Journal of Organometallic Chemistry, 436 (1992) 95–100
Elsevier Sequoia S.A., Lausanne
JOM 22780

Catalytic activity of *cis*-[μ-[bis(1,1-dimethylethyl)-phosphino]]dicarbonyl-μ-chlorobis[tris(1,1-dimethylethyl)-phosphine]dirhodium and of its chiral analog (+)-*cis*-[μ-[bis-(1,1-dimethylethyl)phosphino]]dicarbonyl-μ-chlorobis[[5β-methyl-2α-(1α-methylethyl)cyclohexyl]-diphenylphosphine]dirhodium

Evelina Berkovich, Aharona Jacobson, Jochanan Blum
Department of Organic Chemistry, Hebrew University, Jerusalem 91904 (Israel)

Herbert Schumann, Martin Schäfers and Holger Hemling
Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, W-1000 Berlin 12 (Germany)

(Received February 4, 1992)

Abstract

The title compounds **5a** and **5b**, which contain one bridging phosphido- and one bridging chloro-ligand, have been made by reaction of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ (**1**) with the phosphine $^tBu_3P$ (**2a**) or (+)-neomenthyldiphenylphosphine (**2b**) followed by treatment of the resulting complexes $[(R_2R'P)Rh(CO)(\mu\text{-}Cl)]_2$ (**3**) with $Me_3SiP^tBu_2$ (**4**). Compounds **5a** and **5b** are highly active catalysts for isomerization of allylbenzene, for hydrogenation of styrene and (*Z*)-methyl α-acetamidocinnamate, and for hydroformylation of cyclohexene. The chiral complex **5b** promotes enantioselective hydrogenation of a prochiral dehydroamino acid derivative.

Introduction

Although dinuclear complexes with strong binding ligands should theoretically be better catalysts than mononuclearic species [1], dirhodium compounds with two μ-PR_2 or μ-SR groups have only limited catalytic activity (see, *e.g.*, refs. 2–4). The catalytic ability of the latter type of compounds was, however, significantly increased by substitution of one thiolato group by a chloride bridge [5]. It was not known whether the activity of the phosphido-bridged dirhodium complexes could likewise be increased by introduction of a μ-Cl ligand; a few rhodium complexes

Correspondence to: Professor J. Blum or Professor H. Schumann.

with one PR_2 and one Cl bridge are known (see, *e.g.*, refs. 6–10), but their catalytic potential has not been investigated. In this paper we present the results of a study of the catalytic activity in some hydrogen transfer processes of *cis*-[[(^{t}Bu$_3$P)Rh(CO)]$_2$(μ-Cl)(μ-P^{t}Bu$_2$)] (**5a**) [6,7], and also of that of a chiral analog of **5a** in which the tri-tert-butylphosphine groups have been replaced by (+)-neomenthyldiphenylphosphine {[1αR-]5β-methyl-2α-(1-methylethyl)cyclohexyl]diphenylphosphine} (**2b**) ligands.

Results and discussion

The title compounds were prepared by the reactions outlined in eqs. 1 and 2.

$$\underset{\mathbf{1}}{[Rh(CO)_2(\mu\text{-Cl})]_2} + 2\underset{\mathbf{2}}{R_2R'P} \rightarrow \underset{\mathbf{3}}{[(R_2R'P)Rh(CO)(\mu\text{-Cl})]_2} + 2CO \quad (1)$$

$$\mathbf{3} + \underset{\mathbf{4}}{Me_3SiP^tBu_2} \rightarrow \textit{cis}\text{-}\underset{\mathbf{5}}{[R_2R'PRh(CO)]_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)} + Me_3SiCl \quad (2)$$

a, R = R′ = ^{t}Bu

b, R = Ph R′ = 5β-methyl-2α-(1α-methylethyl)cyclohexyl

Two syntheses of **5a** employing the above reactions were reported previously [6,7]; both gave erratic results. We therefore, had to modify the procedures (see Experimental section) to ensure high reproducibility. The m.p. of complex **5a** so formed, was *ca.* 60°C higher than that previously reported.

Interaction of **1** and **2b** resulted in the formation of **3b** as a 1:4 mixture of *cis* and *trans* isomers. Treatment of this mixture with $Me_3SiP^tBu_2$ (**4**) (prepared by an improved version of the reported procedure [14]) yielded the chiral phosphido-bridged complex **5b**.

The reaction of **1** with a mixture of one equivalent each of **2a** and **2b** gave mainly a mixture of **5a** and **5b**, rather than a dirhodium complex with one ^{t}Bu$_3$P and one neomenthyldiphorylphosphino ligand.

Neither **5a** nor **5b** gave crystals suitable for an X-ray diffraction study. Their identities were, however, unequivocally established from their ^{1}H- and ^{31}P-NMR spectra. The ^{1}H NMR spectrum of **5a** in C_6D_6 consisted of two doublets at 1.442 and 1.946 ppm corresponding to the two kinds of phosphorus-coupled ^{t}Bu protons. The ^{31}P{^{1}H} spectrum showed a triplet of triplets for the bridging phosphorus at 25.11 ppm (indicating coupling with the two equivalent rhodium atoms and the two *cis*-oriented phosphine ligands), and a doublet of doublets of the non-bridging phosphines at 78.42 ppm. The ^{1}H-NMR spectrum of **5b** showed, in addition to the resonance peaks of the phenyl and neomenthyl protons, a single doublet for the bridging P^{t}Bu$_2$ group at 1.870 ppm. As for that of **5a** the ^{31}P{^{1}H} NMR spectrum of **5b** showed a triplet of triplets centred at 16.17 and a doublet of doublets centred at 26.28 ppm.

The catalytic abilities of complexes **5a** and **5b** were studied for some model isomerization, hydrogenation, and hydroformylation processes. The transformation of allylbenzene into *cis*- and *trans*-1-propenylbenzene (eq. 3) was chosen as a representative isomerization process. Typical reaction profiles for this reaction at 120°C are shown in Fig. 1. The initial rate

$$PhCH_2CH{=}CH_2 \rightleftharpoons \textit{cis}\text{- and } \textit{trans}\text{-PhCH=CHMe} \quad (3)$$

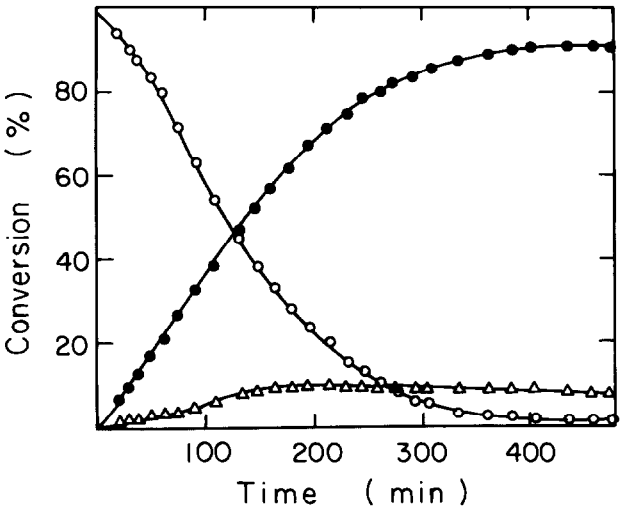

Fig. 1. Composition-time profiles for the isomerization of allylbenzene (1 ml, 7.5 mmol) at 120°C in the presence of **5a** (20 mg, 2.36×10^{-2} mmol). (○) Allylbenzene; (△) *cis*-1-propenylbenzene; (●) *trans*-1-propenylbenzene.

was of the same order of magnitude as that observed in cases in which other Group VIII-metal-phosphine complexes have been employed [12]. But in contrast to some Rh(I) and Rh(III) catalysts, which are deactivated before completion of the process, the dirhodium catalysts retain their full activity until an equilibrium mixture of 8.6% of *cis*-, 90% of *trans*-1-propenylbenzene, and 1.4% of the starting alkene has been formed.

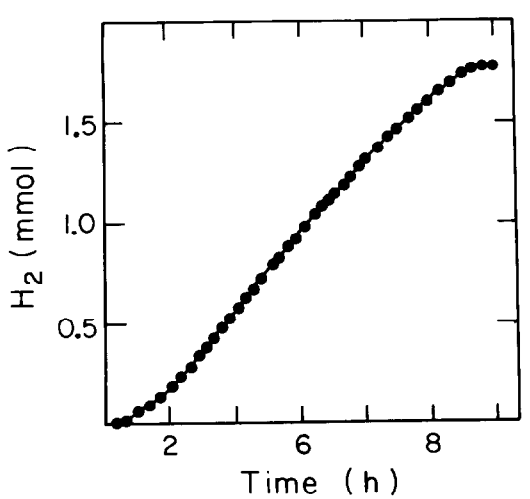

Fig. 2. Hydrogen uptake–time profile during the hydrogenation of styrene (0.2 ml, 1.75 mmol) in 1 ml of PhMe in the presence of **5a** (10 mg, 118×10^{-2} mmol) under 690 mm H_2 at 25°C.

The ability of **5a** and **5b** to serve as hydrogenation catalysts was demonstrated by using styrene and (*Z*)-methyl α-acetamidocinnamate as substrates (eqs. 4, 5).

$$PhCH{=}CH_2 + H_2 \rightarrow PhEt \quad (4)$$

$$PhCH{=}C(NHAc)COOMe + H_2 \rightarrow PhCH_2CH(NHAc)COOMe \quad (5)$$

Styrene was reduced at 25°C and 690 mm H_2 at a rate comparable to that observed with well known hydrogenation catalysts; *e.g.* the maximum rate under the conditions defined in Fig. 2 was 6.6 mmol l^{-1} min^{-1}, while that in the $RhCl_3$-Aliquat 336®-promoted reaction was 9.8 mmol l^{-1} min^{-1} [13]. The reduction of the dehydroamino acid derivative required more severe conditions than those used for styrene; a 91% yield of N-acetylphenylalanine methyl ester was obtained only when the hydrogenation was carried out for 20 h at 70°C under 35 atm H_2. The chiral complex **5b** was found to be able not only to catalyze smooth hydrogenation of the double bonds, but also to induce asymmetry during the reaction with the prochiral acetamidocinnamic ester. Under the conditions we used, however, the optical purity of the product was limited to *ca.* 20%. We attribute this to the ability of the dirhodium complex to promote both asymmetric hydrogenation and racemization of the chiral product initially formed (*cf.* ref. 11).

Hydroformylation of cyclohexene (eq. 6) was found to proceed smoothly at 120°C under 40 atm H_2 and 40 atm CO. After 20 h the mixture consisted of cyclohexanecarboxaldehyde (94%) and 6% of cyclohexane.

$$C_6H_{10} + CO + H_2 \rightarrow C_6H_{11}CHO \quad (6)$$

Experimental

All operations were carried out in freshly dried solvents under dry oxygen-free argon atmosphere.

[Bis(1,1-dimethylethyl)](trimethylsilyl)phosphine (4)

A modification of the method reported previously [14] was used. A mixture of 13 g (0.12 mol) of Me_3SiCl and 0.1 ml of Br_2 was added dropwise to a stirred refluxing suspension of 3.6 g (0.15 mol) of Mg in 140 ml of absolute tetrahydrofuran (THF). The mixture was refluxed for 1 h and 18 g (0.1 mol) of $^tBu_2PCl$ (best prepared by the method described by Fild *et al.* [15]) was added dropwise during 3 h. After 6 days under reflux the pale yellow THF solution was decanted and the residue extracted with three 80 ml portions of pentane. The combined THF-pentane solution was fractionated at 0.1 Torr and the fraction boiling at 41–53°C was collected, (lit. 48–51°C (0.1 Torr) [14]); yield 18 g (80%); ^1H NMR (200 MHz, C_6D_6): δ 0.34 (d, 9H, *J*(H, P) = 3.5 Hz, $SiCH_3$), 1.37 (d, 18H, *J*(H, P) = 14.3 Hz, CCH_3).

cis-[μ-[Bis(1,1-dimethylethyl)phosphino]]dicarbonyl-μ-chlorobis[tris(1,1-dimethylethyl)phosphine]dirhodium (5a)

To a stirred solution of 370 mg (0.94 mmol) of $[Rh(CO_2)(\mu\text{-}Cl)]_2$ (**1**) in 30 ml of hexane was added dropwise a solution of 380 mg (1.88 mmol) of P^tBu_3 (**2a**) in 3 ml of the same solvent. The mixture was refluxed for 40 min during which an orange

solution was formed. Treatment with 240 mg (1.10 mmol) of $Me_3SiP^tBu_2$ (**4**) in 7 ml of hexane followed by refluxing for 2 h afforded a yellow powder. This was washed several times with cold hexane and then dried at 0.05 Torr to give 270 mg (32%) of analytically pure **5a**. M.p. 192–194°C (dec.); (lit. 135°C [6,7]); IR (KBr) ν(CO) 1938, 1925 cm^{-1}; ^1H NMR (200 MHz, C_6D_6): δ 1.442 (d, 54H, J(H, P) = 11.3 Hz, $P[C(CH_3)_3]_3$), 1.946 (d, 18H, J(H, P) = 13.2 Hz, $P[C(CH_3)_3]_2$); $^{31}P\{^1H\}$-NMR (162 MHz, C_6D_6): δ 25.11 (tt, 1P, $J(P^{1,2}, P^3)$ = 219 Hz, $J(P^3, Rh^{1,2})$ = 95 Hz, P3), 78.42 (dd, 2P, $J(P^{1,2}, P^3)$ = 219 Hz, $J(P^1, Rh^{1,2}) = J(P^2Rh^{1,2})$ = 106 Hz, P1, P2). Anal. Found: C, 48.26; H, 8.40; Cl, 4.18. $C_{34}H_{72}ClO_2P_3Rh_2$ (847.13) calcd.: C, 48.21; H, 8.57; Cl, 4.19%.

*(+)-cis-[μ-[Bis(1,1-dimethylethyl)phosphino]]dicarbonyl-μ-chlorobis[[5β-methyl-2α-(1α-methylethyl)cyclohexyl]diphenylphosphine]dirhodium (**5b**)*

As in the previous procedure, 250 mg (0.64 mmol) of **1** was treated with 415 mg (1.28 mmol) of **2b** in 30 ml of hexane. After 2 h under reflux the orange solution was treated with 160 mg (0.73 mmol) of **4**. Further refluxing for 3 h and work-up as above afforded 330 mg (47%) of **5b** as a yellow powder. M.p. 154–156°C (dec.); $[\alpha]_D^{25} = +111°$ (c = 1, PhH); IR (KBr): ν(CO) 1940, 1935 cm^{-1}; ^1H-NMR (400 MHz, C_6D_6): δ 0.893 (d, 6H, J(CH, CH_3) = 6.8 Hz, CH_3CHCH_3), 0.929 (d, 6H, J(CH, CH_3) = 6.8 Hz, CH_3CHCH_3), 1.113 (d, 6H, J(CH, CH_3) = 6.6 Hz, CH_2CHCH_3), 1.184–1.850 (m, 8H), 1.869 (d, 18H, J(H, P) = 13.3 Hz, $[C(CH_3)]_2$), 2.008 (m, 6H), 2.135 (m, 2H), 2.967 (m, 2H), 3.220 (m, 2H), 7.055 (m, 12H, Ar*H*), 7.676 (m, 4H, Ar*H*), 7.917 (m, 4H, Ar*H*); $^{31}P\{^1H\}$-NMR (162 MHz, C_6D_6): δ 16.08 (tt, 1P, $J(P^{1,2}, P^3)$ = 228 Hz, $J(P^3, Rh^{1,2})$ = 95.5 Hz, P3), 26.29 (dd, 2P, $J(P^{1,2}, P^3)$ = 228 Hz, $J(P^1, Rh^{1,2}) = J(P^2, Rh^{1,2})$ = 106 Hz, P1, P2). Anal. Found: C, 58.93; H, 6.87; Cl, 3.18. $C_{54}H_{76}ClO_2P_3Rh_2$ (1091.40) calcd.: C, 59.43; H, 7.02; Cl, 3.25%.

Catalytic isomerization of allylbenzene

In a typical procedure 20 mg (2.36×10^{-2} mmol) of **5a** was added to a stirred sample of 1 ml (0.89 g, 7.5 mmol) of preheated allylbenzene. The mixture was maintained at 120 ± 0.5°C and the progress of the reaction monitored by use of a 2 m GLC column packed with 20% Carbowax 20 M on Chromosorb W. The change in extent of formation of the *cis*- and *trans*-1-propenylbenzene with reaction time is shown in Fig. 1.

Hydrogenation of styrene

In a typical experiment, 10 mg (1.18×10^{-2} mmol) of **5a** was placed under argon in a micro-hydrogenation apparatus at 25 ± 0.5°C, the argon was replaced by H_2 and a solution of 200 μl (0.182 g, 1.75 mmol) of styrene in 1 ml of toluene was injected. The progress of the hydrogenation, during which the temperature and hydrogen pressure were 25°C and 690 mm, respectively, was monitored both by the uptake of H_2 and by GLC analysis of the reaction mixture by use of the Carbowax 20 M column specified above. The formation of the ethylbenzene proved to parallel exactly the consumption of H_2. A typical hydrogen-uptake curve is shown in Fig. 2.

Hydrogenation of (Z)-methyl α-acetamidocinnamate

A mixture of 185 mg (0.84 mmol) of the unsaturated ester, 36 mg (4.2×10^{-2} mmol) of **5a**, 10 ml of PhH, and 5 ml of MeOH was introduced under argon into a

mini-autoclave. The apparatus was sealed, purged with argon, and charged with 35 atm H_2. The mixture was heated to 70°C and stirred at that temperature for 20 h. The vessel was then cooled and opened under argon, and the solvent was evaporated. The residue was dissolved in 3 ml of $CHCl_3$ and chromatographed on silica gel with ethyl acetate as eluent to give 170 mg (91%) of (±)-N-acetylphenylalanine methyl ester, which was identical with an authentic sample [16].

When **5a** was replaced by the chiral catalyst **5b**, (45 mg, 4.2×10^{-2} mmol) the product was optically active. Observed $[\alpha]_D^{25} = +20°$ ($c = 1$, $CHCl_3$).

Hydroformylation of cyclohexene

A 100 ml autoclave was charged under argon with 4 ml (3.24 g, 39 mmol) of cyclohexene, 20 mg (2.36×10^{-2} mmol) of **5a**, and 16 ml of toluene. The apparatus was sealed, purged with argon (20 atm), evacuated, and filled with 40 atm of CO and 40 atm of H_2. The mixture was stirred at 120 ± 0.5°C. After 20 h the autoclave was cooled and the mixture found (by GLC on the above Carbowax 20 M column at 40°C) to consist of 94% of cyclohexanecarboxaldehyde and 6% of cyclohexane.

Ackowledgments

We thank the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the exchange program between the Technical University of Berlin and the Hebrew University of Jerusalem, for financial support of the study. We also thank Degussa, Hanau, for a valuable gift of rhodium trichloride.

References

1 R. Poilblanc, Inorg. Chim. Acta, 62 (1982) 75.
2 P.E. Kreter and D.W. Meek, Inorg. Chem., 22 (1983) 319.
3 R.A. Jones and T.C. Wright, Organometallics, 2 (1983) 470.
4 P. Kalck, Polyhedron, 7 (1988) 2441 and references cited therein.
5 H. Schumann, B. Gorella, M. Eisen and J. Blum, J. Organomet. Chem., 412 (1991) 251 and references cited therein.
6 H. Schumann and M. Heisler, J. Organomet. Chem., 153 (1978) 327.
7 H. Schumann and M. Heisler, Chem. Ber., 112 (1979) 541.
8 E.W. Burkhardt, W.C. Mercer and G.L. Geoffroy, Inorg. Chem., 23 (1984) 1779.
9 A.M. Arif, R.A. Jones, M.H. Seeberger, B.R. Whittlesey and T.C. Wright, Inorg. Chem., 25 (1986) 3943.
10 H. Werner, B. Klingert and A.L. Rheingold, Organometallics, 7 (1988) 911.
11 M. Eisen, J. Blum, H. Schumann and B. Gorella, J. Mol. Catal., 56 (1989) 329.
12 J. Blum and Y. Pickholtz, Isr. J. Chem., 7 (1969) 723.
13 J. Blum, I. Amer, K.P.C. Vollhardt, H. Schwarz and G. Höhne, J. Org. Chem., 52 (1987) 2804.
14 H. Schumann and L. Rösch, Chem. Ber., 107 (1974) 854.
15 M. Fild, O. Stelzer and R. Schmutzler, Inorg. Synth., 14 (1973) 4.
16 R. Glasser and B. Vainas, J. Organomet. Chem., 121 (1976) 249.