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CATALYSIS OF HYDROSILYLATION

XI *. RHODIUM(I)-SILOXYALKYLPHOSPHINE COMPLEXES; SYNTHESIS, CHARACTERISTICS AND CATALYTIC ACTIVITY

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Summary

Rhodium(I) complexes with 1,5-cyclooctadiene (COD) and disiloxydiphosphines $\{O[Si(CH_3)_2(CH_2)_nPPh_2]_2$ where $n = 1$–3; (**B-1**, **B-2**, **B-3**, respectively)$\}$ and/or with trisiloxytriphosphine $Ph_2P(CH_2)_3(CH_3)Si[OSi(CH_3)_2(CH_2)_2PPh_3]_2$ (**C-2**) were synthesized. Their composition and structure were determined using elemental analysis, molecular weight measurements and spectroscopic (IR, ^{1}H NMR and vis) methods, and were then compared with the corresponding data for $RuCl(COD)PPh_3$ (**A**) and $RhCl(COD)_2$ (**D**). The analytical and physico-chemical data all confirm the square planar geometry of the rhodium siloxyphosphine (the same as for rhodium triphenylphosphine) complexes with the general formula $[(COD)RhCl(PPh_2)(CH_2)_n]_mZ$ where $m = 2$ and $Z = (CH_3)_2SiOSi(CH_3)_2$ or $m = 3$ and $Z = (CH_3)_2SiOSi(CH_3)OSi(CH_3)_2$. The structure is independent of the type of phosphine ligand, and the molar ratio of Rh : P is always 1 : 1. Catalytic activity of the complexes prepared was tested in the hydrosilylation of 1-hexene by triethoxysilane which showed a slight decrease in turnover number (**A**–**C**) compared with Wilkinson's catalyst (**E**) but the activation energies for the rhodium-siloxyphosphine complexes (**B** and **C**) are higher than those for the rhodium phosphine complexes (**A** and **E**).

Introduction

Several examples of the high catalytic activity of Rh^I complexes with organosilicon ligands especially in hydrogenation and hydrosilylation have been recently reported. Soluble silylalkylphosphines [1–4] as well as monophosphine derivatives of tetracyclotrisiloxanes, $PPh_2(CH_2)_4\overline{Si(OSiMe_2)_3O}$ [3] or trisiloxanes, $[Me_3SiO]_2SiMe(CH_2)_4PPh_2$ [1] have been tested as monodentate ligands. Polysiloxyal-

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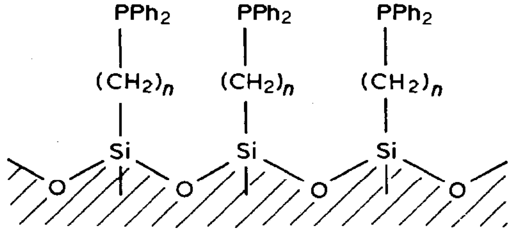
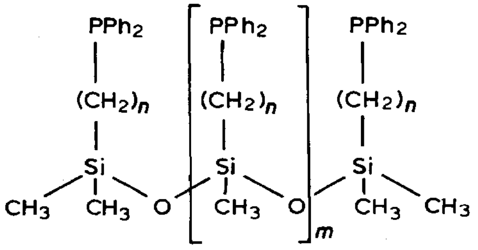
* For Part X see Ref. 18.

kylphosphines [5–7] and finally phosphinated inorganic supports [8–9] however were used as soluble or insoluble ligands of Rh^I complexes.

As a result of silica and silicate treatment the following idealized groups can be attached to the surface:



In order to simulate the idealized system we synthesized model siloxyphosphines, with the generalised structure as given below, which constitute a novel group of organosilicon-phosphorous compounds [10].



where $m = 0, 1$

$n = 1-3$

A rhodium cyclooctadiene dimeric complex $[RhCl(COD)]_2$ was used as a catalyst precursor, which readily forms rhodium phosphine complexes in situ, particularly with chiral ligands [11,12].

Our studies were aimed at the preparation of cyclooctadiene complexes of rhodium(I) with the siloxyphosphines previously mentioned, their molecular formulae and structures were determined and their catalytic activity in the hydrosilylation of 1-hexene by triethoxysilane was evaluated.

Results and discussion

Rhodium siloxyphosphine catalysts were prepared by equilibration of $[RhCl(COD)]_2$ solutions with the following organosilicon ligands: 1,3 bis(ω-diphenylphosphinealkyl)tetramethyldisiloxanes, i.e. $O[Si(CH_3)_2CH_2PPh_2]_2$ (BPS-1) – Catalyst **B-1**, $O[Si(CH_3)_2CH_2CH_2PPh_2]_2$ (BPS-2) – Catalyst **B-2**, $O[Si(CH_3)_2CH_2CH_2CH_2PPh_2]_2$ (BPS-3) – Catalyst **B-3** and 1,3,5-tris-2-(diphenylphosphine)ethylpentamethyltrisiloxane (TPS-2) – Catalyst **C-2**, using the method described in Experimental. A corresponding octadiene rhodium complex with triphenylphosphine (PPh_3) – Catalyst **A** was also prepared. The precursor, $[RhCl(COD)]_2$ – Catalyst **D**, and Wilkinson's catalyst, $RhCl(PPh_3)_3$ – Catalyst **E** were compared under selected conditions.

The synthesized complexes were isolated and identified by various methods. The ratio of rhodium to phosphine in these complexes was determined spectrophotometrically, on the basis of the characteristic bands. Electronic spectra of $[RhCl(COD)]_2$ showed a strong absorption band at 28.4×10^3 cm^{-1} attributable to a metal–ligand

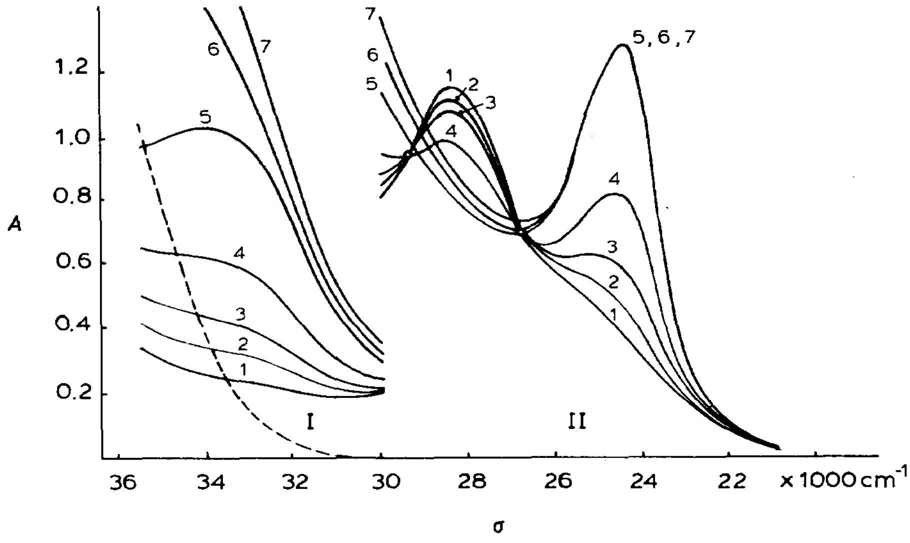


Fig. 1. The effect of disiloxydiphosphine (BPS-2) concentration on the absorption spectra of benzene solutions of $[RhCl(COD)]_2$ (3.213×10^{-4} mol Rh/l); Concentrations of the BPS-2: 1 – 0.0; 2 – 0.37; 3 – 0.76; 4 – 1.58; 5 – 3.28; 6 – 10.84; 7 – 19.10. The dashed line corresponds to a spectrum of BPS-2 (6.26×10^{-4} mol P/l). I – cell 0.5 cm thick. II – cell 2 cm thick.

transfer ($d_{z^2}\rightarrow\pi^*$) [13]. When the phosphines were introduced this band disappeared and two new bands at 24.4 and 33.9×10^3 cm^{-1} appeared. The first is attributed to the metal–phosphine ($d_{z^2}\rightarrow\pi^*$) transfer in the square planar complex. Two very well defined isosbestic points at 26.8 and 29.4×10^3 cm^{-1} were also observed irrespective of the phosphine used. The change in spectra caused by the introduction of the exemplary phosphine (BPS-2) is illustrated in Fig. 1.

By use of the molar ratios method, the composition of the rhodium phosphine complexes were determined. The results presented in Fig. 2 show that the Rh : P ratio is 1 : 1 for all the rhodium phosphine complexes studied, which can be regarded as strong ones. The formation constants of these complexes were evaluated to be greater than 10^6 based on the spectra of the 10^{-4} and 5×10^{-3} mol Rh/l solutions. A general conclusion can be drawn from these results in that in benzene solutions (10^{-3}–10^{-4} mol Rh/l) of $[RhCl(COD)]_2$-phosphine (siloxyphosphine) only one complex is formed even if there is a large excess of phosphine (siloxyphosphine) the structure of which is independent of the type of phosphine ligand and that the molar ratio of Rh : P is always 1 : 1. The rhodium cyclooctadiene complexes formed with all siloxyphosphines and triphenylphosphine were prepared and identified. Elemental analysis and molecular weights of these complexes are shown in Table 1, and the spectroscopic data (IR, ^1H NMR and VIS) are presented in Table 2.

IR spectra of the complexes exhibit absorption bands attributed to Rh–Cl, yet no band at 1650 cm^{-1} is observed, which could be characteristic of C=C bonds of cyclooctadiene. This fact suggests that the cyclooctadiene molecule is coordinated to the rhodium atom via two carbon–carbon double bonds. ^1H NMR spectra confirm such a hypothesis. The chemical shift of the (–CH=CH–) hydrogens in the cyclooc-

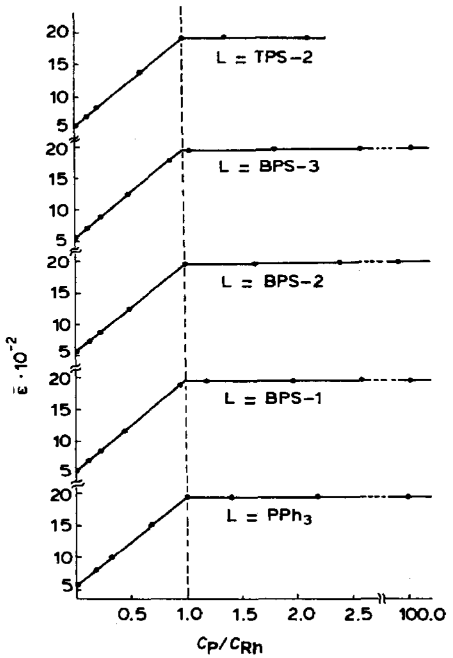


Fig. 2. Molar ratio plots at $\delta = 24.4 \times 10^3$ cm^{-1} for [RhCl(COD)]$_2$phosphine (L) complexes in benzene solutions. $c_{Rh} \approx 3.10^{-4}$ mol/l.

tadiene in [RhCl(COD)]$_2$ complex is determined as δ 4.23 ppm, 4H. This signal is shifted up-field compared with the corresponding ^{1}H chemical shift of non-coordinated (5.43 ppm, 4H). In the spectra of the RhCl(COD)-phosphine systems the signal is split giving two signals. This seems to result from a change in the geometry

TABLE 1

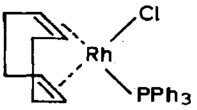
ELEMENTAL ANALYSIS (%) AND MOLECULAR WEIGHTS OF RHODIUM(I) COMPLEXES

Catalyst	Analysis (Found (calcd.))				
	P	Cl	C	H	Molecular weight
A	5.78	6.77	59.29	5.26	504
	(6.09)	(6.96)	(61.32)	(5.31)	(508.8)
B-1	–	7.05	53.0	5.68	905
	(6.06)	(6.93)	(53.92)	(5.86)	(1023.8)
B-2	5.84	7.14	53.0	6.09	1038
	(5.89)	(6.74)	(54.75)	(6.08)	(1051.8)
B-3	5.89	6.24	53.88	6.30	851
	(5.74)	(6.57)	(55.57)	(6.30)	(1079.8)
C-2	5.74	7.02	51.91	5.89	1322
	(5.92)	(6.77)	(54.29)	(5.97)	(1570.6)
D	–	14.26	38.17	5.13	494
	–	(14.38)	(38.98)	(4.91)	(493.0)
E	9.85	4.12	67.70	5.20	–
	(10.04)	(3.83)	(70.10)	(4.90)	(925.2)

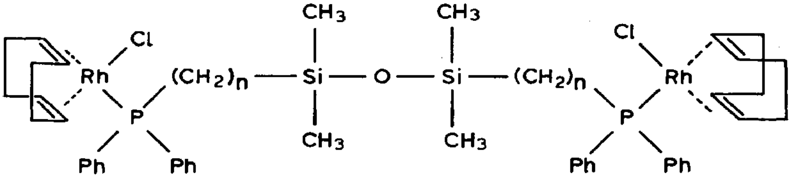
TABLE 2

SPECTROSCOPIC DATA OF RHODIUM(I) COMPLEXES

Spectra	A	B-1	B-2	B-3	C-2	D
Visible						
$\sigma_{max_1}(10^3\ cm^{-1})$	24.4	24.4	24.4	24.4	24.4	28.4
$\epsilon_{max_1}[10^{-3}\ l\ cm^{-1}\ (mole\ Rh)^{-1}]$	1.94	1.96	1.98	1.97	1.96	1.73
$\sigma_{max_2}[10^3\ cm^{-1}]$	33.8	33.9	33.9	33.9	33.9	–
$\epsilon_{max_2}[10^{-3}\ l\ cm^{-1}\ (mole\ Rh)^{-1}]$	6.23	6.27	6.29	6.27	6.26	–
IR (cm^{-1})	490	485	490	490	490	490
C=C (in free COD 1650)	815	830	830	840	840	820
	960	960	960	960	960	965
Si–O–Si	–	1030	1050	1050	1050	–
Si–CH_3	–	1260	1250	1255	1260	–
P–Ph	1435	1435	1430	1435	1435	–
	260	255	250	245	255	255
Rh–Cl	285		280	280	280	280
^{1}*H NMR* (ppm)						
C=C (in complex)	3.16	3.11	3.13	3.13	3.12	4.23
	2H	2H	2H	2H	2H	4H
	5.57	5.55	5.57	5.58	5.56	
	2H	2H	2H	2H	2H	



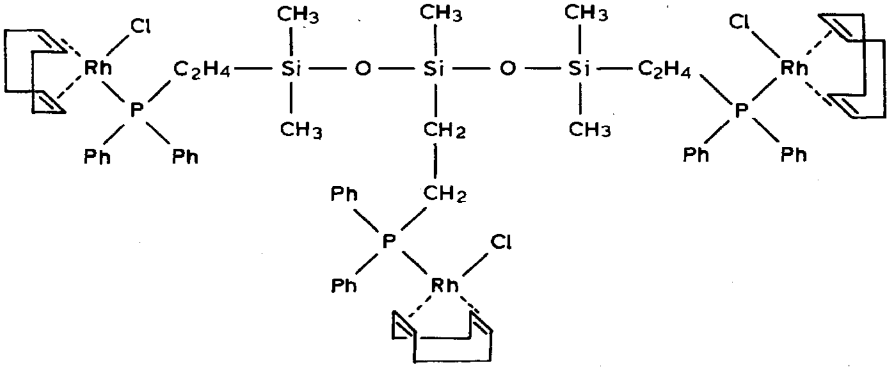
A



$n = 1$ **B-1**

$n = 2$ **B-2**

$n = 3$ **B-3**



C-2

Fig. 3. Proposed structures for the Rh^I – COD – siloxyphosphine complexes.

TABLE 3. THE YIELD OF HEXYLTRIETHOXYSILANE

$(C_2H_5O)_3SiH + C_4H_9CH{=}CH_2 \xrightarrow{Rh^I \text{ catalyst}} (C_2H_5O)_3Si(CH_2)_5CH_3$ $[{\equiv}SiH]:[\text{1-Hexene}]:[Rh(I)] = 1:1:4 \times 10^{-4}$

Catalyst	Yield (%)	
	50 °C, 1.5 h	80 °C, 1.5 h
A	31	48
B-1	52	62
B-2	46	61
B-3	38	48
C-2	51	64
D	17	19
E	61	68

of the square complex leading to different suroundings of the two pairs of hydrogen atoms with –CH=CH– bonds coordinated to the rhodium center. All analytical and physico-chemical data indicate the structure for the rhodium cyclooctadienesiloxyphosphine (triphenylphosphine) complexes as in Fig. 3.

The catalysts were tested in the addition reaction of triethoxysilane to 1-hexene. The yields of triethoxysilane are summarized in Table 3.

All data for kinetic measurements which were carried out (essentially) at 66 °C in the presence of the selected catalysts, are shown in Table 4. The initial rates, which allow the calculation of turnover number (TN) were determined graphically. Error limits are the standard deviations obtained by least-squares regression treatment of the linear form of the respective equations. The kinetic parameters, and TN, which allow the energy of activation to be determined, (see Fig. 4), are also summarized in Table 4. The above kinetic results reveal that the following order of catalytic activity occurs **C-2** > **B-2** ≥ **E** > **A**, while the length of the induction period increases in the sequence **C-2** ≤ **E** < **B-2** < **A**.

The catalyst **C-2** with the trisiloxytriphosphine ligand appears to be the most effective, even more so than Wilkinson's catalyst. It is also noteworthy, that the activation energies for the processes catalyzed by rhodium siloxyphosphine complexes are higher than those of the rhodium-phosphine complexes **A** and **E**. In view

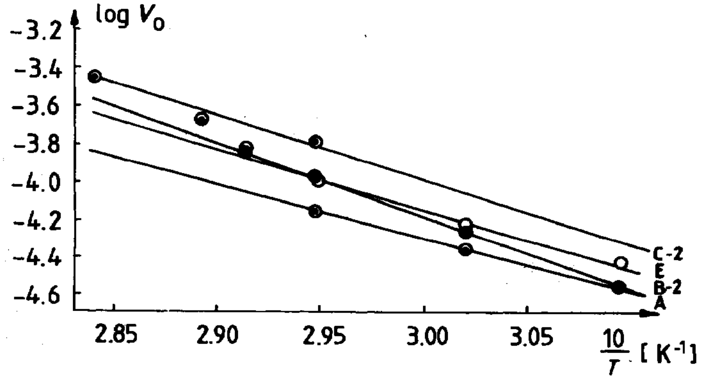


Fig. 4. Arrhenius plot for hydrosilylation of 1-hexene by triethoxysilane in the presence of the catalysts examined.

TABLE 4. KINETIC AND ACTIVATION PARAMETERS FOR THE HYDROSILYLATION OF 1-HEXENE BY TRIETHOXYSILANE IN THE PRESENCE OF RHODIUM(I) COMPLEXES

[$\equiv$SiH] : [1-Hexene] : [Rh(I)] = 1 : 1 : 4×10^{-4}

Catalyst	TN (66 °C) (s^{-1})	Induction period (min)	E_a (kcal/mol)
A	0.11	31–32	13.5 ± 0.4
B-2	0.09	26–27	17.5 ± 0.8
C-2	0.15	5– 6	17.0 ± 0.9
E	0.18	6– 7	14.6 ± 0.8

of the general rules of the mechanism of the hydrosilylation of the C=C bond catalyzed by rhodium(I) octadienephosphine (siloxyphosphine), a complex of square planar geometry, where the dissociation of the phosphine (siloxyphosphine) ligand from the metal center seems to occur at a crucial stage in these consecutive and competitive reactions, involving a coordination of alkene and oxidative addition of the silicon hydride to the rhodium(I) center in order to form an octahedral intermediate. Further reactivity tests of the rhodium siloxy complexes with particular substrates, can throw more light on the individual stages.

Experimental

Materials

Commercially obtained 1-hexene and solvents were dried and subjected to distillation before use. Triethoxysilane was obtained by ethanolysis of trichlorosilane. Preparation of siloxyphosphines has been reported previously [10].

Preparation of catalysts

*Catalyst **A**.* 0.1674 g (0.34 mmol) of $[RhCl(COD)]_2$ and 0.1781 g (0.68 mmol) of triphenylphosphine were dissolved in 5 ml of benzene. The mixture was refluxed for 5 min and cooled. The yellow solid was filtered, washed with ethyl alcohol and dried in vacuo.

*Catalyst **B**.* Equimolar amounts of $[RhCl(COD)]_2$ and BPS-1, (or BPS-2 or BPS-3) (ca. 0.8 mmol) were dissolved in minimal amounts of hot benzene and cooled. Methanol was added to the solution, and an oil separated, which crystallized after some time. The precipitate was recrystallized from a benzene : methanol, 1 : 1 (vol/vol) mixture, washed with methanol, and dried in vacuo.

*Catalyst **C-2**.* The complex was prepared according to the procedure described for catalyst **B**, using $[RhCl(COD)]_2$ (0.65 mmol) and TPS-2 (0.43 mmol) in amounts such that the P : Rh ratio was maintained at 1 : 1. Instead of methanol, cyclohexane was used.

*Catalysts **D** and **E**.* $[RhCl(COD)]_2$ – catalyst **D** [14] and $RhCl(PPh_3)_3$ – catalyst **E** [15] were prepared according to published methods.

All procedures were carried out under an argon atmosphere. Solutions of the catalysts were stored in dry benzene under an argon atmosphere.

Equipment and analytical measurements

The spectrophotometric measurements in the visible region were made using a

Specord UV-VIS spectrophotometer (Carl Zeiss, Jena) in closed glass cells hermetically sealed with silicone rubber.

The molar ratios method was used to determine the composition of the rhodium cyclooctadiene phosphine and siloxyphosphine complexes. Stock solutions of $[RhCl(COD)]_2$ (3×10^{-4} mol Rh/1), and two solutions of this complex with phosphine (5×10^{-4} mol P/l and 5×10^{-3} mol P/l) were employed to prepare a series of solutions with the required Rh/P ratio.

The infrared spectra were recorded on a Perkin–Elmer Model 180 spectrophotometer. ^1H NMR spectra were obtained in $CDCl_3$ solutions using a JEOL FX 900 spectrometer with TMS as an internal standard. Molecular weights were determined on a Knauer Osmometer. Gas chromatographic analyses were carried out on a Chrom 5 (Czech.) instrument using a steel column packed with 10% SE-30 on Chromosorb (with a thermal conductivity detector). Other physico-chemical, as well as elemental C, H, P and Cl analytical, data were determined by commonly employed methods.

Hydrosilylation tests

Catalytic experiments were carried out in sealed glass ampoules under nitrogen and containing equimolar amounts of 1-hexene and triethoxysilane. Kinetic measurements were also carried out under nitrogen in a temperature controlled (thermostat) vessel of 20 ml capacity. The detailed procedures were reported previously [16,17].

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References

1 Z.C. Brzezińska and R. Cullen, Inorg. Chem., 18 (1979) 3132.
2 M. Jakubkova and M. Capka, Collect. Czech. Chem. Commun., 45 (1980) 2219.
3 M.O. Farrell, C.H. Van Dyke, L.J. Boucher and S.J. Metlih, J. Organomet. Chem., 169 (1979) 189.
4 V. Kavan and M. Capka, Collect. Czech. Chem. Commun., 45 (1980) 2150.
5 C.H. Van Dyke, M.O. Farrell and L.J. Boucher in M. Tsutsui (Ed.), Fundamental Research in Homogeneous Catalysis, Vol. 3. Plenum Press, New York, 1979, p. 659.
6 M. Bartholin, J. Conan and A. Guyot, J. Mol. Catal., 2 (1977) 307.
7 Ger. Offen. 3. 029. 599. Chem. Abstr., 97 (1982) 617914.
8 K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.G. Pitkethly and P.J. Robinson, J. Organomet. Chem., 87 (1975) 203.
9 Z.M. Michalska, M. Capka and J. Stock, J. Mol. Catal., 11 (1981) 323.
10 W. Urbaniak and B. Marciniec, Pol. J. Chem., in preparation.
11 A. Vahara and J.C. Bailar, J. Organomet. Chem., 239 (1982) 11.
12 T. Kogure and J. Ojima, J. Organomet. Chem., 234 (1982) 249.
13 R.A. Epstein, G.L. Geoffry, M.E. Keeney and W.R. Mason, Inorg. Chem., 18 (1079) 478.
14 G. Giordano and R.H. Crabtree, Inorg. Synth., 19 (1973) 218.
15 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc., A (1966) 1711.
16 B. Marciniec, Z.W. Kornetka and W. Urbaniak, J. Mol. Catal., 12 (1981) 221.
17 B. Marciniec, W. Urbaniak and P. Pawlak, J. Mol. Catal., 14 (1982) 319.
18 B. Marciniec and J. Guliński in A.E. Shilov (Ed.), Fundamental Research in Homogeneous Catalysis, Vol. 5, Plenum Press, New York, 1986, in press.