*Journal of Organometallic Chemistry*, 390 (1990) 105–111
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20739



# Hex-1-ene hydroformylation catalyzed by $Rh(acac)\{P(OPh)_3\}_2$ modified with amines, formation of reactive $HRh(CO)\{P(OPh)_3\}_3$ and unreactive $Rh_4(CO)_8\{P(OPh)_3\}_4$ species

**A.M. Trzeciak**

*Institute of Chemistry, University of Wrocław, 50-383 Wrocław (Poland)*

(Received January 10th, 1990)

## Abstract

Pyridines and amines have been used as modifying ligands in the hex-1-ene hydroformylation reaction catalyzed by $Rh(acac)\{P(OPh)_3\}_2$. Aldehydes (n + iso) were obtained in 80–85% yield. The active form of the catalyst has been isolated as the solid $HRh(CO)\{P(OPh)_3\}_3$. Another complex formed in the reaction of $Rh(acac)\{P(OPh)_3\}_2$ with $H_2$ and CO in the presence of pyridine, $Rh_4(CO)_8\{P(OPh)_3\}_4$, is catalytically inactive.

## Introduction

Our studies on olefin hydroformylation have shown $Rh(acac)\{P(OPh)_3\}_2$ to have high activity as catalyst precursor [1,2]. This complex exhibits catalytic activity only after the addition of free triphenylphosphite, which plays an essential role in the transformation of $Rh(acac)\{P(OPh)_3\}_2$ into the catalytically active complexes $HRh(CO)\{P(OPh)_3\}_3$ and $HRh\{P(OPh)_3\}_4$ [1,3]. Neither the electronic nor the spacial structure of the various ring substituents in the triphenylphosphites used influence the catalytic activity of the system [4]. However, the systems containing $Rh(acac)\{P(OPh)_3\}_2$ and $PPh_3$, $AsPh_3$ or $SbPh_3$ show very low catalytic ability in the hex-1-ene hydroformylation [5]. The reaction requires very long induction times and yields only small amounts of the aldehydes, (ca. 30%). Much better results were obtained for the system containing $Rh(acac)\{P(OPh)_3\}_2$ and the nitrogen ligands, namely pyridines or amines. The results are discussed here.

## Results and discussion

*Hydroformylation of hex-1-ene catalyzed by $Rh(acac)\{P(OPh)_3\}_2$*

It was found that even 0.6 mole of pyridine per mole of rhodium atom was sufficient to convert $Rh(acac)\{P(OPh)_3\}_2$ into the catalytically active species. The

Table 1

Hydroformylation of hex-1-ene with $Rh(acac)\{P(OPh)_3\}_2$ and 3-picoline. ([Rh] $2.5\times10^{-2}$ mmol, [hex-1-ene] 3.2 mmol $T$ 40 °C; $CO/H_2 = 1$ at $p$ 1 atm)

| [3-pic]/[Rh] | Products (%) [a] | |
|---|---|---|
| | heptanal | hex-2-ene |
| 0.6 | 80 | 20 |
| 1.1 | 90 | 10 |
| 1.7 | 80 | 20 |
| 2.9 | 72 | 24 [b] |
| 5.6 | 56 | 12 [c] |

[a] Reaction time: 3–4 h. [b] Hex-1-ene 4%. [c] Hex-1-ene 32%.

effects of amine concentration on the composition of the hydroformylation products of hex-1-ene was studied for the system containing $Rh(acac)\{P(OPh)_3\}_2$ and 3-picoline (3-pic) (Table 1). The highest hydroformylation rate and selectivity were achieved at [3-pic]/[Rh] = 0.6–1.7. At higher 3-picoline concentrations the reaction rate and the hex-1-ene conversion decreased. The results obtained for the hydroformylation of hex-1-ene with $Rh(acac)\{P(OPh)_3\}_2$ and various amines are given in Table 2. All reactions show induction periods of 18 to 51 min, however it is difficult to quantify the correlation between length of induction period and the electronic or spacial structure of amine used. After induction the reaction proceeds smoothly and ca. 80–85% of aldehydes and 15–20% of hex-2-ene are obtained. The selectivity is higher than that for the $Rh(acac)\{P(OPh)_3\}_2 + P(OPh)_3$ system which gave 70% aldehydes and 30% hex-2-ene.

The catalytic hydroformylation of vinyl acetate with $Rh(acac)\{P(OPh)_3\}_2$ and 3-picoline gives α-acetoxypropionaldehyde in 56–69% yield.

The attractive catalytic properties of the new system, which are practically independent of the structure of the nitrogen donor prompted us to elucidate the reaction mechanism.

Table 2

Hydroformylation of hex-1-ene with $Rh(acac)\{P(OPh)_3\}_2$ and various amines. ([Rh] $2.5\times10^{-2}$ mmol, [hex-1-ene] 3.2 mmol, [amine] $1.5\times10^{-2}$ mmol, $T$ 40 °C, $CO/H_2 = 1$ at $p$1atm)

| Amine | $t_{ind}$ [a] (min) | $t_{40}$ [b] (min) | $t_{90}$ [c] (min) | heptanal (n + iso) (%) | hex-2-ene (%) |
|---|---|---|---|---|---|
| 4-pic | 18 | 82 | 136 | 83 | 17 |
| py | 26 | 104 | 161 | 85 | 15 |
| 3-pic | 27 | 112 | 186 | 80 | 20 |
| 2-CN-py | 25 | 134 | 198 | 85 | 15 |
| 2-Cl-py | 40 | 150 | 211 | 83 | 17 |
| 4-CN-py | 33 | 156 | 224 | 84 | 16 |
| 2-Me-py | 48 | 164 | 232 | 82 | 18 |
| $N(CH_2Ph)_3$ | 33 | 153 | 235 | 83 | 17 |
| 2,4,6-$Me_3$-py | 44 | 178 | 252 | 82 | 18 |
| 3-CN-py | 51 | 189 | 256 | 82 | 18 |
| $NPh_3$ | 48 | 181 | 269 | 81 | 19 |

[a] $t_{ind}$ = induction period. [b] $t_{40}$ = time required to absorb 40 $cm^3$ of $H_2/CO$. [c] $t_{90}$ = time required to absorb 90 $cm^3$ of $H_2/CO$.

*Identification of $HRh(CO)\{P(OPh)_3\}_3$ and $Rh_4(CO)_8\{P(OPh)_3\}_4$*

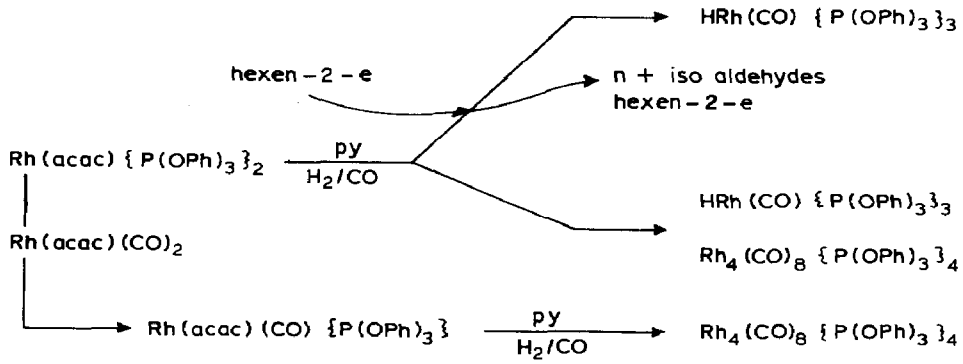
The reaction of $Rh(acac)\{P(OPh)_3\}_2$ with $CO/H_2$ in the presence of 3-picoline was monitored by IR spectroscopy. The appearance of new bands at 2060, 2010 and 1860 $cm^{-1}$ during the reaction, indicated the presence of two species: $HRh(CO)\{P(OPh)_3\}_3$ and $Rh_4(CO)_8\{P(OPh)_3\}_4$. Both complexes were isolated as solids and identified (see Experimental). Introduction of hex-1-ene into the system changes the reaction course such that $HRh(CO)\{P(OPh)_3\}_3$ is the main rhodium complex formed along with only traces of $Rh_4(CO)_8\{P(OPh)_3\}_4$. When the internal olefins, e.g. hex-2-ene or hex-3-ene were used instead of hex-1-ene, no inhibition of the $Rh_4(CO)_8\{P(OPh)_3\}_4$ formation was observed. The reactions are outlined in Scheme 1.

The synthesis carried out by Scheme 1 always gives a mixture of rhodium complexes. However only one complex, $Rh_4(CO)_8\{P(OPh)_3\}_4$, was obtained when $Rh(acac)(CO)\{P(OPh)_3\}$ was used as substrate; this reaction may be regarded as a novel and convenient route to $Rh_4(CO)_8\{P(OPh)_3\}_4$; isolated in ca. 90% yield.

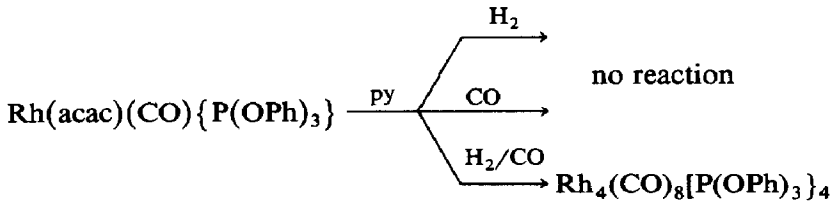
*The mechanism of $HRh(CO)\{P(OPh)_3\}_3$ and $Rh_4(CO)_8\{P(OPh)_3\}_4$ formation*

The role of amine in the formation of $HRh(CO)\{P(OPh)_3\}_3$ and $Rh_4(CO)_8\{P(OPh)_3\}_4$ was elucidated from NMR studies. The most important conclusions are (Scheme 2):

1. The addition of pyridine destabilizes the coordination sphere of rhodium in $Rh(acac)(CO)\{P(OPh)_3\}$; as indicated by the presence of one $CH_3(acac)$ signal ($\delta$ 1.6 ppm) instead of the two at $\delta$ 1.5 and 1.7 ppm observed in $^1H$ NMR spectrum of pure $Rh(acac)(CO)\{P(OPh)_3\}$. After a few hours the signal at 1.4 ppm characteristic for $Rh(acac)\{P(OPh)_3\}_2$ appears in addition to that at 1.6 ppm. Small amounts of $Rh(acac)\{P(OPh)_3\}_2$ complex were isolated and studied by UV-VIS and IR spectroscopy.
2. The Rh–acac chelate bonds in $Rh(acac)(CO)\{P(OPh)_3\}$ are preserved when the complex is treated with pyridine and CO or pyridine and $H_2$. The spectra of the compound do not change even after saturation, of its solution containing pyridine with CO or $H_2$ for a few hours.
3. When a $CO/H_2$ mixture is bubbled through a solution of $Rh(acac)(CO)\{P(OPh)_3\}$ + py (or $Rh(acac)\{P(OPh)_3\}_2$ + py) the Rh–acac chelate bonds are




Scheme 1




Scheme 2

broken and free Hacac forms in 1 h. The presence of Hacac is confirmed from its $^1$H NMR data ($\delta$ 1.7, 1.85, 3.15, 5.15 ppm). IR spectra of the solution showed the presence of $Rh_4(CO)_8\{P(OPh)_3\}_4$ ($\nu$(CO): 2040, 2010, 1840cm$^{-1}$).

4. Reaction of $Rh(acac)\{P(OPh)_3\}_2$ with CO gives $Rh(acac)(CO)\{P(OPh)_3\}$ in which fast exchange of coordinated and free CO takes place, as evidenced by the presence of only one signal from $CH_3$(acac) at 1.6 ppm.

5. $HRh(CO)\{P(OPh)_3\}_3$ reacts with $Rh(acac)(CO)_2$, according to eq. 1:

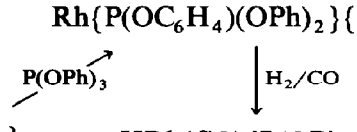
$$HRh(CO)\}P(OPh)_3\}_3 + Rh(acac)(CO)_2 \xrightarrow{\text{fast}} Rh_4(CO)_8\{P(OPh)_3\}_4 + Rh(acac)(CO)\{P(OPh)_3\} + H_2 \quad (1)$$

The next step of the reaction is much slower (eq. 2):

$$HRh(CO)\{P(OPh)_3\}_3 + Rh(acac)(CO)\{P(OPh)_3\} \xrightarrow{\text{slow}} Rh_4(CO)_8\{P(OPh)_3\}_4 + Rh(acac)\{P(OPh)_3\}_2 + H_2 \quad (2)$$

All the reaction products were identified from their IR and $^1$H NMR spectra. These results indicate that $HRh(CO)\{P(OPh)_3\}_3$ could play an important role in the formation of $Rh_4(CO)_8\{P(OPh)_3\}_4$.

In previous studies [3] we have found that the $HRh(CO)\{P(OPh)_3\}_3$ complex can be formed in reaction of $Rh(acac)\{P(OPh)_3\}_2$ with a $H_2/CO$ mixture in the presence of free $P(OPh)_3$. The first step of this reaction involves the formation of an intermediate orthometallated complex $Rh\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}_3$ which is converted into $HRh(CO)\{P(OPh)_3\}_3$ (eq. 3):




(3)

It is very probable that the same orthometallated species is formed in the systems under investigation, namely in $Rh(acac)(CO)\{P(OPh)_3\}$ + py and $Rh(acac)\{P(OPh)_3\}_2$ + py. To confirm the role of orthometallation in the formation of the carbonyl cluster we have repeated the synthesis: $Rh(acac)(CO)(PR_3)$ + py + $H_2$ + CO ($PR_3$ = $PPh_3$, $P(O\text{-}o\text{-}MeC_6H_4)_3$) using $PR_3$ ligands which have a lower ability than $P(OPh)_3$ to form orthometallated bonds to rhodium. The $Rh(acac)(CO)(PPh_3)$ complex shows no structural changes in the presence of the $H_2/CO$ mixture and pyridine, (no changes in IR). The reaction of $Rh(acac)(CO)\{P(O\text{-}o\text{-}MeC_6H_4)_3\}$ was slower than that of $Rh(acac)(CO)\{P(OPh)_3\}$ and finally gave a ca. 50% conversion to carbonyl cluster (eq. 4):

$$Rh(acac)(CO)\{P(O\text{-}o\text{-}MeC_6H_4)_3\} \xrightarrow[\text{py}]{H_2/CO} Rh_4(CO)_8\{P(O\text{-}o\text{-}MeC_6H_4)_3\}_4 \quad (4)$$

A similar, partial conversion of $Rh(acac)\{P(O\text{-}o\text{-}MeC_6H_4)_3\}_2$ into $HRh(CO)\{P(O\text{-}o\text{-}MeC_6H_4)_3\}_3$ was noted for reaction 5:

$$Rh(acac)\{P(O\text{-}o\text{-}MeC_6H_4)_3\}_2 \xrightarrow[P(O\text{-}o\text{-}MeC_6H_4)_3]{H_2/CO} HRh(CO)\{P(O\text{-}o\text{-}MeC_6H_4)_3\}_3 \quad (5)$$

These results are consistent with the suggestion that the ability of phosphorous ligand ($PR_3$ or $P(OR)_3$) to form an orthometallated bond with rhodium is decisive in the formation of $Rh_4(CO)_8\{P(OPh)_3\}_4$ (Scheme 1).

In all the systems studied amine role in the destabilizes the rhodium coordination sphere, and so allows orthometallation. In some systems amine facilitates the heterolytic splitting of $H_2$ molecule, eq. 6 [6] and eq.7 [7]:

$$[RhH_2\{P(OPh)_3\}_4]^+ + NEt_3 \longrightarrow HRh\{P(OPh)_3\}_4 + [HNEt_3]^+ \quad (6)$$

$$RhCl(PPh_3)_3 + NEt_3 + H_2 + CO \longrightarrow HRh(CO)_2(PPh_3)_2 + NEt_3{}^+Cl^- \quad (7)$$

We have found that a similar reaction is a convenient route to $HRh(CO)\{P(OPh)_3\}_3$ (eq. 8):

$$[Rh\{P(OPh)_3\}_4]^+ \xrightarrow[py]{H_2/CO} HRh(CO)\{P(OPh)_3\}_3 + Hpy^+ + P(OPh)_3 \quad (8)$$

The reaction is complete in a few minutes and gives $HRh(CO)\{P(OPh)_3\}_3$ in 80% yield.

*Repetitive hydroformylation with rhodium phosphite complexes*

The complex, $Rh_4(CO)_8\{P(OPh)_3\}_4$, does not catalyse the hydroformylation under mild conditions. This indicates that only $HRh(CO)\{P(OPh)_3\}_3$ is responsible for the catalytic activity shown by the system containing $Rh(acac)\{P(OPh)_3\}_2$ and amine. $HRh(CO)\{P(OPh)_3\}_3$ was also identified as the active form of the catalyst formed under hydroformylation conditions from $Rh(acac)\{P(OPh)_3\}_2$ and $P(OPh)_3$. Up to now, all the hydroformylations with $Rh(acac)\{P(OPh)_3\}_2$ as catalyst precursor are in fact catalyzed by the same complex formulated as $HRh(CO)\{P(OPh)_3\}_3$. Nevertheless the reaction rates and catalyst stability are different, as shown by the data in Table 3. The hydroformylation catalyzed by $HRh(CO)\{P(OPh)_3\}_3$ starts without induction and proceeds at an almost constant

Table 3

Hydroformylation with $Rh(acac)\{P(OPh)_3\}_2$ modified by amine or with $HRh(CO)\{P(OPh)_3\}_3$ in $n$ cycles [a]. ([Rh] $2.5\times10^{-2}$ mmol, [Rh]:[$P(OPh)_3$]:[amine] = 1:1:0.6, $T = 40\,^\circ C$, $CO/H_2 = 1$ at $p$ 1 atm

| Catalytic system | [b] $t_{ind}$ | $t_1$ | $t_2$ (min) | $t_3$ | $t_4$ | heptanal (n + iso) (%) | hex-2-ene (%) |
|---|---|---|---|---|---|---|---|
| $Rh(acac)P_2$ + P + 3-pic | 33 | 240 | not measured | | | 81 | 19 |
| $Rh(acac)P_2$ + P + 4-pic | 31 | 220 | 180 | 240 | – | 62 | 26 |
| $Rh(acac)P_2$ + 4-pic | 31 | 190 | 170 | 240 | – | 72 | 20 |
| $Rh(acac)P_2$ + P | 12 | 160 | 80 | 120 | 180 | 65 | 31 |
| $HRh(CO)P_3$ | 0 | 70 | 60 | 80 | 140 | 61 | 38 |
| $HRh(CO)P_3$ | 0 | 66 | 74 | not measured | | 66 | 34 |

[a] The subsequent dose of hex-1-ene (3.2 mmol) was added when $CO/H_2$ absorption rate slowed down. [b] $t_{ind}$ = induction period; $t_n$ ($n = 1$–4) = time required for conversion of $n$'th dose of hex-1-ene.

rate in three catalytic cycles ($t_1$–$t_3$). The rate in the fourth cycle ($t_4$) is slower (Table 3). The course of the reaction with the Rh(acac){$P(OPh)_3$}$_2$ + $P(OPh)_3$ system is similar but an induction period and a lower reaction rate in the first cycle ($t_1$) were observed. The introduction of pyridine or pyridine with $P(OPh)_3$ as modifying ligands lengthens the induction period and decreases the reaction rate. The rate of hydroformylation measured as a rate at which $CO/H_2$ mixture is consumed decreased only in the third catalytic cycle. The amine-containing system has an important advantage over the system having an excess of free $P(OPh)_3$, in that it shows better selectivity in the distribution of the hydroformylation products, viz., it gives a 10% higher yield of aldehydes. The better selectivity is probably attributable to the absence of HRh{$P(OPh)_3$}$_4$ which isomerises hex-1-ene to hex-2-ene during the hydroformylation catalyzed by Rh(acac){$P(OPh)_3$}$_2$ + $P(OPh)_3$ [2]. This complex, HRh{$P(OPh)_3$}$_4$, was not detected in the amine-containing system.

## Experimental

The rhodium complexes were synthetized by previously published procedures: Rh(acac){$P(OPh)_3$}$_2$ [8], Rh(acac)$(CO)_2$ [9], Rh{$P(OPh)_3$}$_4ClO_4$ [10], $Rh_4(CO)_{12}$ [11], $Rh_4(CO)_8${$P(OPh)_3$}$_4$ [12] and by the procedure described here.

*Synthesis of $Rh_4(CO)_8${$P(OPh)_3$}$_4$*

To a solution of Rh(acac)$(CO)_2$ (0.114 g) in $C_6H_6$ (1 $cm^3$) was added $P(OPh)_3$ (0.14 g) 3-pic (0.2$cm^3$). The solution was stirred for ca. 2h under $CO/H_2$ until its colour turned dark red. Then the solution was evaporated to half of its volume in vacuo, and EtOH (2–3 $cm^3$) was slowly added. The solution was left to crystallize under $CO/H_2$. Yield: 0.18 g (88%).

The composition of the complex was determined from its elemental analysis and its IR spectrum which was identical with that of $Rh_4(CO)_8${$P(OPh)_3$}$_4$ obtained by a different procedure [12]. Anal. Found: C, 50.4; H, 3.4; P, 6.2. $C_{80}H_{60}O_{20}P_4Rh_4$ calc: C, 51.2; H, 3.2; P, 6.6%. IR ($\nu$(CO))/$cm^{-1}$: 2010vs, 1830s (Nujol); 2040m, 2020vs, 2010vs, 1840s ($CHCl_3$)

*Synthesis of HRh(CO){$P(OPh)_3$}$_3$*

*Route 1.* To a solution of Rh(acac){$P(OPh)_3$}$_2$ (0.1 g) in $C_6H_6$ (1 $cm^3$) was added $P(OPh)_3$ (0.03 g) and 3-pic (0.2 $cm^3$). The solution was stirred under $CO/H_2$ atmosphere for 3 h and condensed in vacuo to the half of its volume. Then EtOH (1.5–2 $cm^3$) was added and the mixture was left to crystallize under $CO/H_2$. Yield: 0.07 g (54%).

*Route 2.* The synthesis was carried out as describe above, but 3-pic was not added. Yield: 0.82 g (63%).

*Route 3.* A of Rh{$P(OPh)_3$}$_4ClO_4$ (0.041 g) in $CH_2Cl_2$ (0.5 $cm^3$) was saturated with $CO/H_2$ for 2 min. Then 4-pic (0.02 $cm^3$) was added and the mixture was stirred under $CO/H_2$ for ca. 15 min. The solution was evaporated in vacuo, EtOH (2 $cm^3$) was added, and the solution was left to crystallize under $CO/H_2$. Yield: 0.024 g (80%).

IR ($CHCl_3$)/$cm^{-1}$: 2060m ($\nu$(CO)), 2010w, 1960w. $^{31}$PNMR ($CDCl_3$): $\delta$ 141.2 ppm, $J$(Rh–P) 240 Hz. $^1$HNMR ($CDCl_3$): $\delta$ −10.9 ppm, $J$(Rh–H) = $J$(P–H) = 3 Hz.

(The IR and NMR spectra of the obtained complex are identical with those reported for $HRh(CO)\{P(OPh)_3\}_3$ identified in solution [3]).

The hydroformylations were carried out at 40 °C under $CO/H_2 = 1$ at $p$ 1 atm. The glass vessel was connected to a manometer to measure the volume of gas consumed. The reaction mixture contained $2.5 \times 10^{-2}$ mmol of the catalyst in toluene (0.7 $cm^3$), 3.2 mmol of hex-1-ene or 4.3 mmol of vinyl acetate and $1.5–1.7 \times 10^{-2}$ mmol of amine. The products were analyzed by $^1H$ NMR.

The IR spectra were recorded on a Specord M-80, the NMR spectra on a Tesla 100 MHz and a Bruker MSL 300 spectrometer.

## Acknowledgment

Professor J.J. Ziółkowski is thanked for his continued interest in the work.

## References

1 A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Cat., 34 (1986) 213.
2 A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Cat., 43 (1988) 335.
3 A.M. Trzeciak, J.J. Ziółkowski, S. Aygen, R. van Eldik, J. Mol. Cat., 34 (1986) 337.
4 A.M. Trzeciak, J.J. Ziółkowski, J. Mol Cat., 48 (1988) 319.
5 A.M. Trzeciak, unpublished results.
6 E.K. Barefield, G.W. Parshall, Inorg. Chem., 11 (1972) 964.
7 D. Evans, J.A. Osborn, G. Wilkinson, J. Chem. Soc. A, (1968) 3133.
8 A.M. Trzeciak, J.J. Ziółkowski, Inorg. Chim. Acta, 64 (1982) L267.
9 F. Bonati, G. Wilkinson, J. Chem. Soc., (1964) 3156.
10 L.M. Haines, Inorg. Chem., 9 (1970) 1517.
11 S. Martinengo, G. Giordano, P. Chini, Inorg. Synth., 20 (1980) 209.
12 B.T. Heaton, L. Longhetti, L. Garleschelli, U. Sartorelli, J. Organomet. Chem., 192 (1980) 431.