# RHODIUM–DIPHOSPHINE TOSYLATE COMPLEXES AS HYDROGENATION CATALYSTS*

Jiří Reiss and Jiří Hetflejš

*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6 – Suchdol*

Received July 23rd, 1985

Novel rhodium–diphosphine tosylate complexes of the type $[Rh(COD)L_2]^+ (O_3SC_6H_4CH_3\text{-}p)^-$ ($L_2$ = diphos, prophos, buphos, (−)-DIOP) have been prepared in high yields (87–92%) by the displacement of acac ligand from Rh(COD)(acac) by *p*-toluenesulphonic acid in the presence of $L_2$. The complexes were found to be efficient hydrogenation catalysts comparable in activity to known cationic rhodium complexes. Some differences in the catalytic behaviour of both systems are reported, using hydrogenation of 1-octene and *Z*-α-acetamidocinnamic acid as model reactions.

Our earlier interest in immobilization of asymmetric hydrosilylation and hydrogenation catalysts[1] has led us to investigate the applicability of organic ion exchangers containing sulphonic acid groups as supports for this purpose. Until now, efficient polymer supported asymmetric hydrogenation catalysts have been obtained *via* anchoring chiral phosphines (for recent discussion *cf.*[2]). This route is limited to a few phosphines which could be bound to the polymer surface without deterioration of their chirality.

In the light of the known high catalytic activity of cationic rhodium complexes in hydrogenation of dehydroamino acids[3], it seemed useful to verify whether the noncoordinating ligands such as $ClO_4^-$, $PF_6^-$ *etc.* can be substituted for arenesulphonic acid groups while preserving the efficiency of the catalysts. As the course of reactions leading to immobilization is difficult to follow on polymer surface and no data were available on analogous soluble complexes, we have been interested first in the synthesis of the rhodium–diphosphine arenesulphonate complexes and their hydrogenation activity. The results obtained are reported in the present work.

## EXPERIMENTAL

### Phosphines and Rhodium Complexes

Triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (diphos) were commercial samples (Fluka AG, Buchs). 1,3-Bis(diphenylphosphino)propane (prophos)[4] and 1,4-bis(diphenylphosphi-

* Part LXIX in the series Catalysis by Metal Complexes; Part LXVIII: This Journal *50*, 2647 (1985).

no)butane (buphos)[4] were prepared by the reported procedures. (2*R*, 3*R*)-2,3-0-Isopropylidene--2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((-)-DIOP) was taken from laboratory stock: m.p. 88–89°C, $[\alpha]_{546}^{21}$ — 12·34° (*c* 4·2, benzene). All the phosphines were dried at room temperature at a pressure of $10^{-3}$ Pa and then stored under argon.

Rhodium complexes used as the starting compounds for synthesis of rhodium–phosphine tosylates ($[RhCl(1,5\text{-}COD)]_2$ (ref.[5]) and Rh(acac)(1,5-COD) (ref.[6])) were prepared by the reported procedures as indicated and showed identical IR spectra with those reported in the cited works. The complexes were stored under argon.

## Rhodium–Phosphine Tosylate Complexes

The synthesis of these complexes was made by two procedures illustrated on example of $[Rh(1,5\text{-}COD)(diphos)]^+ (O_3SC_6H_4CH_3\text{-}p)^-$.

*Procedure* A. A mixture of 512 mg (1·65 mmol) of Rh(1,5-COD)(acac), 664 mg (1·67 mmol) od diphos, and 287 mg (1·67 mmol) of *p*-toluenesulphonic acid in 5 ml of dichloromethane was stirred for 15 min at room temperature under argon. To a dark orange solution, 100 ml of diethyl ether were added, the orange precipitate formed was filtered off, washed with diethyl ether and dissolved in 5 ml of dichloromethane. Stirring was continued for another 15 min, the precipitate formed after adding another 100 ml portion of diethyl ether was separated, washed with the ether, dried *in vacuo* at room temperature and stored under argon. The product (1·17 g, 90·4% yield) melted at 145–147°C and its elemental analysis was that expected for $[Rh(1,5\text{-}COD)(diphos)]^+ (O_3S\text{-}C_6H_4CH_3\text{-}p)^-$ (no solvate).

*Procedure* B. A solution of 8·5 g (0·25 mol) of $AgNO_3$ in 100 ml of distilled water was mixed with aqueous KOH solution until dark precipitate was formed. The precipitate was washed several times with about 300 ml of water and then dissolved in 250 ml of solution containing 48 g of *p*-toluenesulphonic acid monohydrate. The solution was filtered, evaporated to half volume and allowed to stand at room temperature. The Ag salt was filtered off, washed with ethanol, dried *in vacuo* and stored under argon.

A total of 205 mg (0·73 mmol) of silver *p*-toluenesulphonate was dissolved in 80 ml of methanol and mixed under stirring with a solution of 181 mg (0·37 mmol) of $[RhCl(1,5\text{-}COD)]_2$ and 293 mg (0·74 mmol) od diphos in 700 ml of methanol. Stirring was continued for another 30 min and then the solution was allowed to stand overnight. The precipitate of silver chloride was filtered off and the solution was evaporated to dryness. The orange-yellow compound was dissolved in 10 ml of dichloromethane, the solution was freed of solid impurities by filtration and then it was evaporated to about 3 ml. After precipitation with 100 ml of diethyl ether, the orange solid was washed with the ether, dried *in vacuo* and stored under argon. The product had m.p. 143–146°C and identical elemental analysis as that obtained by procedure *A* (72% yield). The other rhodium arenesulphonates prepared are presented in Table I, along with m.p. and yields obtained by procedure *A*. Electronic spectra of the complexes were measured on Specord UV-VIS instrument (300–700 nm wavelength, 0·5–5 cm cells) under argon (see Results and Discussion).

## Testing of Catalysts

Hydrogenation activity of the complexes was tested with 1-heptene and *Z*-α-acetamidocinnamic acid as model substrates, using the hydrogenation apparatus described earlier[7]. All manipulations with the substrates, solvents and the catalysts were made under argon. When stock solution of the

catalyst was used, it was prepared fresh prior to measurements, to avoid catalyst aging. Reaction conditions are given in Table II. The activity was evaluated by determining initial reaction rates ($r^0$) from the rate of hydrogen uptake at constant hydrogen pressure.

TABLE I

Rhodium–diphosphine tosylate complexes prepared by procedure *A*

| Complex[a] | M.p., °C | Yield, % |
|---|---|---|
| $[Rh(COD)(diphos)]^+(tos)^-$[b] | 145—147 | 90 |
| $[Rh(diphos)_2]^+(tos)^-$ | 181—184 | 87 |
| $[Rh(COD)(prophos)]^+(tos)^-$ | 146—149 | 92 |
| $[Rh(COD)(buphos)]^+(tos)^-$ | 148—150 | 87 |
| $[Rh(COD)(DIOP)]^+(tos)^-$ | 149—150 | 89 |

[a] tos = $O_3SC_6H_4CH_3$-*p*; [b] $^{31}P$ NMR (in $CDCl_3$): $\delta$ 56·28 ppm, $J$(Rh-P) 148·5 Hz (chemical shift with respect to the external 85% $H_3PO_4$).

TABLE II

Initial reaction rates ($r^0$, mol $H_2$ $s^{-1}$ (mol Rh)$^{-1}$) of hydrogenation of 1-octene and *Z*-α-acetamidocinnamic acid catalysed by rhodium–phosphine complexes (benzene–ethanol (1 : 1, v/v), 40°C, $p(H_2)$ = 149 kPa, Rh conc. 2 . $10^{-3}$ mol $l^{-1}$, Rh : P molar ratio = 1 : 2)

| No | Catalysts | $r^0$ . $10^3$ | |
|---|---|---|---|
| | | 1-octene[a] | *Z*-α-acetamidocinnamic acid[b] |
| *1* | $[RhCl(COD)]_2$ + diphos | 23·7 | 3·0 |
| *2* | $[RhCl(COD)]_2$ + $P(C_6H_5)_3$ | 28·9 | —[c] |
| *3* | $[RhCl(COD)]_2$ + diphos + tos Ag | 65·9 | 67·5 |
| *4* | $[RhCl(COD)]_2$ + $P(C_6H_5)_3$ + tos Ag | 96·5 | —[c] |
| *5* | Th(COD)(acac) + diphos | 37·8 | 67·0 |
| *6* | Rh(COD)(acac) + diphos + tos H | 60·7 | 122·5 |
| *7* | $[Rh(COD)(diphos)]^+(tos)^-$ | 67·4 | 118·8 |
| *8* | $[Rh(diphos)_2]^+(tos)^-$ | 28·9 | —[c] |
| *9* | $[Rh(COD)(prophos)]^+(tos)^-$ | —[d] | 144·9 |
| *10* | $[Rh(COD)(buphos)]^+(tos)^-$ | —[d] | 223·5 |
| *11* | $[Rh(COD)(DIOP)]^+(tos)^-$ | —[d] | 420·1 |

[a] Concentration 0·58 mol $l^{-1}$; [b] concentration 0·231 mol $l^{-1}$; [c] catalysts inactive under given reaction conditions; [d] not measured.

## RESULTS AND DISCUSSION

### *Synthesis of Rhodium–Phosphine p-Toluenesulphonate Complexes*

By analogy to the synthesis of cationic rhodium complexes[8,9], we have tested the applicability of two procedures for preparing arenesulphonate complexes: *a*) the displacement of acac ligand from Rh(1,5-COD)(acac) by *p*-toluenesulphonic acid with coordination of diphosphine ligand ($L_2$) (Eq. (*A*)) and *b*) the reaction of $[RhCl(1,5\text{-COD})]_2$ with silver *p*-toluenesulphonate in the presence of $L_2$, (Eq. (*B*)).

$$Rh(1,5\text{-COD})(acac) + L_2 + CH_3C_6H_4SO_3H \rightarrow$$
$$\rightarrow [Rh(L_2)(1,5\text{-COD})]^+(O_3SC_6H_4CH_3)^- + acacH \qquad (A)$$

$$\tfrac{1}{2}[RhCl(1,5\text{-COD})]_2 + L_2 + CH_3C_6H_4SO_3Ag \rightarrow$$
$$[Rh(L_2)(1,5\text{-COD})]^+(O_3SC_6H_4CH_3)^- + AgCl \qquad (B)$$

Although, as shown in experimental part on example of the synthesis of $[Rh(diphos)(1,5\text{-COD})]^+(O_3SC_6H_4CH_3\text{-}p)^-$ complex, both procedures yield the expected complexes in comparable purity, the procedure *B* is less convenient in this case, both due to the low solubility of the silver salt and to difficult separation of fine precipitate of silver chloride. Of several solvents tested in procedure *A*, the reaction in dichloromethane followed by precipitation of the product by diethyl ether turned out to be the most suitable. Re-dissolution of the complex so prepared in dichloromethane and subsequent precipitation with the ether gives the pure product. Procedure *A* has been used to prepare several Rh–diphosphine complexes in high chemical yields (Table I).

The reaction can be followed by electronic spectra; Rh(1,5-COD)(acac) shows a weak absorption band with maximum at 362 nm (27 600 $cm^{-1}$, $\varepsilon_{362} = 4{\cdot}98 \cdot 10^2$); in the presence of *p*-toluenesulphonic acid this band is shifted to 350 nm (28 550 $cm^{-1}$, $\varepsilon_{350} = 5{\cdot}05 \cdot 10^2$). In both cases the coordination of a diphosphine leads to immediate formation of a band at 443 nm (22 600 $cm^{-1}$), attaining maximum intensity ($\varepsilon_{443} = 1{\cdot}77 \cdot 10^3$) at Rh: diphosphine molar ratio = 1 : 1; further addition of the diphosphine results in formation of a new band with maximum at 403 nm (24 800 $cm^{-1}$), the intensity of which increases up to Rh : diphosphine molar ratio = = 1 : 2 ($\varepsilon_{403} = 2{\cdot}96 \cdot 10^3$) with simultaneous decrease of the 443 nm band. The same electronic spectra were obtained with the isolated complexes. This situation is shown in Figs 1*a*,*b* for formation of the $[Rh(COD)(diphos)]^+$ (band at 443 nm) and $[Rh(diphos)_2]^+$ (band at 403 nm) complexes. The equilibrium constant for $[Rh(diphos)(1,5\text{-COD})]^+(O_3SC_6H_4CH_3\text{-}p)^-$ was found to be $10^5$ $mol^{-1}$ l.

*Hydrogenation Activity of the Arenesulphonate Complexes*

To estimate the effect of tosylate ligand on the catalytic behaviour of rhodium–phosphine complexes, their activity (expressed by initial rates, $r^0$) was compared

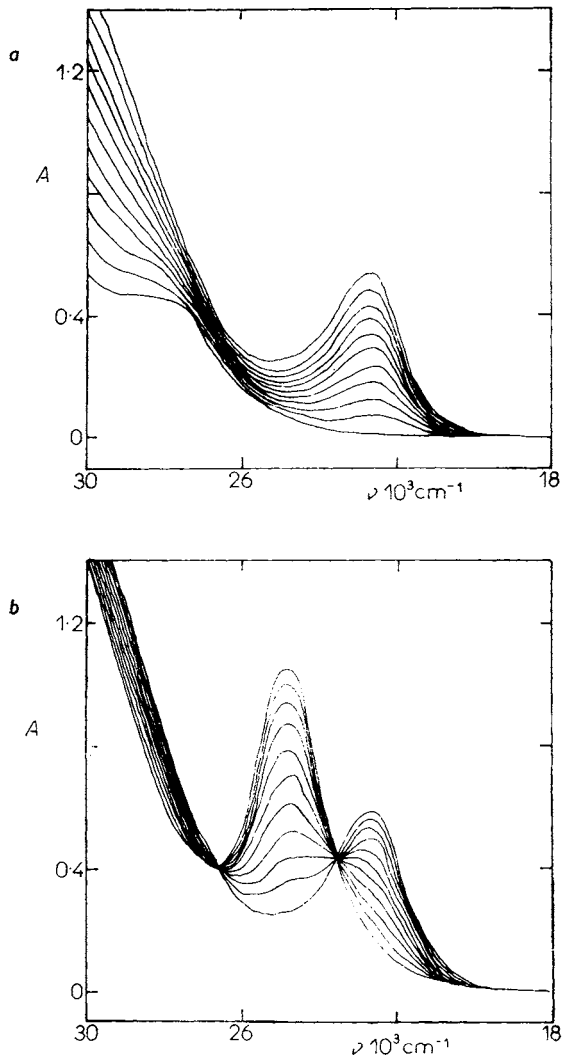


FIG. 1

Changes in the electronic spectrum of Rh(COD)(acac) due to the reaction with diphos and *p*-toluenesulphonic acid (both components in 1 : 1 molar ratio) in benzene–ethanol (1 : 1, v/v) at 20°C. *a*) The diphos: Rh molar ratio increases by 0·1 from 0 to 1·0; *b*) the diphos: Rh molar ratio increases by 0·1 from 1·0 to 2·0

with the complexes of Wilkinson type prepared *in situ* from $[RhCl(COD)]_2$ and diphos or $P(C_6H_5)_3$ (Rh : P = 1 : 2), using hydrogenation of 1-octene and *Z*-α-acetamidocinnamic acid as model reactions. The results presented in Table II show that: *a*) Rh(I) complexes containing bidentate phosphine (diphos) catalyze both reactions, while $Rh–P(C_6H_5)_3$ complexes are inactive in hydrogenation of *Z*-α--acetamidocinnamic acid (lines *2*, *4*), the increase in the Rh : diphos ratio to 1 : 2 has the same effect (line *8*), in accordance with earlier reports[10,11]; *b*) as expected, Rh–diphos complexes are in general the less efficient catalysts for hydrogenation of simple alkenes compared to the complexes with similarly substituted monodentate phosphines (lines *1*, *2* or *3*, *4*); *c*) the tosylate ligand introduced by two ways used to prepare the rhodium–phosphine arenesulphonate complexes (lines *3* and *6*) increases the activity of the catalysts in both hydrogenations, their efficiency being comparable to that of known cationic rhodium complexes; *d*) the activity of the *in situ* catalysts (lines *3*, *6*) is further comparable within experimental error with the activity of the isolated complex (line *7*), this speaks not only for the same type of catalytically active species in both systems but also for fast formation of these complexes *in situ* under reaction conditions, in accordance to the results obtained by measurements of the electronic spectra discussed in the preceding part; *e*) as far as the effect of diphosphine ligand is concerned, the activity of the catalysts in hydrogenation of *Z*-α-acetamidocinnamic acid increases with increasing chelate ring size (diphos < < prophos < buphos, lines *7*, *9*, *10*), *i.e.* in the sequence already observed for cationic Rh complexes (ref.[12]), the behaviour of the Rh-DIOP catalyst is consistent with this trend (line *11*).

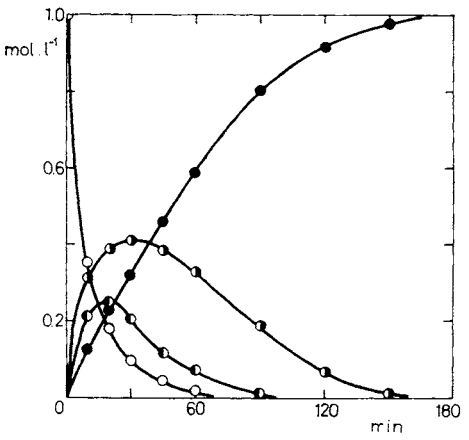


FIG. 2

Hydrogenation of 1-heptene catalyzed by $[Rh(COD)(diphos)]^+ (tos)^-$ (benzene–ethanol 1 : 1, v/v, 40°C, Rh concentration $3{\cdot}4 \cdot 10^{-2}$ mol $l^{-1}$, alkene concentration 1 mol $l^{-1}$, $p(H_2) = 149$ kPa) ○ 1-heptene, ● heptane, ◑ *trans*-2-heptene, ◐ *cis*-2-heptene

It is worth mentioning that the hydrogenation of Z-α-acetamidocinnamic acid catalysed by the tosylate complexes proceeds at constant hydrogen pressure at a rate independent of the acid concentration, indicating thus zero order of the hydrogenation in the acid. This speaks for the similarity in the behaviour of the above catalysts and cationic rhodium complexes for which the same situation was already reported[13], in contrast to the complex kinetics of hydrogenation of the acid catalysed by analogous neutral Rh complexes[11].

As shown on example of 1-heptene in Fig. 2, its hydrogenation is accompanied by fast isomerization to 2-alkenes, with the *trans* isomer prevailing. 3-Heptenes have not been detected. The complexes are not isomerization catalysts and the reaction does not proceed under given reaction conditions in the absence of hydrogen. In this connection it is of interest that isomerization of alkenes has not been reported for cationic Rh–diphos complexes[14]. This different course of the reaction indicates that in the case of alkenes the analogy to the structure of catalytically active species[14] evidenced for the cationic complexes is unwarranted. In contrast to the noncoordinating anions used in known cationic Rh complexes (*e.g.* $ClO_4^-$, $BF_4^-$, $PF_6^-$), the tosylate ligand seems thus to affect the coordination sphere of the metal at least in some steps of the reaction.

Summarizing, in the present work it has been documented that *p*-tosylate can be used to prepare well defined rhodium–diphosphine complexes which exhibit hydrogenation activity comparable to that of known cationic rhodium complexes. This finding opens the possibility of synthesizing the catalysts anchored to ion exchangers containing sulphonic acid groups as an alternative route of immobilization.

REFERENCES

1. Kolb I., Černý M., Hetflejš J.: React. Kinet. Catal. Lett. *7*, 199 (1977).
2. Pittman C. U., jr in the book: *Comprehensive Organometallic Chemistry* (G. Wilkinson, Ed.), Vol. 8, Chapter 55. Pergamon Press, Oxford 1982.
3. Kagan H. B., in the book: *Comprehensive Organometallic Chemistry* (G. Wilkinson, Ed.), Vol. 8, Chapter 53. Pergamon Press, Oxford 1982.
4. Sacconi I., Gelsomini J.: Inorg. Chem. *7*, 291 (1968).
5. Chatt J., Venanzi L. M.: J. Chem. Soc. A *1957*, 4738.
6. Cramer R.: J. Amer. Chem. Soc. *86*, 217 (1964).
7. Vilím J., Hetflejš J.: Chem. Listy *70*, 188 (1976).
8. Garralda M. A., Oro L. A.: Trans. Met. Chem. *5*, 132 (1980).
9. James B. R., Mahajan D.: Can. J. Chem. *58*, 996 (1980).
10. Kagan H. B., Dang T. P.: J. Amer. Chem. Soc. *94*, 6429 (1972).
11. Vilím J., Hetflejš J.: This Journal *43*, 122 (1978).
12. Landis C. R., Halpern J.: J. Organometal. Chem. *250*, 485 (1983).
13. Vaisarová V., Hetflejš J.: 2nd Symposium Italian–Czechoslovak on Catalysis (Bologna 1979), Abstract B 10.
14. Halpern J., Riley D. P., Chan A. S. C., Pluth J. J.: J. Amer. Chem. Soc. *99*, 8055 (1977).

Translated by the author (J. H.).