



## COMPLEXES WITH HETEROCYCLIC NITROGEN LIGANDS—III†. CATIONIC RHODIUM(I) DERIVATIVES AND APPLICATIONS IN CATALYSIS

SERGIO A. MOYA,\* RUBEN PASTENE and RENATO SARIO

Departamento de Química Aplicada, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 307-2, Santiago, Chile

REBECA SARTORI\*

Departamento de Bioquímica, Facultad de Medicina, Universidad de Chile, Casilla 70086-7, Santiago, Chile

PEDRO AGUIRRE

Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile

and

HUBERT LE BOZEC

Université de Rennes I, Campus Beaulieu, 35042, Rennes, France

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**Abstract**—The preparation and spectroscopic properties of mononuclear cationic complexes of rhodium(I) coordinated to the diolefin 2,5-norbornadiene (NBD) and to the heterocyclic nitrogen ligands 6,7-dihydrodipyrido-[2,3-b:3',2'-j]-1,10-phenanthroline (**2-4N**), 7,8-dihydro-6H-cyclohepta-[2,1-b:3,4-b]-di-1,8-naphthyridine (**3-4N**) and 2,2'-bi-(3-methyl)-1,8-naphthyridine (**Me-4N**) are described. The complexes show the characteristic intraligand bands of the ligands and an electronic low energy band insensitive to solvent changes and of low intensity, which may be assigned to a ligand field band. The NMR properties agreed with the IR results showing the equivalence of the two naphthyridine fragments in the complexes. Electrochemically all the complexes display two reductions and one oxidation waves, in the potential region from +1.5 to −2.4 V *vs* Fc<sup>+</sup>/Fc. The water gas shift reaction (WGS) and the selective reduction of nitrobenzene to aniline under WGS conditions are effectively catalysed by these complexes.

In recent years it has become clear that some nitrogen donor ligands can form stable complexes with low oxidation state transition metals. This is particularly true with ligands containing *sp*<sup>2</sup> hybridized

nitrogen donors where  $\pi$  back-bonding effects can be expected.<sup>3</sup> The well-known cationic complexes with arylphosphine ligands of type [Rh(NBD)L<sub>2</sub>]<sup>+</sup> have shown important catalytic activity in many reactions.<sup>4–6</sup> Some similar complexes of Rh<sup>I</sup> with L<sub>2</sub> = Schiff base ligands have been reported to have catalytic activity in hydrogen transfer reactions.<sup>7</sup> Many rhodium complexes have been investigated

\* Authors to whom correspondence should be addressed.

† See refs 1 and 2.

in the WGSR, and a kinetic study of the behaviour of the *in situ* generated  $[\text{Rh}(\text{CO})_2(4\text{-picoline})_x]^+$  complex has been reported.<sup>8</sup> The intermediate hydride produced in the WGSR may react with a suitable substrate and, as the elimination of  $\text{H}_2$  from the intermediate hydride is frequently the key step in the catalytic cycle, the reaction of this hydride with a reducible substrate may be much faster.<sup>9</sup>

The preparation of a series of catalyst precursors of rhodium(I) with variations only in the polypyridine ligands could be the beginning of a systematic study of the relationships between the structural, spectroscopic and electrochemical properties with the catalytic activity in a homogeneous process. In this paper the preparations of cationic species of the type  $[\text{Rh}(\text{NBD})(\text{L})]^+$  where NBD = bicyclo[2,2,1]hepta-2,5-diene (2,5-norbornadiene) and  $\text{L} = 6,7\text{-dihydrodipyrido-[2,3-b:3',2'-j]-1,10-phenanthroline}$  (**2-4N**), 7,8-dihydro-6H-cyclohepta-[2,1-b:3,4-b]-di-1,8-naphthyridine (**3-4N**) and 2,2'-bi-(3-methyl)-1,8-naphthyridine (**Me-4N**) (Fig. 1), the spectroscopic and electrochemical properties are described. The effect of the nature of the polypyridine ligand on the catalytic activity of these complexes in the WGSR and in the process of reduction of nitrobenzene under WGSR conditions has also been studied.

## EXPERIMENTAL

### Physical measurements

IR spectra were determined as KBr disks using a Bruker IFS-66V Fourier-transform spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu UV-160 spectrophotometer using different solvents in quartz cells at ambient temperature. Proton NMR spectra of the polypyridine ligands were recorded using a Varian T-60 spectrometer (100 MHz) and the spec-

tra of the complexes in a Bruker AM 300 (300 MHz) spectrometer. Conductivity measurements were carried out in acetonitrile and chloroform anhydrous on  $10^{-3} \text{ mol l}^{-1}$  solutions at  $25^\circ\text{C}$  using a Cole-Parmer 01481 conductivity meter. Electrochemical measurements were carried out on a classical three-electron potentiostatic set-up consisting of a Bank-Wenking POS 73 potentiostat, an XY Linseis recorder model OS 17100 and a Gould oscilloscope model OS 4100. Working and auxiliary electrode were a Pt disk electrode and a Pt wire, respectively. The reference electrode (an aqueous saturate sodium chloride calomel) was connected to the cell by a Vycor bridge (porous glass No. 7930) filled with corresponding solvent and supporting electrolyte. A  $0.1 \text{ mol l}^{-1}$  solution of purified and dried tetrabutylammonium perchlorate (TBAP) in acetonitrile or methylene chloride was used as supporting electrolyte. The reference electrode was calibrated against  $\text{Cp}_2\text{Fe}$ , which is used as the reference in this work. The separation between the anodic and the cathodic peaks for the  $\text{Cp}_2\text{Fe}$  oxidation was 80–85 mV in acetonitrile. All measurements were carried out under extreme conditions of inertness.

Microanalyses were performed by the Centre de Microanalyses du CNRS at Lyons, France.

The catalytic studies on the WGSR were carried out following the methods and apparatus reported in the literature.<sup>10</sup> The reduction of nitrobenzene was accomplished as previously described,<sup>11</sup> in ethoxyethanol in the presence of KOH,  $\text{H}_2\text{O}$  and nitrobenzene. The  $\text{H}_2$  produced in the WGSR was analysed by GC in a Perkin-Elmer 8500 GC, with a Carbosieve SII column. The hydrogenation of the nitrobenzene was followed by GC in a Perkin-Elmer Sigma 3 GC, equipped with an OV 17 column, using *p*-cymene as internal standard. In both cases the batch reactor was charged with 0.9 atm of CO and heated at  $130^\circ\text{C}$ .

### Materials

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and 2,5-norbornadiene from Aldrich, were used as received. The ligands 6,7-dihydrodipyrido-[2,3-b:3',2'-j]-1,10-phenanthroline (**2-4N**), 7,8-dihydro-6H-cyclohepta-[2,1-b:3,4-b]-di-1,8-naphthyridine (**3-4N**) and 2,2'-bi-(3-methyl)-1,8-naphthyridine (**Me-4N**) were prepared according to published procedures<sup>12</sup> and were recrystallized from ethanol before use. Solvents used for the preparations and spectroscopic studies were obtained from J.T. Baker Chemical Co. as HPLC grade. Acetonitrile anhydrous for electrochemical studies was obtained dried using  $\text{CaH}_2$  under nitrogen atmosphere at reflux for 2 h and distilled prior to use. Methylene chloride was dried

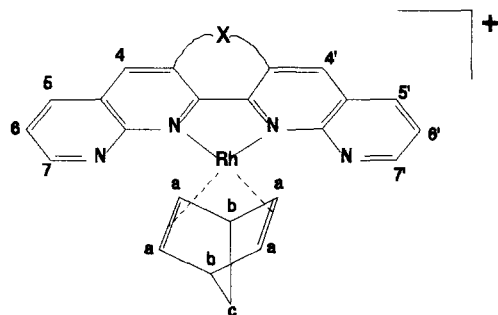


Fig. 1. Schematic perspective of the complexes. Polypyridine ligands: **2-4N** ( $\text{X} = -(\text{CH}_2)_2-$ ), **3-4N** ( $\text{X} = -(\text{CH}_2)_3-$ ) and **Me-4N** ( $\text{X} = -(\text{CH}_3)_2-$ ). Ligand numbering are shown.

under nitrogen by distillation from phosphorus pentoxide. The supporting electrolyte for the electrochemical measurements, TBAP was recrystallized from ethanol–water and rigorously dried under vacuum at 80°C for 12 h.

#### Preparation of the complexes

The dimeric starting complex,  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  was prepared by the literature methods.<sup>13</sup> To a solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (0.70 g) in ethanol (10 cm<sup>3</sup>) norbornadiene (2 cm<sup>3</sup>) was added, and the resulting solution was stirred for 3 days at ambient temperature in the dark. The yellow solid product that appeared was filtered and washed with small portions of ethanol–diethyl ether. Recrystallization from chloroform–light petroleum, gave pure  $[\text{Rh}(\text{NBD})\text{Cl}]_2$ .

#### General method of preparations of Rh complexes

To a stirred solution of  $[\text{Rh}(\text{NBD})(\text{Cl})]_2$  (50.60 mg, 0.110 mmol) in acetone a solution in the same solvent of  $\text{AgClO}_4$  (45.5 mg, 0.220 mmol) was added (**CAUTION**: perchlorate salts are potentially explosive. Although no detonation tendencies have been observed, caution is advised and handling of only small quantities is recommended). After about 30 min the solution was separated from the white precipitate of  $\text{AgCl}$  by filtration and stirred with a solution of the ligand (0.110 mmol). The solution of the formed complex was evaporated about to dryness and the complex was precipitated as a microcrystalline solid by addition of diethyl ether.

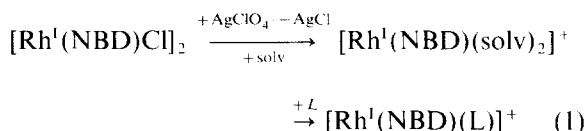
1.  $[\text{Rh}(\text{NBD})(2\text{-}4\text{N})]\text{ClO}_4$  was obtained as an orange solid in 68% yield. IR absorptions  $[\text{ClO}_4(\text{T}_d)]$ : 1090 and 615 cm<sup>-1</sup>. Molar conductivity: 141 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in methylene chloride at 25°C. Found: C, 48.8; H, 3.4; N, 8.9. Calc for  $\text{C}_{25}\text{H}_{20}\text{N}_4\text{O}_4\text{ClRh} \cdot 2\text{H}_2\text{O}$ : C, 48.8; H, 3.9; N, 9.1%.

2.  $[\text{Rh}^{\text{I}}(\text{NBD})(3\text{-}4\text{N})]\text{ClO}_4$  was obtained as an orange solid in 90% yield. IR absorptions  $[\text{ClO}_4(\text{T}_d)]$ : 1115 and 620 cm<sup>-1</sup>. Molar conductivity: 122 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in methylene chloride at 25°C. Found: C, 49.0; H, 3.8. Calc for  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{ClRh} \cdot 2\text{H}_2\text{O}$ : C, 49.7; H, 4.1%.

3.  $[\text{Rh}^{\text{I}}(\text{NBD})(\text{Me-}4\text{N})]\text{ClO}_4$  was obtained as an orange solid in 70% yield. IR absorptions  $[\text{ClO}_4(\text{T}_d)]$ : 1085 and 618 cm<sup>-1</sup>. Molar conductivity: 131 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in methylene chloride at 25°C. Found: C, 50.0; H, 3.8; N, 9.6. Calc for  $\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_4\text{ClRh} \cdot \text{H}_2\text{O}$ : C, 50.1; H, 4.0; N, 9.4%.

## RESULTS AND DISCUSSION

The reaction of the dimer  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  in coordinating solvent with  $\text{Ag}^+$ , followed by the addition of the respective polypyridine bidentate ligand derived from 1,10-phenanthroline gives cationic monometallic rhodium(I) species as stable salts, soluble in organic polar solvents and moderately soluble in water (eq. (1))



The ionic character of the rhodium complexes are manifested by conductivity measurements (all are 1:1 electrolytes). The IR spectra of the new complexes show the absorption bands due to the anion  $\text{ClO}_4^-$  ( $\text{T}_d$ ) (one strong band at about 1100 cm<sup>-1</sup> and other medium at about 610 cm<sup>-1</sup>) together with the bands due to the diolefin at 1310–1320 cm<sup>-1</sup> and those of the coordinated nitrogen donor ligands. These results indicate that the polypyridine ligands bind to rhodium in a bidentate chelating fashion and the perchlorate anion is in the outer sphere of coordination.

The electronic spectra of the rhodium complexes obtained using solvents of different polarities, contain bands in the UV region, which have intensity, shape and energy similar to those found in the spectra of the uncoordinated polypyridine ligands. These are assigned as intraligand transitions. In the low energy region (around 500 nm) the electronic spectra also show a very low intensity band which is solvent independent and can be assigned to a  $d$ – $d$  transition.

The <sup>1</sup>H NMR spectra show the proton signals of the polypyridine ligands together with those of the NBD ligand (Table 1). The values and intensities of the chemical shifts indicate that both ligands are bound to the metal atom in a 1:1 molar ratio. Coordination shifts the aromatic proton signals of the ligands, except  $\text{H}_7$  and  $\text{H}_7'$ , to low field. This is a consequence of the deshielding contributions from both polarization of the  $\sigma$  framework and resonance within the  $\pi$  framework (Table 2).<sup>14</sup> The protons  $\text{H}_7$  and  $\text{H}_7'$  undergo a shift to high field after coordination. This behaviour may be ascribed to predominance of the strong shielding effect induced by the electron current of the NBD coordinated to the same metal atom and the reduction of the effect of the noncoordinating N atom on their adjacent  $\text{H}_7$ . In the complex with the Me-4N ligand, this effect is negligible as a consequence of the torsion of the plane of the polypyridine ligands.<sup>2</sup>

These observations support our belief that the

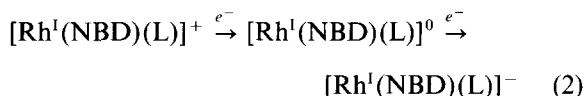
Table 1. Chemical Schiff data for the complexes of Rh(I) and the free ligands<sup>a</sup>

Comp <sup>b</sup>	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>77'</sub>	H <sub>44'</sub>	H <sub>55'</sub>	H <sub>66'</sub>	—(CH <sub>2</sub> ) <sub>n</sub> —
<b>1<sup>c</sup></b>	5.33 (d)	3.89 (d)	1.49 (s)	8.88 (s)	8.62 (s)	8.34 (d)	7.56 (d)	3.41 (s)
<b>2<sup>c</sup></b>	5.02 (s)	3.82 (s)	1.51 (s)	8.95 (s)	8.69 (s)	8.43 (d)	9.61 (dd)	2.82 (t) 2.50 (m)
<b>3<sup>d</sup></b>	3.95 (t)	3.75 (m)	1.10 (t)	9.15 (m)	8.67 (t)	8.52 (dd)	7.39 (t)	2.50 (s)
<b>2-4N<sup>d</sup></b>				9.20 (dd)	8.17 (s)	8.15 (dd)	7.50 (dd)	3.31 (s)
<b>3-4N<sup>d</sup></b>				9.13 (dd)	8.25 (s)	7.50 (dd)	7.50 (dd)	2.57 (t) 2.06 (q)
<b>Me-4N<sup>e</sup></b>				9.10 (dd)	8.20 (d)	8.15 (dd)	7.50 (dd)	2.50 (s)
<b>NBD<sup>f</sup></b>	6.7 (t)	3.55 (m)	2.00 (t)					

<sup>a</sup>In CDCl<sub>3</sub>, in ppm downfield from TMS; <sup>b</sup>**1**: [Rh(NBD)(2-4N)]<sup>+</sup>; **2**: [Rh(NBD)(3-4N)]<sup>+</sup>; **3**: [Rh(NBD)(Me-4N)]<sup>+</sup>; <sup>c</sup>300 MHz; <sup>d</sup>200 MHz; <sup>e</sup>100 MHz; <sup>f</sup>from literature<sup>20</sup>.

coordination of the polypyridine ligand is occurring through the nitrogen atoms localized in positions I and I'. On the other hand, the methylene protons of the 2-4N and 3-4N ligands show chemical shifts to low field probably due to the torsion effect of the ligand molecule produced by coordination. This effect, however, is not observed in the protons of the methyl groups of the Me-4N ligand, probably due to the greater rotational freedom of these protons. The signals of the protons H<sub>a</sub> of the 2,5-norbornadiene are shifted to high field (over 1 ppm) after coordination as a consequence of the decreasing electronic density on the olefinic bonds because of the coordination. In the less distorted complexes this effect is nearly compensated by the electronic current of the naphthyridine rings. The protons H<sub>b</sub>, close to the double bonds of the NBD, are shifted to lower field due to the coordination to the metal. H<sub>c</sub> is slightly shifted to higher fields in all the complexes.

Cyclic voltammetry experiments were carried out under rigorously anhydrous conditions due to the high reactivity of the complexes. The compounds showed two reduction waves in the range of  $-0.90$  to  $-2.40$  V *vs* Fc<sup>+</sup>/Fc.  $\Delta E_p$ , the difference in potential between anodic and cathodic peak currents varied from 70 to 140 mV. When an equimolecular amount of ferrocene was added to the acetonitrile solutions of the complexes, cyclic wave forms of the same size and shape were obtained for the ferrocene couple, verifying that these are single electron couples, which can be assigned<sup>15</sup> to the processes (eq. (2)) attributed to reduction of the metal atom:



It was not possible to obtain the oxidation potentials of the complexes in acetonitrile, however in

Table 2. Redox potentials for the complexes with the polypyridine ligands<sup>a</sup>

Complex	$E_{\text{P}_{1/2}}^{\text{red}}$ , Rh <sup>I</sup> /Rh <sup>0</sup>	$V^b$ , Rh <sup>0</sup> /Rh <sup>-1</sup>	$E_{\text{P}_{1/2}}^{\text{ox}}$ , Rh <sup>II</sup> /Rh <sup>I</sup>
<b>1.</b> [Rh(NBD)(2-4N)] <sup>+</sup>	-1.04	-1.51	+0.34
<b>2.</b> [Rh(NBD)(3-4N)] <sup>+</sup>	-1.39	-1.88	+0.36
<b>3.</b> [Rh(NBD)(Me-4N)] <sup>+</sup>	-0.58	-1.16	+0.43

<sup>a</sup> $E_{\text{P}_{1/2}} = (E_c + E_a)/2$ , in V *vs* Fc<sup>+</sup>/Fc in Pt electrode; <sup>b</sup> $E_{\text{P}_{1/2}}^{\text{red}}$  in CH<sub>3</sub>CN/0.1 mol l<sup>-1</sup> of TBAP at 100 mV s<sup>-1</sup>; <sup>c</sup> $E_{\text{P}_{1/2}}^{\text{ox}}$  in CH<sub>2</sub>Cl<sub>2</sub>/0.1 mol l<sup>-1</sup> of TBAP at 200 mV s<sup>-1</sup>.

Table 3. Catalytic activity of the complexes<sup>a</sup>

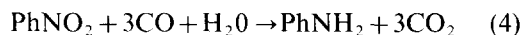
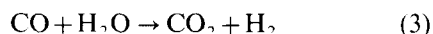
Complex	H <sub>2</sub> , h <sup>-1</sup> <sup>b</sup>	Aniline, h <sup>-1</sup> <sup>c</sup>	Azobenzene <sup>c</sup>
[Rh(NBD)(2-4N)] <sup>+</sup>	14	46	4
[Rh(NBD)(3-4N)] <sup>+</sup>	14	49	—
[Rh(NBD)(Me-4N)] <sup>+</sup>	13	41	—

<sup>a</sup>In turnover mol of product (mol of catalyst)<sup>-1</sup> h<sup>-1</sup>; <sup>b</sup>production of H<sub>2</sub> in the WGS; <sup>c</sup>in the reduction of nitrobenzene under WGS conditions.

methylene chloride and at 200 mVs<sup>-1</sup> all the complexes showed a reversible oxidation wave between +0.3 and +0.4 V vs Fc<sup>+</sup>/Fc, assignable to the couple Rh<sup>II</sup>/Rh<sup>I</sup> couple (Table 2).

The observed reduction potentials are related to the stability of the intermediate d<sup>9</sup>, owing to the high  $\pi$  acceptor capacity of the ligands (otherwise a single two electron reduction step should be observed).<sup>15,16</sup>

Under mild conditions, these complexes are active catalysts for WGS and for the reduction of nitrobenzene to aniline in the WGS conditions (eqs (3) and (4)).



The activity of these complexes in the WGS is quite high and comparable to that showed by carbonyl clusters with arylphosphines.<sup>11</sup> Conversions of over 80% of nitrobenzene to aniline were observed after only 2 h, in the presence of [Rh(NBD)(3-4N)]<sup>+</sup> and [Rh(NBD)(2-4N)]<sup>+</sup>, and values slightly lower were found when [Rh(NBD)(Me-4N)]<sup>+</sup> was used as a catalyst. The activity of these catalysts is higher than other previously reported systems with complexes of Rh, Ru or Co.<sup>17–19</sup> The selectivity of this reaction to aniline is also remarkable. These results show the prevalence of the sigma donor properties of the ligands over the steric effects. On the other hand, the higher activity shown by these complexes in the reduction of nitrobenzene than in the WGS, stress the importance of the H<sub>2</sub> elimination step in this last reaction.

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## REFERENCES

1. S. A. Moya, R. Pastene, R. Schmidt, J. Guerrero, R. Sartori, *Polyhedron* 1992, **11**, 1665.
2. S. A. Moya, J. Guerrero, R. Pastene, R. Schmidt, R. Sariego, R. Sartori, J. Sanz, I. Fonseca, M. Martinez, *Inorg. Chem.* 1994, **33**, 2341.
3. A. Togni and L. M. Venanzi, *Ang. Chem., Int. Ed. Engl.* 1994, **33**, 497.
4. R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.* 1971, **93**, 3089.
5. R. Sariego, I. Carkovic, M. Martinez and M. Valderrama, *J. Mol. Catal.* 1986, **35**, 161.
6. R. Sariego, M. Martinez, I. Carkovic, R. Contreras and S. Moya, *J. Mol. Catal.* 1988, **51**, 67.
7. R. Sariego, I. Carkovic, M. Martinez and M. Valderrama, *Trans. Met. Chem.* 1984, **9**, 106.
8. B. S. L. Neto, K. H. Ford, A. J. Pardey, R. G. Rinker and P. C. Ford, *Inorg. Chem.* 1991, **30**, 3837.
9. P. A. Chaloner, M. A. Esteruelas, F. Joó and L. A. Oro, *Homogeneous Hydrogenation*, p. 224. Kluwer Academic, Dordrecht (1993).
10. Ch. Ungermann, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Pearson, R. G. Rinker and P. C. Ford, *J. Am. Chem. Soc.* 1979, **101**, 5922.
11. S. A. Moya, R. Sariego, P. Aguirre, R. Sartori and P. Dixneuf, *Bull. Soc. Chim. Belg.* 1995, **104**, 19.
12. R. P. Thummel, F. Lefoulon, D. Cantu, R. Mahadevan, *J. Org. Chem.* 1984, **49**, 2208.
13. E. W. Abel, M. A. Bennett, G. Wilkinson, *J. Chem. Soc.* 1959, 3178.
14. G. Orellana, C. Alvarez Ibarra and J. Santoro, *Inorg. Chem.* 1988, **27**, 1025.
15. J. Hanzlik, A. Camus, G. Mestroni, G. Zassinovich, *J. Organometal. Chem.* 1981, **120**, 115.
16. E. Makrlík, J. Hanzlik, A. Camus, G. Mestroni, G. Zassinovich, *J. Organometal. Chem.* 1977, **142**, 95.
17. F. Joó and H. Alper, *Can. J. Chem.* 1985, **63**, 1157.
18. K. Januszkiewicz and H. Alper, *J. Mol. Catal.* 1983, **19**, 139.
19. M. Miura, M. Shinohara and M. Nomura, *J. Mol. Catal.* 1988, **45**, 151.
20. C. J. Pouchert and J. Behnke, *The Aldrich Library of <sup>13</sup>C and <sup>1</sup>H FT-NMR Spectra*. Aldrich Chemical Co. (1993).