

# Synthesis, Characterisation of Cycloocta-1,5-Diene Ruthenium(II) Nitrile Complexes and their Activity as Hydroformylation Catalysts

Haleden Chiririwa, and CT Parekh

**Abstract**—The synthesis and characterization of a range of cycloocta-1,5-diene complexes of ruthenium(II) containing organonitrile ligands is described. The complexes were characterized by elemental analysis, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Single-crystal X-ray diffraction analysis for complex **5** revealed that the ruthenium(II) COD dimer contains triply-bridging chloride ligands and both ruthenium atoms possess octahedral coordination geometries. Furthermore, the ruthenium complexes 1-4 were tested as potential catalysts in the hydroformylation reaction of 1-octene.

**Keywords**—Cycloocta-1,5-diene, hydroformylation, nitrile, X-ray crystal structure

## I. INTRODUCTION

**H**YDROFORMYLATION of alkenes is a versatile reaction for the direct insertion of CO to the olefinic double bond of alkenes for the production of commercially important  $\text{C}_{n+1}$  aldehydes and alcohols useful in the manufacture of paint and other pharmaceutical products [1]-[3]. Modern research in hydroformylation reactions is based mainly on cobalt and rhodium complexes modified by phosphorous based ligands [4]-[8]. However, a number of metal complexes other than those of Co and Rh have been used in the hydroformylation reaction. The generally accepted order of activity for unmodified monometallic catalysts is:  $\text{Rh} > \text{Co} > \text{Ru/Ir} > \text{Os} > \text{Pt} > \text{Pd} > \text{Fe} > \text{Ni}$  [9]. Ruthenium is attracting researchers' attention after rhodium and cobalt. Ru and Pt catalysts have been studied and reported as active catalysts for hydroformylation [10]-[11]. Specifically, platinum(II) catalysts containing bidentate diphosphine ligands have demonstrated good activities and selectivities toward the linear aldehyde [12]-[13]. The steric effect of the ligand generally decides the approach of alkenes towards the metal centre [14], while the electron density of the metal centre is determined by electronic effect [15].

There are reports that metal complexes with bulky ligands

H. Chiririwa was with Department of Chemistry, University of Johannesburg, P.O. Box 524, Auckland Park, Johannesburg 2006 South Africa. He is now with the Department of Chemistry, National University of Science & Technology, P.O Box AC939 Ascot Bulawayo, Zimbabwe (phone: +263-9- 2828442 ext 2445; fax: +263-9-286803; e-mail: harychiririwa@yahoo.com).

C. T. Parekh is with the Department of Chemistry, National University of Science & Technology, P.O Box AC939 Ascot Bulawayo, Zimbabwe. (e-mail: ctparekh@nust.ac.zw).

are found to be the most active catalysts for the hydroformylation reaction [16]. The bite angle has been reported to have a decisive effect on activity, stability and selectivity achieved by catalysts in hydroformylation reactions [17]-[18]. Herein, we report the synthesis and characterization of new ruthenium(II) complexes containing organonitrile ligands as well as the catalytic activity of the complexes in the hydroformylation of 1-octene.

## II. EXPERIMENTAL

All manipulations were performed in air on a water bath. Acetonitrile, propionitrile, acrylonitrile and isobutyronitrile were purchased from Sigma-Aldrich and used as received. The polymeric material  $[\{\text{RuCl}_2(\text{COD})\}_x]$  was prepared from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  by the published procedure [19]. Melting points were determined on a Stuart Melting point Apparatus SMP10, and are uncorrected. Infrared spectra (KBr pellets) were recorded on a Bruker Tensor FT-IR instrument and all data are given in wavenumbers ( $\text{cm}^{-1}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  at room temperature on a Bruker-400 spectrometer operating at 400.13 and 100.6 MHz. Microanalyses were determined using a Fisons EA 1108 CHNO-S instrument. X-ray intensity data were collected on an APEX2 (Bruker, 2010) diffractometer with 1.5 kW graphite monochromated Mo-K $\alpha$  radiation.

### A. General procedure for the synthesis of complexes 1-5

A suspension of  $[\{\text{RuCl}_2(\text{COD})\}_x]$  (0.5 g) in the appropriate organonitrile (25 ml) was heated under reflux for 12 h. The bright orange solution was filtered hot and concentrated on a steam bath to *ca* half the original volume and cooled to  $-5^\circ\text{C}$ . The resultant precipitate was collected by filtration and washed with the chilled respective organonitrile (5 ml) and diethyl ether (2 X 5 ml) affording orange crystals in yields ranging from 50 – 70 %. Complex **5** was prepared by heating complex **1** in acetone (10 ml) for 30 min. The orange solution was filtered hot and concentrated on a steam bath to *ca* half volume and cooled to  $0^\circ\text{C}$  overnight affording orange crystals

### B. Preparation of 1

$[\text{RuCl}_2(\text{C}_8\text{H}_{12})(\text{C}_2\text{H}_3\text{N})_2] \cdot \text{C}_2\text{H}_3\text{N}$  Orange crystals. Yield: 68%. M.p.: decomposes above  $170^\circ\text{C}$ . Anal.: found, C 41.9, H 5.4, N 10.6 %. Calc. for  $\text{C}_{14}\text{H}_{21}\text{Cl}_2\text{N}_3\text{Ru}$ , C 41.7, H 5.3, N 10.4 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$  (ppm): 4.27 (4H, br m, CH),

2.62 (6H, s, Me), 2.43 (4H, br m, CH<sub>2</sub>), 2.01 (4H, br m, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 125.8, 90.6, 84.8, 84.6, 30.0, 29.8, 29.7. IR (cm<sup>-1</sup>): 2969(m), 2919(m), 2359(m), 2331(m), 2250(m), 1864(w), 1419(m), 1339(m), 1035(m), 948(m), 839(s), 781(s).

#### C. Preparation of 2

[RuCl<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>3</sub>H<sub>5</sub>N)<sub>2</sub>] Orange crystals. Yield: 65%. M.p.: 140-142 °C. Anal.: found, C 42.3, H 5.9, N 7.4 %. Calc. for C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>Ru, C 43.1, H 5.7, N 7.2 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> (ppm): 4.27 (4H, br m, CH), 2.50 (4H, br m, CH<sub>2</sub>), 2.43 (4H, br m, CH<sub>2</sub>), 2.01 (4H, br m, CH<sub>2</sub>), 1.34 (t, 6H, CH<sub>3</sub>), <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 129.6, 89.9, 29.4, 13.68, 10.2. IR (cm<sup>-1</sup>): 2914(s), 2264(s), 1452(s), 1425(m), 1376(m), 1318(m), 1069(s), 1009(m), 842(s), 788(s).

#### D. Preparation of 3

[RuCl<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>3</sub>H<sub>5</sub>N)<sub>2</sub>] Orange crystals. Yield: 50%. M.p.: 160-162 °C. Anal.: found, C 43.6, H 4.9, N 7.5 %. Calc. for C<sub>14</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>Ru, C 43.5, H 4.7, N 7.3 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> (ppm): 6.56 (2H, br m, CH), 6.31 (2H, br m, CH), 6.16 (2H, br m, CH), 4.27 (4H, br m, CH), 2.43 (4H, br m, CH<sub>2</sub>), 2.01 (4H, br m, CH<sub>2</sub>), <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 140.5, 125.8, 107.7, 91.0, 29.5. IR (cm<sup>-1</sup>): 2951(w), 2361(m), 2341(sh), 2234(s), 1408(m), 1334(m), 968(s), 831(m), 679(m).

#### E. Preparation of 4

[RuCl<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>4</sub>H<sub>7</sub>N)<sub>2</sub>] Yellow crystalline powder. Yield: 70%. M.p.: decomposes above 190 °C. Anal.: found, C 45.7, H 6.4, N 6.9 %. Calc. for C<sub>16</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>Ru, C 45.9, H 6.3, N 6.7 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> (ppm): 4.27 (4H, br m, CH), 2.62 (6H, s, Me), 2.43 (4H, br m, CH<sub>2</sub>), 2.01 (4H, br m, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 128.7, 119.3, 45.1, 28.1, 19.8. IR (cm<sup>-1</sup>): 2159(w), 1966(w), 1579(w), 1476(s), 1427(s), 1390(w), 741(s), 710(s).

#### F. Preparation of 5

[Ru<sub>2</sub>Cl<sub>4</sub>(C<sub>8</sub>H<sub>12</sub>)CH<sub>3</sub>CN] Orange crystals. Yield: 65% M.p.: decomposes above 190 °C. Anal.: found, C 35.7, H 4.4, N 2.5 %. Calc. for C<sub>18</sub>H<sub>27</sub>Cl<sub>4</sub>NRu<sub>2</sub>, C 35.9, H 4.5, N 2.3 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> (ppm): 4.66 (2H, m, CH), 4.51 (2H, m, CH), 4.43 (2H, m, CH), 4.24 (2H, m, CH), 2.66 (3H, s, Me), 2.58 (2H, m, CH<sub>2</sub>), 2.53 (2H, m, CH<sub>2</sub>), 2.44 (2H, m, CH<sub>2</sub>), 2.29 (2H, m, CH<sub>2</sub>), 1.98 (4H, br m, CH<sub>2</sub>), 1.90 (2H, m, CH<sub>2</sub>), 1.81 (2H, m, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 123.5, 122.0, 90.5, 89.9, 84.6, 84.4, 30.0, 29.7, 29.6, 29.4. IR (cm<sup>-1</sup>): 2960(m), 2469(m), 2451(m), 2280(w), 1794(w), 1519(m), 1439(m), 1235(m), 930(m), 750(s).

#### G. General procedure for 1-octene hydroformylation reactions

In a typical experiment, the ruthenium complex (0.029 mmol) were added to a solution of dry decane (11 mL) and 1-octene (8.9 mL, 0.06 mmol) in a stainless steel autoclave reactor. The reactor was initially pressurized to 60-bar total pressure (CO:H<sub>2</sub> = 1:1) heated at 120 °C for 10 min with stirring. The total pressure was then increased to 80 bar, and syngas was supplied on demand to maintain the reaction pressure at 80 bar throughout the reaction period. After the

desired reaction time was reached, the syngas supply was shut down and the reactor was allowed to cool to room temperature. The excess pressure was then vented from the cooled reactor, and a sample of the resulting solution was taken for GC analysis. The yield of aldehyde was calculated by using the mass of the decane solvent as an internal reference.

#### H. X-ray crystal structure determination

Crystals suitable for single crystal X-ray diffraction for complex **5** were obtained by slow evaporation of a concentrated solution of the complex at room temperature. All X-ray intensity data were collected on a Bruker APEX-II 4K-CCD diffractometer with 1.5 kW graphite monochromated Mo-Kα radiation.

The structure was solved by direct methods using SHELXS-97 and refined employing full-matrix least-squares with the program SHELXL-97 refining on F<sup>2</sup>. Packing diagrams were produced using the program PovRay and graphic interface X-seed [20]. Crystallographic data for the structure determinations are listed in Table I.

TABLE I  
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS FOR  
COMPLEX 5

Complex	5
Empirical formular	C <sub>18</sub> H <sub>27</sub> Cl <sub>4</sub> N Ru <sub>2</sub>
Formular weight	601.35
T/K	100(2)
λ/Å	0.71073
Crystal system	monoclinic
Space group	C2/c
a	21.119(4)
b	7.1230(14)
c	26.723(5)
α(deg)	90
β(deg)	93.262(5)
γ(deg)	90
V(Å <sup>3</sup> )	4013.5(13)
Z	8
Density <sub>calc</sub> (mg/ml)	1.99
Absorption coefficient (mm <sup>-1</sup> )	2.04
F(000)	2384
Crystal size (mm)	0.145x0.038x0.031
θ range for data collection (deg)	1.53– 27.55

Limiting indices	-26<=h<=27,-9<=k<=6,-34<=l<=34
Reflections Collected/ Unique	13998/ 4621[R(int) = 0.0826]
Completeness of theta max. and min. transmission	27.55 (99.6%)
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / Restraints/ Parameters	4621 / 0 / 227
Goodness-of-fit on F <sup>2</sup>	0.971

### III. RESULTS AND DISCUSSION

The 1,5-cyclooctadiene ruthenium(II) polymer has been prepared in very good yields (85 to 95 %) from ruthenium halides and 1,5-cyclooctadiene in boiling ethanol. This polymer is a very useful starting material for the preparation of a series of ruthenium complexes with bulky phosphine ligands. All the compounds can be handled in air although solutions are oxidized slowly. The polymer  $[\{\text{RuCl}_2(\text{COD})\}_x]$  dissolves slowly over several hours in the respective organonitriles to give dark orange solutions after filtration and products crystallize readily on cooling the solutions at  $-5^\circ\text{C}$ . The major species in the solution are the neutral complexes, and the formation of byproducts can be suppressed by adding an excess of cycloocta-1,5-diene to the reaction mixture. All the complexes are soluble in dichloromethane, acetonitrile, alcohols and less soluble in ethers and alkanes. Complex **1** is soluble in water and may therefore have an extensive aqueous chemistry. This compound was initially reported by Johnson *et al.*, [21] and previously reported by Singleton *et al.* [22] as to contain one water molecule of crystallization. Under the experimental conditions that we used we obtained the compound with an acetonitrile solvent molecule and we elucidated the structure [23]. This does however not seem to have an effect on the stereochemistry of the product. Compounds **2**, **3** and **4** could also be readily prepared from the reaction of  $[\text{RuCl}_2(\text{C}_8\text{H}_{12})(\text{C}_2\text{H}_3\text{N})_2]$  with the propionitrile, acrylonitrile [24]-[25] and isobutyronitrile. In these reactions the acetonitrile ligand is effectively being replaced and this could be attributed to the fact that the acetonitrile is a good leaving group and this has been observed when **1** reacts with diimine and diamine chelate ligands [26].

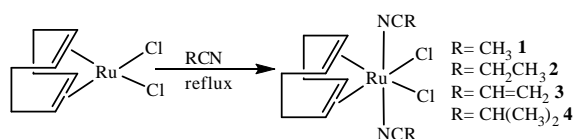


Fig. 1 Synthesis of the ruthenium nitrile complexes

Complexes **1-4** exhibit a variety of reactivity patterns which demonstrate their usefulness as precursors to a range of ruthenium(II) complexes. They possess labile halide and organonitrile ligands, which allow both cationic and neutral

substituted derivatives to be obtained. Under extreme conditions the COD ligand can actually get displaced. Dimeric complexes with triple halide bridges are obtained by heating acetone solutions of the neutral complex  $[\text{RuCl}_2(\text{C}_8\text{H}_{12})(\text{C}_2\text{H}_3\text{N})_2]$  as shown in Fig. 2. The ease with which these compounds are formed is a consequence of the lability of the nitrile ligands.

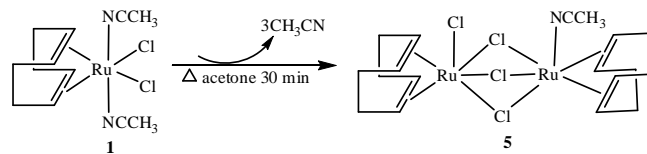


Fig. 2 Spontaneous dimerization of  $[\text{RuCl}_2(\text{cod})(\text{NCR})_2]$

The IR spectra of the complexes all contain  $\nu(\text{CN})$  absorption bands which are observed to be at higher frequency than is observed for the free nitrile ligands. This behavior is consistent with coordination via the nitrogen atom only, as has been found with a majority of nitrile complexes [27]-[29].

The most interesting feature of the NMR spectra of the complexes is the use of the chemical shift value of the respective organonitrile proton resonances to assign the stereochemistry of the complexes **1-4**. In complex **1** resonances observed at 2.45 and 2.70 are assigned to the mutually *trans* acetonitrile ligands and the resonance at 1.95 is assigned to the free acetonitrile protons in the complex, strongly suggesting *trans* acetonitrile ligands. In all the four complexes the cod alkene protons were observed to resonate at two positions, and the cod methylene protons were observed at 4.27 ppm. For complex **2** the methyl protons are observed as a triplet at 1.31 ppm whilst the methylene protons resonate as a multiplet at 2.45 ppm. Complex **3** exhibits 3 distinct peaks at 6.56, 6.31 and 6.16 ppm and these represent the ethylene protons. Complex **4** has the expected absorption at 1.08 which represents the methyl protons and a peak at 1.85 ppm for the aliphatic protons.

#### A. Structural description of complex 5

The selected bond lengths and angles for complexes **5** are summarized in Table II, and the molecular structure is shown in Fig. 1.

TABLE II  
SELECTED BOND DISTANCES AND ANGLES FOR COMPLEX 5

Bond Distances (Å)		Bond Angles(°)	
N1 Ru1	2.029(5)	N1- C1- C2	176.5(7)
Cl1 Ru1	2.4428(15)	Cl3- Ru2- Cl2	78.82(5)
Cl1 Ru2	2.4965(16)	Cl3- Ru2- Cl1	77.84(5)
Cl2 Ru1	2.4290(15)	Cl4- Ru2- Cl1	87.45(6)
Cl2 Ru2	2.4515(15)	Ru1- Cl1- Ru2	81.82(5)
Cl3 Ru1	2.4038(14)	Ru1- Cl3- Ru2	83.87(4)
Cl3 Ru2	2.4363(15)		
Cl4 Ru2	2.4080(16)		

The ruthenium complex **5** is a Ru(II) dimer and contains bridging chloride ligands. The Ru atoms each contain axial COD ligands and both ruthenium atoms exhibit octahedral geometries and the structure can be described as being composed of a pair of face-sharing octahedra. One Ru metal atom contains a coordinated acetonitrile which is slightly bent and the other a chloride ligand. Bonds to the COD ligands by the metal atoms range from 2.179(6) to 2.213(6) Å and similar to those observed in Ru(II) complexes containing similar ligands [27]-[29].

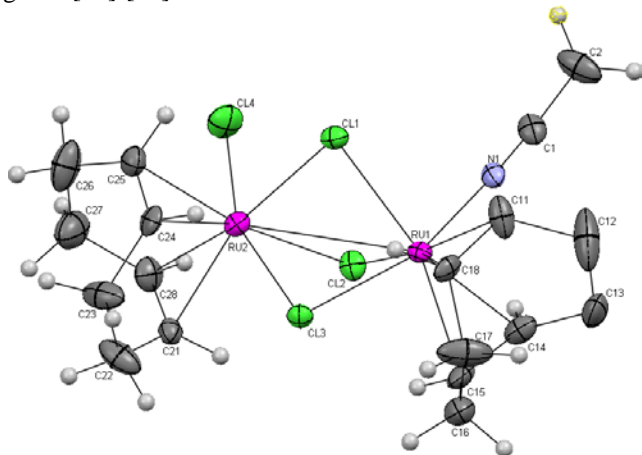


Fig. 1 The molecular structure of complex 5 showing the atomic numbering. All non-hydrogen atoms were presented with ellipsoidal model with probability level 50%. All hydrogen atoms are omitted for clarity.

#### B. Hydroformylation of 1-octene

The ruthenium complexes (**1-4**) were evaluated as catalyst precursors for the hydroformylation of 1-octene. In the present work, the complexes gave active ruthenium catalysts, although demonstrating low activity in the hydroformylation of 1-octene (Table 3). All the experiments were performed in triplicate, and the mean values were taken as the final results.

TABLE III  
HYDROFORMYLATION OF 1-OCTENE USING COMPLEXES 1- 4

Complex	Time (h)	Conv <sup>a</sup> (%)	Hyd <sup>b</sup> (%)	Yield <sup>c</sup> (%)	n:i <sup>d</sup>	TOF <sup>e</sup> (h <sup>-1</sup> )
(1)	6	15	18	22	6	35
(2)	6	18	20	24	6	35
(3)	6	25	35	26	3	25
(4)	6	20	25	24	6	30

Reaction conditions: 80-bar syngas (CO:H<sub>2</sub> = 1:1), 120 °C

<sup>a</sup> % Conversion = 100 - (n(1 - octene)<sub>out</sub>/n(1 - octene)<sub>in</sub>) x 100

<sup>b</sup> % Hydrogenation = n(octane)/n(1 - octene converted) x 100

<sup>c</sup> % Yield Nonanal = n(nonanal)/n(1 - octene converted) x 100

<sup>d</sup> n:i = normal:iso ratio representing the linear-to-branched selectivity

<sup>e</sup> TOF = n(1 - octene converted)/{n(Ru) 6 h}

Complexes **1-4** represent ruthenium complexes containing an organonitrile ligand. These ligands are no doubt not the best ligands in ruthenium-catalyzed hydroformylation. However, they are still worth investigating for posterity. The complexes are air-stable solids and thermally stable, which did not melt nor decompose below 140 °C, due to strong coordination to the metal center provided by the nitrogen atoms.

The complexes **1-4** exhibited low activities in 1-octene hydroformylation when subjected to 80 bar syngas at 120 °C for periods of 6 h. Increasing the length of reaction time did not greatly increase the conversion. This suggests that the complexes were retarding the catalytic reaction, and either a structural or electronic effect was causing the low activity rather than an induction period required for the catalysis to commence. The hydrogenation observed for complexes **1** and **2** (18 and 20 %) was less than that observed for complexes **3** and **4**, It was higher for complex **3** (35%). The presence of a double bond in complex **3** appears to increase the hydrogenating ability of the complex. The yield of nonanal with the complexes where all not too impressive ranging from 32-36 %. The n:i ratios revealed that a large proportion of the products formed were linear aldehydes.

#### IV. CONCLUSION

The complexes exhibit low catalytic activity in the hydroformylation of 1-octene. Given the usefulness of the labile-ligand nitrile ruthenium 1,5-COD complexes [**1-4**], the present complexes promise to find applications not only in our own work, but also the work of others.

#### A. Supplementary materials

CCDC 924232 contains the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

#### ACKNOWLEDGEMENTS

The author gratefully acknowledges the University of Johannesburg for funding this project and the South African National Research Foundation for award of a Post Doctoral Fellowship. Opinions, findings, conclusions or recommendations expressed in this manuscript are those of the author and do not necessarily reflect the views of the NRF. The author is also grateful to Professor R. Meijboom (University of Johannesburg) for the freedom to pursue his own research within the MetaCatalysis group.

#### REFERENCES

- [1] Dabbawala AA, Parmar DU, Bajaj HC, Jasra RV (2011) Indian Journal of Chemistry, Vol 50A: 27-32.
- [2] Jessop, P.G.; Leitner, W., Eds. Chemical Synthesis Using Supercritical Fluids (1999) Wiley-VCH:Weinheim
- [3] Leitner, W. Supercritical Carbon Dioxide as a Green Reaction Medium for Catalysis (2002) Acc Chem Res 35: 746-756.
- [4] Cornils B (1980) New Syntheses with Carbon Monoxide, edited by J Falbe, Springer, Berlin:1
- [5] Frohning CD, Kohlpaintne CW (1996) Applied Homogenous Catalysis with Organometallic Compounds: A Comprehensive handbook, edited by B Bornils & WA Herrmann (VCH, Weinheim) Vol 1: 27
- [6] Cornils B, Herrmann WA (2000) Applied Homogenous Catalysis with Organometallic Compounds (Wiley-VCH, Weinheim): 29
- [7] Dabbawala AA, Parmar DU, Bajaj HC, Jasra RV (2008) J Mol Catal A Chem 282: 99
- [8] Dabbawala AA, Parmar DU, Bajaj HC, Monflier E (2009) Catal Commun 10: 1808

- [9] Pruchnik FP (1990) *Organometallic Chemistry of Transition Metals*, Plenum Press, New York: 691
- [10] Suss-fink G, Schmidt GF (1987) *J Mol Catal* 42: 361
- [11] Ancilotti F, Lamiaand M, Marchionna M (1990) *J Mol Catal* 63: 15
- [12] van Duren R, van der Vlugt J, Kooijman H, Spek AL, Vogt D (2007) *Dalton Trans* 1053.
- [13] van der Veen LA, Keeven PK, Kamer PCJ, van Leeuwen PWNM (2000) *Chem Commun*333.
- [14] Rooy AV, Bruijn JNH, Roobeek KF, Kamer PCJ, Van Leeuwen PWNM (1991) *J Chem Soc Chem Commun* 16: 1096.
- [15] Magee MP, Luo W, Hersh WH (2002) *Organometallics* 21: 362
- [16] Rooy AV, Orij EN, Kamer PCJ, Van Leeuwen PWNM (1995) *Organometallics* 14: 34
- [17] Casey CP, Whiteker GT (1990) *Isr J Chem* 30:299
- [18] Kranenburg M, van der Burgt YEM, Kamer PCJ, van Leeuwen PWNM, Vogt D, Keim W (1995) *J Chem Soc Chem Commun* 2177
- [19] Albers MO, Singleton E, Yates JE (1989) *Inorg Synth* 26: 2
- [20] Barbour LJ (2001) X-Seed: a software tool for supramolecular crystallography. *J Supromol Chem* 1:189
- [21] Schrock RR, Johnson BFG, Lewis J (1974) *J Chem Soc Dalton* 951
- [22] 22. Ashworth TV, Liles DC, Robinson DJ, Singleton E, Coville NJ, Darling E, Markwell AJ (1987) *S. Afr. J. Chem* 40: 3
- [23] Chiririwa H, Meijboom R, Owulude SO, Eke UB, Arderne C, (2011) *Acta Cryst E*67:m1096
- [24] Chiririwa H, Meijboom R (2011) *Acta Cryst E*67:m1336
- [25] Chiririwa H, Meijboom R (2011) *Acta Cryst E*67:m1335
- [26] Kasper C, Alborzinia H, Can S, Kitanovic I, Meyer A, Geldmacher Y, Oleszak M, Ott I, Wolf S , Sheldrick WS, *Journal of Inorganic Biochemistry* 106 (2012) 126-133  
<http://dx.doi.org/10.1016/j.jinorgbio.2011.08.027>
- [27] Ashworth TV, Nolte MJ, Reinmann RH, Singleton E (1977) *J Chem Soc Chem Commun* 757
- [28] Ashworth TV, Nolte MJ, Reinmann RH, Singleton E (1978) *J Chem Soc Dalton Trans* 1043.
- [29] Ashworth TV, Liles DC, Singleton E (1984) *J Chem Soc Chem Commun* 1317.