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Synthesis and Structural Characterization of some Ruthenium(II) Alkoxide Complexes

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Abstract

The complex $[RuCl_2(COD)(OR)_2]$ (COD = cyclo-octa-1,5-diene and R = CH_3 or C_2H_5) has been prepared by treatment of the polymeric specie $[\{RuCl_2(COD)\}_x])$ with appropriate LiOR solution and has been characterized by elemental analysis, IR and ^1H NMR spectroscopic analyses. The reaction of the alkoxide complex with two or more equivalent of phosphine ligands gave the complex $[Ru(COD)(OR)_2L_2]$ (R = CH_3 or C_2H_5; L = o-methoxyphenyldiphenylphosphine and tri(m-tolyl)phosphine) while the subsequent reaction with diphenylphosphine yielded $[Ru(OR)_2(Ph_2P)_4]$ (R = C_2H_5). Spectroscopic and elemental analysis data revealed symmetric alkoxide-bridged diruthenium phosphine complexes.

Key words: Ruthenium, alkoxide, cycloocta-1,5-diene, phosphine ligands

1.   Introduction

Transition metal alkoxides were first reported by Ugo and co-workers in the synthesis of trans - R'OM(PR$_3$)$_2$L (M = Rh, Ir; L = CO, PR,; R' = H, alkyl, aryl) derivatives. They combined sodium alkoxides and trans-C1Rh(PR$_3$)(CO) in water to generate the hydroxide, (HO)Rh(PR$_3$)$_2$(CO) (Ugo et al., 1969). Roper et al also prepared later the iridium analogue by adding NaOH to trans-[(CH$_3$CN)Ir(PPh$_3$)$_2$(CO)]C1O$_4$ (Read and Ropa, 1973). Since then many other metal alkoxides have been reported (Yoshida et al., 1981; Bryndza and Tam, 1988; Lai et al., 2003; Hashimoto et al, 2007). These metal alkoxide complexes have reactivity similar to that previously established for metal-carbon and metal-hydrogen bonds. The presence of lone pairs of electron on these substituents

gives them additional capabilities in terms of interacting with small molecules and weak acids. These

interactions can result in lowering activation barriers for bimolecular reactions (Bryndza and Tam,

1988).

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Metal-oxygen and metal-nitrogen bonds can form easily yet they are reactive enough to demonstrate interesting reactivity. In binding to late transition-metal centers oxygen and nitrogen ligands are not hard relative to carbon and hydrogen; however, because of increased electron affinity of the heteroatoms involved, these bonds can easily undergo heterolysis more than metal-hydrogen or metal-carbon linkages (Blum and Milstein, 1995). This increased ability to heterolyze gives these compounds another mode of reactivity not normally open to the alkyls and hydrides. While the roles of these metal-alkoxides in many catalytic transformations have not been fully explored, they could be designed as catalysts (or precursors) to carry out reactions that would be difficult to effect by other methods (Malcolm *et al*, 2000). In view of the richness and importance of the metal-alkoxide complexes in structural studies and catalysis (Baratta *et al*, 2008), we therefore attempted the preparation of a number of ruthenium alkoxide complexes starting from the polymer [{RuCl$_2$(COD)}$_x$]. Utility of the synthesized ruthenium alkoxide complexes in the preparation of stable ruthenium(II) phosphine compounds are discussed.

2.   Experimental

*General procedures***:** The starting material [{RuCl$_2$(COD)}$_x$] **1** was prepared as described previously (Albers *et al*, 2007). Argon-saturated ethanol and methanol, which had been dried and distilled over magnesium ethoxide and methoxide respectively, were used as solvents. *o*-methoxyphenyldiphenylphosphine, diphenylphosphine and tri(*m*-tolyl)phosphine were purchased from Aldrich. The reactions involving the phosphines were carried out under a purified nitrogen atmosphere using standard Schlenk techniques. Melting points were obtained on a Kofler hot stage apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrophotometer. The NMR spectra were recorded on a Bruker Avance 300 MHz instrument. NMR spectra were referenced internally to residual solvent resonances (^{1}H) or

externally to 85% H_3PO_4 (^{31}P). Elemental analyses were determined at the Center for Nanotechnology, Department of Chemistry, Rhodes University, South Africa

Synthesis of (ethoxy)(cycloocta-1,5-diene)ruthenium(II) dimer [Ru(COD)(OC$_2$H$_5$)]$_2$ **(2):** Lithium metal (0.10 g, 14.3 mmol) was cut into pieces and added to a freshly distilled ethanol (20 cm^3) to produce $LiOC_2H_5$. The polymer, [$RuCl_2(COD)$] (0.2 g, 0.71 mmol) was added to the above solution and well shaken, a dark brown suspension was obtained. The brown suspension was refluxed for 10 min under nitrogen at 80 ^{o}C. The polymer dissolved completely to give a light brown clear solution. The solution was cooled down to -5 ^{o}C for several hours and no precipitate was formed. The solvent was then removed under reduced pressure; brown crystalline solids were obtained. The brown solid was dissolved in CH_2Cl_2 and filtered to remove the LiCl. The filtrate was cooled to 0 ^{o}C, after 12 h a yellow precipitate was obtained. The precipitate was collected through filtration and then dried in vacuo to obtain a yellow powder. Yield: 0.142 g, (40%) Anal. Calcd for $C_{20}H_{34}O_2Ru_2$: C, 47.24; H, 6.69. Found: C, 47.43; H, 6.71. m.p. Decomp. > 240 ^{o}C; IR (cm^{-1}): Sym CH_2: 1450-1354, Ru-O-C vib: 1100-881, bridging C-O: 1032; ^{1}H-NMR (ppm): 1.24, 3.74 (protons of OC_2H_5); 1.63, 5.58, 2.37(m) COD protons; Calcd)

Synthesis of bis(methoxy)(cycloocta-1,5-diene)ruthenium(II) [Ru(COD)(OCH$_3$)$_2$] **(3):** Lithium metal (0.55 g, 0.08 mol) was cut into pieces and added to a freshly distilled methanol (20 cm^3) to produce $LiOC_2H_5$. The excess methanol was removed under a reduced pressure to obtain white crystalline solids. $LiOC_2H_5$ (0.152 g, 4 mmol) was dissolved in dry methanol (15 cm^3) and the polymer, [{$RuCl_2(COD)$}$_x$] (0.56 g, 2 mmol) was added, the suspension was well shaken and then refluxed for 10 min under nitrogen at 70 ^{o}C. The polymer dissolved completely to give a clear light brown solution. The brown solution was kept at 0 ^{o}C for 12 hours, a yellow precipitate was formed. The precipitate obtained was collected through filtration and `then dried in the

vacuum. Yield: 0.21 g (39%) Anal. Calcd for $C_{10}H_{18}O_2Ru$: C, 44.28; H, 6.64. Found: C, 44.39; H, 6.81. m.p. Decomp. > 185 °C; IR(cm^{-1}): sym CH_2: 1450-1354, Ru-O-C vib: 1052; ^{1}H-NMR (ppm): Not soluble enough for NMR study)

Preparation of [Ru(COD)(OC₂H₅)₂(C₁₉H₁₇OP)₂] (**4**): Excess of *o*-methxyphenyldiphenyphosphine (1 g, 3.4 mmol) was added to a solution of [Ru(COD)(OC₂H₅)]₂ (0.5 g, 1mmol) in dry ethanol (20 mL). The suspension was refluxed under nitrogen at 80 °C (*ca* 30 min) until all the solid ligand dissolved to give a pale red solution. The volume of the solution was then evaporated under reduced pressure to obtain a brown crystalline solid. The solid was further dried in the vacuum. Yield: 0.28 g (32%) Anal. Calcd for $C_{50}H_{56}O_4P_2Ru$: C, 67.95; H, 6.34. Found: C, 68.01; H, 6.29. m.p. 178-181 °C; IR(cm^{-1}): Ru-O-C vib: 1142-896 νCH: ν aromatic: 3056, 2984; ^{1}H-NMR (ppm): 7.45 – 7.71(m) (phenyl protons); 1.24 and 3.56 (protons of OC_2H_5); 1.85 and 3.83 (COD protons); ^{31}P (ppm): 27.9.

Preparation of [Ru(OC₂H₅)₂(C₁₂H₁₀P)₄] (**5**): Diphenyphosphine (0.5 mL, 0.25 mmol) was added to [Ru(COD)(OC₂H₅)₂] ((0.5 g, 1 mmol)) in ethanol (30 mL). The solution was then refluxed for 12 h at 80 °C. An orange solution was obtained after filtration; the volume of the solution was then reduced under reduced pressure and cooled to 0 °C for several hours. An orange precipitate was formed at the bottom of the flask which was collected through filtration and dried in the vacuum to obtain an orange powder. Yield: 0.32 g (34%). Anal. Calcd for $C_{52}H_{50}O_2P_4Ru$: C, 67.02; H, 5.37. Found: C, 66.89; H, 5.43. m.p. 185-188 °C; IR(cm^{-1}): νCH 1048, 1127, 1584: ν aromatic: 3053, 2971, Ru-O-C vib: 1127-884; ^{1}H-NMR (ppm): 1.23, 2.31 (protons of OC_2H_5); 7.47 – 7.52 (phenyl protons); ^{31}P (ppm): 118.4.

Preparation of [Ru(COD)(OCH₃)₂(C₂₁H₂₁P] (**6**): Tri(*m*-tolyl)phosphine (0.1 g, 0.33 mmol) was added to a solution of [Ru(COD)(OCH₃)₂] (0.27 g, 1mmol) in methanol (20 mL). The suspension

was heated on the steam bath until the entire solid dissolved; the heating is continued for another 30 min. The light brown solution was obtained and the solvent was removed under reduced pressure to obtain a brown solid. Yield: 0.51 g (58%). Anal. Calcd for $C_{52}H_{60}O_2P_2Ru$: C, 70.99; H, 6.83. Found: C, 71.48; H, 6.57. m.p. Decomp. > 200 °C; IR(cm^{-1}): Ru-O-C vib: 1132-885; ν aromatic: 3054, 2983; 1H-NMR (ppm): 2.30 (s) (CH$_3$ protons); 1.96, 3.49 (COD protons); 7.03 – 7.34 (phenyl protons); ^{31}P (ppm): 60.48.

3.   Results and Discussion

The FTIR spectrum of complex **2** exhibits sharp bands around 2971, 2926 and 2876 cm^{-1} due to symmetric stretch of the ethoxy ligands and sharp bands around 1450−1354 cm^{-1} due to the (CH$_2$) vibrations (Yang *et al*, 2008). Bands at 1100−881 cm^{-1} correspond to the Ru—O—C vibrations of ethoxy groups bound to Ru. Complex **2** is also characterized by the existence of C–O stretching frequencies at 1052 and 1032 cm^{-1} (Barraclough *et al*, 1961). The band at 1032 cm^{-1} suggests the presence of a bridging ethoxide while the Ru–O stretching mode appeared at 667 and 619 cm^{-1} (Barraclough *et al*, 1961). The presence of two individual bands, instead of one broad band, is indicative of the dimeric nature of ethoxide (Seubold, 1956; Hashimoto *et al*, 2007). The IR data for this complex also show the presence of an additional strong band at 996 cm^{-1} and two bands in the region 550 – 700 cm^{-1} in agreement with the literature which supports the assignment of a bridging ethoxide in this complex (Seubold, 1956; Hashimoto *et al*, 2007). Absence of band at 1030 cm^{-1} region in **3** (the methoxide analogue) rules out a bridging group in this complex, however the Ru–O and C–O were observed at the expected regions (Wentworth and Brubaker, 1964). It is therefore suggested that **3** may be monomeric.

The ethoxide protons are observed in the NMR spectrum of **2** at δ 3.74 and 1.63 ppm while the cyclooctadiene protons are present at the expected regions. Complex **3** is not soluble enough for an NMR study. Based on the spectroscopic evidence, the following structure is proposed for **2.** The structure proposed in Figure 1 is in agreement with structures of similar compounds reported in the literature (Selent, 1996; Selent and Ramm, 1995; Hashimoto *et al*, 2007).
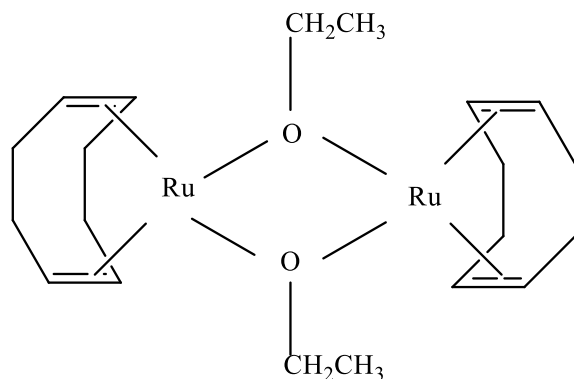

Figure 1: Proposed structure for [Ru(COD)(OC$_2$H$_5$)]$_2$

Complex **4** was obtained as brown crystalline solid. Phenyl protons of the ligand o-methoxyphenyldiphenylphosphine were observed in the ^{1}H-NMR of **4** between 7.45-7.71 ppm. This showed a good chemical shift when compared with the ^{1}H-NMR of the free ligand which appeared between 6.67 – 6.85 ppm. The protons of the ethoxide were observed in the complex at 1.24 and 3.56 ppm as expected for a coordinated ethoxide. ^{31}P NMR spectra showed a good shift from -15.9 ppm in the free ligand to 27.9 in the complex. The cyclooctadiene protons were not clearly observed at the expected regions in the complex. Treatment of a solution of [Ru(COD)(OC$_2$H$_5$)]$_2$ in ethanol with diphenylphosphine produced the compound [Ru(OC$_2$H$_5$)$_2$(Ph$_2$P)$_4$] which is a clear deviation from **4** and **6** where COD protons were observed. The absence of cyclooctadiene protons at the expected regions in the NMR of this complex as well as the microanalytical data supports the proposed stoichiometry. The

characteristic ethoxide peaks were observed at 1.23 and 2.31 ppm. Appearance of a peak at 118.4 ppm in the ^{31}P NMR of this complex also supports the presence of diphenylphosphine in this complex. Complex **6** was obtained as a yellow crystalline solid. The methoxide protons were observed as a singlet at δ 2.3 ppm while the cyclooctadiene protons appeared at the expected regions at δ 2.03 and 3.49 ppm in ratio 2:1 (Kolle et al, 1990). A good chemical shift was also observed in the ^{31}P NMR of this complex at 60.48 ppm when compared to the free ligand which appeared at -15.76 ppm.

4.   Conclusions

A simple reaction of the polymeric species [{RuCl$_2$(COD)}$_x$] with LiOR in refluxing methanol or ethanol gave an air stable ruthenium(II) alkoxide complex [RuCl$_2$(COD)(OR)$_2$] (R = CH$_3$ or C$_2$H$_5$). Some representative reactions to demonstrate their usefulness in the preparation of ruthenium(II) alkoxide phosphine complexes are reported.

Acknowledgement

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