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Journal of Organometallic Chemistry 691 (2006) 27–34

Journal of Organo metallic Chemistry

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Synthesis, characterization, and reactivity of a novel ruthenium carbonyl cluster containing tri-*O*-benzyl-D-glucal as a chiral carbohydrate ligand ☆

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Received 5 August 2005; received in revised form 11 August 2005; accepted 12 August 2005
Available online 4 October 2005

Abstract

A chiral carbohydrate ligand 3,4,6-tri-*O*-benzyl-D-glucal (L) reacts with the cluster triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ giving a novel chiral cluster $Ru_3(\mu\text{-}H)_2(CO)_9(L\text{-}2H)$ (**I**) that shows fluxional behavior at room temperature. The reaction of $Ru_3(\mu\text{-}H)_2(CO)_9(L\text{-}2H)$ (**I**) with triphenylphosphine and diphenylphosphinoethane (dppe) gives two new clusters $Ru_3(\mu\text{-}H)_2(CO)_7(L\text{-}2H)(PPh_3)_2$ (**II**) and $Ru_3(\mu\text{-}H)_2(CO)_7(L\text{-}2H)(dppe)$ (**III**). The new compounds **I**, **II** and **III** have been characterized by a combination of elemental analysis, mass spectrometry, infrared and variable temperature NMR spectroscopy.

Keywords: Tribenzyl glucal; Triruthenium dodecacarbonyl; Chiral ligand; Triphenylphosphine; Diphenylphosphinoethane; Variable temperature; NMR spectra

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1. Introduction

Ruthenium carbonyl clusters have been used in several catalytic reactions. Considerable interest generated in the synthesis of ruthenium clusters [1] containing chiral ligands because of their potential use in asymmetric reactions [2]. This paper describes the synthesis, characterization, and reactivity of a novel triruthenium carbonyl cluster $Ru_3(\mu\text{-}H)_2(CO)_9(L\text{-}2H)$ (**I**) obtained from the reaction of 3,4,6-tri-*O*-benzyl-D-glucal (tribenzyl glucal) with $Ru_3(CO)_{12}$. Compounds **II** and **III** were prepared from the reaction of compound **I** with triphenylphosphine and diphenylphosphinoethane. Compounds **I**, **II** and **III** will be explored in the synthesis of glycosylated amino acids. The rapidly developing area of glycoproteins is currently under intense study by glycobiologists [3]. As a result, synthetic organic chemistry is required for the synthesis of glycosylated amino acids and peptides.

2. Results and discussion

The reaction of tribenzyl glucal with $Ru_3(CO)_{12}$ in benzene at reflux temperature yields a yellow syrupy compound which could be separated on a silica gel flash column with hexane/dichloromethane (2:1) as well as by preparative thin layer chromatography with hexane/dichloromethane (1:1). It is not been possible to obtain X-ray quality crystals due to the fact that compound **I** is a syrupy liquid. Compound **I** has been characterized by FT-IR and NMR spectroscopy, mass spectrometry, and by elemental analysis. The FT-IR spectrum in dichloromethane exhibits stretching vibrations in the carbonyl region between 1900 and 2100 cm^{-1} indicating that all carbonyl groups are terminal: 2107(m), 2080(vs), 2054(vs), 2041(s, sh), 2012(s, br) cm^{-1}.

^{1}H NMR spectrum of **I** in $CDCl_3$ in the organic region shows signals corresponding to all of the hydrogens of

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☆ Dedicated with admiration and appreciation to Prof. Richard Franck at Hunter College/CUNY on the occasion of his 69th birthday.

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doi:10.1016/j.jorganchem.2005.08.018

tribenzyl glucal except two, each on C-1 and C-2 carbons. However, these two hydrogens were found in the hydride region of the ^{1}H NMR spectrum as a broad resonance at δ −18.33 due to the rapid exchange of the two bridging hydride ligands on the NMR time scale at room temperature. This is the first example in which C-1 and C-2 carbons of the 3,4,6-tri-*O*-benzyl-D-glucal are bonded to two ruthenium atoms of $Ru_3(CO)_9$ framework. It is well documented in the literature that the reaction of $Ru_3(CO)_{12}$ with olefins (L) gives $H_2Ru_3(CO)_9(L\text{-}2H)$ [1]. ^{1}H–^{1}H COSY spectrum (Fig. 1) of **I** shows two cross-peaks that reveal the coupling between H-5 (quartet, centered at 4.48 ppm) and both H-4 (triplet, centered at 3.92 ppm), and to H-6 (AB quartet, centered at 3.89–3.81 ppm). ^{1}H NMR shows 15 hydrogens due to three phenyl rings, 6 hydrogens due to benzylic hydrogens in three benzyl groups, and 5 hydrogens of carbohydrate moiety. No coupling between H-1 and H-2 is observed. Apparently, they have been transferred to ruthenium skeleton. ^{13}C NMR spectrum in $CDCl_3$ shows peaks for both aliphatic and aromatic carbons of the carbohydrate portion of the cluster, and four peaks at 206.5, 197.6, 192.8, and 192.1 due to terminal CO groups. ^{13}C APT spectrum in CD_3COCD_3 shows four peaks at 207.1, 198.5, 193.9 and 192.3 due to four carbonyl carbons of ruthenium, three peaks at 138.9, 138.5 and 138.2 due to three quaternary carbons of phenyl groups of benzyl groups in tribenzyl glucal, and four peaks due to benzylic CH_2 carbons as positive peaks; CH carbons of the six-membered carbohydrate ring and CH carbons of phenyl groups as negative peaks. Additional characterization of **I** was performed using variable temperature (VT) ^{1}H NMR and ^{13}C NMR spectroscopic measurements. The variable-temperature ^{1}H NMR spectra in the hydride region are shown in Fig. 2. The ^{1}H NMR spectrum at +20 °C exhibits a broad resonance at δ −18.33, which can be assigned to the two bridging hydride ligands migrating over all three edges of the ruthenium framework in a rapid fluxional process [4,7] as shown in Scheme 1. Upon cooling to −50 °C, the broad resonance becomes two sharp singlets at δ −16.27 and δ −20.41 with the integrated ratio 1:1 similar to the compound $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}AsCF_3)]$ [4]. ^{1}H NMR suggests that there are two inequivalent hydrides. The singlet at δ −20.41 may be associated with the bridging hydride ligand between the two-ruthenium atoms that are sigma bonded to the tribenzyl glucal. The singlet at δ −16.27 may be due to the bridging hydride between the ruthenium atom bonded to the double bond and the other ruthenium atom sigma bonded to the tribenzyl glucal. At −8 °C, the two singlets become featureless (slow to fast exchange rate at $T_c = \sim -8$ °C is 3681/s.); above −8 °C, two peaks coalesces to a broad peak. The fluxional process at room temperature can be rationalized in terms of two hydride ligands migrating over all three edges of the triruthenium skeleton producing a broad peak. Variable temperature ^{13}C NMR of **I** in $CDCl_3$ at −50 °C shows expected three peaks at 206.5, 198.1, and 186.4 due to three

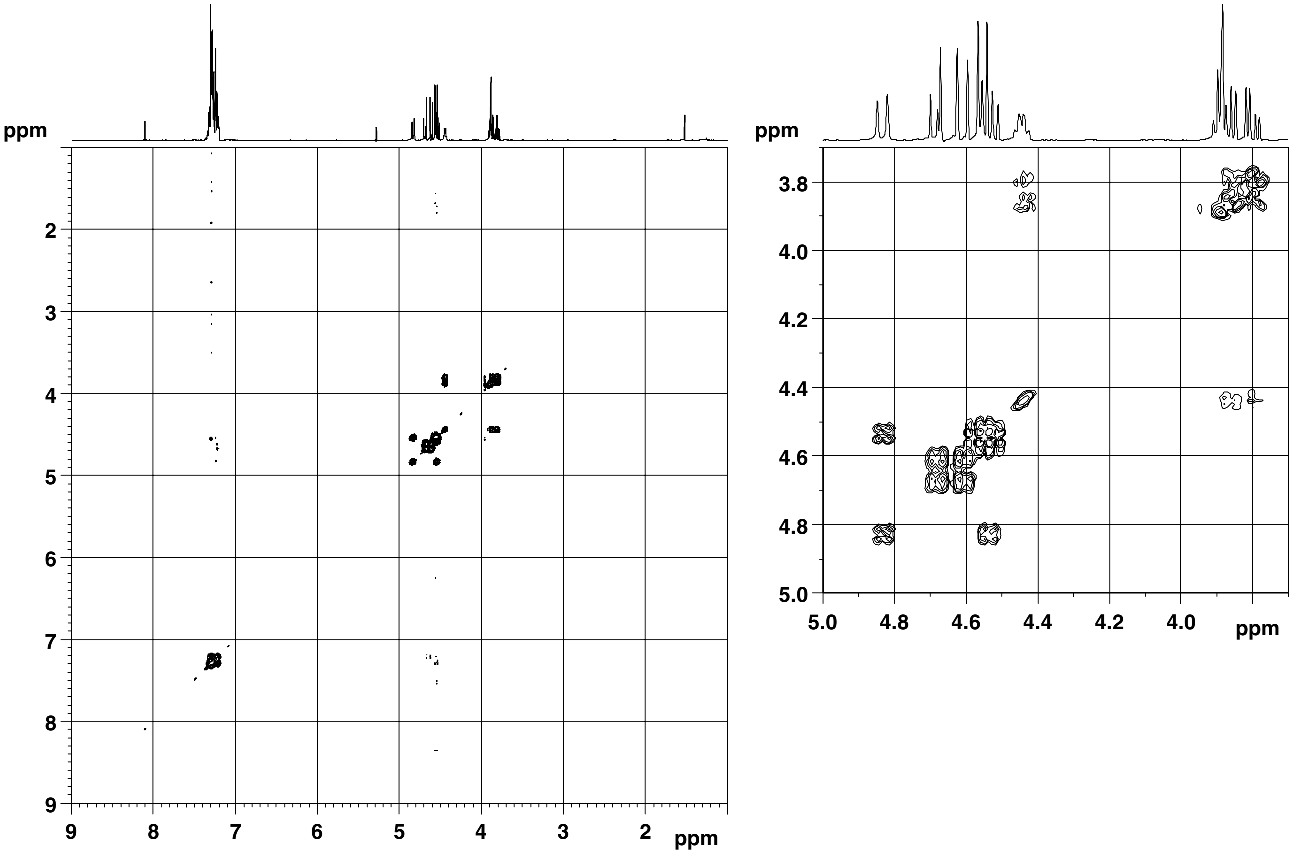

Fig. 1. ^{1}H–^{1}H COSY spectrum of compound **I** in $CDCl_3$.