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Formation and reactivity of the chloromethyl π-allyl complex $(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$

John L. Hubbard *, Christopher R. Zoch

Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300, USA

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Abstract

Treatment of $(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}C_3H_5)Cl_2$ in CH_2Cl_2 with ethereal diazomethane in the presence of copper powder produces $(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$ in moderate yield with no detectable formation of the bis(chloromethyl) derivative. Deuterium labeling with CD_2N_2 shows no methylene scrambling into the allyl ligand. Evidence from NMR spectroscopy supports an *endo* allyl conformation in the chloromethyl complex. Mass spectroscopy experiments indicate that the d^4 (Ru^{IV}) metal center is relatively ineffective in stabilizing the $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(=CH_2)Cl]^+$ fragment. The new chloromethyl complex reacts under photochemical conditions to give polymethylene with the regeneration of the starting dichloride. No intramolecular transfer of methylene to the allyl or $(\eta^5\text{-}C_5Me_5)$ ligands is observed.

Keywords: Ruthenium; Allyl; Chloromethyl

1. Introduction

Organometallic compounds of the general formula $(\eta^5\text{-}C_5R_5)Ru(\eta^3\text{-}C_3H_5)X_2$, first described by Itoh and co-workers, contain ruthenium in a relatively high +4 oxidation state (R = H (Cp); R = Me (Cp*); X = Cl, Br, I) [1]. The Cp* derivatives are now known to be easily obtained from the addition of allyl halides to $[Cp^*RuCl_2]_x$ [2]. The detection of allyl σ–π interconversion has been noted in the reaction of the $Cp^*Ru(\eta\text{-}C_3H_5)Cl_2$ with DMSO [3]. Of particular interest are C–C bond forming reactions arising from $Cp^*Ru(\eta\text{-}C_3H_5)(alkyl)_2$ derivatives [3–6].

Over the past few years we have been interested in intramolecular C–C bond formation arising in a variety of transition metal–halomethyl complexes [7–8]. The $Cp^*Ru(\eta\text{-}C_3H_5)Cl_2$ complex was especially attractive in relation to our work on the structurally similar $Cp^*Ru(NO)X_2$ systems. Specifically, the reaction of $Cp^*Ru(NO)(CH_2Cl)_2$ to form ethylene with the regeneration of $Cp^*Ru(NO)Cl_2$ is proposed to proceed through a carbene-like $[Ru=CH_2^{\delta+}Cl^{\delta-}]$ transition state [8]. We describe here our characterization of the allyl(chloromethyl) complex $Cp^*Ru(\eta\text{-}C_3H_5)(CH_2Cl)Cl$ in an effort to probe for possible C–C bond formation between an allyl ligand and a CH_2 moiety introduced from diazomethane.

2. Results and discussion

The repeated addition of ethereal diazomethane to a dichloromethane solution of $Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$ in the presence of Cu powder produces $Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$ as a yellow, hexane-soluble product in ca. 50% yield (Eq. (1)). The use of CD_2N_2 leads to the similar formation of the $-CD_2Cl$ derivative. In comparison with the similar conversion of $(\eta^5\text{-}C_5R_5)Ru(NO)Cl_2$ to the $Cp^*Ru(NO(CH_2Cl)Cl$ and $Cp^*Ru(NO)(CH_2Cl)_2$

$$Cp^*Ru(\eta\text{-}C_3H_5)Cl_2 + \text{excess } CH_2N_2 \xrightarrow{\text{Cu dust}} Cp^*Ru(\eta\text{-}C_3H_5)(CH_2Cl)Cl + N_2 \quad (1)$$

derivatives, methylene insertion to produce just $Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$ is rather sluggish, requiring a large excess of ethereal CH_2N_2. This may be a result of a stronger Ru–Cl bond in the formally Ru^{IV} complex. In contrast to the treatment of Cp*

* Corresponding author.

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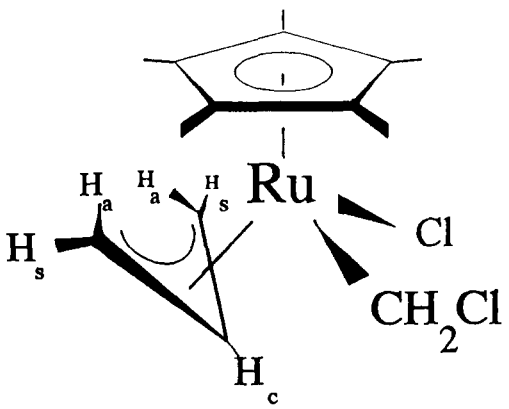

Fig. 1. A sketch of Cp*Ru(η-C_3H_5)(CH_2Cl)Cl showing *endo* allyl configuration.

$Ru(NO)Cl_2$ with CH_2N_2, no traces of Cp*Ru(η-C_3H_5)$(CH_2Cl)_2$ or any other organometallic products were detectable in the crude reaction mixtures by ^1H NMR spectroscopy. The need for a great excess of ethereal CH_2N_2 causes the build-up of colorless, partially soluble polymethylene residues, making it necessary to filter the reaction onto fresh Cu powder at frequent intervals in order to see product formation. Repeated recrystallization of the product is required to free the product of the polymethylene residues. Attempts to purify the complex by chromatography on various SiO_2 or Al_2O_3 supports result in the loss of the chloromethyl ligand and the regeneration of Cp*Ru(η-C_3H_5)Cl_2.

The ^1H NMR spectrum for Cp*Ru(η^3-C_3H_5)(CH_2-Cl)Cl reflects the lack of C_s symmetry found in dichloride starting complex (Fig. 1). The two *anti* protons as well as the two *syn* protons of the allyl ligand are no longer chemical shift equivalent. An AB pattern is seen for the diastereotopic protons of the CH_2Cl ligand. In samples of Cp*Ru(η-C_3H_5)(CD_2Cl)Cl these resonances are noticeably reduced in intensity and broadened due to the presence of the chloromethyl ligand as the -CD_2Cl and -CHDCl isotopomers. The signals from the Cp* and allyl ligands are unaffected by CD_2 substitution on the chloromethyl ligand.

The ^{13}C NMR spectrum of Cp*Ru(ω-C_3H_5)(Ch_2-Cl)Cl clearly shows the presence of the -CH_2Cl ligand with a resonance at δ 42.6. The presence of dissimilar terminal allylic carbon atoms is shown by resonances at δ 62.1 and 63.8, slightly shifted from the position of the terminal allylic carbon atoms in Cp*Ru(η-C_3H_5)Cl_2. Resonances typical for the skeletal and methyl group carbon atoms of the Cp* ring are observed.

The EI-mass spectrum of Cp*Ru(η^3-C_3H_5)(CH_2-Cl)Cl reveals information about the stability of Cp*Ru(η-C_3H_5)(CH_2Cl)Cl and its tendency to lose part or all of the chloromethyl ligand. The presence of a low intensity molecular ion supports limited thermal stability of the complex. From the presence of the $[Cp^*Ru(\eta\text{-}C_3H_5)Cl]^+$ as the base peak in the spectrum, it is apparent that the loss of the chloromethyl ligand is the most predominant process. The low abundance of the fragment at *m/e* 327 (corresponding to either $[Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2)Cl]^+$ or $[Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)]^+$) indicates that the formally d^4 Ru^{IV} metal center is not very effective in stabilizing a [Ru = CH_2^+] interaction due to the lack of metal d electron back donation into the CH_2 moiety. In contrast, loss of chloride from d^6 chloromethyl complexes gives rise to intense fragments in the mass spectrum [7,8]. In the d^6 systems, frontier molecular orbital theory predicts significant metal $\rightarrow CH_2$ π-backdonation to stabilize the $[L_nM = CH_2]^+$ ion produced from the loss of a chloride on the chloromethyl ligand.

Itoh has shown by VT-NMR spectroscopy that an *endo* allyl configuration persists for the Cp*Ru(η^3-C_3H_5)B_2 complex over a range of temperature [4]. We have independently determined by X-ray crystallography that Cp*Ru(η-C_3H_5)Cl_2 is essentially isostructural to Cp*Ru(η-C_3H_5)Br_2 [9]. Indeed, selective $^1H\{^1H\}$ NOE and 2-D NOESY experiments on Cp*Ru(η^3-C_3H_5)(CH_2Cl)Cl show correlation between the *anti* protons of the allyl ligand and the methyl groups on the Cp* ligand but no detectable through-space interaction between the central allylic proton (H_c) with the Cp* methyl groups. This data would support an *endo* allyl conformation for the Cp*Ru(η-C_3H_5)(CH_2Cl)Cl complex in solution (Fig. 1).

Clear yellow solutions of Cp*Ru(η^3-C_3H_5)(CH_2-Cl)Cl in C_6D_6 react quickly in direct sunlight and more slowly under thermal conditions to produce a milky, insoluble residue on the walls of the tube together with a dark orange supernatant solution. Subsequent ^1H NMR measurements show the presence of Cp*Ru(η^3-C_3H_5)Cl_2 in addition to signals in the region characteristic of polymethylene residues (Eq. (2)).

$$Cp^*Ru(\eta\text{-}C_3H_5)(CH_2Cl) \rightarrow Cp^*Ru(\eta\text{-}C_3H_5)Cl_2 + \text{-}(CH_2)_x\text{-} \quad (2)$$

Throughout the similar formation and reactions of the deuterated complex Cp*Ru(η^3-C_3H_5)(CD_2Cl)Cl, no incorporation of the CD_2 label into the allyl or Cp* ligands is observed by NMR spectroscopy.

In summary, we have shown that Cp*Ru(η-C_3H_5)Cl_2 can be converted only to Cp*Ru(η-C_3H_5)(CH_2Cl)Cl with diazomethane in the presence of Cu powder. The complex is reactive under photolysis and thermal conditions to liberate CH_2 but no intramolecular methylene transfer occurs to either the allyl or Cp* ligands.

3. Experimental reaction

Manipulation of all compounds was carried out using standard Schlenk techniques. Chemical reagents were obtained from Aldrich unless otherwise indicated. $Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$ was prepared by the method of Itoh and co-workers [2,3] from the Ru^{III} oligomer $[Cp^*RuCl_2]_x$, prepared by literature methods [10]. Reagent grade solvents (Baker) were distilled under a nitrogen atmosphere over appropriate drying agents prior to use. Proton NMR spectra were measured using a Varian XL 300 spectrometer and ^{13}C NMR data were recorded at 69.8 MHz using a JEOL GSX 270 spectrometer. Chemical shifts were referenced to the solvent peaks (residual C_6D_5H at δ 7.15 (^1H), δ 128 for C_6D_6 (^{13}C)). Electron impact mass spectra (70 eV) were measured with an LKB 2091 Spectrometer with a direct insertion probe at 100°C. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA.

Diazomethane (CH_2N_2) was generated using the "alcohol-free" method from Diazald (Aldrich) [11]. *CAUTION: Diazomethane is exceedingly toxic and solutions have been known to explode unaccountably! All work must be carried out in a well-ventilated fume hood.* CD_2N_2 was prepared from 1-methyl-3-nitro-1-nitrosoguanidine (MNNG, Aldrich) using KOD/D_2O (vide infra). The dropwise addition of the diazomethane solutions was carried out with a peristaltic pumping device as previously reported [7]. Copper powder (as electrolytic dust, Baker) was used as received.

3.1. Preparation of $Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$

$Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$ (0.13 g, 0.37 mmol) was dissolved in 60 ml of dichloromethane and the solution poured over 5 g copper powder. Ethereal diazomethane was peristaltically pumped to the reaction vessel at the rate of 20–40 drops/min for three 15 min addition periods. After each addition the reaction mixture was filtered through Analytical Filter Pulp (Schliesser and Schuller) onto fresh Cu powder. Following the additions, the solution was again filtered, and the solvent removed *in vacuo*. A final extraction with 40 ml of hexane followed by filtration, concentration to 10 ml, and placement at −40°C produced 0.070 g, (0.19 mmol, 52%) of $Cp^*Ru(\eta\text{-}C_3H_5)(CH_2Cl)Cl$ as a yellow, microcrystalline powder.

^1H NMR: (C_6D_6) δ 4.31 (tt, 1H, $H_{cent.}$ on allyl, $^3J(H_c - H_{anti}) = 10$ Hz, $^3H(H_c - H_{syn}) = 6$ Hz); δ 4.21 (d, 1H, $-CH_aH_b$); δ 4.11 (d, 1H, $-CH_aH_b$) ($^2J(CH_aH_b) = 8$ Hz); δ 3.77 (dd, 1H, H_{syn} *trans* to CH_2Cl, $^2J(H_{syn} - H_{anti}) = 3$ Hz, $^3J(H_{syn} - H_c) = 6$ Hz); δ 3.45 (dd, 1H, H_{syn} *cis* to CH_2Cl, $^2J(H_{syn} - H_{anti}) = 3$ Hz, $^3J(H_{syn} - H_c) = 6$ Hz); δ 1.74 (d, 1H, H_{anti} *trans* to CH_2Cl, $^3J(H_{anti} - H_c) = 11$ Hz); δ 1.34 (d, 1H, H_{anti} *cis* to CH_2Cl, $^3J(H_{anti} - H_c) = 10$ Hz); δ 1.17 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR: (C_6D_6) δ 101.4 ($\eta^5\text{-}C_5Me_5$); δ 96.8 (central allyl); δ 63.8, 62.1 (terminal allyl); δ 46.6 (CH_2Cl); δ 8.7 ($\eta^5\text{-}C_5Me_5$). Mass Spec. (EI): [M +] *m/e* 362 (5%); [M − Cl] *m/e* 327 (4%); [M − CH_2Cl] *m/e* 313 (100%); [M − (C_3H_5)CH_2Cl] *m/e* 271 (98%) Anal. Calc. for $C_{14}H_{22}RuCl_2$: C, 46.41; H, 6.12%. Found: C, 46.95; H, 6.44; mp. 78–82°C (dec).

3.2. Preparation of $Cp^*Ru(\eta^3\text{-}C_3H_5)(CD_2Cl)Cl$

A procedure identical to that for the preparation of $Cp^*Ru(\eta\text{-}C_3H_5)(CH_2Cl)Cl$ was followed, substituting ethereal CD_2N_2 for CH_2N_2. CD_2N_2 was prepared by adding 0.5 g of MNNG (1-methyl-3-nitro-1-nitrosoguanidine, Aldrich) in 0.1 g portions to a 250 ml flask containing 50 ml of a 50% solution of KOD in D_2O covered by 100 ml of Et_2O while swirling at 0°C. The ether layer was carefully separated (do not expose to KOH!) and used without rigorous drying. Examination by ^1H NMR spectroscopy showed the product to be ca. 70% labeled as $Cp^*Ru(\eta^3\text{-}C_3H_5)(CD_2Cl)Cl$.

3.3. Photolysis of $Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$

Two 5 mm NMR tubes were each charged with 0.015 g of $Cp^*Ru(\eta^3\text{-}C_3H_5)(CH_2Cl)Cl$ and 0.5 ml of C_6D_6. One tube was placed in direct sunlight and the other was wrapped in Al foil and heated in a 50°C oil bath. The ^1H NMR spectra were monitored over a 90 min period, revealing the disappearance of the starting complex and the appearance of $Cp^*Ru(\eta^3\text{-}C(_3H_5)Cl_2$ in both cases (^1H NMR of $Cp^*Ru(\eta\text{-}C_3H_5)Cl_2$ in C_6D_6: δ 5.36 (m, 1H, H_c on allyl); δ 4.00 (d, 2H, H_{syn}, $^3J(H_{syn} - H_c) = 7$ Hz); δ 1.77 (d, 2H, H_{anti}, $^3J(H_{anti} - H_c) = 10$ Hz); δ 1,06 (s, 15H, Cp*). Slow evaporation of these solutions produced $Cp^*Ru(\eta^3 = \text{-}C_3H_5)Cl_2$ as orange, single crystals that were suitable for X-ray analysis [9].

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Supplementary Material

A complete description of the X-ray structure of $Cp^*Ru(\eta\text{-}C_3H_5)Cl_2$ (10 pages) is depicted at the Cambridge Crystallographic Data Centre.

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