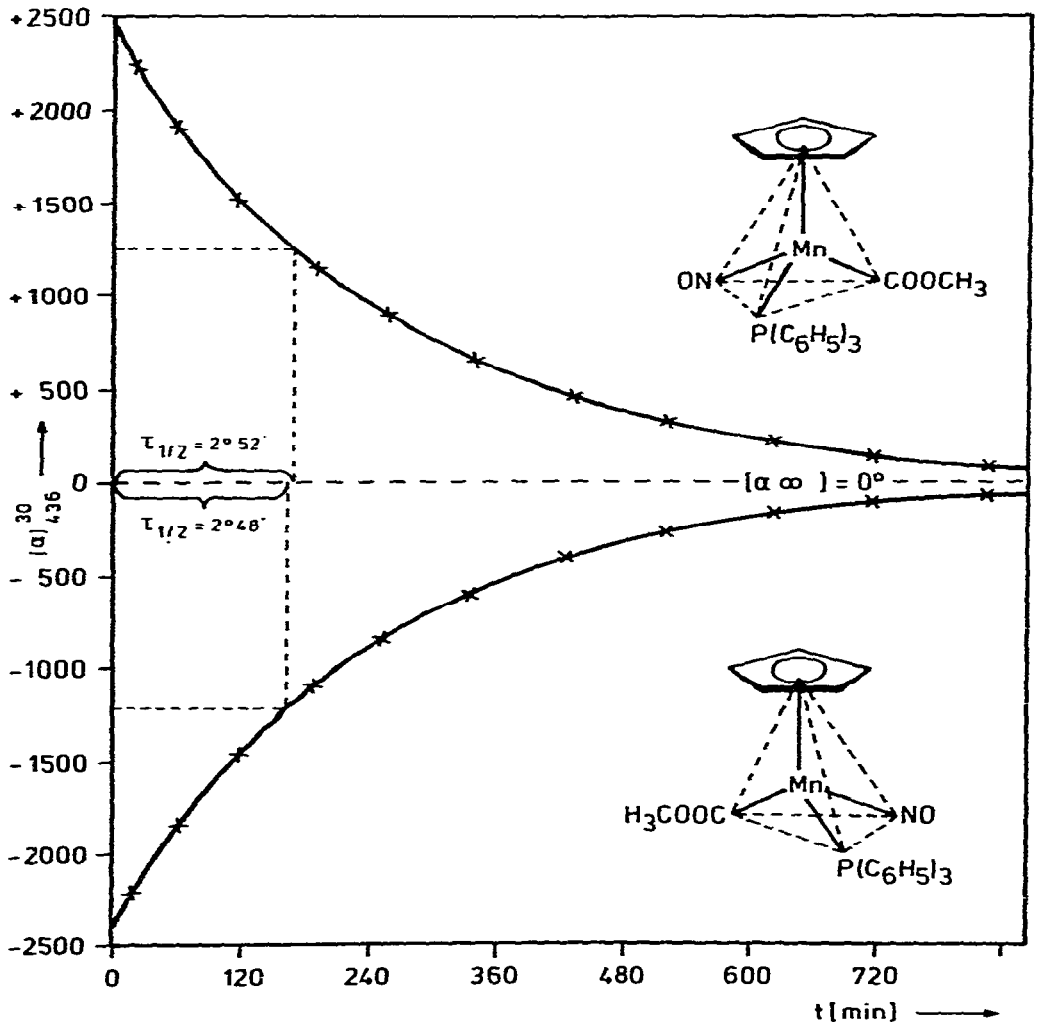
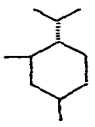


Fig. 1. Racemisation of (+)- and (−)-$C_5H_5Mn(COOCH_3)(NO)P(C_6H_5)_3$ (+I and −I) in benzene solution at 30°C.

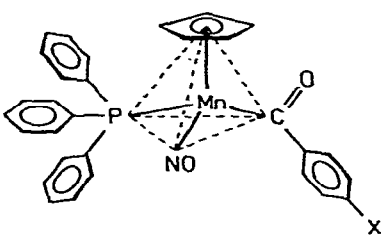
TABLE 1

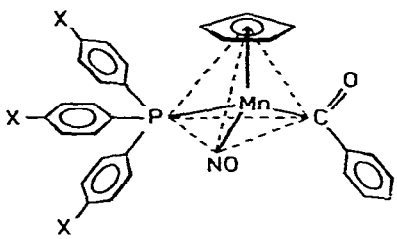
HALF LIVES OF THE RACEMISATION REACTION OF (+)- AND (—)-$C_5H_5Mn(COOR)(NO)P(C_6H_5)_3$ IN BENZENE SOLUTION AT 30°C

R	$\tau_{1/2}$
CH_3	170 min
C_2H_5	115 min
	71; 52 min (two different diastereoisomers)

of racemisation of +I and —I is unaffected by the presence of triphenylphosphine [2-4]. The simple S_N1 mechanism of Scheme 1 will have to be refined after consideration of the benzoyl compounds +II and —II.

The rates and half lives of the racemisation of the $C_5H_5Mn(COOR)(NO)P(C_6H_5)_3$ compounds are dependent on the group R in the ester function. Table 1 shows that the half lives at 30°C in benzene solution decrease if the alkyl group changes from methyl to ethyl to menthyl [2,4,5]. The increasing size of R should favor the dissociation of triphenylphosphine, but the steric effect is superimposed by an electronic effect. To investigate only the electronic effect without changing the steric situation around the reaction center the benzoyl compounds (+)- and (—)-$C_5H_5Mn(CO\text{-}p\text{-}C_6H_4X)(NO)P(C_6H_5)_3$ of Fig. 2 with different *p*-substituents X were prepared [6]. These optically active





X	$\tau_{1/2}$ (toluene, 20°C)	$\tau_{1/2}$ (toluene, 20°C)
$N(CH_3)_2$	3.6 min	very large
OCH_3	18.5 "	337 min
CH_3	26.7 "	151 "
H	49.5 "	49.5 "
C_6H_5	56.5 "	84.4 "
F	87 "	34 "
Cl	145 "	25.2 "
CF_3	418 "	5.9 "

Fig. 2. Effect of *p*-substituents X in (+)- and (—)-$C_5H_5Mn(CO\text{-}p\text{-}C_6H_4X)(NO)P(p\text{-}C_6H_4X)_3$ on the half lives ($\tau_{1/2}$) of the first order racemisation in toluene at 20°C (complex concentration 2 mg/ml).

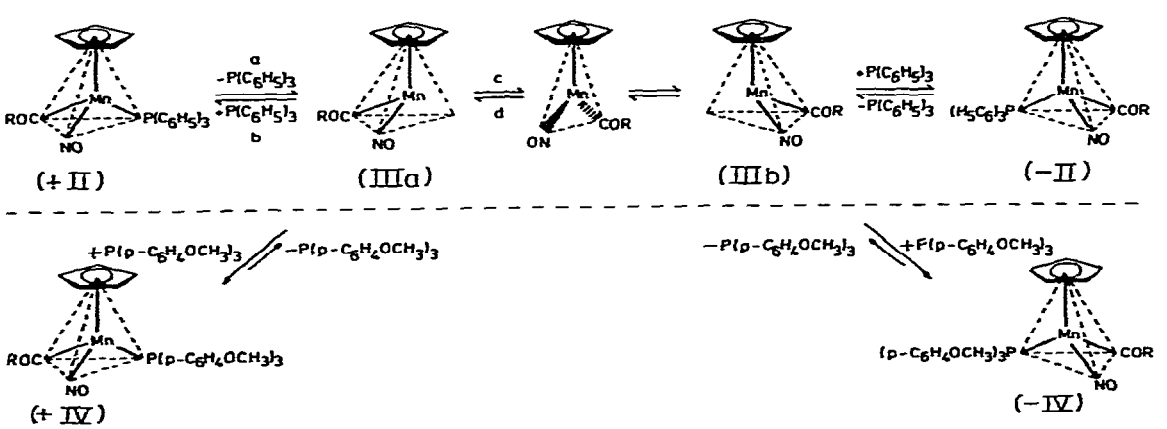
complexes racemise in solution in the same way as the corresponding esters +I and —I. A comparison of the half lives for the first order racemisation reactions of the benzoyl derivatives in toluene at 20°C (Fig. 2, left part) shows that electron-releasing substituents increase and electron-attracting substituents decrease the rate of racemisation appreciably [6]. Whereas the dimethylamino and the methoxy compounds only can be handled at low temperatures without racemisation, the racemisation of the trifluoromethyl complex is fast at relatively higher temperatures [4,6].

To vary the electron density at the phosphorus atom in the same way as at the manganese atom, compounds with substituents X in the *p*-positions of the triphenylphosphine ligand were prepared and resolved [7]. The half lives of the complexes on the right hand side of Fig. 2 demonstrate that *p*-substitution in the phenyl rings of the phosphine ligand leads to exactly the opposite effect as *p*-substitution in the benzoyl system at the manganese atom [7]. It can be concluded that the cleavage of the manganese—phosphorus bond is fast if electron-donating substituents are attached to the metal atom and electron-attracting substituents are bound to the phosphorus atom whereas the cleavage of the metal—phosphorus bond is slow if the substituent effects are the other way round [4,6,7].

For both series of compounds good Hammett correlations between the substituent constants and the half lives of the racemisation reaction can be established. The half lives of the racemisation reaction are much more sensitive probes to the investigation of variations in the electron density at the manganese or phosphorus atoms than the small shifts of the IR stretching vibrations or the NMR signals [6,7].

It was mentioned earlier that the racemisation of the optically-active manganese methyl esters +I and —I is independent of whether triphenylphosphine is present or not [2]. However, the racemisation of the corresponding benzoyl complexes +II and —II turned out to be $P(C_6H_5)_3$-dependent [6,8]. Figure 3 shows that on addition of increasing amounts of triphenylphosphine the configurational stability of (+)-$C_5H_5Mn(COC_6H_5)(NO)P(C_6H_5)_3$ (+II) is increased. The triphenylphosphine dependence of the racemisation of +II was studied at complex/triphenylphosphine concentrations up to 1/20 [4,6,8].

SCHEME 2



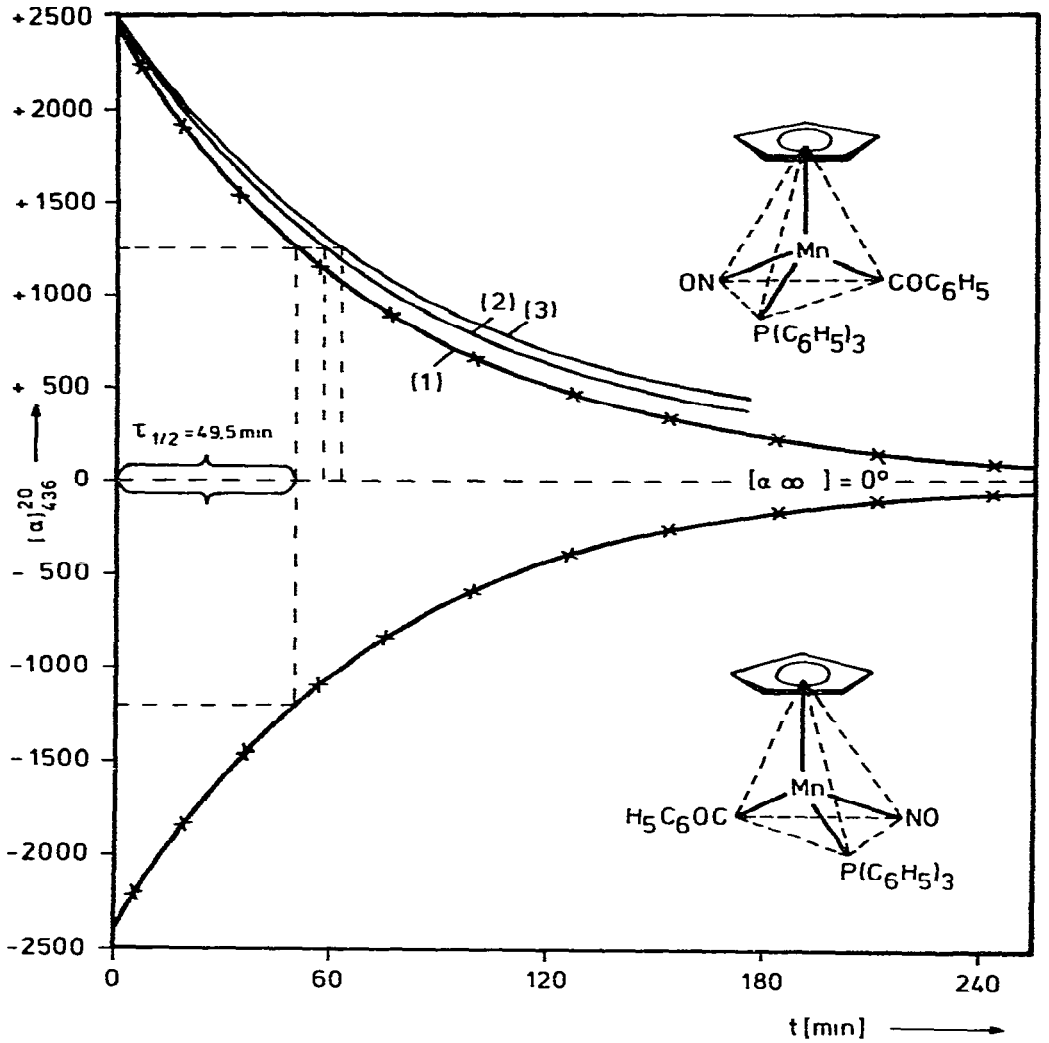


Fig. 3. Racemisation of (+)- and (—)-$C_5H_5Mn(COC_6H_5)(NO)P(C_6H_5)_3$ +II and —II in toluene solution at 20°C (complex concentration 2 mg/ml); (1) in the absence of $P(C_6H_5)_3$, (2) in the presence of $P(C_6H_5)_3$ in a 3-fold excess, (3) in the presence of $P(C_6H_5)_3$ in a 6-fold excess.

To account for the triphenylphosphine dependence the chiral intermediates IIIa and IIIb are introduced into the S_N1 racemisation mechanism of Scheme 1.

The chiral tripod IIIa, formed by triphenylphosphine dissociation from +II in the rate-determining reaction step a of Scheme 2, may either rearrange according to step c, to give a planar intermediate or transition state, or it may react in step b with triphenylphosphine to give the original compound +II [6,8]. As the bimolecular step b is favored in the presence of increasing amounts of triphenylphosphine the decrease of the rate of racemisation on addition of $P(C_6H_5)_3$ can be rationalized [4,6,8].

If the Bodenstein steady state approximation is applied to the upper part of Scheme 2 and small quantities are neglected, equation 1 is obtained [6,8].

$$\frac{k_c}{k_b} = \frac{k_{with} \cdot [P(C_6H_5)_3]}{k_{without} - k_{with}} \quad (1)$$

k_b and k_c are the rate constants for steps b and c in Scheme 2 and k_{with} and $k_{without}$ the rate constants for the racemisation of +II with and without addition of $P(C_6H_5)_3$. As the competition ratio k_c/k_b remains constant for complex/triphenylphosphine concentrations from 1/1 to 1/20, the $P(C_6H_5)_3$ dependence of the racemisation is not only qualitatively but also quantitatively consistent with Scheme 2 [4,6,8].

Besides this kinetic argument there is also stereochemical evidence for chiral intermediates in the racemisation of +II. Treatment of the benzoyl complex +II with an excess of tri-*p*-anisylphosphine leads to phosphine exchange and the substitution product +IV is formed (Scheme 2) [8]. After one half life of +II the unchanged starting material +II and the reaction product +IV, which is optically active and has the same configuration as +II, can be separated by low temperature chromatography [8]. Although a dissociation reaction, phosphine substitution according to Scheme 2, occurs with at least partial retention of configuration at the manganese atom due to the formation of a chiral intermediate [4,8].

An explanation of the stereochemical results by the assumption of a rapid migration of group R from the acyl substituent to the metal atom to give an intermediate of the type $C_5H_5Mn(CO)(NO)R$, either in an additional reaction starting from IIIa in Scheme 2 or by a concerted process directly from +II, is not considered likely because preliminary results show that compounds of the type $C_5H_5Mn(CO)(NO)R$ are stable molecules [9]. Coordinatively unsaturated intermediates similar to IIIa have also been postulated in the reaction of $C_5H_5Fe(COR)(CO)_2$ with nucleophiles on the basis of kinetic results in different solvents [10].

The mechanism of Scheme 2 should also be valid for the racemisation of the esters +I and —I. Probably because of the unfavorably large competition ratio k_c/k_b, this hypothesis could not be supported by kinetic and stereochemical arguments as in the case of the benzoyl compounds +II and —II [4,8].

References

1 H. Brunner, Ann. N.Y. Acad. Sci., 239 (1974) 213.
2 H. Brunner and H.-D. Schindler, Chem. Ber., 106 (1971) 2467.
3 H. Brunner and H.-D. Schindler, Z. Naturforsch. B, 26 (1971) 1200.
4 H. Brunner, Top. Curr. Chem., in press.
5 M. Langer, Diplomarbeit, TU München, 1971.
6 H. Brunner and M. Langer, J. Organometal. Chem., 87 (1975) 223.
7 H. Brunner and J. Aclasis, J. Organometal. Chem., in press.
8 H. Brunner, J.Aclasis, M. Langer and W. Steger, Angew. Chem., 86 (1974) 864; Angew. Chem. Int. Ed. Engl., 13 (1974) 810.
9 H. Brunner and W. Steger, unpublished results.
10 K. Nicholas, S. Raghu and M. Rosenblum, J. Organometal. Chem., 78 (1974) 133.