Journal of Organometallic Chemistry, 159 (1978) 91—98

CATALYTIC HYDROGENATION OF PROPENE OVER POLYMER SUPPORTED RHODIUM COMPLEXES

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(Received April 3rd, 1978)

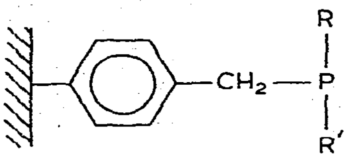
Summary

Hydrogenation of propene and other substrates has been studied in flow and batch reactors using various rhodium catalysts. The results show that in some cases rhodium metal is probably formed, but only if solvent is present. A possible explanation is given.

Introduction

Polymer-attached rhodium complexes have been proved to be effective catalysts in the hydrogenation of a variety of unsaturated compounds [1—4]. Under certain experimental conditions, selective hydrogenation of olefins and ketones catalyzed by rhodium(I) polyphosphine complexes of the type $[Rh(NBD)LL]^+$ (L = polyphosphine ligand) was also found [5]. In a more detailed study of these reactions a solvent-dependent induction period was observed [6,7]. Reuse of the catalyst gave a strong increase in catalytic activity and the disappearance of the induction time. This catalyst activation by H_2 could correspond to the formation of rhodium metal [6]. However, if the P/Rh ratio is increased (for example to 10) the compounds are more stable and no reduction to metal is observed. Complexes of the same type, $[Rh(NBD)LL']^+$, but having only one ligand (L or L′) polymeric, are stable toward reduction, even at high H_2 pressures, suggesting some sort of destabilization of the immobilized complexes with increasing rhodium content at constant phosphorus content and hence with increasing "chelating" ability of the polymer. The mobility of the resin with low divinylbenzene content entails the possibility of linkage by even remote phosphines, reducing possible strain in the polymeric chain [5,8] and enhance complex stability toward reduction.

To provide a better understanding of the factors causing possible reduction to rhodium metal we have examined the hydrogenation of a variety of substrates catalyzed by rhodium compounds bound to polymeric phosphines of type I.



(I)

$R = R' = Ph; R = Ph, R' = Menthyl$

The results obtained in flow reactors are compared to those found in batch reactors, where solvent is always present.

Results and discussion

We studied three different catalysts: A: $[Rh(NBD)(PolyPPh_2)_2]ClO_4$; B: $[Rh(NBD)(PolyPPh_2)_2]ClO_4$ (used after hydrogen treatment; see Experimental); C: $[Rh(NBD)(PolyPPh\ Menthyl)_2]ClO_4$ (used after hydrogen treatment; see Experimental). (NBD = norbornadiene, Poly = styrene 2% divinylbenzene copolymer). Analytical data are reported in Table 2.

The activities in flow reactors of catalysts A, B, and C for propene hydrogenation are shown in Fig. 1.

Catalysts B and C behave rather similarly, but catalyst A displays a much smaller activity. As shown in Table 2 the catalysts have the same rhodium content, and compounds A and B have also the same P/Rh ratio which, as we have

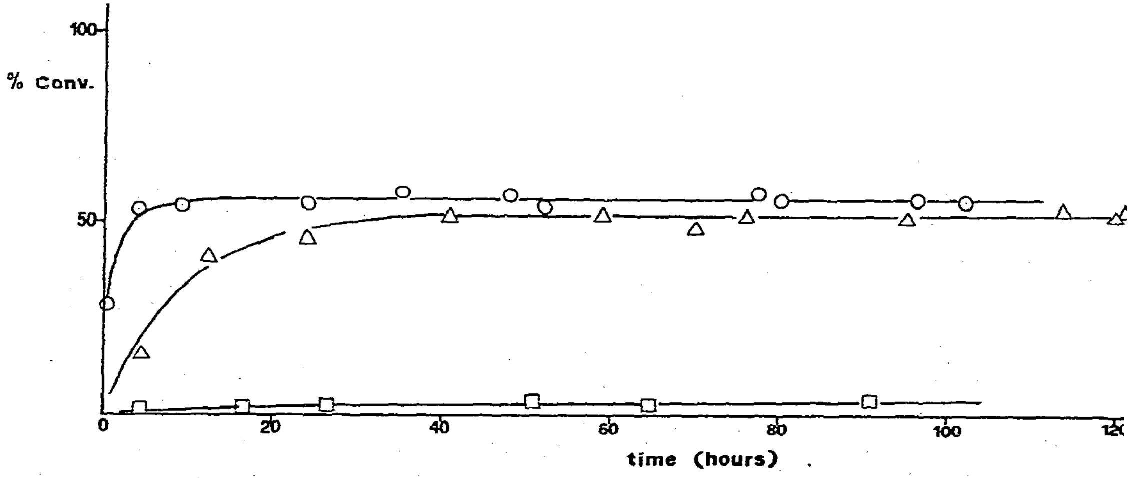


Fig. 1. Hydrogenation of propene: T 88°C; τ 38.6 g h mol^{-1}; p_{total} 1 Atm; $p(H_2)$ 0.77; H_2/propene = 3.3. Catalysts: (A) □ $[Rh(NBD)(PolyPPh_2)_2]^+$; (B) ○ $[Rh(NBD)(PolyPPh_2)_2]^+$ recycled; (C) △ $[Rh(NBD)(PolyPPhMenthyl)_2]^+$ recycled.

previously reported [5] is important in determining the behaviour of this type of catalysts [5,9]. In batch reactors, rhodium metal or rhodium(II) was formed at the end of the hydrogenation; depending on the conditions with increasing P/Rh ratio, the stability of this type of complex toward hydrogen reduction increases, but at the same time the catalytic activity decreases, due to uncoordinated phosphines present on the resin [5,10]. As shown in Fig. 1, catalysts B (P/Rh = 5.9) and C (P/Rh = 2.9), display a much higher activity than A (P/Rh = 5.9), even when the rhodium content is the same in the three cases. Compound A, however, catalyzes hydrogenation of olefins in batch reactor, but it loses its catalytic activity in the presence of a good coordinating agent such as CH_3CN. If the same reaction is carried out with a catalyst which has been already used in the presence of solvent as a hydrogenation catalyst (e.g. compound B), the catalytic activity is almost the same both in the presence or absence of CH_3CN, showing that such a catalytic species is insensitive to competition with a good ligand such as CH_3CN. These results may be interpreted in terms of catalysis by rhodium metal. Formation of rhodium metal has also been proposed for hydrogenation of hexene catalyzed by rhodium complexes [13]. We feel, however, that the polymeric support also plays an important role. Heating at 130—140°C causes cracking of the polymer, with formation of rhodium metal and complete loss of catalytic activity, probably due to the formation of large aggregates. Catalyst $[Rh(NBD)(PolyPPh_2)_2]^+$ (A) is rather active in olefin hydrogenation in batch reaction [5], but it displays a very poor activity in flow reactor (Fig. 1). Pretreatment of A in dry state with H_2 at 88°C for 24 h does not improve the catalytic activity. This lack of activity can be related to the difficulty of forming hydrido complexes of rhodium(III) in absence of solvent, and/or to a much slower hydrogenation of the diolefin in the first catalytic cycle arising from the impossibility of forming $[Rh(PolyPPh_2)_2H_2S_2]^+$ (where S is a molecule of solvent) under these conditions [5].

The behavior of catalyst B in the hydrogenation of propene, at constant pressure, and contact time, defined as $\tau = w/Q$ (w = g of catalyst; Q = mol of substrate flowing in 1 h), is shown in Fig. 2. A steady increase in the conversion

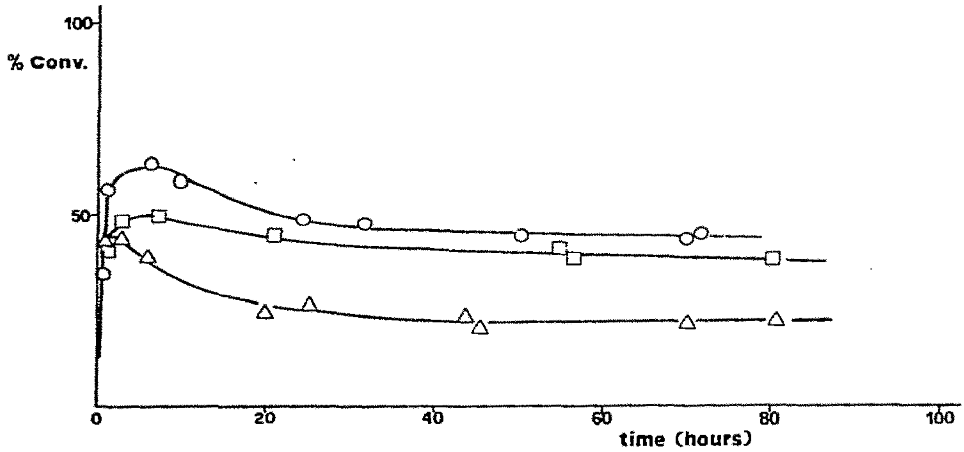


Fig. 2. Hydrogenation of propene; catalyst $[Rh(NBD)(PolyPPh_2)_2]^+$ recycled (B); τ 41.6 g h mol^{-1}; p_{total} 1 Atm; $p(H_2)$ 0.8 Atm; H_2/propene = 4. ○ 106.6°C; □ 98.6°C; △ 73.0°C.

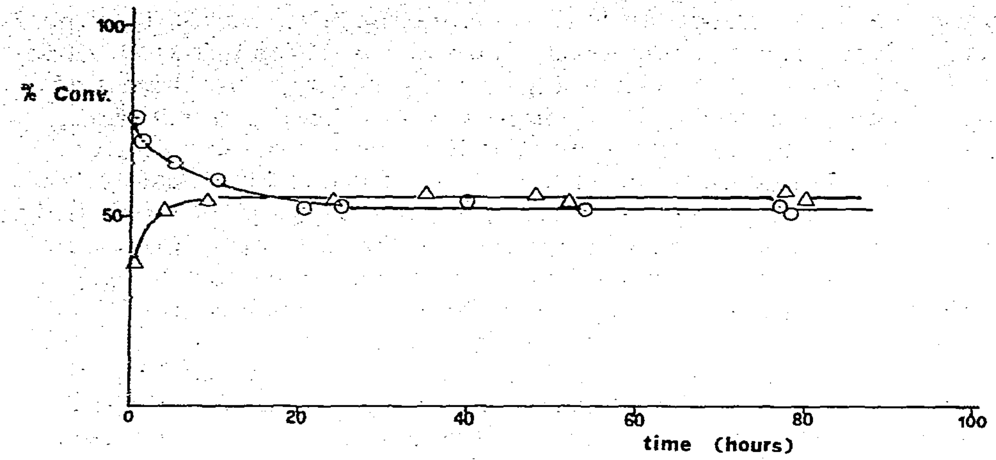


Fig. 3. Hydrogenation of propene; catalyst $[Rh(NBD)(PolyPPh_2)_2]^+$ recycled (B); T 88°C; τ 38.6 g h mol^{-1}; p_{total} 1 Atm; $p(H_2)$ 0.77 Atm; H_2/propene = 3.3. △ no activation; ○ activated with H_2 for 24 h at 88°C.

is observed at the beginning of the reaction, and a constant value is reached after some time. These results can be interpreted in terms of a hydrogen activation to form a more reactive species. Catalyst B was then treated with a stream of H_2 for 24 h, and the results are shown in Fig. 3. When there is activation, this is quickly lost, to give a product having the same activity of the catalyst used without hydrogen pretreatment.

The effect of time of contact (τ) has been studied for the hydrogenation of various substrates such as propene, cyclohexene, benzene, etc. for compounds B and C (Fig. 4, 5). Chemical and physical effects appear to be important in these reactions; the greater reactivity of propene could be related, among other factors, to its smaller size and hence to its easier diffusion within the polymer, since the active centers are mainly located inside the polymeric network and

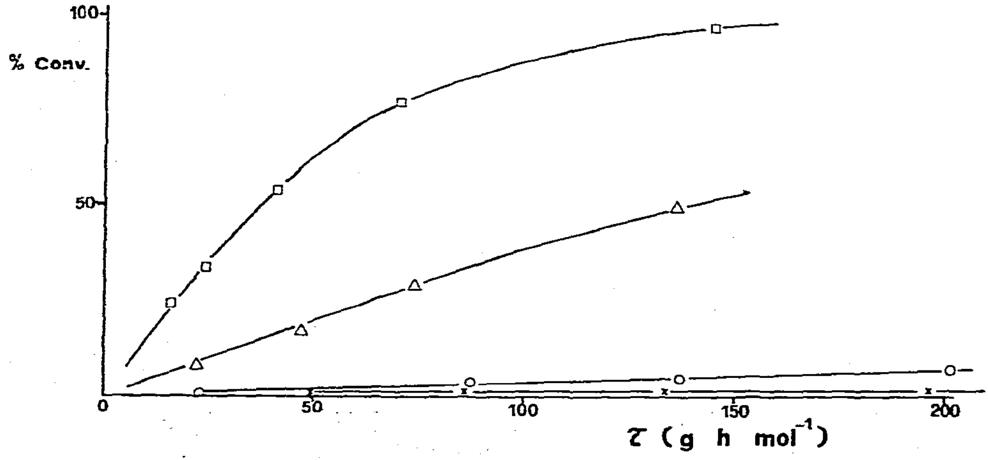


Fig. 4. Hydrogenation of various substrates. Catalyst: $[Rh(NBD)(PolyPPh_2)_2]^+$ recycled (B); T 88°C; p_{total} 1 Atm; $p(H_2)$ 0.77 Atm; H_2/substrate = 3.3. □ propene; △ cyclohexene; ○ benzene; X acetone.

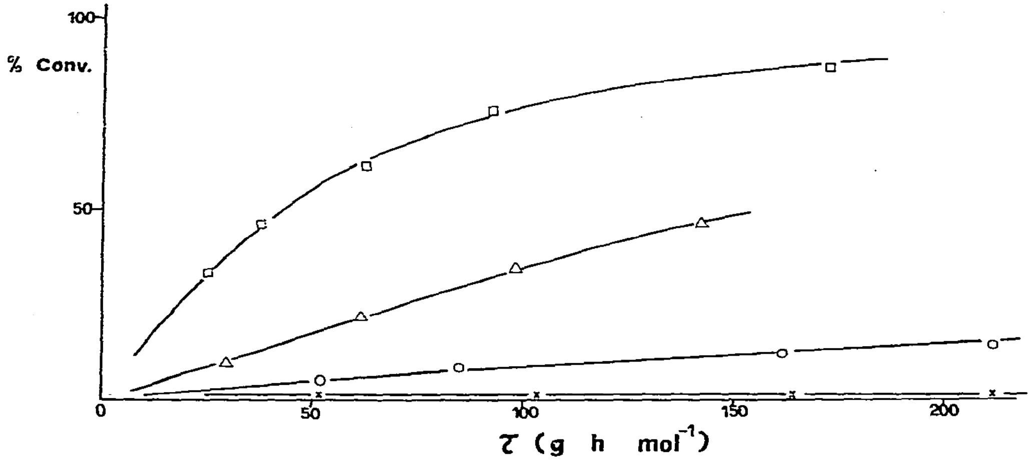


Fig. 5. Hydrogenation of various substrates. Catalyst: $[Rh(NBD)(PolyPPhMenthyl)_2]^+$ recycled (C); T 88°C; p_{total} 1 Atm; $p(H_2)$ 0.77 Atm; H_2/substrate = 3.3. □ propene; △ cyclohexene; ○ benzene; × acetone.

not on the surface [14,15]. Under more drastic conditions benzene is also hydrogenated in good yield to cyclohexane, but the unsaturated intermediates never exceeded 1% (Table 1).

Acetone is not hydrogenated under these conditions. In contrast, catalysts B and C in a batch reactor at 25°C and $p(H_2)$ 1 Atm gave a conversion into 2-butanol of 27% after 50 h, and of 100% after 5 h, respectively. The effect of the temperature in the hydrogenation of propene catalyzed by compound B has been studied. The results obtained as function of contact time (τ) and $p(H_2)$ are shown in Fig. 6 and 7, respectively.

Our data support the hypothesis that rhodium metal is formed by treatment with H_2 of polymers supported rhodium(I) catalysts, but only if solvent is present, and this behavior can be attributed to a lack of mobility in the polymer in the absence of solvent. A dissociative equilibrium causing rhodium complexes to be detached from the polymer could also operate [16]. When detached, rhodium(I) complexes are probably easily reduced to rhodium(0). Our results could also be interpreted in the same way, showing that the dissociative equilibrium, if present, is dependent on the solvent and on the P/Rh ratio.

TABLE 1

HYDROGENATION OF BENZENE

(T 108°C; $P_{total}(H_2 + C_6H_6)$ 1 Atm; τ 1100 g h mol^{-1})

Catalyst	Cyclohexane (%)	Cyclohexene (%)	Cyclohexadiene (%)	$p(H_2)$ (Atm)
B	12.5	0.9	0.03	0.74
	13.5	0.7	0.03	0.48
C	50.5	0.3	0.05	0.74
	50.5	0.4	0.05	0.48

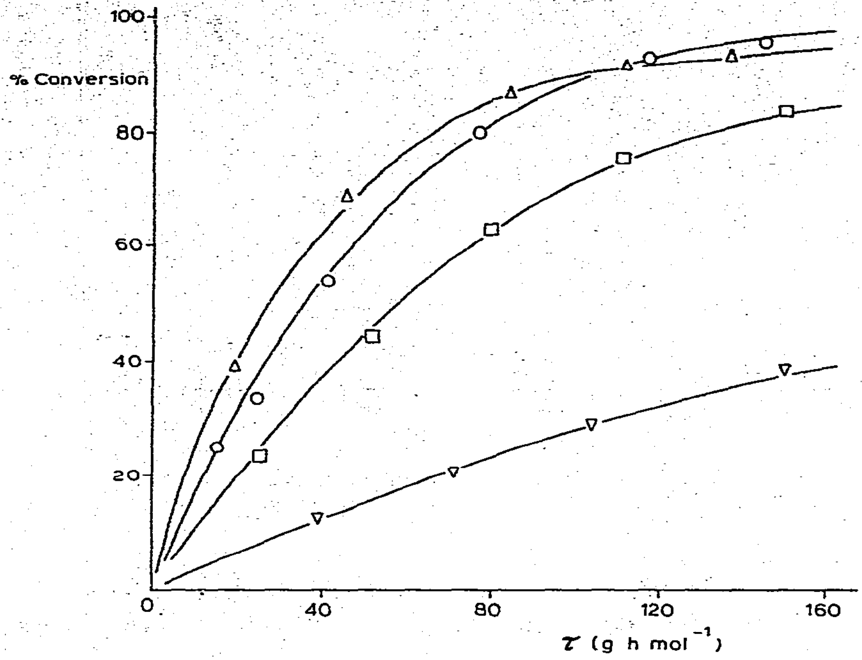


Fig. 6. Hydrogenation of propene. Catalyst: $[Rh(NBD)(PolyPPh_2)_2]^+$ recycled (B); p_{total} 1 Atm; $p(H_2)$ 0.77 Atm; H_2/propene = 3.3. ▽ 46.0°C; □ 73.3°C; ○ 88.0°C; △ 107.0°C.

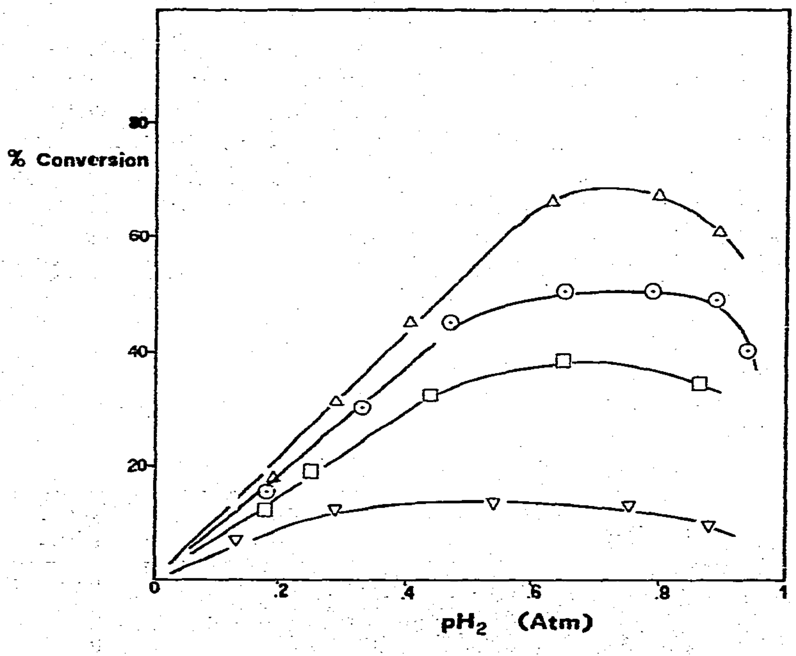


Fig. 7. Hydrogenation of propene. Catalyst: $[Rh(NBD)(PolyPPh_2)_2]^+$ recycled (B); p_{total} 1 Atm; τ 38.6 g h mol^{-1}. ▽ 46.0°C; □ 73.3°C; ○ 88.0°C; △ 107.0°C.

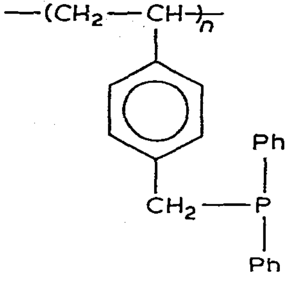
Experimental

Materials

Analytical grade chemicals and solvents were employed, and usually used without purification. Propene was obtained from Fluka AG. The purity of solvents and substrates used for hydrogenation experiments were checked by GLC.

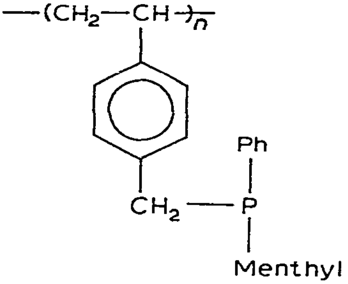
The complex [Rh(NBD)(acac)] was prepared by the method reported in literature for [Rh(ethylene)$_2$(acac)] [17].

Merrifield polymers Fluka (200—400 mesh), 2% divinylbenzene, 0.7 meq. Cl/g and/or 3.5 meq. Cl/g were used throughout. This polymer was treated in THF with Li[PPh$_2$] or with Li[PPhMenthyl] [5,18] to give the organic polymers II and III using methods reported in literature [19].



(PolyPPh$_2$)

(II)



(PolyPPhMenthyl)

(III)

Synthesis of catalysts

[Rh(NBD)(PolyPPh$_2$)$_2$] ClO$_4$ and [Rh(NBD)(PolyPPhMenthyl)$_2$]ClO$_4$, were prepared as previously reported [5] according to the following eq. 1.

$$[\mathrm{Rh(NBD)(acac)}] + 2\mathrm{PolyPRR'} \xrightarrow[\mathrm{HClO_4}]{\mathrm{THF}} [\mathrm{Rh(NBD)(PolyRR')_2}]\mathrm{ClO_4} + \mathrm{acacH} \quad (1)$$

R = R′ = Ph; R = Ph; R′ = Menthyl

Complex [Rh(NBD)(PolyPPh$_2$)$_2$]ClO$_4$ was used as prepared (catalyst A, Table 2). It was used to catalyze hydrogenation of cyclohexene in CH$_3$OH in batch reactor, and the yellow green compound obtained after catalytic turnover was used as catalyst in flow reactor (catalyst B, Table 2). Similarly using [Rh(NBD)(PolyPPhMenthyl)$_2$]ClO$_4$ was obtained catalyst C (Table 2).

TABLE 2

ANALYTICAL DATA

Catalyst	Rh ($\times 10^4$)/polymer (mol/g)	P (%)	P/Rh
A	2.82	5.1	5.9
B	2.82	5.1	5.9
C	2.77	2.5	2.9

Apparatus and procedure

Experiments were performed in a microflow system. The reactant gases, with nitrogen diluent, were first passed through a preheated coil and then down through the catalyst bed (2 mm) located about half way down the length of a glass tubular reactor (200 mm high, 15 mm diameter). The gas flows were measured by simple construction type flow meters [20]. Reaction products were directly injected into the gas chromatograph (Perkin—Elmer, model 3920 with a T.C. detector and equipped with H.P. Digital Integrator model 3927/3) for the quantitative analysis. Two stainless steel columns, one filled with silica gel (50—80 mesh) and the other with Carbowax 1500 on Cromosorb W-AW (80—100 mesh), were used for the analyses.

The fresh catalyst samples were used in the reactions to stationary conditions (at least 5 h). This procedure garanteed good reproducibility of the kinetic data.

When one of the reagents was liquid at room temperature, a hydrogen/nitrogen mixture of the appropriate ratio was passed through a feed saturator containing the liquid reactant. All lines beyond the saturator were heated in order to prevent condensation.

Infrared spectra were recorded on a Perkin—Elmer 457 spectrophotometer. Microanalyses were performed by A. Bernhard Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

Acknowledgements

The authors thank C.N.R. (Roma) and SNAM Progetti (Milano) for financial support.

References

1 N.K. Kohler and F. Dawans, Rev. Inst. Fr. Petr., 27 (1972) 105.
2 J. Bailar, Catal. Rev. Sci. Eng., 10 (1974) 17.
3 E.M. Cernia and M. Graziani, J. Appl. Polym Sci., 18 (1974) 2725.
4 R.H. Grubbs, Chemtech., (1977) 512.
5 G. Strukul, M. Bonivento, M. Graziani, E. Cernia and N. Palladino, Inorg. Chim. Acta, 12 (1975) 15.
6 G. Strukul, P. D'Olimpio, M. Bonivento, E. Pinna and M. Graziani, J. Mol. Catal., 2 (1977) 179.
7 L. Horner and F. Schumacher, Liebigs Ann. Chem., (1976) 633.
8 S.L. Davydova and N.A. Plate, Coord. Chem. Rev., 16 (1975) 195.
9 C.U. Pittman and R.L. Smith, J. Amer. Chem. Soc., 97 (1975) 1749.
10 J.P. Collman, L.S. Hegedus, M.P. Cooke, J.P. Norton, G. Dolcetti and D.N. Marquart, J. Amer. Chem. Soc., 94 (1972) 1789.
11 J.R. Shapley, R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 91 (1969) 2816.
12 R.R. Schrock and J.A. Osborn, Chem. Commun., (1970) 567.
13 A. Guyot, Ch. Graillat and M. Bartholin, J. Mol. Catal., 3 (1977/78) 39.
14 R.H. Grubbs and L.C. Kroll, J. Amer. Chem. Soc., 93 (1971) 3062.
15 F. Pinna, M. Bonivento, G. Strukul, M. Graziani, E. Cernia and N. Palladino, J. Mol. Catal., 1 (1975/76) 309.
16 W.H. Lang, A.T. Jurewicz, W.O. Haag, D.D. Whitehurst and L.D. Rollman, Coatings and Plastics Preprints, 173rd Amer. Chem. Soc. Meeting, New Orleans, 37 (1977) 304.
17 R. Cramer, J. Amer. Chem. Soc., 86 (1964) 217.
18 K. Issleib, Rev. Pure Appl. Chem., 9 (1967) 205.
19 British Petroleum Co. Ltd., Belgian Patent, 739.607 (1969).
20 J.H. Sinfelt, Chem. Eng. Sci., 23 (1968) 1181.