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Note

Reactivity studies on cationic non-hydridic triruthenium carbonyl clusters. Reactions of $[Ru_3(\mu_3\text{-ampy})(CO)_{10}][BF_4]$ with hydrogen, triethylsilane and triphenylstannane

Javier A. Cabeza *, Ignacio del Río, Víctor Riera

Instituto de Química Organometálica 'Enrique Moles', Facultad de Química, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain

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Abstract

The cationic cluster complex $[Ru_3(\mu_3\text{-ampy})(CO)_{10}][BF_4]$ (**1**) (Hampy = 2-amino-6-methylpyridine) reacts with hydrogen at room temperature undergoing an oxidative substitution of CO to give the cationic dihydrido derivative $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$. However, under similar conditions, the reactions of compound **1** with triethylsilane and triphenylstannane lead to mixtures of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ with the corresponding $[R_3E][BF_4]$ salts ($R_3E = Et_3Si, Ph_3Sn$). © 1998 Elsevier Science S.A.

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1. Introduction

In a recent paper, we have described a high-yield synthesis of the cluster complex $[Ru_3(\mu_3\text{-ampy})(CO)_{10}][BF_4]$ (**1**) (Hampy = 2-amino-6-methylpyridine) [1]. This compound is interesting because it is the first cationic non-hydridic 48-electron triruthenium carbonyl cluster ever reported [2].

The cationic character, the fact that it does not contain hydride ligands, its high thermal and air stability, and its efficient preparation make complex **1** an excellent candidate for reactivity studies. In previous reports, we have reported that compound **1** presents a high reactivity towards neutral [1] and anionic [3,4] nucleophilic reagents, as observed previously with hydrido cationic clusters [5], but without the complication of competitive deprotonation reactions. Compound **1** has also proven to be a convenient starting material for the preparation of high-nuclearity clusters, by reaction with anionic clusters [3,4].

On the other hand, the addition of hydrogen to neutral and anionic carbonyl cluster compounds generally results in dihydrido derivatives containing one CO ligand less than the corresponding starting materials [6]. In other cases, the addition of hydrogen is accompanied by the scission of metal–metal bonds [7]. Similarly, the addition of silanes and stannanes to carbonyl cluster compounds generally results in hydrido-silyl and hydrido-stannyl derivatives containing fewer CO ligands than the starting materials [8], although cases in which these reactions lead to cluster fragmentation are also known [9]. In all these reactions, it can be considered that the H–X reagent ($X = H, SiR_3, SnR_3$) oxidatively adds to the metal clusters.

Due to its cationic character, compound **1** was expected to be less capable than neutral or anionic clusters to undergo oxidative addition reactions. However, compound **1** had so far proven to be so reactive towards neutral and anionic nucleophiles [1,3,4], that we thought it would be interesting to treat it with hydrogen, silanes, and stannanes.

2. Results and discussion

Bubbling hydrogen through a dichloromethane solution of compound **1** at room temperature gave the cationic dihydride $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) in quantitative yield (Scheme 1). Compound **2** has previously been made by protonation of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**3**) and its structure has been determined by X-ray diffraction methods [5a]. The very mild conditions required by this reaction confirm the great reactivity of compound **1**. In fact, complex **1** was not reformed when carbon monoxide was bubbled through a solution of the dihydride **2** in 1,2-dichloroethane at reflux temperature.

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* Corresponding author. Tel.: +34 8 510 3501; fax: +34 8 510 3446; e-mail: jac@sauron.quimica.uniovi.es

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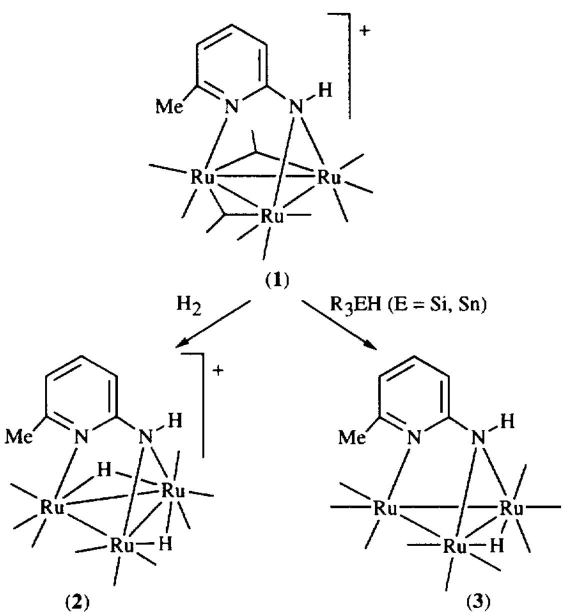

Scheme 1.

On the other hand, compound **1** reacted with triethylsilane and triphenylstannane to give the neutral hydride **3**. The reactions proceeded in dichloromethane at room temperature. When the solvent was not carefully dried, small amounts of the cationic dihydride **2** were also produced. These results are consistent with the equations given below, which involve the transfer of a hydride anion from the silane or stannane to the cationic cluster, with release of carbon monoxide, and concurrent formation of $[R_3E][BF_4]$ ($R_3E = Et_3Si, Ph_3Sn$) (Eq. (1)). Moisture in the solvent would produce the hydrolysis of the $[R_3E]^+$ cations to give R_3EOH (or other hydrolysis products) and $H[BF_4]$ (Eq. (2)). A subsequent reaction of $H[BF_4]$ with complex **3** would give the cationic dihydride **2** (Eq. (3)).

$$[Ru_3(\mu_3\text{-ampy})(CO)_{10}][BF_4]\ (\mathbf{1}) + R_3EH \rightarrow [Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]\ (\mathbf{3}) + CO + [R_3E][BF_4] \quad (1)$$

$$[R_3E][BF_4] + H_2O \rightarrow R_3EOH + H[BF_4] \quad (2)$$

$$\mathbf{3} + H[BF_4] \rightarrow [Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]\ (\mathbf{2}) \quad (3)$$

An alternative mechanism that would account for the formation of **3** from **1** and R_3EH (Eq. (1)) would imply the oxidative addition of the R_3EH reagent to compound **1**, with elimination of carbon monoxide, to give a cationic hydridosilyl (or stannyl) cluster intermediate that would finally release the $[R_3E]^+$ cation to give **3**. In an attempt to elucidate the mechanism of this reaction, solutions of complex **1** in CD_2Cl_2 were treated with the corresponding R_3EH reagent in NMR tubes, but the only new cluster compound that was observed by ^1H NMR spectroscopy was compound **3**.

As far as we are aware, this type of reactivity with silanes and stannanes has no precedent in cluster chemistry [8,9], since the abstraction of a hydride anion from these reagents has never been reported to occur using metal complexes as hydride abstractors. The $[R_3E]^+$ cations have been previously generated by treatment of tertiary silanes and stannanes with trityl salts of non-nucleophilic anions ($[ClO_4]^-$, $[B\{C_6H_3(CF_3)_2\}_4]^-$, $[B(C_6F_5)_4]^-$) in polar solvents of very low nucleophilicity. They are highly reactive species which readily undergo solvolysis processes [10–12]. The tetrafluoroborate salts of $[R_3Si]^+$ cations decompose easily to silyl fluorides [11]. In this respect, the trafluoroborate salts of $[R_3Sn]^+$ cations are much more stable [12].

3. Concluding remarks

In spite of its cationic constitution, compound **1** oxidatively substitutes hydrogen for CO to give the cationic dihydride $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ under very mild conditions. In contrast, it does not form hydridosilyl or hydridostannyl derivatives in its reactions with tertiary silanes and stannanes, but abstracts a hydride from these reagents to give the neutral derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$. This type of reactivity with silanes and stannanes is new in cluster chemistry and is definitely due to the cationic nature of compound **1**.

4. Experimental

4.1. General data

Dichloromethane and 1,2-dichloroethane were distilled over CaH_2 under nitrogen prior to use. The reactions were carried out under nitrogen at room temperature, using Schlenk vacuum line techniques, and were monitored by solution IR spectroscopy (carbonyl stretching region). Compound **1** was prepared as described previously [1]. All other reagents and chromatographic supports were purchased from commercial suppliers. IR spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. NMR spectra were run at 20°C with a Bruker AC-300 instrument.

4.2. Reaction of compound 1 with hydrogen

Hydrogen was gently bubbled through a solution of compound **1** (50 mg, 0.064 mmol) in dichloromethane (20 ml) for 30 min. The colour changed from red to yellow. After addition of hexane (10 ml), the solvent was removed under reduced pressure to give $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) in quantitative yield. Its analytical and spectroscopic data matched those reported in the literature [5a].

4.3. Reaction of compound **1** *with Et_3SiH*

A solution of triethylsilane (100 μl) and compound **1** (50 mg, 0.064 mmol) in dichloromethane (10 ml) was stirred for 30 min. The colour changed from red to orange. After removal of the solvent, the residue was separated by column chromatography (2 × 10 cm) in neutral alumina (activity I). Hexane–dichloromethane (1:1) eluted an orange band. The solvent was removed under vacuum to give $[Ru_3(\mu\text{-H})(\mu\text{-ampy})(CO)_9]$ (**3**) as an orange solid (36 mg, 85%). Its analytical and spectroscopic data matched those reported in the literature [13].

4.4. Reaction of compound **1** *with Ph_3SnH*

A solution of triphenylstannane (22.6 mg, 0.064 mmol) and compound **1** (50 mg, 0.064 mmol) in dichloromethane (10 ml) was stirred for 1 h. The colour changed from red to orange. After removal of the solvent, the residue was separated by column chromatography (2 × 10 cm) in neutral alumina (activity I). Hexane–dichloromethane (1:1) eluted an orange band. The solvent was removed under vacuum to give $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**3**) as an orange solid (34 mg, 84%). Its analytical and spectroscopic data matched those reported in the literature [13].

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