Journal of Organometallic Chemistry 693 (2008) 2327–2337

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

CO substitution in $HRu_3(CO)_{10}(\mu\text{-}COMe)$ by the unsaturated diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd): Synthesis and reactivity studies of the face-capped cluster $Ru_3(CO)_7(\mu_3\text{-}COMe)[\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)]$

Simon G. Bott [a,*], Huafeng Shen [b], Shih-Huang Huang [b], Michael G. Richmond [b,*]

[a] Department of Chemistry, University of Houston, Houston, TX 77004, United States
[b] Department of Chemistry, University of North Texas, Denton, TX 76203, United States

ARTICLE INFO

Article history:
Received 15 March 2008
Received in revised form 2 April 2008
Accepted 2 April 2008
Available online 10 April 2008

Keywords:
Ruthenium clusters
Ligand substitution
Diphosphine ligand
P–C bond activation
Cluster expansion

ABSTRACT

The reaction of the methylidyne-bridged cluster $HRu_3(CO)_{10}(\mu\text{-}COMe)$ (**1**) with the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) and Me_3NO furnishes $HRu_3(CO)_8(\mu\text{-}COMe)(bpcd)$ (**2**) and $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)CH_2C(O)]$ (**3**) as the major and minor products, respectively. The ^1H and ^{31}P NMR data indicate that the bpcd ligand in **2** is chelated to one of the ruthenium atoms that is bridged by the hydride and methylidyne ligands. Thermolysis of **2** is accompanied by P–Ph bond cleavage and elimination of benzene to yield $Ru_3(CO)_7(\mu_3\text{-}COMe)[\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)]$ (**4**). Compound **4** consists of a triangular ruthenium core that is face-capped by μ_3-COMe methylidyne and $\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)$ phosphido ligands. The kinetics for the conversion of **2** → **4** have been measured in toluene solvent over the temperature range 320–343 K, and based on the observed activation parameters and the inhibitory effect of added CO on the reaction, a rate-limiting step involving a dissociative loss of CO is supported. Heating **4** in the presence of H_2 afforded the phosphinidene-capped cluster $H_3Ru_3(CO)_7(\mu_3\text{-}PPh)[\mu\text{-}C{=}C(PPh_2)C(O)CH_2C(O)]$ (**5**). Crystallographic analysis of **5** has confirmed the loss of the methylidyne moiety and the cleavage of the phosphido PhP–C(dione) bond, and the presence of three edge-bridging hydrides is supported by ^1H NMR spectroscopy. The reaction of **4** with added PPh_3 and PMe_3 has been investigated; the uptake of a single phosphine ligand occurs regiospecifically at one of the phosphido-bound ruthenium centers to give $Ru_3(CO)_6L(\mu_3\text{-}COMe)[\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)]$ (PPh_3, **6**; PMe_3, **7**). Compound **6** contains 48e- and exhibits a structural motif similar to that found in **4**. Compound **7** readily adds a second PMe_3 ligand to yield the bis-substituted cluster $Ru_3(CO)_6(PMe_3)_2(\mu_2\text{-}COMe)[\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)]$ (**8**). The solid-state structure of **8** confirms the loss of two ruthenium–ruthenium bonds and the conversion of the original face-capping μ_3-COMe ligand to a μ_2-COMe moiety that tethers two non-bonding ruthenium centers. The two PMe_3 ligands in **8** coordinate to the same ruthenium center, and the 9e- $P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)$ ligand binds all three ruthenium atoms through the phosphine, phosphido, alkene, and carbonyl moieties. Near-UV irradiation of **8** leads to loss of CO and polyhedral contraction of the triruthenium frame to yield the 48e- cluster $Ru_3(CO)_5(PMe_3)_2(\mu_3\text{-}COMe)[\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)]$ (**9**).

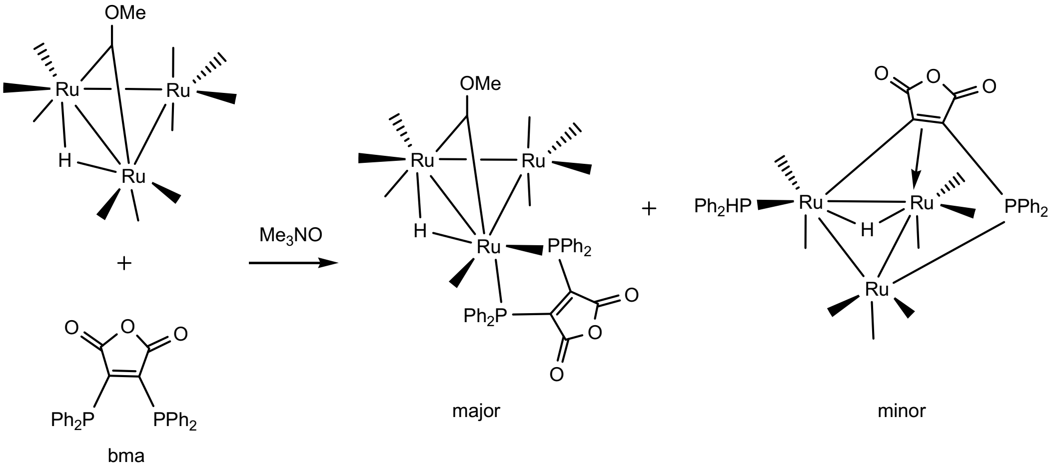
1. Introduction

Activation of the methylidyne-bridged cluster $HRu_3(CO)_{10}(\mu\text{-}COMe)$ (**1**) by the oxidative-decarbonylation reagent Me_3NO in the presence of the rigid diphosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride (bma) gives the chelated cluster $HRu_3(CO)_8(bma)(\mu\text{-}COMe)$ and the diphenylphosphine-substituted cluster $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)OC(O)]$ as the major and minor products, respectively [1]. Eq. (1) summarizes the reaction between **1** and the bma ligand. Controlled thermolysis of **1** with bma yields only trace amounts of $HRu_3(CO)_8(bma)(\mu\text{-}COMe)$ due to its facile decomposition under the reaction conditions. Also exacerbating the situation is the extensive loss of all bma-substituted products during chromatographic work-up due to the deleterious support-induced hydrolysis of the anhydride ring [2].

---

* Corresponding authors. Tel.: +1 713 743 2771 (S.G. Bott); tel.: +1 940 565 3548 (M.G. Richmond).
E-mail addresses: sbott@uh.edu (S.G. Bott), cobalt@unt.edu (M.G. Richmond).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.04.007



(1)

Since a detailed mechanistic study on the degradation pathway(s) exhibited by the bma-chelated cluster $HRu_3(CO)_8(bma)(\mu\text{-}COMe)$ during thermolysis and was hampered, in part, due to the unavoidable decomposition of the bma-derived products during chromatographic separation, the reaction between **1** and the related diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) was next explored. While both ligands are structurally similar in terms of the their cluster binding properties, the dione moiety associated with the bpcd ligand is stable to chromatographic supports. Treatment of **1** with bpcd in the presence of Me_3NO furnishes the bpcd-chelated cluster $HRu_3(CO)_8(bpcd)(\mu\text{-}COMe)$ (**2**), which unlike its bma counterpart $HRu_3(CO)_8(bma)(\mu\text{-}COMe)$, is easily purified by column chromatography and isolated in high yields. The ready availability of **2** has greatly facilitated our investigation on the reactivity of the ancillary methylidyne and bpcd ligands in this and other related clusters under thermal and photochemical activation. Previous reports from our groups have demonstrated low-energy manifolds for the activation of the diphosphine ligands bma and bpcd in a variety of polynuclear systems containing face-capping carbyne and alkyne ligands [3].

2. Experimental

2.1. General

The carbonylation of $RuCl_3 \cdot xH_2O$ to give $Ru_3(CO)_{12}$ was conducted in a 1000 mL Parr Series 4000 rocking autoclave and employed the procedure of Bruce [4], while the starting cluster **1** was prepared according to the procedure of Keister et al. [5]. The bpcd ligand used in this study was synthesized from 4,5-dichloro-4-cyclopenten-1,3-dione and Ph_2PSiMe_3 [6]. All reaction solvents were distilled from an appropriate drying agent under argon using Schlenk techniques and stored in Schlenk storage vessels equipped with high-vacuum Teflon stopcocks [7]. The IR and NMR solvents were reagent grade and were typically degassed by three pump-thaw-degas cycles prior to their use. The reported combustion analyses were performed by Atlantic Microlab, Norcross, GA.

The infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in a 0.1 mm NaCl cell, using PC control and OMNIC software. The reported ^1H and ^{31}P NMR spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer and 121 MHz on a Varian 300-VXR spectrometer, respectively. The reported ^{31}P chemical shifts, which were recorded in the proton-decoupled mode unless otherwise stated, are referenced to external H_3PO_4 (85%), taken to have $\delta = 0$. The reported ESI mass spectral data for cluster **9** were collected at the UNT mass spectrometry facility in the positive ion mode, using a MeOH matrix containing 1% AcOH. The spectroscopic data for clusters **2**–**9** are summarized in Table 1.

2.2. Reaction of $HRu_3(CO)_{10}(\mu\text{-}COMe)$ with bpcd in the presence of Me_3NO to give $HRu_3(CO)_8(\mu\text{-}COMe)(bpcd)$ (**2**) and $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)CH_2C(O)]$ (**3**)

To 0.35 g (0.52 mmol) of **1** and 0.27 g (0.58 mmol) of bpcd in a large Schlenk flask under argon was added 50 mL of CH_2Cl_2 by cannula. The solution was stirred at room temperature for 1 h and then examined by both TLC and IR spectroscopy. Only the two reactants were observed, at which point 84 mg (1.1 mmol) of Me_3NO was next added, causing an immediate change in the color of the solution from red to yellow-brown. Stirring was continued for an additional 0.5 h and the solution was examined by TLC, which revealed the presence of one major yellow-brown spot corresponding to **2** ($R_f = 0.25$ using 1:1 CH_2Cl_2/hexane), in addition to a trace amount of **1** ($R_f = 0.90$ same eluent) and red-black material at the origin of the plate. After the solvent was removed under vacuum, the residue was purified by column chromatography over silica using hexane to first elute unreacted **1**, after which the mobile phase was changed to CH_2Cl_2 to furnish **2**. Washing the column with acetone allowed for the separation of a small amount of the red **3**. Both new products were recrystallized from benzene/hexane at room temperature to yield 0.46 g (82%) of **2** and 15 mg (2.9%) of **3**. Compound **2**: Anal. Calc. for $C_{39}H_{26}O_{11}P_2Ru_3 \cdot 1/4C_6H_6$: C, 46.05; H, 2.61. Found: C, 45.89; H, 2.85%. Compound **3**: Anal. Calc. for $C_{37}H_{24}O_{10}P_2Ru_3 \cdot 1/2C_6H_6$: C, 46.48; H, 2.61. Found: C, 46.34; H, 2.69%.

2.3. Thermolysis of $HRu_3(CO)_8(\mu_2\text{-}COMe)(bpcd)$ (**2**) to $Ru_3(CO)_7(\mu_3\text{-}COMe)[\mu\text{-}P(Ph)C{=}C(PPh_2)C(O)CH_2C(O)]$ (**4**)

To a Schlenk tube was charged 0.20 g (0.19 mmol) of **2** under argon flush, followed by 30 mL of 1,2-dichloroethane (DCE). The vessel was sealed and heated at ca. 80–90 °C for period of 2 h, with the solution slowly turning from yellow-brown to red in color. Upon cooling, TLC analysis using a 10:1 mixture of CH_2Cl_2/acetone as the eluent revealed trace amounts of **1** ($R_f = 0.95$) and **2** ($R_f = 0.60$), along with a large red spot corresponding to **4** ($R_f = 0.25$) and some black material at the origin. The solvent was removed and **4** subsequently isolated by column chromatography using the aforementioned eluent. The desired product was recrys-