Full Paper

Home-Made Syn-Gas: Hardware And Application To The Hydroformylation Of Styrene

Corresponding Author

Mauro Marchetti
Istituto Di Chimica Biomolecolare - CNR,
Sede Di Sassari, Traversa La Crucca 3 - Località
Baldinca, Li Punti, I-07049 Sassari (ITALY)
Email : mauro@ss.cnr.it

Received: 10th February, 2007
Accepted: 15th February, 2007

Co-Authors

Elisabetta Alberico[1], Stefano Paganelli[2]
[1]Istituto Di Chimica Biomolecolare - CNR, Sede Di Sassari, Traversa La Crucca 3 - Località Baldinca, Li Punti, I-07049 Sassari (ITALY)
[2]Dipartimento Di Chimica - Università Ca' Foscari Di Venezia, Calle Larga S.Marta 2137, I-30123 Venezia (ITALY)

ABSTRACT

Home production of syn-gas by ruthenium catalyzed decomposition of methylformate or paraformaldeyde avoids gas storage and compression and it is well suited for top-bench hydroformylation. The rhodium catalyzed hydroformylation of styrene in the presence of syn-gas generated from decomposition of methylformate either at 140°C or 180°C showed a very low chemoselectivity, substrate hydrogenation being the prevailing reaction. Better results were obtained by using a CO/H_2 mixture generated from decomposition of paraformaldeide although, in order to obtain an almost complete chemoselectivity to oxo-aldehydes, the syn-gas generating reaction and the hydroformylation of styrene had to be carried out in two different autoclaves.   © 2007 Trade Science Inc. - INDIA
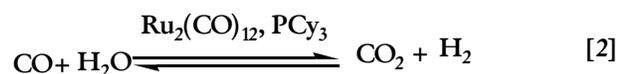
INTRODUCTION

Hydroformylation is the largest volume homogeneous catalytic industrial process employing organometallic catalysts for the production of bulk chemicals[1]. Recently, the hydroformylation of olefins containing other functional groups has been successfully employed for the preparation of several valuable intermediates for the synthesis of fine chemicals[1b,2]. In the last years many efforts have been devoted to render the *oxo*-process more attractive to industry by tackling its economical and safety weak points[3]. Along

this line, the use of formates as carbon monoxide generators is described in the literature[4]. Methyl formate, the most accessible industrial formate, may act as a source of carbon monoxide via decarbonylation to methanol in the presence of different homogeneous catalyst systems based on ruthenium and osmium compounds: in particular, the catalytic system formed by $Ru_3(CO)_{12}$ and tricyclohexylphosphine shows excellent turnovers and selectivities[4a, 4d]. Interestingly, the addition of a small amount of water to the reacting system strongly increases the catalytic activity up to a doubling of the turnover number: a plausible expla-

Full Paper

$$HCOOCH_3 \rightleftharpoons CO + CH_3OH \qquad [1]$$

$$CO + H_2O \overset{Ru_2(CO)_{12}, PCy_3}{\rightleftharpoons} CO_2 + H_2 \qquad [2]$$

[$HCOOCH_3$] = 130 mmol, [$HCOOCH_3$]/[H_2O] = 1.56,
[$HCOOCH_3$]/[Ru] = 498, [PCy_3]/[Ru] = 2.1, T = 140 °C

Scheme 1 : Syn-gas via decomposition of methyl formate

nation of this phenomenon has been given by assuming the formation of anionic ruthenium hydride carbonyl species formed by reaction of the catalytic system with water[4a, 4d]. As ruthenium compounds are also known to catalyze the water-gas shift reaction[5], syn-gas can be synthesized from aqueous methyl formate under the action of a single ruthenium catalyst via the reaction sequence depicted in Scheme 1.

The advantage of the procedure is self-evident as it generates synthesis gas in a very simple manner avoiding gas storage and compression and it is well suited for top-bench hydroformylation.

The one-pot hydroformylation of a number of 1-alkenes and internal alkenes, catalyzed by this system, has been described[4a]. Since the efficiency of the catalytic system, in terms of formate decomposition and developed pressure, is very high at 180°C, the reported reactions have been performed at this temperature. Although hydroformylation does take place, hydrogenation, either of the starting olefin or of the *oxo*-products, is by far the prevailing reaction. As a matter of fact, in all cases, only alcohols were produced and aldehydes were never detected in the reaction mixtures. For example, styrene was completely converted at 180°C but the substrate hydrogenation was the prevailing reaction (75%) and the regioselectivity of the process was rather low[4a]. This result is not surprising in view of the high efficiency of ruthenium - phosphine systems as catalysts for the reduction of aldehydes[6].

EXPERIMENTAL

$HCOOCH_3$, $(CH_2O)_n$, *n*BuOH, DMF, ethylene glycol and toluene were purchased from Aldrich. Solvents were dried by standard procedures and stored over molecular sieves under inert atmosphere. $Ru_3(CO)_{12}$, Tricyclohexylphosphine, 1,4-bis (diphenylphosphino) butane,[$HRh(CO)(PPh_3)_3$]and [$Rh(acac)(CO)_2$] were purchased from Strem. [$(COD)Rh(BPh_4)$] was prepared according to a published procedure[8]. NMR spectra were recorded on a Varian Mercury Plus spectrometer operating at 400 MHz (for ^1H) and 182 MHz (for ^{13}C). GC-MS spectra were recorded on a Hewlett-Packard G1800B GCD system equipped with an Rtx-5MS Restek capillary column (30 m, i.d. 0.25 mm, df 0.25 μm). GC analysis was performed on a 8500 Perkin Elmer GC using a 30-50 mesh molecular sieves column (2 m) using argon as carrier gas.

The reactions were performed in 150 ml double-wall stainless steel autoclaves equipped with a manometer.

One-pot syn-gas production with $HCOOCH_3$ and hydroformylation of styrene

In a typical experiment, $HCOOCH_3$ (8 ml, 0.13 moles), $Ru_3(CO)_{12}$ (56 mg, 0.087 mmoles) and tricyclohexylphosphine (158 mg, 0.55 mmoles) were placed in a glass vial and stirred to give a clear orange solution. Distilled water (1.5 ml, 0.083 moles) was then added. Styrene (100 mg, 0.96 mmoles), the Rh-catalyst ($3.84 \cdot 10^{-3}$ mmoles) (see TABLE1) and toluene (2 ml) were placed in a smaller glass vial which was placed inside the first vial (see figure 1). The glass apparatus was placed inside the steel autoclave and the sequence vacuum/nitrogen carefully applied three times to replace air with the inert gas. The autoclave was heated at 140°C for the reported time (see TABLE 1), after which it was

TABLE 1 : Hydroformylation of styrene[a] in the Matrioska reactor using $HCOOCH_3$ as syn-gas source

Entry	Syn-Gas source[b]	P[c] (bars)	t (hours)	[Rh]	Conv.[d] (%)	2/3[d]	iso/n[d]
1	$HCOOCH_3$	25	15	[$Rh(CO)_2(acac)$]	40	0/100	-
2	$HCOOCH_3$	25	19	[$RhH(CO)(PPh_3)_3$]	77	0/100	-
3	$HCOOCH_3$	25	22	[$(COD)Rh(BPh_4)$]	40	0/100	-

Set up of experiment in the Matrioska reactor is detailed in the experimental part.
a) Reagents and conditions are reported in Scheme 2.
b) Reagents and conditions are reported in Scheme 1.
c) Max. pressure developed at 140°C under the conditions reported in Scheme 1.
d) Determined by means of NMR or gas-chromatography.

Full Paper

TABLE 2 : Hydroformylation of styrene[a) in the Matrioska reactor using (HCOH)$_n$ as syn-gas source[b)

Entry	Solv.[c)	P[d) (bars)	t (h)	[Rh]	Conv.[e)(%)	2/3[e)	iso/n[e)
1	nBuOH	20-25	25	[Rh(CO)$_2$(acac)]	> 99	29/71	40/60
2	DMF	20-25	25	[Rh(CO)$_2$(acac)]	85	100/0	28/72[f)
3	Glycole	20-25	18	[Rh(CO)$_2$(acac)]	> 99	13/87	51/49[g)
4	nBuOH	20-25	24	[Rh(CO)$_2$(acac)]/3 dppb	97	48/52	46/54[h)

Set up of experiment in the Matrioska reactor is detailed in the experimental part.
a) Reagents and conditions are reported in Scheme 2.
b) Reagents and conditions are reported in Scheme 4.
c) Solvent used to dissolve (HCOH)$_n$.
d) Max. pressure developed at 180° under the conditions reported in Scheme 2.
e) Determined by means of NMR or gas-chromatography. f) 26 % of the linear product n is due to the alcohol derived from reduction of the corresponding aldehyde. g) 73% of the branched product iso is due to the alcohol derived from reduction of the corresponding aldehyde; 63% of the linear product n is due to the alcohol derived from reduction of the corresponding aldehyde.
h) 96 %of the branched product iso is due to the alcohol derived from reduction of the corresponding aldehyde; 90 % of the linear product η is due to the alcohol derived from reduction of the corresponding aldehyde.

rapidly cooled down and the residual pressure released. The hydroformylation reaction mixture was filtered through a short pad of celite to remove the catalyst and the solvent evaporated under reduced pressure. The crude product was analyzed by NMR and GC.

One-pot syn-gas production with (CH$_2$O)$_n$ and hydroformylation of styrene

In a typical experiment Ru$_3$(CO)$_{12}$ (128 mg, 0.20 mmoles), tricyclohexylphosphine (179 mg, 0.64 mmoles) and the solvent (11 ml) were placed in a glass vial and stirred for 30 min. to give a clear orange solution. (CH$_2$O)$_n$ (4 g, 0.133 moles) was then added. Styrene (100 mg, 0.96 mmoles), the Rh-catalyst (3.84 · 10^{-3} mmoles) (see TABLE 2) and toluene (2 ml) were placed in a smaller glass vial which was placed inside the first vial (see Figure 1). The glass apparatus was placed inside the steel autoclave and the sequence vacuum/nitrogen carefully applied three times to replace air with the inert gas. The lower part of the autoclave was immersed in an oil bath (oil level above autoclave bottom 5 cm) and heated at 180 °C for the reported time, after which it was rapidly cooled down and the residual pressure released. The hydroformylation reaction mixture was filtered through a short pad of celite to remove the catalyst and the solvent evaporated under reduced pressure. The crude product was analyzed by NMR and GC.

Hydroformylation using (HCOH)$_n$ as syn-gas source produced in a separate autoclave

In a typical experiment Ru$_3$(CO)$_{12}$ (128 mg, 0.20 mmoles), tricyclohexylphosphine (179 mg, 0.64 mmoles) and nBuOH (11 ml) were placed in a glass vial and stirred for 30 min. to give a clear orange solution. (CH$_2$O)$_n$ (4 g, 0.133 moles) was then added. The glass vial was placed inside a steel autoclave (called autoclave A) and the sequence vacuum/ nitrogen carefully applied three times to replace air with the inert gas. The autoclave was heated at 180 °C until the maximum pressure had developed. Styrene (260 mg, 2.5 mmoles), [Rh(acac)(CO)$_2$] (2.6

TABLE 3 : Hydroformylation of styrene[a) using (HCOH)$_n$ as syn-gas source[b) produced in a separate autoclave A

Entry	P[c) (bars)	t (h)	T (°C)	Catalyst	Conv.[d) (%)	2/3[d)	iso/n[d)
1	15	21	80	[Rh(CO)$_2$(acac)]/3 dppb	47	94/6	60/40
2	15	45	80	[Rh(CO)$_2$(acac)]/3 dppb	70	97/3	61/39
3[e)	15	19	80	[Rh(CO)$_2$(acac)]/3 dppb	48	97/3	53/47
4[d)	15	20	80	[Rh(CO)$_2$(acac)]/3 dppb	48	96/4	60/40

Set up of experiment using two autoclaves is detailed in the experimental part.
a) [Styrene] = 260 mg, [Styrene]/[Rh] = 250, toluene = 6 ml.
b) Reagents and conditions are reported in Scheme 4; n-BuOH was used to dissolve (HCOH)$_n$.
c) Initial pressure in the hydroformylation autoclave.
d) Determined by means of NMR or gas-chromatography.
e) This experiment has been carried out using the syn-gas developed in autoclave A after the first withdrawal of gas for experiment in entry 2.
d) This experiment has been carried out using the syn-gas developed in autoclave A after addition of fresh (HCOH)$_n$.
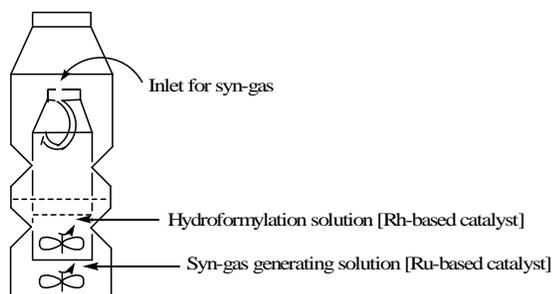
Full Paper

Figure 1 : Matrioska reactor

mg, 0.01 mmoles), dppb (0.03 mmoles, 12 mg) and toluene (6 ml) were placed in a glass vial which was sealed inside a different steel autoclave (called autoclave B). The sequence vacuum/nitrogen was carefully applied three times to replace air with the inert gas. The autoclave B was heated to 80°C and then connected to the autoclave A via a steel capillary to allow flow of syn-gas until equilibration had been reached. The capillary was then removed and the autoclave B heated for the reported time after which it was rapidly cooled down and the residual pressure released. The hydroformylation reaction mixture was filtered through a short pad of celite to remove the catalyst and the solvent evaporated under reduced pressure. The crude product was analyzed by NMR and GC.

RESULTS AND DISCUSSION

Pursuing our long lasting interest in the application of the oxo-reaction to the synthesis of fine chemicals[7], we set out to improve the chemoselectivity of the hydroformylation with home-made syn-gas: we speculated about the possibility of confining the syn-gas generator system while
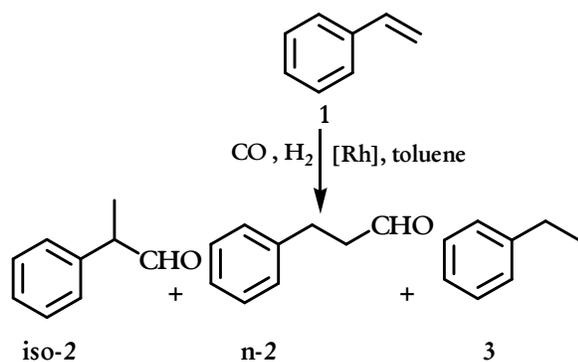
[Styrene] = 100 mg, 0.48M ; [Styrene]/[Rh] =250
Scheme 2 : Hydroformylation of styrene

$$HCOOCH_3 \rightleftharpoons CO + CH_3OH \qquad [1]$$

$$CO + H_2O \underset{Ru_2(CO)_{12}, PCy_3}{\rightleftharpoons} CO_2 + H_2 \qquad [2]$$

$[HCOOCH_3]$ = 130 mmol, $[HCOOCH_3]/[H_2O]$ = 1.56,
$[HCOOCH_3]/[Ru]$ = 498, $[PCy_3]/[Ru]$ = 2.1, T = 140 °C

Scheme 3 - Competing decomposition of methyl formate

allowing the flow of the generated gases into the hydroformylation reaction vessel. This would allow to carry out formate decomposition in the presence of a ruthenium catalyst and to perform the hydroformylation process in the presence of rhodium complexes which, for this reaction, are more active and selective than the related ruthenium catalysts[1]. In order to accomplish this task in a single autoclave, we devised a special glass liner that we named matrioska because it actually consists of two glass vials one inside the other as shown in figure 1.

In a series of experiments, the syn-gas generating mixture was prepared from methylformate and water, using Ru_3CO_{12} and tricyclohexyl phosphine as catalyst precursor according to reference 4a. Styrene was chosen as a standard substrate and its hydroformylation (Scheme 2) was attempted with three rhodium catalyst precursors $[HRh(CO)(PPh_3)_3]$, $[Rh(CO)_2(acac)]$ and $[(COD)RhBPh_4]$, respectively. The reactions were performed at 140 °C and the maximum syn-gas pressure developed was 25 bars (TABLE 1).

Under the conditions reported in TABLE 1, only reduction of styrene to ethylbenzene was detected and the presence of metallic rhodium was observed in the hydroformylation vial. Contamination of the hydroformylation vial with the syn-gas generating mixture was also evident.

Likely, syn-gas pressure does not develop quickly enough to prevent the hydrolysis of methyl formate to formic acid that, in turn, generates carbon dioxide and hydrogen (Scheme 3) which would reduce Rh(I) to Rh(0) and thus favour hydrogenation over hydroformylation.

To overcome this problem, formaldehyde was chosen as an alternative syn-gas source[4c]. In particular, easy to handle paraformaldehyde was used to generate the CO/H$_2$ mixture at 180°C in the presence of the catalytic system $Ru_3(CO)_{12}/PCy_3$

Full Paper

$$HCHO \xrightarrow{\text{Ru}_2(CO)_{12}, PCy_3} CO + H_2$$
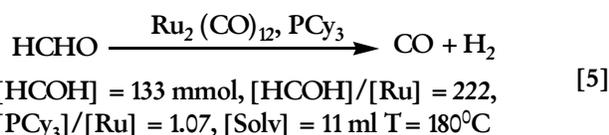
[HCOH] = 133 mmol, [HCOH]/[Ru] = 222,   [5]
[PCy$_3$]/[Ru] = 1.07, [Solv] = 11 ml T = 180°C
Scheme4: Syn-gas via decomposition of paraformaldehyde
(HCHO)n

(Scheme 4).

In this case, only the lower part of the matrioska autoclave was immersed in the oil bath at 180 °C: this would assure a lower temperature in the upper part hosting the hydroformylation vial while allowing (HCOH)$_n$ decomposition at the bottom. Besides, solvents with increasing boiling points, n-butanol (bp 116-118°C), N,N-dimethylformamide (bp 153 °C) and ethylene glycol (bp 196-198) respectively were tested for (HCOH)$_n$ decomposition in order to minimize contamination of the hydroformylation vial before maximum syn-gas pressure had developed.

TABLE 2 summarises the results obtained in the hydroformylation of styrene: the use of paraformaldehyde as source of syn-gas boosts conversion which is practically complete in all cases except when decomposition of (HCOH)$_n$ is carried out in DMF (85%, entry 2). Noteworthy, in this case the hydroformylation vial is not contaminated by the syn-gas generating solution, styrene is hydroformylated and no trace of ethylbenzene is detected. Moreover, only a small amount of the linear aldehyde is further reduced to the corresponding alcohol, while hydrogenation of styrene is still the prevailing reaction in the other two cases (entries 1 and 3). When n-butanol was used as the solvent, however, aldehydes are not reduced furtherly (entry 1), while, when using ethylene glycol, alcohols are the main products (entry 3). In an attempt to prevent formation of rhodium black, which was observed in all the three experiment described so far, and thus stabilize the catalyst, hydroformylation of styrene was carried out in the presence a chelating diphosphine, 1,4-bis (diphenylphosphino) butane, dppb (entry 4). Unfortunately, metallic rhodium formed despite the ligand and reduction of the product aldehydes to alcohols was almost complete.

Although we were able in one case to successfully carry out the hydroformylation of styrene using the matrioska reactor (TABLE 2, entry 2), contamination

of the hydroformylation vial with the syn-gas source solution appears to be the main reason for failure in the other cases.

Therefore we considered the possibility of confining the syn-gas generating system and the hydroformylation vessel in two separate autoclaves, A and B respectively, which would then be connected by a steel capillary when the maximum syn-gas pressure available had developed in autoclave A (about 25 bars). By using this device, the initial syn-gas pressure available for hydroformylation after equilibration of the two autoclaves was 15 bars and the oxo-processes could be carried out at 80°C.

When hydroformylation of styrene, carried out in the autoclave B, was accomplished with the in-situ catalyst system generated from [Rh(CO)$_2$(acac)] and 3 equivalents dppb, the branched and linear aldehydes were almost exclusively formed and no metallic rhodium was detected in the reaction mixture (entry 1, TABLE 3). It is noteworthy that despite a prolonged reaction time (up to 45 h), styrene conversion did not exceed 70% (entry 2, TABLE 3).

However, after this time, by charging the hydroformylation autoclave B with additional CO and H$_2$ from a conventional tank, olefin conversion went to completion. Partial conversion of styrene is then ascribed to insufficient gas pressure, not to deactivation of the metal catalyst. Interestingly, after a first withdrawal of syn-gas, further pressure develops in the syn-gas generating autoclave A so allowing to perform a new hydroformylation experiment on fresh styrene, the results of which are consistent with the first one (entry 3, TABLE 3). When no further pressure develops, the syn-gas generating solution containing Ru$_3$(CO)$_{12}$ and tricyclohexylphosphine in η - butanol can be loaded with some more paraformaldehyde and again pressure develops so showing the robustness of the ruthenium catalyst: it is then possible to carry out another experiment (entry 4, TABLE 3).

The H$_2$/CO ratio of the home made syn-gas mixture, measured by gas chromatography, resulted to be 16/84 in volume. It is known that the branched aldeyde is strongly favoured in the case of styrene because the branched rhodium-alkyl species from which it ensues is stabilized due to resonance[1b]. This is not observed in the experiments we have carried out, neither with unmodified- nor with dppb-

CHEMICAL TECHNOLOGY
An Indian Journal

Full Paper

modified catalysts, for which the branched to normal aldehyde ratio is, in most cases, close to one: we believe that the observed regiochemistry might be due to the low pressure and the high temperature at which the hydroformylation reactions are carried out.

CONCLUSION

The rhodium catalyzed hydroformylation of styrene carried out at 140°C in the presence of home-made syn-gas generated from methylformate showed to be scarcely chemoselective, hydrogenation of the substrate being the prevailing reaction. Better results, although not yet satisfactory, were obtained by using paraformaldehyde as syn-gas source: a complete conversion was achieved at 180°C but the aldehyde yield did not exceed 30%. Only when the syn-gas generating system was separated from the hydroformylation vessel it was possible to hydroformylate styrene with high chemoselectivity: the branched and linear aldehydes were almost exclusively formed, the substrate hydrogenation product not exceeding 5%. This device might represent a useful alternative to CO and H_2 tanks to supply syn-gas to the hydroformylation reaction vessel while allowing to run the reaction under mild conditions.

Further investigations are underway in order to assess the exact composition of the developed gas mixture and to test the applicability of this system to other substrates.

REFERENCES

[1] a) B.Cornils, W.A.Hermann (Eds.); 'Applied Homogeneous Catalysis with Organometallic Compounds', Wiley-VCH, Weinheim, **(1996)**.
b) P.W.N.M.van Leeuwen, C.P.Casey, G.T.Whiteker in: P.W.N.M.van Leeuwen, C.Claver (Eds); 'Rhodium Catalyzed Hydroformylation', Kluwer Acad.Publ., Dordrecht, **(2000)**.

[2] a) C.Botteghi, M.Marchetti, S.Paganelli; In, C.Bolm, M. Beller, (Eds.) 'Transition Metals for Organic Synthesis', Vol.1, VCH, Weinheim, **(1998)**.
b) M.Beller, K.Kumar; in, M.Beller, C.Bolm (Eds.); 'Transition Metals for Organic Synthesis', 2nd Ed.,Vol.1, VCH, Weinheim, **(2004)**.
c) B.Breit, W.Seiche; Synthesis, 1 and references therein **(2001)**.
d) H-W.Bohnen, B.Cornils; In, B.C.Gates, H.Knözinger (Eds), 'Advances in Catalysis', Academic Press, San Diego (USA), vol. **47**, p.1 **(2002)**.
e) J.L.Leighton; In, P.A.Evans (Ed.), 'Modern Rhodium-Catalyzed Organic Reactions', Wiley-VCH, Weinheim, **(2004)**.

[3] a) B.Cornils, W.A.Hermann (Eds.); 'Aqueous-Phase Organometallic Catalysis', 2nd Ed., Wiley-VCH, Weinheim, **(2004)**.
b) F.Joo; 'Aqueous Organometallic Catalysis', Kluwer Acad.Publ.Dordrecht, **(2001)**.
c) B.Cornils, W.A.Hermann, I.T.Horvath, W.Leitner, S.Mecking, H.Olivier-Bourbigou, D.Vogt; (Eds.) 'Multiphase Homogeneous Catalysis', Wiley-VCH, Weinheim, **(2005)**.

[4] a) G.Jenner; Appl.Catal., **75**, 289 **(1991)**.
b) G.Jenner; Tetrahedron Lett., **32**, 505 **(1991)**.
c) G.Jenner, E.M.Nahmed, S.Libs-Konrath; J.Mol.Catal., **64**, 337 **(1991)**.
d) G.Jenner; Appl.Catal.A:General, **121**, 25 **(1995)**.

[5] R.M.Laine; J.Am.Chem.Soc., **100**, 6451 **(1978)**.

[6] R.A.Sanchez-Delgado, N.Valencia, R.L.Marquez-Silva, A.Andriollo, M Medina; Inorg. Chem., **25**, 1106 **(1986)**.

[7] a) C.Botteghi, M.Marchetti, S.Paganelli, F.Persi-Paoli; Tetrahedron, **57**, 1631 **(2001)**.
b) C.Botteghi, C.Dei Negri, S.Paganelli, M.Marchetti; J.Mol.Catal.A:Chem, **175,** 1725 **(2001)**.
c) M.Marchetti, S.Scognamillo, S.Paganelli, C.Botteghi; J.Mol.Catal.A:Chem, **179** 79 **(2002)**.
d) C.Botteghi, T.Corrias, M.Marchetti, S.Paganelli, O.Piccolo; Org.Proc.Res. & Dev., **6,** 379 **(2002)**.
e) C.Botteghi, S.Paganelli, F.Moratti, M.Marchetti, R.Lazzaroni, R.Settambolo, O.Piccolo; J.Mol.Catal. A: Chem., **200**, 147 **(2003)**.
f) M.Marchetti, S.Paganelli, E.Viel; J.Mol. Catal.A:Chem., **222**, 143 **(2004)**.
g) S.Paganelli, L.Spano, M.Marchetti, O.Piccolo; Chimica e Industria, **87(6)**, 94 **(2005)**.
h) S.Paganelli, F.Battois, M.Marchetti, R.Lazzaroni, R.Settambolo, S.Rocchiccioli; J.Mol.Catal. A: Chem., **246,** 195 **(2006)**.
i) S.Paganelli, A.Ciappa, M.Marchetti, A.Scrivanti, U.Matteoli; J.Mol.Catal.A: Chem., **247,** 138 **(2006)**.
j) H.S.Parker, E.Alberico, H.Alper; J.Am.Chem. Soc., **121**, 11697 **(1999)**.

[8] R.R.Schrock, J.Osborn; Inorg.Chem., **9**, 2339 **(1970)**.