RuCl$_2$(PPh$_3$)$_3$ catalyzed liquid phase hydroformylation of propene under mild pressure conditions in alcoholic media: isolation and characterization of species separated out during the reaction

Vivek K. Srivastava, Ram S. Shukla, Hari C. Bajaj[1], Raksh V. Jasra[*]

*Silicates and Catalysis Discipline, Central Salt and Marine Chemicals Research Institute, G.B. Marg,
Bhavnagar 364002, Gujarat, India*

Abstract

Dichlorotris(triphenylphosphine)ruthenium(II), RuCl$_2$(PPh$_3$)$_3$, catalyzed liquid phase hydroformylation of propene was carried out in ethanol. Mixture of two complexes, which get separated, were observed to form along with hydroformylation products under mild pressure of 9 bar at 175 °C. These two complexes were identified as dicarbonylchlorohydridobis(triphenylphosphine)ruthenium(II), HRuCl(CO)$_2$(PPh$_3$)$_2$ and dicarbonyldichlorobis(triphenylphosphine)ruthenium(II), RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ which have been isolated and characterized. The crystal structure of one of the intermediates as determined by single crystal X-ray diffraction established this as *cis* form of RuCl$_2$(CO)$_2$(PPh$_3$)$_2$. The isolated complexes were found to be inactive towards hydroformylation of propene. A possible mechanism for the formation of these intermediate species and lower conversion for hydroformylation products is discussed.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Hydroformylation; Propene; Ruthenium; Phosphine; Liquid phase

1. Introduction

Synthesis of aldehydes and other oxo compounds via catalytic hydroformylation of alkenes is one of the industrially important homogeneous reactions. Catalytic hydroformylation of alkenes for the production of approximately 6–7 metric tonnes per year of aldehydes for use in the manufacture of soaps, detergents and plastisizers [1,2] is commercially done. However, in some cases, the deviation from the desired product due to the formation of various intermediate species, par-ticularly because of complicated reaction cycle, may occur. For example, it has been reported [3] that with the Co$_2$(CO)$_8$ as a catalyst, the formation of alcohol occurs after the formation of aldehyde and in this case HCo(CO)$_3$ acts as a reducing agent. The hydroformylation reaction may also undergo Aldol reaction, acetal formation, Tishchenko reaction, isomerization, polymerization and hydrogenation of reactants [4] depending on the conditions and catalysts used.

The use of cobalt and rhodium carbonyl complexes in the homogeneous hydroformylation of alkenes has been the subjects of meticulous reviews [5–13]. However, some other metal complexes including ruthenium complexes were also reported [14,15] to be efficient hydroformylation catalysts with high linear/branched product isomer ratio [16,17].

* Corresponding author. Tel.: +91-278-2471793/2567760;
fax: +91-278-2566970/2567542.
E-mail addresses: rvjasra@csir.res.in, salt@csir.res.in (R.V. Jasra).
[1] Co-corresponding author.

The tricarbonylrutheniumphosphine complexes [17] have been found to be potential hydroformylation catalysts under slightly high temperature and pressure. We have also been exploring the possibility of such non-rhodium-based complexes, which are well known for other homogenous reactions except hydroformylation, to understand the basic intricacy of their low activity for the hydroformylation reactions. In this progression, we have investigated dichlorotris-(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$ (**1**) catalyzed hydroformylation of propene and observed low activity of this complex towards hydroformylation reaction under employed conditions.

In this paper, we are reporting the formation, isolation and characterization of dicarbonylchlorohydrido-bis(triphenylphosphine)ruthenium(II), $HRuCl(CO)_2$ $(PPh_3)_2$ (**2**) and dicarbonyldichlorobis(triphenylphosphine)ruthenium(II), $RuCl_2(CO)_2(PPh_3)_2$ (**3**) complexes formed during hydroformylation of propene at 9 bar and 175 °C. In addition to other physicochemical characterization of the isolated complexes, to understand the isomerism present in complex **3**, we have also determined the single crystal X-ray structure of one of the intermediates. The crystal structure clearly revealed the *cis* form of dicarbonyl-dichlorobis(triphenylphosphine)ruthenium(II), $RuCl_2$ $(CO)_2(PPh_3)_2$ (**3**) complex as reported by Batista et al. [18]. The lower conversion towards hydroformylation products in ethanol as a solvent with complex **1** is discussed in terms of precipitation of species **2** and **3**.

2. Experimental

2.1. Materials

Propene (99.5%) and syn-gas (99.8%) were purchased from Hydro Gas Ltd., Mumbai, India and Alchemie Gases and Chemicals Pvt. Ltd., Mumbai, India, respectively. $RuCl_2(PPh_3)_3$ was prepared by literature method [19]. Ruthenium trichloride trihydrate $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Mathew (UK). Triphenylphosphine was purchased from E. Merck. Ethanol was purchased from Baroda Chemical Industries Ltd., Baroda, India and purified by literature method [20]. Argon gas was used to maintain inert atmosphere wherever necessary.

2.2. Product analysis and characterization

The reaction products analysis were carried out using gas chromatography (GC; Shimadzu 17A) using 5% diphenyl and 95% dimethyl siloxane universal capillary column and flame ionization detector (FID). Quantification was done after considering the response factors of the reactants and products obtained using standard mixture. NMR (^{1}H, ^{31}P) and IR analysis were done on Bruker Advance DPX 200 MHz FT-NMR and Perkin-Elmer spectrum GX FT-IR systems, respectively. C, H and N analysis was performed on Perkin-Elmer CHN analyzer, 2400.

2.2.1. Single crystal X-ray analysis

Cell parameters and diffracted intensities for the compound were measured at room temperature on an Enraf-Nonius CAD-4 X-ray diffractometer using graphite monochromatized Mo Kα radiation (0.7107 Å) in the range $\theta = 2–25°$. Twenty-five reflections with θ in the range 7–10° were used for getting the accurate cell dimensions. Three standard reflections were monitored after every 100 reflections during the entire period of data collection, which showed no significant variation, indicating the stability of the crystal. The crystal orientation, refinement of the cell parameters and intensity measurements were carried out using the program CAD-4 PC [21]. The raw intensity data were corrected for Lorentz polarization effects but not for absorption. The Lorentz polarization corrections and data reduction was carried out using NRCVAX [22] program. The structure was solved by heavy atom method using the program SHELEXL97 [23]. The full matrix least-squares refinement of all non-hydrogen atoms with isotropic temperature factors was carried out till the convergence. After the complete convergence of non-hydrogen atoms anisotropically, the H-atoms were either fixed stereochemically by riding model using SHELEXL97 or located from the difference Fourier map. The final cycles of least-squares refinements, yielded the R-value $R_1 = 0.0512$ ($wR_2 = 0.1380$) for the complex.

2.3. Catalytic reaction

The hydroformylation reactions were carried out in a 300 ml, stainless-steel autoclave Parr reactor (Parr, USA). In a typical experiment, the desired quantity of

catalyst **1** dissolved in ethanol (50 cm^3) was charged in the autoclave. The autoclave was twice flushed with nitrogen prior to successively introducing syn-gas and propene at desired pressure. The reactor was then brought to desired reaction temperature and the hydroformylation reaction was initiated by stirring with magnetic stirrer. After the set reaction time, the autoclave was cooled to room temperature and pressure drops were also noted. The reaction was then quenched. It was observed that during the course of hydroformylation reaction, small amount of solid material gets separated from reaction mixture, which were collected by filtration/decantation. The reaction mixtures were subjected to GC analysis and solid material was analyzed using physicochemical techniques.

3. Results and discussion

The C, H and N analysis obtained for the separated solid mixture during hydroformylation reaction was as: C, 63.3; H, 4.3. The IR spectra (Fig. 1) of the isolated mixture showed bands at 1881, 1999 and 2061 cm^{-1}. The IR band observed at $\nu = 1881$ cm^{-1} [24,25] confirms the presence of Ru–H bond. The ν(CO) bands at 2061 and 1999 cm^{-1} indicate the presence of two carbonyls coordinated to ruthenium center in *cis* configuration. The ^{31}P NMR spectrum of the isolated solid gives two singlets at 34.81 and 72.75 ppm indicative of two non-equivalents phosphorous. If these two non-equivalents phosphorous

are present in the same complex, one should get two doublets due to the presence of two non-equivalents phosphorous with P–P coupling. As ^{31}P NMR spectra gave only two singlets, it is inferred that these two ^{31}P singlets are originating from two different complexes. The ^{1}H NMR (Fig. 2) spectra of the isolated solid mixture gave one symmetrical triplet in the high field resonance at -4.5 ppm [J (P–H) $= 19$ Hz] in CH$_2$Cl$_2$, which implies the presence of a hydride *cis* to two equivalent phosphine [26]. James and Markham [27] have reported the interaction of H$_2$ and then CO to the coordinatively unsaturated 16-electron complex **1** in dimethylacetamide (dma), and isolated a mixture of complexes **2** and **3** as depicted in Scheme 1.

The symmetrical triplet structure of the high field hydride resonance in the ^{1}H NMR spectra implies that complex **2** may have one of the following isomeric structures.
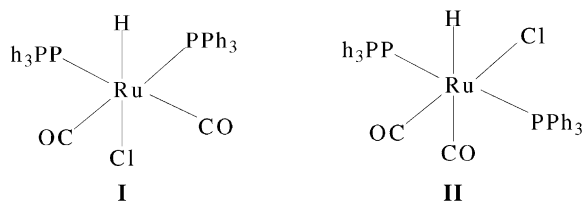
CO, a good π-acceptor ligand *trans* to hydride [28], makes isomer (II) more stable than isomer (I). In addition, the singlet obtained in ^{31}P NMR spectra at 72.75 ppm also confirms the *trans* position of phosphorous to each other {isomer (II)}.
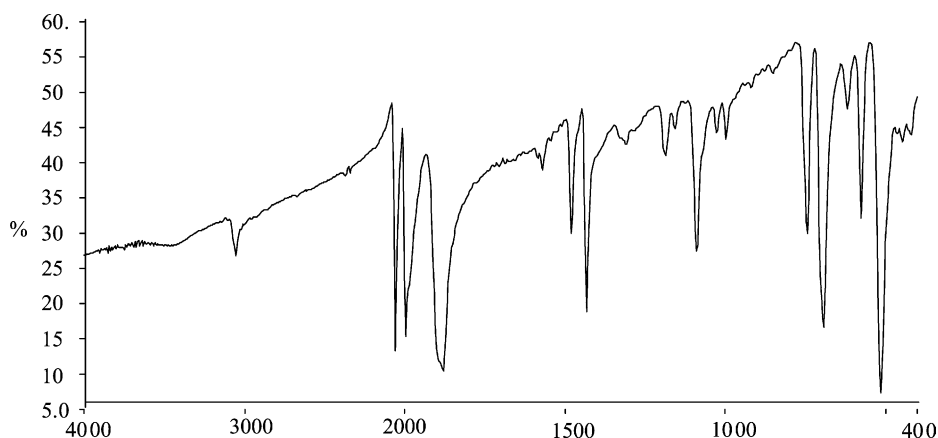

Fig. 1. The IR spectra of solid mixture obtained during hydroformylation reaction (KBr pellets).

Fig. 2. ^{1}H NMR of solid mixture obtained during hydroformylation reaction (inset: magnification of the triplets obtained at -4.5 ppm).

cis-Ruthenium dicarbonyl complex **3** may exist in three isomeric forms; (III)–(V). However, IR spectra of the isolated mixture gave ν(CO) [26] bands at 2061 and 1999 cm^{-1} and a ^{31}P NMR gave singlet at 34.81 ppm, thereby, inferring that *cis*-ruthenium dicarbonyl complex **3** may exist as isomer (III). The downfield shift of 38 ppm in ^{31}P NMR chemical shift from the hydrido–ruthenium complex may be due to change in the electronic environment in the complex **3** be-

cause of the presence of *cis* carbonyls and chlorides groups.

The first sight of crystals obtained during hydroformylation reaction emerged to be a mixture of blackish hexagonal and light yellowish needle-shaped crystals. It was found that only light yellowish needle-shaped crystals were suitable for single crystal X-ray diffraction studies. The single crystal X-ray analysis of complex **3** has already been established by Batista et al. [18]. However, a summary of crystallographic data and selected bond lengths and angles around the coordination sphere is given in Tables 1 and 2. The structure (Fig. 3) and crystal data were

Scheme 1.

Table 1
Summary of crystallographic data for complex **3**

Empirical formula	$C_{38}H_{30}Cl_2O_2P_5Ru1$
Formula weight	752.59
a (Å)	10.312 (10)
b (Å)	26.042 (4)
c (Å)	12.620 (4)
α (°)	90.00
β (°)	100.1 (5)
γ (°)	90.00
Z	4
V (Å^3)	3337 (3)
Crystal system	Monoclinic
Space group	$P2_1/n$
Radiation used, λ (Å)	0.7107
$\rho_{calcd.}$ (g cm^{-3})	1.545
Absolute coefficient, μ (cm^{-1})	7.62
Temperature (°C)	23
Final R (F_0^2)[a]	0.0512
Weighted R (F_0^2)[b]	0.1380

[a] $R = \sum ||F_0| - |F_c|| / \sum |F_0|$.
[b] $Rw = [Sw(F_0^2 - F_c^2)^2]/S[w(F_0^2)^2]^{1/2}$, $w = 1/\sigma(F_0)^2$.

Table 2
Selected bond lengths and angles for complex **3** around the coordination sphere

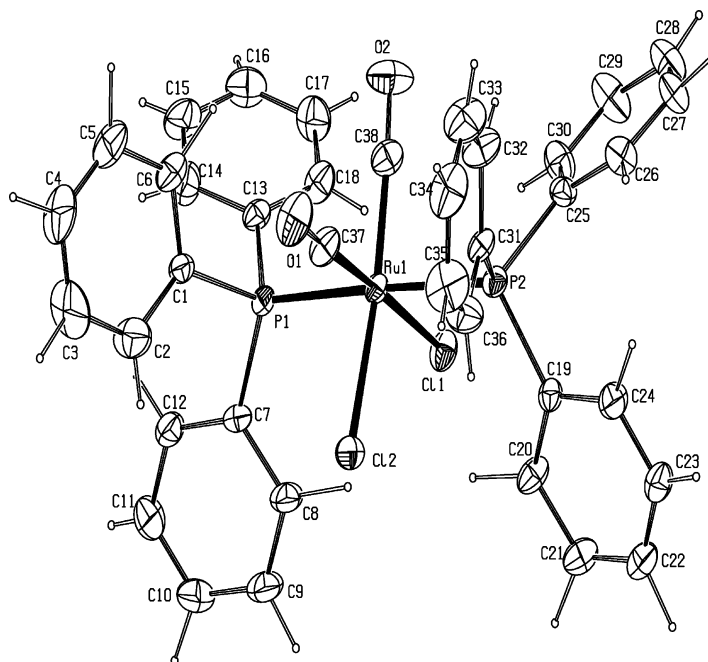| Bond lengths (Å)	
Ru1–Cl1	2.418 (3)
Ru1–Cl2	2.5050 (17)
Ru1–Pl	2.4147 (18)
Ru1–P2	2.4161 (18)
Ru1–C38	1.862 (8)
Ru1–C37	1.867 (3)
Bond angles (°)	
C38–Ru1–C37	89.9 (3)
C38–Ru1–P1	89.5 (2)
C37–Ru1–P1	93.1 (2)
C38–Ru1–P2	91.1 (2)
C37–Ru1–P2	91.1 (2)
P1–Ru1–P2	175.75 (5)
C38–Ru1–Cl1	92.9 (2)
C37–Ru1–Cl1	177.2 (2)
P1–Ru1–Cl1	87.31 (7)
P2–Ru1–Cl1	88.46 (7)
C38–Ru1–Cl2	170.7 (2)
C37–Ru1–Cl2	80.8 (2)
P1–Ru1–Cl2	90.36 (6)
P2–Ru1–Cl2	89.72 (6)
Cl1–Ru1–Cl2	96.35 (7)

Fig. 3. ORTEP diagram of complex **3** with atom numbering scheme (50% probability for the thermal ellipsoid).

exactly matching with the results obtained by Batista et al. [18].

The complexes **2** and **3** have been synthesized and studied by several workers [24–27,29], however, it is for the first time that we are reporting the separation and characterization of complexes **2** and **3** as intermediates under the hydroformylation conditions which result into lower catalytic activity of complex **1**. The formation and precipitation of intermediate complexes **2** and **3** during hydroformylation of propene by complex **1** as a catalyst may be one of the reasons for its low activity towards hydroformylation under mild pressure conditions. To establish the catalytic inactivity of the isolated complexes **2** and **3**, hydroformylation of propene catalyzed by isolated mixture was done using dichloromethane as a solvent. Although, 38% conversion to isomerized/hydrogenated products was observed, but no hydrofomylation activity was observed for these complexes as seen from the absence of C_4-aldehydes and C_4-alcohols in the product mixture (Table 3). The $RuCl_2(PPh_3)_3$ catalyzed hydroformylation of propene was also investigated in a solvent in which the complexes **2** and **3** are soluble along with complex **1**. It gave 35% conversion of propene with 9.6% selectivity for C_4-aldehydes and 7.4% selectivity for C_4-alcohols. These conversion data are similar to those obtained in the solvent where complexes **2** and **3** are insoluble and precipitate out (Table 3). This confirms that formation of complexes **2** and **3** is responsible for the low hydroformylation activity of $RuCl_2(PPh_3)_3$ catalyzed hydroformylation of propene. The possible mechanism for the formation of inactive intermediates **2** and **3**, and thereby lower activity of complex **1** for hydroformylation of propene (Table 3) is discussed below.

Table 3
$RuCl_2(PPh_3)_3$ catalyzed hydroformylation of propene[a]

Sl. No.	[Cat] (mmol)	Conversion (%)	C_4-aldehydes (%)	C_4-alcohol (%)
1	2.5	37.86	10.49	5.91
2	5.0	30.08	9.81	15.07
3	7.5	33.32	5.05	5.03
4	10.0	33.57	6.98	13.39
5	2.5[b]	34.44	9.63	7.38
6	1.0[c]	38.28	–	–

[a] Conditions: $P_{(CO/H_2)} = 6$ bar, $P_{(propene)} = 3$ bar, $T = 175\,°C$, solvent (ethanol) $= 50\,cm^3$, reaction time $= 5\,h$, $CO:H_2:propene = 1:1:1$.

[b] Conditions: $P_{(CO/H_2)} = 6$ bar, $P_{(propene)} = 3$ bar, $T = 120\,°C$, solvent (chloroform) $= 50\,cm^3$, reaction time $= 5\,h$, $CO:H_2:propene = 1:1:1$.

[c] Conditions: catalyst = isolated solid containing complexes **2** and **3**; $P_{(CO/H_2)} = 6$ bar, $P_{(propene)} = 3$ bar, $T = 175\,°C$, solvent (dichloromethane) $= 50\,cm^3$, reaction time $= 5\,h$, $CO:H_2:propene = 1:1:1$.

The complex **1** may interact with propene to give alkene complexes as have been reported [30] or it may interact with syn-gas to give the complexes **2** and **3** as reported by James and Markham [27]. These two possibilities strongly depend on the solubility of these gases in ethanol. The ethoxide–ruthenium complex from ethanol–ruthenium system as reported by Chatt et al. [24] is also one of the possibilities for the formation of ruthenium hydride complex. Although this reaction was base promoted, may be in our case, the hydroformylation conditions can promote the formation of Ru–H complex.

Thus, during the hydroformylation of propene, the complex **1** may have higher tendency to form insoluble complexes **2** and **3** [31] than complex **5**, an intermediate complex responsible for hydroformylation products (Scheme 2).
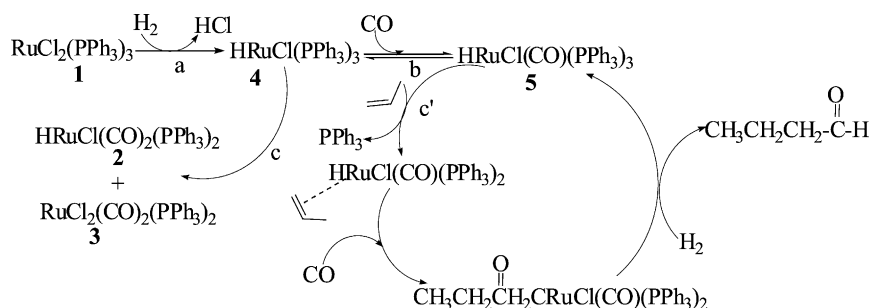
Scheme 2. The possible mechanism of formation of complexes **2** and **3** together with hydroformylation products.

Here, in the first step (a) the interaction of hydrogen with coordinatively unsaturated 16-electron complex **1** gives the hydride complex **4**. This complex **4** has tendency to form either complexes **2** and **3** through step (c) (Scheme 2) or hydroformylation products through steps (b) and (c′) via formation of complex **5**. The hydride complex **2** and *cis*-dicarbonyl complex **3** (vide supra) gets separated in alcoholic solution as a solid material during hydroformylation reaction showing preferred formation of these intermediates. Consequently, the conversion of propene to hydroformylated products is low, which can only be envisaged if the interaction of propene to complex **5** is very weak and hence lower conversions of hydroformylation products.

4. Conclusions

A mixture of intermediate complexes, dicarbonylchlorohydridobis(triphenylphosphine)ruthenium(II), $HRuCl(CO)_2(PPh_3)_2$ (**2**) and dicarbonyldichlorobis(triphenylphosphine)ruthenium(II), $RuCl_2(CO)_2(PPh_3)_2$ (**3**) formed in situ during the liquid phase hydroformylation of propene using dichlorotris(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$, complex as a catalyst, has been isolated and characterized. The single crystal X-ray structural analysis of the isolated complex **3** further confirms our preposition for the complex **3** based on the physicochemical studies. Isolated complexes **2** and **3** observed to be inactive for hydroformylation of propene are shown to be responsible for the low hydroformylation activity for the complex, $RuCl_2(PPh_3)_2$ under studied experimental reaction conditions.

Acknowledgements

References

[1] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Wiley–VCH, Weinheim, vol. 1, 2000, 29 pp.

[2] P.N.W.M. van Leeuwen, C. Claver, Rhodium Catalyzes Hydroformylation, Kluwer Academic Publishers, Dordrecht, 2000.

[3] C.L. Aldridge, H.B. Jonassen, J. Am. Chem. Soc. 85 (1963) 886.

[4] J. March, Advance Organic Chemistry, fourth ed., Wiley-Interscience, New York, 1992, 810 pp.

[5] W.A. Herrmann, B. Cornils, Angew. Chem. Int. Ed. Engl. 36 (1997) 1048.

[6] F. Joo, A. Katho, J. Mol. Catal. A: Chem. 116 (1997) 3.

[7] B. Li, X. Li, K.A. Sami, K. Fujimoto, Chem. Lett. (2002) 836.

[8] S. Rojas, P. Terreros, J.L.G. Fierro, J. Mol. Catal. A Chem. 184 (2002) 19.

[9] P. Kandanarachchi, A. Guo, Z. Petrovic, J. Mol. Catal. A: Chem. 184 (2002) 65.

[10] Y. Huang, Li.-e. Min, Y. Li, H. Chen, P. Cheng, X. Li, J. Mol. Catal. A: Chem. 185 (2002) 41.

[11] A. Aghmiz, A.M. Masdeu-Bulto, C. Claver, D. Sinou, J. Mol. Catal. A: Chem. 184 (2002) 111.

[12] L. Ropartz, R.E. Morris, D.F. Faster, D.J. Cole-Hamilton, J. Mol. Catal. A: Chem. 182–183 (2002) 99.

[13] P.N.W.M. van-Leeuwen, A.J. Sandee, J.N.H. Reek, P.C.J. Kamer, J. Mol. Catal. A: Chem. 182–183 (2002) 107.

[14] L. Alvila, T.A. Pakkanen, T.T. Pakkanen, J. Mol. Catal. 73 (1992) 325.

[15] P. Pino, F. Piacenti, H. Bianchi, R. Lazzaroni, Chim. Ind. 50 (1968) 318.

[16] H. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann, R. Pettit, J. Am. Chem. Soc. 99 (1977) 8323.

[17] R.A. Sanchez-Delgado, J.S. Bradley, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1976) 399.

[18] A.A. Batista, J. Zukerman-Schpector, O.M. Porcu, S.L. Queiroz, M.P. Araujo, Polyhedron 13 (1994) 689.

[19] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.

[20] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, second ed., Pergamon Press, Oxford, 1980, 249 pp.

[21] CAD-4 PC Software, Version 5, Enraf-Nonius, Delft, 1989.

[22] E.I. Gabe, Y. Le Page, I.P. Charland, F.L. Lee, P.S.J. White, Appl. Cryst. 22 (1989) 384.

[23] G.M. Sheldrick, SHELEXL97, Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1997.

[24] J. Chatt, B.L. Shaw, A.E. Field, J. Chem. Soc. A (1964) 3466.

[25] F. L'Eplattenier, F. Calderazzo, Inorg. Chem. 7 (1968) 1290.

[26] B.R. James, L.D. Markham, B.C. Hui, G.L. Rampel, J. Chem. Soc., Dalton Trans. (1973) 2247.

[27] B.R. James, L.D. Markham, Inorg. Nucl. Chem. Lett. 7 (1971) 373.

[28] H.D.F. Kaesz, R.B. Saillant, Chem. Rev. 72 (1972) 231.

[29] K.R. Grundy, Inorg. Chim. Acta 53 (1981) L225.

[30] D.J. Cole-Hamilton, G. Wilkinson, J. Chem. Soc., Chem. Commun. (1977) 57.

[31] D. Evans, J.A. Osborn, F.H. Jardine, G. Wilkinson, Nature 5016 (1965) 1203.