Reduction of aromatic nitro compounds as catalyzed by rhodium trichloride under water–gas shift reaction conditions ☆

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Described are quantitative studies of the CO/H_2O reduction of various nitroaromatics to the respective anilines under water–gas shift reaction (WGSR) conditions catalyzed by solutions of $RhCl_3$ in aqueous amines. The most active media were aqueous tetramethylethylenediamine and 2-picoline solutions. The reduction rates exhibited first-order dependence on $P(CO)$ over the 0.3–1.5 atm range, but turnover frequencies decreased as the total rhodium concentration increased over the range 5–40 mM. The latter behavior was interpreted in terms of the coexistence of mononuclear and polynuclear Rh species in the system, the mononuclear being the more catalytically active. Relative shift reaction and reduction rates indicate that the nitroaromatics must be reduced by an independent catalytic cycle rather than by the WGSR produced H_2.
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1. Introduction

It is well established that the water–gas shift reaction (WGSR) (Eq. (1)) is catalyzed in homogeneous solutions by various transition metal complexes [1,2]. Furthermore, under WGSR conditions, the CO/H_2O couple has proved effective for the hydrogenation and hydroformylation of alkenes (e.g. Scheme 1) as well as the reduction of various other substrates [1]. Studies in these laboratories have long been concerned with homogeneous catalysis of the water–gas shift reaction as well as its applications in organic transformations ("Reppe chemistry") [3]. Among the most active and consistently stable WGSR catalysts we have studied are those based on $RhCl_3$ dissolved in aqueous aromatic nitrogen heterocycles (such as 4-picoline) and other amine solvents [4,5]. These and related systems including rhodium complexes heterogenized on amine functionalized polymers (e.g. poly-4-vinylpyridine) have also proved effective for the Reppe hydroformylation and hydrogenation of alkenes and carbonylation of alkynes and reductions of chlorocarbons and nitroaromatics [6–16]. In this context, we describe here quantitative studies of the CO/H_2O reductions of several nitrobenzene derivatives to the respective anilines by a homogeneous catalytic system prepared by $RhCl_3 \cdot 3H_2O$ dissolved in aqueous N,N,N'',N'-tetramethylethylenediamine (TMEDA) and in other aqueous amines.
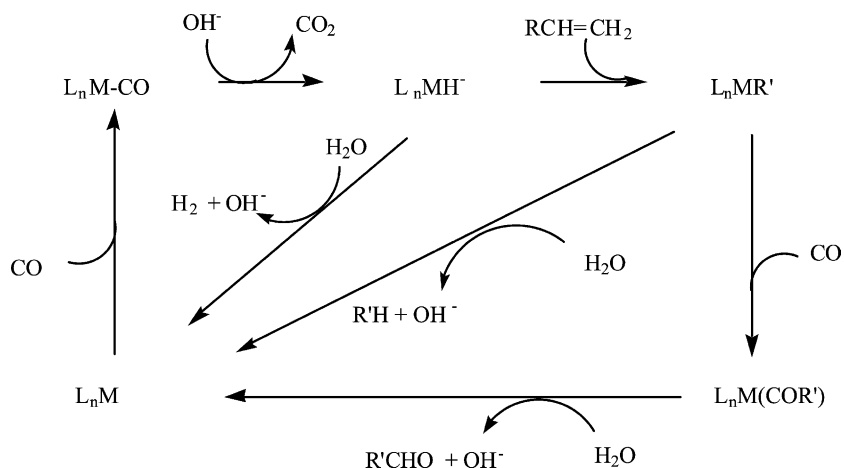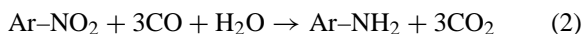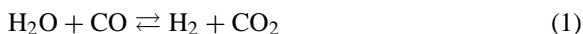
Scheme 1. Hypothetical mechanism for "Reppe" type hydroformylation or hydrogenation of an alkene.

$$H_2O + CO \rightleftarrows H_2 + CO_2 \qquad (1)$$

$$Ar-NO_2 + 3CO + H_2O \rightarrow Ar-NH_2 + 3CO_2 \qquad (2)$$

2. Experimental

Materials: *N,N,N′,N′*-Tetramethylethylenediamine *p*-nitrotoluene, *p*-nitroaniline, *p*-flouronitrobenzene, *p*-chloronitrobenzene, and *p*-nitrobenzonitrile were obtained from Aldrich and distilled prior to use. Double distilled water was used to prepare solutions. Nitrobenzene (Mallinckrodt), rhodium trichloride (Johnson-Matthey, Ltd.) were used as received. The gas mixture CO/CH_4 (94/6 (v/v)), He/H_2 (91.5/8.5%) were obtained from Liquid Carbonics. A gas mixture of $CO/CO_2/CH_4/H_2$ (85.05/5.13/4.94/4.88%) was obtained from Linde and used to generate calibration curves for CO, CO_2, CH_4 and H_2.

Instrumentation: Analyses of liquid samples were done on a Hewlett-Packard 5980 Series II programmable gas chromatograph–mass spectrometer (GC–MS) fitted with PONA (cross-linked methyl silicone gum) capillary column (50 m × 0.2 mm × 0.5 mm). Gas samples analyses were performed on a Hewlett-Packard 5980 Series II programmable gas chromatograph fitted with carbosieve-B (80–100 mesh) column and a thermal conductivity detector. The column temperature was programmed from 60 to 175 °C (ramp rate = 30 °C/min at He/H_2 carrier-gas flow rate of 30 ml/s.

Batch reactor procedures: Catalytic and kinetic runs were conducted in all-glass reactor vessels consisting of a round bottom flask (100 ml) connected to an "O" ring sealed joint to a two-way Rotoflow Teflon stopcock attached to the vacuum line [4]. In a typical catalytic experiment, a known amount of the nitroaromatic compound was dissolved in 8.0 ml of solvent amine and added to the glass reactor vessel, containing $RhCl_3 \cdot 3H_2O$ (typically 13.2 mg, 0.5 mmol) dissolved in 2.0 ml of H_2O, then the solution was degassed by three freeze-pump-cycles. The reaction vessel was charged with CO/CH_4 mixture at the desired pressure (typically 0.9 atm at 100 °C), then suspended in a thermostated silicone oil bath. Gas samples of 1.0 ml were periodically removed from the reaction vessel at bath temperature, analyzed by gas chromatography. The CH_4 was used as internal standard to allow calculation of absolute quantities of CO consumed and CO_2 produced during a time interval (typically 3 h). Subsequent to gas samples analyses, the catalytic solution was removed from the reactor, passed through a column of neutral alumina and liquid samples of the worked-up solution were analyzed by GC–MS using *o*-xylene as an internal standard.

3. Results

Solvent effects: The CO/H_2O reduction of nitrobenzene catalyzed by $RhCl_3 \cdot 3H_2O$ under WGSR

Table 1
p-Nitrotoluene reduction to aniline by CO/H_2O catalyzed by a solution prepared from $RhCl_3 \cdot 3H_2O$ in various aqueous amines[a]

Solvent amine	TF(aniline) (per day)	Conversion (%)
Diethylamine	17	7
Trimethylamine	13	6
Triethylamine	31	14
Tetramethylenediamine	20	9
2-Picoline	78[b]	–
TMEDA	131	57

[a] 8/2 (v/v) amine/H_2O, $RhCl_3 \cdot 3H_2O$ = 5 mM, [*p*-CH_3PhNO_2] = 250 mM, $P(CO)$ = 0.9 atm, T = 100 °C, reaction time = 3 h.
[b] Value inferred from the measured TF(CO_2).

conditions in several aqueous amine solutions was examined. Aniline was the only organic product detected by GC–MS, and in each case a 1/3 aniline/CO_2 stoichiometric ratio as predicted by Eq. (2) was observed. The observed turnover frequencies for the production of aniline (TF(aniline) = moles of aniline/mole of Rh per day) are given in Table 1. Aqueous TMEDA and aq. 2-picoline (20/80 (v/v), H_2O/amine) were the most active media for this reduction.

Concentration effects: The effects of varying the substrate concentration, carbon monoxide pressure ($P(CO)$), rhodium concentration ([Rh]), and temperature on the CO/H_2O reduction of *p*-nitrotoluene were all studied in the 80% aq. TMEDA medium. The CO_2 formation was monitored owing to simplicity and speed of the gas sample analyses. Several checks of *p*-toluidine formation confirmed the predicted 1/3 *p*-toluidine/CO_2 ratio (±5%). Similar studies were carried out using *p*-nitrotoluene as the substrate in 80% aq. 2-picoline.

Figs. 1 and 2, respectively, illustrate the effects of varying $P(CO)$ over the 0.3–1.5 atm range and of [Rh] over the 5–40 mM range on the rates of *p*-nitrotoluene reduction in aq. TMEDA while holding other variables constant. In the former case, the plot of TF(CO_2) versus $P(CO)$ is linear, indicating a first-order dependence on CO concentration in solution. In the latter case, TF(CO_2) decreases as [Rh] increases, thus the catalytic efficiency of the system decreases. Closely analogous behavior was seen for *p*-nitrotoluene reduction by CO/H_2O in aq. 2-picoline as well, and such patterns have also been noted for the WGSR catalytic activity of analogous systems [4].

The effect of substrate concentration was probed by examining the CO_2 and H_2 production rates over
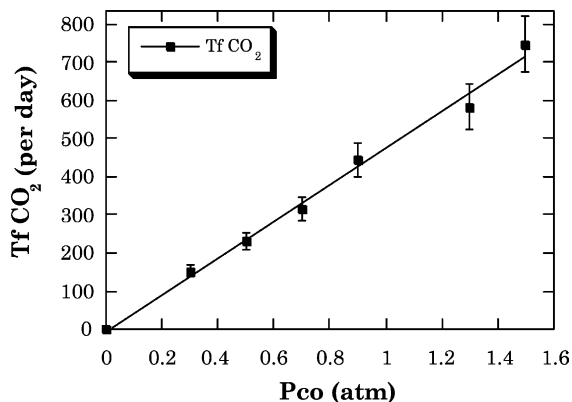

Fig. 1. Effect of $P(CO)$ on the on the TF(CO_2) associated with the reduction of *p*-nitrotoluene in 80% aq. TMEDA at 100 °C ([*p*-nitrotoluene] = 250 mM, [Rh] = 5 mM, T = 100 °C).

the [*p*-nitrotoluene] range 35–350 mM with [Rh] = 5 mM, $P(CO)$ = 0.9 atm at 100 °C. These data are presented in Table 2. At low [substrate], H_2 was also found as the result of competing water–gas shift catalysis. TF(H_2) decreased and TF(CO_2) increased with rising [*p*-nitrotoluene], and little dihydrogen production was seen for substrate concentrations greater than 150 mM and CO_2 production leveled off in this region. A similar pattern for TF(CO_2) with respect to [nitrobenzene] was also seen in aq. 2-picoline ($P(CO)$
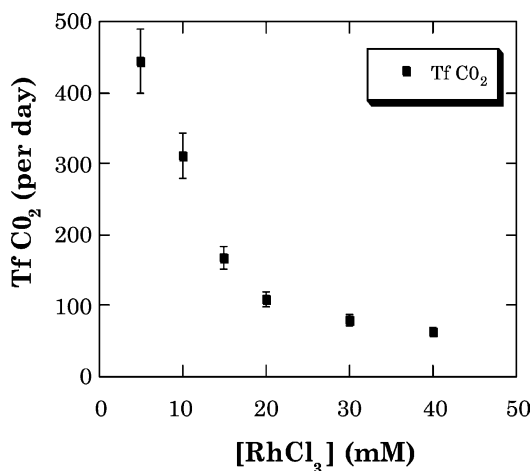

Fig. 2. Dependence of TF(CO_2) on the concentration of added $RhCl_3$ associated with the CO/H_2O reduction of *p*-nitrotoluene in 80% aq. TMEDA at 100 °C ([*p*-nitrotoluene] = 250 mM, $P(CO)$ = 0.9 atm).

Table 2
Effect of substrate concentration on the catalysis rates for the CO/H_2O reduction of *p*-nitrotoluene in aq. TMEDA[a]

[*p*-Nitrotoluene] (mM)	TF(CO_2) (per day)	TF(H_2) (per day)
0	75	63
35	165	36
75	274	16
150	420	<10
250	444	<5
350	437	<5

[a] $T = 100\,°C$, [Rh] $= 5\,mM$, $P(CO) = 0.9\,atm$, 80% aq. TMEDA.

Fig. 3. Plot of log(TF(CO_2)) vs. Hammett σ-values for the CO/H_2O reduction of the nitrobenzene derivatives *p*-X-PhNO_2 (TF(CO_2) is in per day with an experimental uncertainty of ∼10%, [RhCl$_3$·3H_2O] $= 10\,mM$, [substrate]$_0$ $= 250\,mM$, $P(CO) = 0.9\,atm$ at $100\,°C$, σ-values for the substituents were taken from [18]).

$= 0.9\,atm$, $100\,°C$) with TF(CO_2) leveling off at a value of ∼500 per day at substrate concentrations >400 mM, but with the key difference that the rates of H_2 and CO_2 production dropped to near zero (∼3 per day) at low [substrate] owing to the poor activity of the WGSR catalysis in this medium [4].

Temperature effects: The catalytic activity of these systems (as reflected by the TF(CO_2) value) for a solution with [Rh] $= 5\,mM$, $P(CO) = 0.9\,atm$, and [*p*-nitrotoluene] $= 250\,mM$, was assayed over the temperature range 80–100 °C. The TF(CO_2) values increased from 225 per day at 80 °C to 325 at 90 °C to 444 at 100 °C. This gives an apparent activation energy of $8.9 \pm 0.4\,kcal\,mol^{-1}$ over this relatively narrow range of T. A similar study of *p*-nitrotoluene (550 mM) reduction in aq. 2-picoline gave an apparent E_a of $5.2 \pm 0.5\,kcal\,mol^{-1}$.

Substrate substituent effects: The electronic effects of phenyl ring substituents X for a series of nitrobenzene derivatives *p*-X-PhNO_2 were examined for X = NH_2, CH_3, H–, F–, Cl– and NC– in 80% aq.

TMEDA solutions. The TF(aniline) values are seen to decrease as the substituents become more electron withdrawing (Table 3). A Hammett plot of these data (log(TF(aniline)) versus the substituent constant σ [18]) was linear giving a ρ-value of −0.28. An analogous plot of the CO_2 turnover frequencies determined for such solutions is shown in Fig. 3 and gave the same value for ρ.

4. Discussion

As noted above, the marked dependence of the catalytic activity on the concentration of RhCl$_3$ ini-

Table 3
Reduction of the aromatic nitro compounds *p*-X-PhNO_2 to the respective anilines by CO/H_2O catalyzed by a solution prepared from RhCl$_3$·3H_2O in aqueous TMEDA[a]

Substituent X on *p*-X-PhNO_2	Product[b] (% conversion)	σ-value for X[c]	TF(amine) (per day)
NH_2	*p*-Phenylenediamine (52)	−0.66	104
CH_3	*p*-Toluidine (51)	−0.17	102
H	Aniline (36)	0.00	73
F	*p*-Fluoroaniline (34)	0.06	67
Cl	*p*-Chloroaniline (31)	0.23	62
CN	*p*-Aminobenzonitrile (24)	0.66	48

[a] [RhCl$_3$·3H_2O] $= 10\,mM$, [substrate] $= 250\,mM$, 8 ml of TMEDA, 2 ml of H_2O, $P(CO) = 0.9\,atm$ at $100\,°C$, reaction time = 3 h.
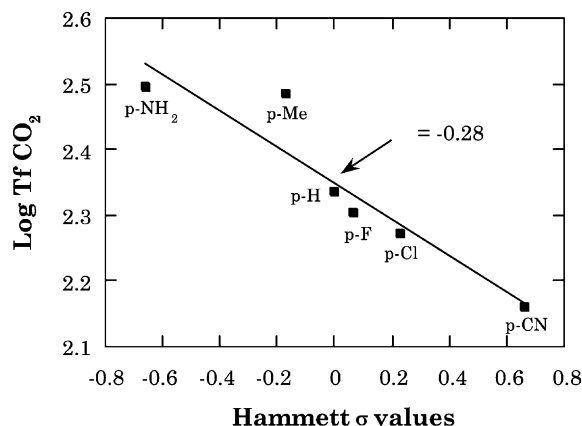[b] Selectivity (>99%).
[c] Taken from [18].

tially added was observed previously for the activity of water–gas shift reaction catalysis ($TF(H_2)$ and $TF(CO_2)$) by rhodium salts in aqueous amine solvents. Such behavior was interpreted to involve the presence under these conditions of a relatively labile mixture of mononuclear and polynuclear rhodium complexes, both of which are catalytically active, but the mononuclear catalysts being much more active on a per rhodium basis [4,5]. In situ ^{13}C NMR and IR spectral analyses were consistent with the presence of at least two different active species in solution [4]. In this context, it is notable that Fachinetti et al. found the cluster $[Rh_5(CO)_{13}(py)_2]^-$ ($L = H_2O$, py) to accumulate during WGSR catalysis by solutions prepared from *cis*-$[Rh(CO)_2(py)_2]PF_6$ or $RhCl_3 \cdot 3H_2O$ in 80% aq. pyridine [17]. They proposed a catalytic cycle where *cis*-$[Rh(CO)_2(py)_2]^+$ and $[Rh_5(CO)_{13}(py)_2]^-$ are the active species. We conclude that a similar mixture of mono- and polynuclear Rh complexes is responsible for the catalytic nitro group reactions described here.

Scheme 2 is a proposed catalytic cycle for the CO/H_2O reduction of nitrobenzene derivatives to anilines based on analogies drawn from earlier studies

of rhodium based WGSR and Reppe hydrogenation catalysis [4,5] and ruthenium based nitrobenzene carbonylation [19,20]. In this scheme, the resting state of the catalyst(s) is represented by {Rh}, and this undoubtedly is a mixture of mono- and polynuclear rhodium species leading to the activity pattern seen in Fig. 2. For a constant rhodium concentration the rate-limiting step of the catalytic cycle is first-order in [CO] (Fig. 1). This is attributed in the scheme to the equilibrium

$$\{Rh\} + CO \rightleftarrows \{Rh(CO)\} \qquad (3)$$

The WGSR catalysis activity of analogous systems displays similar first-order dependence on [CO] [4,5], and this behavior suggests that the same equilibrium precedes the rate-limiting steps of both the WGSR and the nitroaromatic reduction catalytic cycles. Scheme 2 accounts for this in terms of competition for the key {Rh(CO)} intermediate(s). The WGSR involves first the reversible reaction with OH^- (or H_2O activated by a general base) to give the hydroxycarbonyl intermediate(s) generically represented as $\{Rh(CO_2H)\}$. The competing nitroaromatic reduction cycle would be initiated by substrate trapping of {Rh(CO)} to
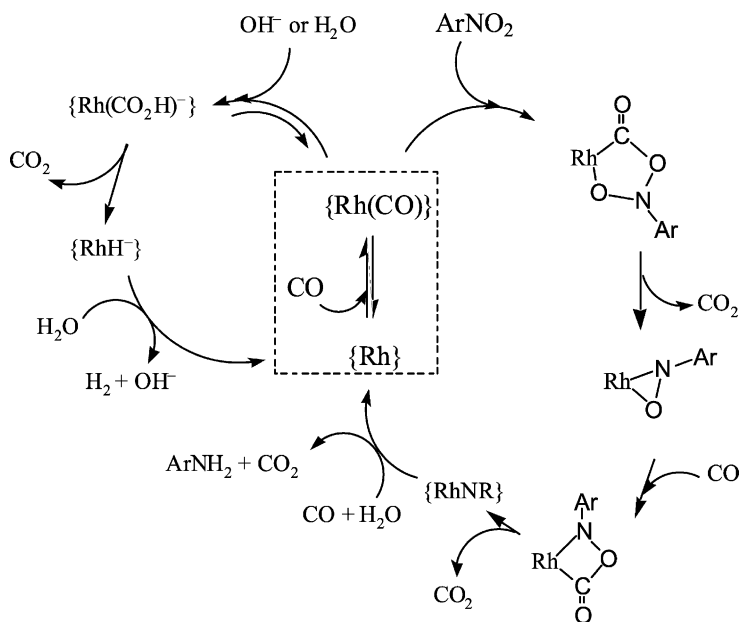
Scheme 2. Hypothetical pathway for the catalytic CO/H_2O reduction of Ar–NO_2 to the respective anilines showing the competing WGSR cycle.

begin a sequence of events such as represented by the right side of Scheme 2. Notably, there is precedence for structures proposed for the reduction cycle, for example, in mechanism studies of ruthenium catalyzed nitroaromatic carbonylation, Gladfelter and co-workers [19,20] isolated and determined the X-ray crystal structure of a $\{Ru(\eta^2\text{-ON-Ar})\}$ intermediate.

The dependence of the reduction rates in aq. TMEDA (Table 2) on substrate concentration can be explained in terms of this competition. At higher [substrate], the reaction rate reaches a maximum and little H_2 formation was seen, so under these conditions nearly all the $\{Rh(CO)\}$ must be trapped by $Ar–NO_2$. In that case, $\{Rh(CO)\}$ formation via Eq. (3) must be rate limiting and the reaction is independent of [substrate]. At lower [substrate], the two catalytic cycles are competitive and both $Ar–NO_2$ reduction and H_2 production are seen. The substituent effects on the reduction rates (Hammett $\rho = -0.28$) suggest that association of $Ar–NO_2$ with $\{Rh(CO)\}$ is affected by the electron density at the nitro group. Since electron donating substituents accelerate the reaction, and we favor a mechanism proceeding via nucleophilic attack of a nitro oxygen on the coordinated CO. This aspect does contrast with the ruthenium catalyzed carbonylation of nitroaromatics [19], where a strong substituent effect with a large and positive Hammett ρ-value was observed and it was concluded that the reaction was initiated by electron transfer from the catalyst to the substrate.

An important point to emphasize is that both in aq. TMEDA and (especially) in aq. 2-picoline the rates of the rhodium catalyzed nitroaromatic reduction by the CO/H_2O are dramatically higher than the water–gas shift catalysis by the same systems in the absence of such substrates. This remains the case even when the 3/1 stoichiometry of CO_2 production by the reduction cycle is taken into account. In this context, therefore, it is clear that the WGSR cycle does not precede the reduction cycle, that is, the nitroaromatics are not being reduced by WGSR generated H_2. Instead the $X\text{-}PhNO_2$ substrate must be competing for the $\{Rh(CO)\}$ species in the manner shown by Scheme 2.

In summary, quantitative studies of the CO/H_2O reduction of various nitroaromatics to the respective anilines catalyzed by solutions of $RhCl_3$ dissolved in aqueous amines show the most active media to be aqueous TMEDA and 2-picoline solutions. The reduc-

tion rates exhibited first-order dependence on $P(CO)$ over the 0.3–1.5 atm range, but decreased as the total Rh concentration increased consistent with an equilibrium between mononuclear and polynuclear catalytic species, the mononuclear being the more catalytically active. Relative shift reaction and reduction rates, and substrate concentration and substituent effects were interpreted as indicating that the $X\text{-}PhNO_2$ substrate must be reduced by a catalytic cycle independent of (and in competition with) the water–gas shift also catalyzed under these conditions.

References

[1] P.C. Ford, A. Rokicki, Adv. Organomet. Chem. 28 (1988) 187.
[2] P.C. Ford, E. Trabuco, M.M. Mdleleni, Encyclopedia of Catalysis, Wiley, New York, 2002.
[3] P.C. Ford, Acc. Chem. Res. 14 (1981) 31.
[4] A.J. Pardey, P.C. Ford, J. Mol. Catal. 53 (1989) 247.
[5] B.S. Lima Neto, K.H. Ford, A.J. Pardey, P.C. Ford, Inorg. Chem. 30 (1991) 3837.
[6] M.M. Mdleleni, R.G. Rinker, P.C. Ford, J. Mol. Catal. 89 (1994) 283.
[7] E. Trabuco, P.C. Ford, J. Mol. Catal. A: Chem. 148. (1999) 1.
[8] M.M. Mdleleni, R. Rinker, P.C. Ford, Inorg. Chem. Acta 270 (1998) 345, and references therein.
[9] A.J. Pardey, J. Brito, M. Fernandez, A.B. Rivas, M.C. Ortega, C. Longo, P.J. Baricelli, E. Lujano, S.A. Moya, React. Kinet. Catal. Lett. 74 (2001) 111.
[10] A.J. Pardey, M. Mediavilla, M. Canestrari, D. Moronta, C. Urbina, E. Lujano, P. Baricelli, C. Longo, R. Pastene, S.A. Moya, Catal. Lett. 56 (1999) 231.
[11] A.J. Pardey, M. Fernandez, A.B. Rivas, M.C. Ortega, C. Urbina, D. Moronta, C. Longo, M. Mediavilla, P.J. Baricelli, S.A. Moya, Inorg. Chim. Acta 329 (2002) 22, and references therein.
[12] C. Longo, J. Alvarez, M. Fernandez, A.J. Pardey, S.A. Moya, P. Baricelli, M.M. Mdleleni, Polyhedron 19 (2000) 487.

[13] S.A. Moya, R. Pastene, R. Sariego, R. Sartori, P. Aguirre, H. Le Bozec, Polyhedron 15 (1996) 1823.

[14] K. Nomura, I. Kotohiro, H. Masaru, T. Motoo, J. Mol. Catal. 66 (1991) L1.

[15] K. Kaneda, K. Fujita, T. Takemoto, T. Imanaka, Univ. Bull. Chem. Soc. Jpn. 64 (1991) 602.

[16] S.-W. Zhang, S. Takahashi, Chem. Commun. (2000) 315; E. Yoneda, T. Sugioka, K. Hirao, S.-W. Zhang, S. Takahashi, JCS, Perkin Trans. 1 (1998) 477–484.

[17] G. Fachinetti, G. Fochi, T. Funaioli, Inorg. Chem. 33 (1994) 1719.

[18] K.B. Wiberg, Physical Organic Chemistry, Wiley, New York, 1963.

[19] S.J. Skoog, W.L. Gladfelter, J. Am. Chem. Soc. 119 (1997) 11049.

[20] S.J. Skoog, J.P. Campbell, W.L. Gladfelter, Organometallics 13 (1994) 4137.