Journal of Organometallic Chemistry, 308 (1986) 345–351
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

OLEFIN ENANTIOFACE SELECTION IN OPTICALLY ACTIVE $[(\eta\text{-}C_5H_5)Ru\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(OLEFIN)]^+ PF_6^-$ COMPLEXES

GIAMBATTISTA CONSIGLIO,

Swiss Federal Institute of Technology, Department of Industrial and Engineering Chemistry, CH-8082 Zürich (Switzerland)

PAUL PREGOSIN

Swiss Federal Institute of Technology, Department of Inorganic Chemistry, CH-8092 Zürich (Switzerland)

and FRANCO MORANDINI

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, I-35131 Padova (Italy)

(Received January 15th, 1986)

Summary

Enantioface selection for various olefins has been investigated by ^{31}P and ^1H NMR spectroscopy for pseudotetrahedral ruthenium complexes of the type $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(CH_2{=}CHR)]PF_6$ (where R = H, CH_3, C_6H_5, $CH(CH_3)_2$, $COOCH_3$, CH_2COCH_3 and $COCH_2CH_3$). For the olefinic species the diastereomeric equilibrium composition largely favours one species; for the styrene complex ($R = C_6H_5$) only one product is detected. In the case of methyl acrylate and of ethyl vinyl ketone, however, the diastereomeric ratio is close to unity. It is concluded that enantioface selection is influenced by both steric and electronic factors.

In recent years there has been considerable interest in olefin complexes of the type $[(\eta\text{-}C_5H_5)MLL'(olefin)]^{n+}$ ($n = 0$ or 1; L and L′ are equal or different ligands) [1–20]. The structures of such complexes have been investigated both in solution [1–5,18,19] and in the solid state [14,20]. The preferred geometry of these pseudotetrahedral complexes has the double bond roughly parallel to the plane of the cyclopentadienyl ligand [1,9,18,20]. The complexed olefin is susceptible to attack by nucleophiles [16,21], thus leading to formation of new bonds, sometimes with very high stereospecificity [16]. In these complexes, when $L \neq L'$ the metal is stereogenic [22] and therefore enantioface selection can take place, and this has been confirmed

0022-328X/86/$03.50

in a few cases [3,8,15,17–20]. However, even for complexes in which L and L′ were very different in size, the extent of the asymmetric induction was found to be rather low [8,15,18]. As far as we are aware, no example of chiral olefin complexes of the above type has been reported in which enantioface selection is determined by chiral L and/or L′. This contrasts with the numerous studies for chiral square planar or pentacoordinated platinum olefin complexes [23–28]. In view of our interest in the asymmetric hydrocarbonylation reaction of olefinic substrates using diphosphine ligands as the chiral cocatalysts [29–32] we have synthesized and investigated some complexes of the formula $[(\eta\text{-}C_5H_5)Ru\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}\text{-}(CH_2{=}CHR)]PF_6$. We report here on their properties and on asymmetric induction phenomena.

Results and discussion

The olefin complexes were prepared according by published methods [10,11,13] involving reaction of the parent chloro compound [33] $(\eta\text{-}C_5H_5)RuCl\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}$ with an excess of olefin in MeOH the presence of NH_4PF_6 as the halogen scavenger. The complexes precipitate out as yellow microcrystalline materials. In no case were we able to obtain crystals suitable for an X-ray structure determination. Moreover, attempts to prepare the corresponding iron complexes starting with $(\eta\text{-}C_5H_5)FeBr\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}$ [34] failed, as expected [35].

Solutions of the complexes are very sensitive, and slowly develop a blue color even under nitrogen.

A solution of the ethylene complex in CD_2Cl_2 shows the expected AX $^{31}P\{^1H\}$ NMR spectrum (Table 1) due to the two diastereotopic phosphorus atoms, and shows a singlet resonance for the $\eta\text{-}C_5H_5$ group in the ^1H NMR spectrum. By contrast, the propylene complex in the same solvent shows two AX spin systems in the phosphorus spectrum both at room temperature or when a solution is made up and examined quickly at −70°C. The ratio between the two species (d_1/d_2) is 89/11, based on the integrals of the $\eta\text{-}C_5H_5$ resonances. The 3-methyl-1-butene complex shows the same behaviour; in this case the d_1/d_2 ratio is ca. 23/77. For the styrene complex only one set of ^{31}P resonances is recognizable. In the spectrum

TABLE 1

SOME NMR PARAMETERS [a] AND DIASTEREOMERIC COMPOSITIONS FOR THE COMPLEXES $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(CH_2{=}CHR)]PF_6$

R	d_1				d_2				d_1/d_2 [b]
	$\delta(C_5H_5)$	$\delta(P^1)$	$\delta(P^2)$	$J(P\text{–}P)$	$\delta(C_5H_5)$	$\delta(P^1)$	$\delta(P^2)$	$J(P\text{–}P)$	
H	4.56	78.7	73.6	42.7	–	–	–	–	
CH_3	4.62	80.3	66.3	43.9	4.27	76.9	73.9	43.9	89/11
$CH(CH_3)_2$	4.60	77.8	71.8	43.5	4.43	78.2	71.4	42.8	23/77
C_6H_5	4.06	79.0	70.2	41.0	n.d.	n.d.	n.d.	n.d.	95/5
$COOCH_3$	4.62	74.6	73.8	45.1	4.39	74.9	69.9	45.1	55/45
CH_2OCH_3	4.65	77.9	67.9	44.0	4.45	76.6	74.7	42.8	83/17
$COCH_2CH_3$	4.67	74.4	73.8	42.9	4.38	77.8	72.4	41.1	43/57

[a] In CD_2Cl_2. δ in ppm, J in Hz. [b] d_1/d_2 = diastereomeric ratio at the equilibrium.

of a freshly prepared solution of the methyl acrylate complex in CD_2Cl_2 two species again appear in the proton and phosphorus spectra, in a molar ratio of ~ 20/80. This ratio changes with time and reaches an equilibrium value of 55/45 in about 10 h. The rate with which the equilibrium composition is reached is not influenced by the presence of an excess of methyl acrylate. The analogous complex containing the 1,2-ethanediylbis(diphenylphosphine) ligand shows only one doublet of doublets (due to diastereotopic phosphorus atoms) in the ^{31}P spectrum and only one singlet for the η-C_5H_5 ligand in the ^1H spectrum; the spectra do not change with time.

The behaviour of the complex containing the vinyl ethyl ketone ligand is analogous to that of the methyl acrylate complex. The intensity of the η-C_5H_5 signal at δ 4.38 decreases with time, and a new signal at δ 4.67 correspondingly increases; an equilibrium composition of 43/57 is reached in 8–10 h. In contrast, the complex containing allylmethyl ether behaves similarly to the propylene complexes, and gives a d_1/d_2 ratio of 83/17.

In principle the presence of two sets of signals in the NMR spectra of the complexes investigated (with the exception of the styrene and ethylene complexes) can be associated either with the presence of diastereomers (due to preferential complexation of either olefin enantioface) or with the presence of rotamers (arising from rotation of the olefin around the metal double bond axes). We assign the two species to diastereomeric olefin complexes arising from enantioface selection, since (a) rotational barriers in related complexes are rather low [3,18], and (b) the analogous methyl acrylate diphos complex gives only one set of signals; in this case complexation of a prochiral olefin leads to the formation of enantiomeric complexes. Furthermore we have shown that the barrier to rotation for unsaturated ligands is practically independent of the two diphosphine ligands, at least in the case of alkylidene carbene complexes [34,36].

The fact that the rate of epimerization at the olefinic enantioface is not influenced by an excess of olefin is in agreement with the expectation that coordinatively saturated complexes epimerize via dissociation of the olefinic ligand. The lower rate of epimerization for olefins containing electron-withdrawing groups can be understood in terms of a stronger coordination of the olefinic double bond.

Enantioface selection is rather large even in the case of the propylene complexes, but it does not depend only on steric factors. Asymmetric induction for 3-methyl-1-butene is somewhat lower than that for propylene. In the case of the methyl acrylate and of the ethyl vinyl ketone the two diastereomers are present in a ratio close to unity; in contrast, asymmetric induction for the allyl methyl ether complex is comparable to that observed for propylene. Comparison of the last three complexes suggests that the carbonyl group might have some additional interaction within the complexes so as to reduce the differences in the complexation energy of the two enantiofaces. Since these molecules are coordinatively saturated, it appears more probable that such interactions involve the ligands (e.g., the phenyl groups of the diphosphine) not the metal [37].

The lack of suitable crystals prevents identification of the predominantly complexed enantioface. Comparison of the CD spectra of the ethylene, propylene and styrene complexes suggests that the same enantioface is complexed for styrene and propylene, if the band at ~ 430 nm is influenced by the olefin enantioface, which is implied by the fact that this band is about an order of magnitude smaller in the ethylene complexes (Fig. 1) which do not have enantiofaces. There is no apparent

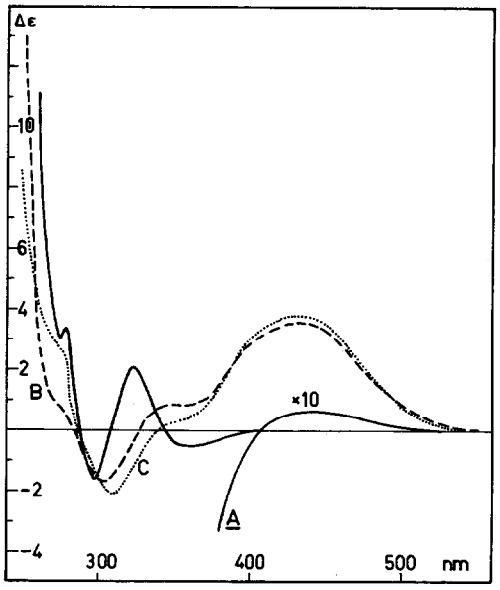


Fig. 1. CD spectra of the complexes $[(\eta\text{-}C_5H_5)Ru\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(CH_2{=}CHR)]PF_6$: **A**, R = H; **B**, R = CH_3; **C**, R = C_6H_5.

concordance, however, between the CD spectra of the methyl acrylate complex (Fig. 2) before and after epimerization, which is not surprising in view of the possible interaction of the carbonyl group of the ester moiety mentioned above.

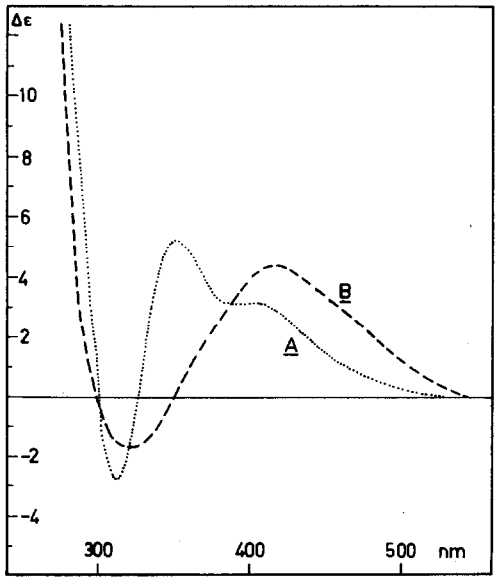
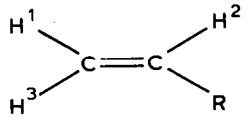


Fig. 2. CD spectra of the $[(\eta\text{-}C_5H_5)Ru\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(CH_2{=}CHCOOCH_3)]PF_6$: **A**, immediately after dissolution; **B**, after 15 h.

Experimental

All experiments were carried out under nitrogen using standard inert gas techniques. Diethyl ether was purified by distillation from $LiAlH_4$, methanol from $Mg(OMe)_2$, and methylene chloride from P_2O_5.

NMR spectra were recorded on a Bruker WM 250 spectrometer; for ^{31}P NMR external 85% H_3PO_4 was used as the reference. The ^1H NMR parameters of the olefinic protons (where assignment was possible) refer to the following numbering:



CD spectra were measured on a Jasco J-40AS recording spectropolarimeter and UV spectra on a Cary 14 recording spectrophotometer.

The complexes (η-C_5H_5)Ru{(*S,S*)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}Cl and ($\eta$-$C_5H_5$)Ru($Ph_2PCH_2CH_2PPh_2$)Cl were prepared by previously described procedures [38,39].

General procedure for the preparation of the complexes

0.15 g (0.24 mmol) of (η-C_5H_5)RuCl(diphosphine) were treated at room temperature with an excess of the appropriate olefin in 20 ml of anhydrous methanol containing NH_4PF_6 (1.3 mmol). The solvent was removed under reduced pressure and the white or pale-yellow products were recrystallized form dichloromethane/diethyl ether. Yields were in the range 75–90%.

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=$CH_2$)]$PF_6$. Anal. Found: C, 54.12; H, 5.01. $C_{35}H_{37}P_3F_6Ru$ calcd.: C, 54.90; H, 4.87%. ^1H NMR (CD_2Cl_2) δ 0.75 (dd, CH_3), 0.99 (dd,CH_3), 2.22 and 2.64 (m,CHCH), 2.38 and 2.50 (m,CH_2=CH_2), 4.56 (s,C_5H_5), 6.60–7.72 (m,C_6H_5).

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=$CHCH_3$)]$PF_6$. Anal. Found: C, 54.76; H, 4.86. $C_{36}H_{39}P_3F_6Ru$ calcd.: C, 55.46; H, 5.04%. ^1H NMR (CD_2Cl_2) for the major diastereomer: 0.56 (dd,CH_3), 0.68 (d, CH_3C=), 0.80 (dd,CH_3), 2.26 (m, H^1), 2.55 (m, H^2), 3.52 (m, H^3), 4.62 (s, C_5H_5) 6.53–7.80 (m, C_6H_5).

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=$CHCH(CH_3)_2$]$PF_6$. Anal. Found: C, 55.67; H, 5.28. $C_{38}H_{43}P_3F_6Ru$ calcd.: C, 56.51; H, 5.37%. ^1H NMR (CD_2Cl_2) for the major diastereomer: 0.66 (d, CH_3), 0.74 (d,CH_3), 0.88 (dd, CH_3), 0.92 (dd, CH_3), 1.47 (m, H^1), 2.68 (m, H^2), 2.97 (m, H^3), 4.43 (s, C_5H_5), 6.60–7.80 (m, C_6H_5).

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=$CHC_6H_5$)]$PF_6$. Anal. Found: C, 58.42; H, 4.85. $C_{41}H_{41}P_3F_6Ru$ calcd.: C, 58.50; H, 4.90%. ^1H NMR (CD_2Cl_2) 0.80 (dd, CH_3), 0.99 (dd,CH_3), 3.02 and 2.29 (m, CH), 1.75 (m, H^1), 3.26 (m, H^2), 4.26 (m, H^3), 4.06 (s, C_5H_5), 6.75–8.00 (m, C_6H_5).

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=$CHCOOCH_3$)]$PF_6$. Anal. Found: C, 52.20; H, 4.65. $C_{37}H_{39}O_2P_3F_6Ru$ calcd.: C, 51.65; H, 4.57%. ^1H NMR (CD_2Cl_2) for the diastereomer prevailing soon after dissolution: 0.88 (dd, CH_3), 1.12 (dd, CH_3), 3.66 (s, CH_3), 1.58 (m, H^1), 3.02 (m, H^2), 3.38 (m, H^3), 4.39 (s, C_5H_5), 6.51–8.00 (m, C_6H_5).

[(η-C_5H_5)Ru($Ph_2PCH_2CH_2PPh_2$)(CH_2=CHCOOCH_3)]PF_6. Anal. Found: C, 52.62; H, 4.44. $C_{35}H_{35}O_2P_3F_6Ru$ calcd.: C, 52.83; H, 4.43%. ^{1}H NMR (CD_2Cl_2) δ 1.83–3.02 (m, CH_2CH_2 and CH_2=CH), 3.31 (s, CH_3), 4.95 (s, C_5H_5), 6.80–7.60 (m, C_6H_5). ^{31}P NMR (CD_2Cl_2) P^1 80.2; P^2 77.0; *J*(P–P) 22.0 Hz.

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=CH-$CH_2OCH_3$)]$PF_6$. Anal. Found: C, 54.64; H, 5.01. $C_{37}H_{41}OP_3F_6Ru$ calcd.: C, 54.88; H, 5.10%. ^{1}H NMR (CD_2Cl_2) for the major diastereomer: δ 0.55 (dd,CH_3), 0.78 (dd,CH_3), 2.91 (s,CH_3), 4.65 (s,C_5H_5), 6.72–8.01 (m, C_6H_5).

[(η-C_5H_5)Ru{(S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($CH_2$=CHCO$CH_2CH_3$)]$PF_6$. Anal. Found: C, 55.62; H, 5.10. $C_{38}H_{41}OP_3F_6Ru$ calcd.: C, 55.54; H, 5.03%. ^{1}H NMR (CD_2Cl_2) for the diastereomer prevailing soon after dissolution: δ 0.80 (dd,CH_3), 1.03 (dd,CH_3), 0.94 (t,CH_3), 1.62 (m, H^1), 3.09 (m, H^2), 3.22 (m,H^3), 4.38 (s, C_5H_5), 6.70–7.92 (m, C_6H_5).

Acknowledgement

G.C. thanks the Schweizer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Grant Nr. 2.028 - 0.83) for financial support. F.M. thanks Mr. A. Ravazzolo (CNR, Padua) for technical assistance.

References

1 J.W. Faller and B.W. Johnson, J. Organomet. Chem., 88 (1975) 101.
2 A. Cutler, D. Ehntholt, P. Lennon, K. Nicholas, D.F. Marten, M. Madhavarao, S. Raghu, A. Rosan and M. Rosenblum, J. Am. Chem. Soc., 97 (1975) 3149.
3 H. Alt, M. Herberhold, C.G. Kreiter and H. Strack, J. Organomet. Chem., 102 (1975) 491.
4 M. Herberhold and H. Alt, Liebigs Ann. Chem., (1976) 292.
5 D. Reger and C.J. Coleman, Inorg. Chem., 18 (1979) 3155.
6 B.E.R. Schilling, R. Hoffmann and D.L. Lichtenberger, J. Am. Chem. Soc., 101 (1979) 585.
7 B.E.R. Schilling, R. Hoffmann and J.W. Faller, J. Am. Chem. Soc., 101 (1979) 593.
8 D.L. Reger, C.J. Coleman and P.J. McElligott, J. Organomet. Chem., 171 (1979) 73.
9 D.E. Laycock and M.C. Baird, Inorg. Chim. Acta, 42 (1980) 263.
10 P.M. Treichel and D.A. Komar, Inorg. Chim. Acta, 42 (1980) 277.
11 S.G. Davies and F. Scott, J. Organomet. Chem., 188 (1980) C41.
12 E.K.G. Schmidt and C.H. Thiel, J. Organomet. Chem., 220 (1981) 87.
13 M.I. Bruce and F.S. Wong, J. Organomet. Chem., 210 (1981) C5.
14 M.I. Bruce, T.W. Hambley, J.R. Rodgers, M.R. Snow and F.S. Wong, Aust. J. Chem., 35 (1982) 1323.
15 H. Werner and R. Feser, J. Organomet. Chem., 232 (1982) 351.
16 J.E. Jensen, L.L. Campbell, S. Nakanishi and T.C. Flood, J. Organomet. Chem., 244 (1983) 61.
17 W.A. Kiel, G.-Y. Lin, G.S. Bodner and J.A. Gladysz, J. Am. Chem. Soc., 105 (1983) 4958.
18 H. Lehmkuhl, J. Grundke and R. Mynott, Chem. Ber., 116 (1983) 159.
19 H. Lehmkuhl, J. Grundke, G. Schroth and R. Benn, Z. Naturforsch. B, 39 (1984) 1050.
20 M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, J. Organomet. Chem., 273 (1974) 361.
21 M. Rosenblum, Acc. Chem. Res., 7 (1974) 22.
22 K. Mislow and J. Siegel, J. Am. Chem. Soc., 106 (1984) 3319.
23 G. Paiaro, Organometal. Chem. Revs. A, 6 (1970) 319.
24 H. Boucher and B. Bosnich, J. Am. Chem. Soc., 99 (1977) 6253.
25 S. Shinoda, Y. Yamaguchi and Y. Saito, Inorg. Chem., 18 (1979) 673.
26 A. De Renzi, B. Di Blasio, A. Saporito, M. Scalone and A. Vitagliano, Inorg. Chem., 19 (1980) 960.
27 H. van der Poel and G. van Koten, Inorg. Chem., 20 (1981) 2950.
28 R. Lazzaroni, G. Uccello-Barretta, S. Bertozzi, C. Bertucci and F. Marchetti, J. Chem. Res. (S), (1984) 286; J. Chem. Res. (M), (1984) 2570.
29 G. Consiglio and P. Pino, Topics Curr. Chem., 105 (1982) 77.

30 G. Consiglio and P. Pino, Adv. Chem. Ser., 196 (1982) 371.
31 G. Consiglio, F. Morandini, M. Scalone and P. Pino, J. Organomet. Chem., 279 (1985) 193.
32 P. Haelg, G. Consiglio and P. Pino, J. Organomet. Chem., 296 (1985) 281.
33 F. Morandini, G. Consiglio, B. Straub, G. Ciani and A. Sironi, J. Chem. Soc., Dalton Trans., (1983) 2293.
34 G. Consiglio, F. Bangerter, C. Darpin, F. Morandini and V. Lucchini, Organometallics, 3 (1984) 1446.
35 G. Balavoine, M.L.H. Green and J.P. Sauvage, J. Organomet. Chem., 128 (1977) 247.
36 G. Consiglio and F. Morandini, submitted for publication.
37 R. Lazzaroni and B.E. Mann, J. Organomet. Chem., 164 (1979) 79, compare also ref. 28.
38 G. Consiglio, F. Morandini and F. Bangerter, Inorg. Chem., 21 (1982) 455.
39 G.S. Ashby. M.I. Bruce, I.B. Tomkins and R.C. Wallis, Aust. J. Chem., 32 (1979) 1003.