Journal of Organometallic Chemistry, 302 (1986) 259–264
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ASYMMETRIC HYDROGENATION CATALYZED BY RHODIUM COMPLEXES OF 2,3-BIS(DIMENTHYLPHOSPHINO)MALEIC ANHYDRIDE AND 2,3-BIS(DIMENTHYLPHOSPHINO)-*N*-PHENYLMALEIMIDE

ANNEGRET KINTING* and HANS-WALTER KRAUSE
Central Institute of Organic Chemistry, Academy of Sciences of G.D.R., Rostock (G.D.R.)

(Received September 25th, 1985)

Summary

2,3-Bis(dimenthylphosphino)maleic anhydride and the phenylimide derivative have been prepared from 2,3-dichloromaleic anhydride and 2,3-dichloro-*N*-phenylmaleimide, respectively, and dimenthyl(trimethylsilyl)phosphine. These compounds have been used as ligands for Rh complexes and have been tested in the asymmetric hydrogenation of α-acetamidocinnamic acid, methyl-α-acetamidocinnamate and itaconic acid. Optical yields of up to approximately 70% were obtained with α-acetamidocinnamic acid.

Introduction

In 1974 Fenske and Becher prepared 2,3-bis(diphenylphosphino)maleic anhydride [1] and its derivatives [2] and metal carbonyl complexes therefrom.

We searched for optically active ligands with a planar arrangement of the chelating backbone and suggested as a possible route the preparation of 2,3-bis(dimenthylphosphino)maleic derivatives, which should be available via phosphinylation of 2,3-dichloromaleic anhydride and its analogous phenylimide with suitable dimenthylphosphines.

Since five-membered metal chelates should be achieved and as additional rigidity is exerted by the anhydride ring, relatively high optical yields were expected [3], although in this case the stereoselectivity was promoted by the menthyl groups and not by the backbone.

Results and discussion

Synthesis of 2,3-bis(dimenthylphosphino)maleic anhydride and its derivatives

By treating dimenthyl(trimethylsilyl)phosphine (**1**) with 2,3-dichloromaleic anhydride (**2**) [4] and 2,3-dichloro-*N*-phenylmaleimide (**3**), respectively [5], compounds **4**

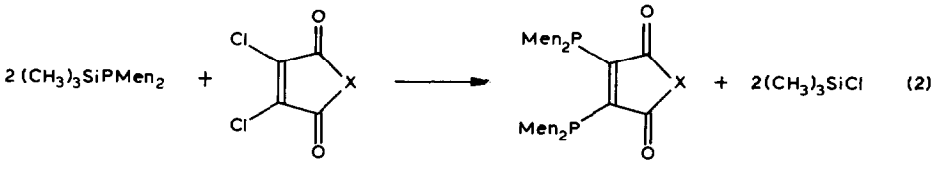
0022-328X/86/$03.50 © 1986 Elsevier Sequoia S.A.

and **5** were synthesized. Dimenthyl(trimethylsilyl)phosphine, which has not yet been described in the literature, was obtained from dimenthylchlorophosphine [6], trimethylchlorosilane and magnesium in tetrahydrofuran using the method for the synthesis of organoelement (Group IVB)-phosphines [7,8] (eq. 1).

$$(CH_3)_3SiCl + Men_2PCl + Mg \xrightarrow{THF} (CH_3)_3SiPMen_2 + MgCl_2 \quad (1)$$

(1)

The diphosphines were prepared according to eq. 2. Compounds **4** and **5** were

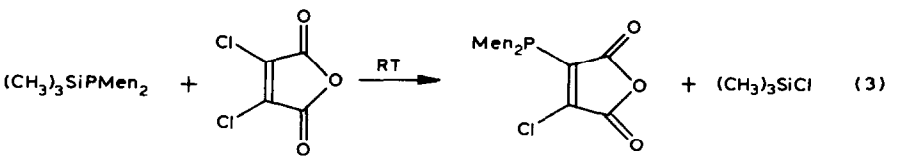


(**2** X = O, **3** X = NC_6H_5) (**4** X = O, **5** X = NC_6H_5)

(Men = (−)-(1*R*,3*R*,4*S*)-menthyl)

obtained as dark red crystals.

The monosubstituted compound **6**, which is orange coloured, was prepared from **1** and **2** under relatively mild conditions (eq. (3)). It offers the principal possibility of preparing mixed phosphines by treating the remaining Cl with another P compound.



(6)

The structures of the chiral maleic derivatives were confirmed by IR, ^{31}P-NMR and mass spectrometry. Typical IR bands are given in the Experimental.

Compounds **2** and **3** display medium bands at 1620 and 1635 cm^{-1}, respectively, expected for ν(C=C) which for compounds **4** and **5** are very weak, making assignment impossible.

As for the analogous Ph_2P derivatives [9], the ^{31}P NMR spectra of **5** displays one signal at δ 14.76 ppm (benzene), thus excluding any phosphine oxide.

We tried to prepare crystalline Rh complexes from **4** and $[Rh(C_8H_{14})_2Cl]_2$ but failed. On the other hand, from $[Rh(NBD)_2]BF_4$ and **5** a crystalline complex could be isolated which from analytical data for C, H and P corresponded to [Rh(NBD)-5]BF_4 but differed markedly in the Rh values.

Asymmetric hydrogenation of α,β-unsaturated acids and esters

Ligands **4**, **5** and **6** were used in the hydrogenation of *Z*-α-acetamidocinnamic acid, its methyl ester and itaconic acid under mild conditions (25°C, 0.1 MPa) using catalysts generated in situ from $[Rh(COD)Cl]_2$ [11] or $[Rh(NBD)_2]BF_4$ [12] and ligands **4**, **5** and **6**. The results are summarized in Table 1. Methanol is the most favourable solvent in these hydrogenations. In the case of ligand **4**, THF was added

to increase the solubility of this ligand. However, the amount of THF added was small because the use of THF as a solvent reduces the optical and chemical yield. The in situ prepared neutral complexes exhibited only a low activity (runs 1, 2 and 13). A higher enantioselectivity and rate were found when the cationic complexes were applied. Ligand **4** gave the best results at molar ratio L/Rh = 1 (run 5), with a small decrease when this ratio was increased to 2 (compare runs 5, 7 and 8 with 6, 9 and 10). Even in small amounts THF lowered the rate. This is shown for **5** (runs 7 and 8), revealing **5** to be less stereoselective than **4**.

The preformed [Rh(NBD)-**5**]BF_4 proved to be less active than the in situ complex. It is worth mentioning that during the hydrogenation reactions slight deposition of rhodium was observed.

Changing the substrate to α-acetamidocinnamic ester generally gave lower optical yields. Again **4** displayed the best results (run 14) and **5** reacted with a higher rate in CH_3OH than CH_3OH/THF (runs 15 and 16).

The hydrogenation of itaconic acid proceeded almost unselectively. Since the reaction rate was rather high and simultaneously rhodium metal was deposited, the result may be influenced by rhodium metal catalyzed unspecific hydrogenation.

Ligand **6** proved to be unsuitable for the asymmetric hydrogenation of α-acetamidocinnamic acid and ester, even in the molar ratio L/Rh = 2.

In comparison with the monodentate dimenthylphosphinoalkylsilanes we investigated recently with respect to their catalytic and stereoselective effects [13], the enantiomeric excess of the bidentate ligands **4** and **5** is rather low, indicating that chelate ring formation has no promoting effect on the enantioselectivity.

Experimental

General procedures

All reactions were carried out under argon, using freshly distilled, dry solvents. The optical yields were determined using a POLAMAT A polarimeter (Carl Zeiss, Jena) or by GLC with an HP-5880 A Gas Chromatograph using *N*-stearoyl-L-valin-t-butylamide in a fused silica capillary column (6.2 m) after transformation of the amino acid to the corresponding methyl ester.

IR spectra were recorded on a Beckman IR 12-spectrophotometer either in Nujol mull or as a KBr disk. ^{31}P NMR spectra were recorded on a Varian CFT-20 spectrometer using H_3PO_4 as external standard.

Preparations

Dimenthyl(trimethylsilyl)phosphine (1). To a vigorously stirred suspension of 1.7 g (0.058 mol) of magnesium in 40 ml of THF, which was heated under reflux, 6.9 ml (0.054 mol) of trimethylchlorosilane mixed with 0.5 ml of ethyl bromide was added dropwise. After addition of trimethylchlorosilane the mixture was heated under reflux for 2 h. Then 11.8 g (0.034 mol) of dimenthylchlorophosphine in 20 ml of THF was added dropwise to the boiling suspension and the heating was continued for a further 30 h. The precipitate formed was filtered off was washed with 50 ml of hexane. The washings were combined with the filtrate and the solvents were removed. Again 50 ml of hexane was added if a precipitate formed during evaporation of the solvent.

TABLE 1

ASYMMETRIC HYDROGENATION OF 1 mmol OF SUBSTRATE IN 15 ml OF SOLVENT AT 25°C, $P(H_2) = 0.1$ MPa and substrate/catalyst = 100

Run	Substrate [a]	Catalyst [b]	Rh/L	Solvent [d]	Time (h)	Conversion (%)	Optical yield [e] (%)	Conf.
1	A	**4**+$[Rh(COD)Cl]_2$	1/1	CH_3OH/THF	24	69.3	30.7	*R*
2		**5**+$[Rh(COD)Cl]_2$	1/1	CH_3OH/THF	45.5	71.9	58.0	*R*
3		**5**+$[Rh(COD)Cl]_2$	1/1	CH_2Cl_2	24	0	–	–
4		**4**+$[Rh(NBD)_2]BF_4$	1/1	THF	22	11.3	33.9	*R*
5		**4**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH/THF	8	100	69.7	*R*
6		**4**+$[Rh(NBD)_2]BF_4$	1/2	CH_3OH/THF	8	100	68.2	*R*
7		**5**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH/THF	22	100	56.9	*R*
8		**5**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH	7	100	59.2	*R*
9		**5**+$[Rh(NBD)_2]BF_4$	1/2	CH_3OH/THF	23	89.3	35.8	*R*
10		**5**+$[Rh(NBD)_2]BF_4$	1/2	CH_3OH	8	100	56.0	*R*
11		[NBDRh-**5**]BF_4 [c]		CH_3OH/THF	23	89.1	37.9	*R*
12		[NBDRh-**5**]BF_4 [c]		CH_3OH	25	100	37.1	*R*
13	B	**5**+$[Rh(COD)Cl]_2$	1/1	CH_3OH/THF	72	59	56.1	*R*
14		**4**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH/THF	2.5	100	41.0	*R*
15		**5**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH/THF	23	96.6	40.7	*R*
16		**5**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH	4	100	38.3	*R*
17	C	**4**+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH/THF	4.5	100	6.3	*S*
		5+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH/THF	4.5	100	5.3	*S*
		5+$[Rh(NBD)_2]BF_4$	1/1	CH_3OH	2	100	8.9	*S*

[a] A = α-acetamidocinnamic acid, B = methyl-α-acetamidocinnamate, C = itaconic acid. [b] Prepared in situ. [c] Preformed complex. [d] CH_3OH/THF = 14 ml/1 ml. [e] *N*-Acetylphenylalanine and its methyl ester were determined by GLC [14]; methylsuccinic acid was calculated from the specific rotation of the pure enantiomers [15].

The residue was distilled under reduced pressure, b.p. 125°C/5 × 10^{-3} mmHg. The resulting oil crystallized after a short time. The yield was 5.9 g (45.4%), $[\alpha]_D^{10}$ −177° (*C* 4.78, benzene). Found: C, 72.35; H, 12.25; P. 8,7. $C_{23}H_{47}PSi$ calcd.: C, 72.18; H, 12.38; P, 8.09%. IR (cm^{-1}): 1460s(CH_3); 1390m, 1370m($(CH_3)_2CH$); 1250m, 845s($(CH_3)Si$).

2,3-Dichloromaleic anhydride (2). The preparation was modified as follows. Mucochloric acid (10 g) was heated under reflux over a period of about 10 h with fuming nitric acid. The solution was concentrated under reduced pressure and the precipitate formed was filtered and purified by sublimation, giving a 46% yield, m.p. 119°C. Found: C, 28.75; Cl, 42.4. $C_4O_3Cl_2$ calcd.: C, 28.78; Cl, 42.47%.

2-Chloro-3 dimenthylphosphinomaleic anhydride (6). To a solution of 7.7 mmol of **2** in 40 ml of ether at 0°C, 7.8 mmol of **1** in 20 ml of ether was added dropwise over a period of 1 h. Immediately the solution turned an intensive yellow colour and then red-brown. The ether was evaporated and 5 ml of petroleum ether (b.p. 30–50°C) was added to the residue. After cooling to −78°C, the orange-coloured precipitate was filtered after 24 h and recrystallized from hexane, giving only a 30% yield, m.p. 152–153°C. Found: C, 65.85; H, 8.65; P, 6.7, Cl, 8.3. $C_{24}H_{38}O_3ClP$ calcd.: C, 65.36; H, 8.68; P, 7.02; Cl, 8.04%.

2,3-Bis(dimenthylphosphino)maleic anhydride (4). To a solution of 0.01 mol of **2** in 50 ml of ether at 0°C, 0.025 mol of **1** in 30 ml of ether was added dropwise over a period of 90 min. The solution immediately turned an intense yellow colour and afterwards red-brown. After addition of **1**, the solution was heated under reflux for 3 h, concentrated and diluted with 10 ml of petroleum ether (b.p. 30–50°C). At +5–0°C a dark-red substance precipitated, which was filtered, washed with petroleum ether (b.p. 30–50°C), dried in vacuo and recrystallized from benzene, giving a 56% yield, m.p. 199–201°C (dark-red needles). Found: C, 73.90; H, 10.82; P, 8.7. $C_{44}H_{76}P_2O_3$ calcd.: C, 73.91; H, 10.71; P, 8.66%. *m/e* 714 (mol. peak), 699 ($M^+ - CH_3$), 671 ($M^+ - CH(CH_3)_2$), 575 ($M^+ -$ Men), 310 ($HPMen_2$), 139 (Men). IR (cm^{-1}): 1825 w, 1765s (C=O); 1460m(CH_3); 1390m, 1370m ($(CH_3)_2CH$).

2,3-Bis(dimenthylphosphino)-N-phenylmaleimide (5). **5** was prepared as described above for **4** according to equation 2, using THF instead of ether. The impurities of the dark-red crude product were extracted with methanol, leaving the product in a 60% yield, m.p. 217–219°C. Found: C, 75.98; H, 10.36; P, 7.59; N, 1.82. $C_{50}H_{81}P_2O_2N$ calcd.: C, 76.00; H, 10.33; P, 7.84; N, 1.77%. IR (cm^{-1}): 1765w, 1710s (C=O); 1460m (CH_3); 1390m, 1370m ($(CH_3)_2CH$).

Bicyclo[2.2.1]heptadiene-[2,3-bis(dimenthylphosphino)-N-phenylmaleimide]rhodium(I) tetrafluoroborate. 0.188 mmol of $[Rh(NBD)_2]BF_4$ (**12**) and 0.36 mmol of **5** in 1.5 ml of CH_2Cl_2 and 1.5 ml of THF were stirred at room temperature for 1 h. Then the solution was reduced to a volume of 0.5 ml and 5 ml of petroleum ether (b.p. 30–50°C) was added, which caused precipitation of a brown complex. The precipitate was filtered, washed three times with 5 ml of petroleum ether (b.p. 30–50°C) and dried in vacuo, giving a 79.6% yield. Found: C, 63.77; H, 8.41; P, 5.89; Rh, 7.84. $RhC_{57}H_{89}F_4N\,O_2P_2B$ calcd.: C, 63.86; H, 8.37; P, 5.78; Rh, 9.60%.

Hydrogenation experiments

1 mmol of substrate and 0,01 mmol of Rh catalyst precursor were placed in a hydrogenation vessel. Under argon 14 ml of methanol was added. The mixture was stirred until dissolution was complete. The ligand, dissolved in 1 ml of THF, was

added (in the absence of THF, the ligand was placed with the Rh catalyst precursor in the flask and 15 ml of methanol was added). This mixture was stirred for 5 min under argon and then the flask was connected to the hydrogenation apparatus under hydrogen. The hydrogenation was carried out at 0.1 MPa and 25°C. The solvents were removed and the extent of conversion and optical rotation were determined.

References

1 D. Fenske and H. Becher, Chem. Ber., 107 (1974) 117.
2 D. Fenske and H. Becher, Chem. Ber., 108 (1975) 2115.
3 H. Brunner, Angew. Chem., 95 (1983), 921.
4 G.L. Ciamician and P. Silber, Chem. Ber., 16 (1883) 2396.
5 H.M. Relles and R.W. Schluenz, J. Org. Chem., 37 (1972) 1742.
6 H.W. Krause and A. Kinting, J. Prakt. Chem., 322 (1980) 485.
7 H. Schuhmann and L. Rösch, Chem. Ber., 107 (1974) 854.
8 H. Schuhmann and W.-W. du Mont, Chem. Ber., 108 (1975) 2261.
9 H.J. Becher, W. Bensmann, D. Fenske and B. Pfenning, Monatsh. Chem., 109 (1978) 1023.
10 A. van der Ent and A.L. Onderdelinden, Inorg. Synth., 14 (1973) 92.
11 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
12 R. Usón, L.A. Oro, M.A. Garralda, M.C. Claver and P. Lahuerta, Trans. Met. Chem., 4 (1979) 55.
13 A. Kinting, M. Capka and H.-W. Krause, J. Mol. Catal., 33 (1985) 215.
14 R. Charles, U. Beitler, B. Feibusch and E. Gil-Av. J. Chromatogr., 112 (1975) 121.
15 E.P. Kyba, R.E. Davis, P.N. Juri and K.R. Shirley, Inorg. Chem., 20 (1981) 3616.