ELSEVIER

Reproducible high-yield syntheses of [Ru$_3$(CO)$_{12}$], [H$_4$Ru$_4$(CO)$_{12}$], and [Ru$_6$C(CO)$_{16}$]$^{2-}$ by a convenient two-step methodology involving controlled reduction in ethylene glycol of RuCl$_3$·nH$_2$O

Elena Lucenti [a], Elena Cariati [b], Claudia Dragonetti [b], Dominique Roberto [b,*]

[a] *Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM), Via C. Golgi 19, 20133 Milan, Italy*
[b] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Milano and Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM), via Venezian 21, 20133 Milan, Italy*

Abstract

[Ru$_3$(CO)$_{12}$], [H$_4$Ru$_4$(CO)$_{12}$], and [Ru$_6$C(CO)$_{16}$]$^{2-}$ have been synthesized in reproducible high yields and under mild conditions (1 atm) by a two-step methodology involving (i) first carbonylation of RuCl$_3$·nH$_2$O dissolved in ethylene glycol to give a mixture of tri- and di-carbonyl ruthenium(II) species, probably of the kind [Ru(CO)$_3$Cl$_2$(ethylene glycol)] and [Ru(CO)$_2$Cl$_2$(ethylene glycol)$_x$] (x = 1, 2), and (ii) addition of specific amounts of alkali carbonates and further reductive carbonylation to give the desired ruthenium carbonyl cluster. The selectivity of the second step is controlled by the: (i) nature and quantity of the alkali carbonate (Na$_2$CO$_3$ or K$_2$CO$_3$); (ii) gas-phase composition (CO or CO+H$_2$); (iii) temperature.
© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Although the reported syntheses in solution of high nuclearity ruthenium and osmium carbonyl clusters usually require [M$_3$(CO)$_{12}$] (M = Ru, Os) as starting material, it appeared that various neutral or anionic ruthenium [1] and osmium [2,3] carbonyl clusters can be synthesized in high yields and rather easily by controlled reduction at atmospheric pressure of silica-supported [M(CO)$_3$Cl$_2$]$_2$ or silica-bound [M(CO)$_3$Cl$_2$(HOSi≡)] (generated in situ by controlled reductive carbonylation of silica-supported MCl$_3$·nH$_2$O) [4] in the presence of specific amounts of alkali carbonates. These silica-mediated syntheses were the springboard of new convenient syntheses of [M$_3$(CO)$_{12}$], [H$_4$M$_4$(CO)$_{12}$], [H$_3$M$_4$(CO)$_{12}$]$^-$, [Ru$_6$C(CO)$_{16}$]$^{2-}$, and [H$_4$Os$_{10}$(CO)$_{24}$]$^{2-}$ starting from [M(CO)$_3$Cl$_2$]$_2$ or MCl$_3$·nH$_2$O and working in ethylene glycol solution, a high boiling

solvent carrying non acidic OH groups that could mimic the role and polarity of the OH groups of the silica surface [5,6]. The selective and facile direct reductive carbonylation of MCl$_3$·nH$_2$O (M = Ru, Os) was particularly convenient on a synthetic point of view but quite unexpected because silica-supported MCl$_3$·nH$_2$O gives a low selectivity and very low yields when reduced under similar conditions in the presence of alkali carbonates [1–3]. However, it appeared that the syntheses of [Ru$_3$(CO)$_{12}$], [H$_4$Ru$_4$(CO)$_{12}$], and [Ru$_6$C(CO)$_{16}$]$^{2-}$ by direct reduction of RuCl$_3$·nH$_2$O dissolved in ethylene glycol are not always reproducible, probably due to various factors such as amount of water present in the reaction mixture and nature of the commercial salt [7]. For this reason and because the syntheses starting from [Ru(CO)$_3$Cl$_2$]$_2$ dissolved in ethylene glycol were well reproducible [5], we investigated a modified two-step methodology, inspired by the two-step route to convert silica-supported RuCl$_3$·nH$_2$O into ruthenium carbonyl clusters via [Ru(CO)$_3$Cl$_2$(HOSi≡)] [1], involving (i) preparation of tri- and di-carbonyl ruthenium(II) species by carbonylation of RuCl$_3$·nH$_2$O at 110 °C in ethylene

---

* Corresponding author. Fax: +39-02-5031-4405.
E-mail address: dominique.roberto@unimi.it (D. Roberto).

glycol, as previously reported [5] and (ii) addition of specific amounts of alkali carbonates and further reductive carbonylation to give selectively the desired neutral or anionic cluster.

2. Results and discussion

When, in a flask equipped with a condenser, $RuCl_3 \cdot nH_2O$ (ca. 0.2 g, see Section 3) dissolved in ethylene glycol is heated at 110 °C for 2 h under 1 atm of CO a mixture of tri- and di-carbonyl ruthenium(II) species probably of the kind [$Ru(CO)_3Cl_2$(ethylene glycol)] ($\nu_{CO} = 2136$ (m) and 2065 (s) cm^{-1}) and [$Ru(CO)_2$-Cl_2(ethylene glycol)$_x$] ($x = 1, 2$; $\nu_{CO} = 2067$ (s) and 1999 (s) cm^{-1}) is formed, as evidenced by infrared spectroscopy [5,8]. Addition at 25–40 °C of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:2) followed by further reaction under CO (1 atm) at 80 °C for 7 h affords an orange material which precipitates in the reaction flask whereas, in parallel, some orange powder sublimes on the cold walls of the condenser. Extraction of the sublimate and reaction mixture with dichloromethane affords [$Ru_3(CO)_{12}$] in reproducible excellent yields (91%). By working on a high preparative scale (starting from ca. 2 g of $RuCl_3 \cdot nH_2O$), the second reduction step is slightly slower affording after 15 h [$Ru_3(CO)_{12}$] in 61% yield; under these conditions the formation of small amounts of anionic clusters such as [$H_3Ru_4(CO)_{12}$]$^-$ and [$HRu_6(CO)_{18}$]$^-$ [1] cannot be avoided (see Section 3). When the second reduction step is carried out with the same amount of Na_2CO_3 at 95 °C for 7 h under a mixture of CO + H$_2$ (molar ratio = 1:3; 1 atm) instead of CO, some [$H_4Ru_4(CO)_{12}$] precipitates in the reaction flask whereas, in parallel, some [$H_4Ru_4(CO)_{12}$] sublimes on the cold walls of the condenser. Besides, the infrared spectrum of the ethylene glycol solution shows the presence of [$H_3Ru_4(CO)_{12}$]$^-$ ($\nu_{CO} = 2036$ (m), 2016 (s), 1998 (s) and 1977 (m, br) cm^{-1}). Acidification of the ethylene glycol solution with H_2SO_4 leads to the precipitation of more [$H_4Ru_4(CO)_{12}$]. Successive extraction of the sublimate and the reaction mixture with dichloromethane at room temperature, gives [H_4Ru_4-$(CO)_{12}$] in 73% yield (working on a high preparative scale). Such yields of [$Ru_3(CO)_{12}$] and [$H_4Ru_4(CO)_{12}$] are similar to those obtained in ethylene glycol starting from [$Ru(CO)_3Cl_2$]$_2$ [5] or on the silica surface starting from $RuCl_3 \cdot nH_2O$ via [$Ru(CO)_3Cl_2$(HOSi$\equiv$)] that requires a much longer reaction time (ca. 5 days) [1]. In fact, both the reduction of $RuCl_3 \cdot nH_2O$ to Ru(II) carbonyl species and the subsequent formation of carbonyl clusters occur much more rapidly in ethylene glycol than on the silica surface due to a higher mobility of reagents and intermediate species in solution than on a solid surface [1,5].

It is worth pointing out that the new one-pot two-step synthesis in solution of [$Ru_3(CO)_{12}$] and [$H_4Ru_4(CO)_{12}$] must be carried out under well defined conditions with the stream of CO at the top of the condenser in order to obtain reproducible high yields of the clusters. In fact, if the reaction is carried out by bubbling CO in the flask, a non reproducible quantity of HCl is lost during the first step working at 110 °C; consequently, during the second step, a considerable amount of anionic ruthenium carbonyl complexes can be formed as by-products even using a molar ratio Na_2CO_3:Ru = 3:2. These results confirm that, in the case of the [$Ru_3(CO)_{12}$] and [$H_4Ru_4(CO)_{12}$] syntheses, the reduction must be carried out in the presence of the stoichiometric amount of Na_2CO_3 necessary to remove the chloro ligands from the coordination sphere of ruthenium (molar ratio Na:Cl = 1:1), because, when working in solution, use of even a small excess of Na_2CO_3 leads to the formation of anionic carbonyl clusters as by-products [5]. Therefore, before the preparation of the clusters it is crucial to control the exact Ru content of the salt which is very hygroscopic. Besides, in our preparation of [$Ru_3(CO)_{12}$], it is worth pointing out that if the second step is carried out in the presence of a molar ratio Na:Cl inferior to 1, a mixture of [$Ru_3(CO)_{12}$] and unreacted tri- and di-carbonyl ruthenium(II) species is obtained. This result is in contrast with a recently reported similar two-step preparation of [$Ru_3(CO)_{12}$] (86% yield) involving (i) reductive carbonylation of $RuCl_3 \cdot nH_2O$ in 2-methoxyethanol at 125 °C followed by addition of ca. one equivalent of KOH per Ru and successive reductive carbonylation at 85 °C [9], but it was then observed that it is better to use a higher amount of KOH (ca. two equivalents per Ru) in this latter synthesis [10].

In contrast to the syntheses of [$Ru_3(CO)_{12}$] and [$H_4Ru_4(CO)_{12}$] that of [$Ru_6C(CO)_{16}$]$^{2-}$ can be carried out under CO bubbling since it occurs in the presence of a large excess of alkali carbonate and, therefore, it is not sensitive to the exact quantity of base. Thus, when CO (1 atm) is bubbled through a solution of $RuCl_3 \cdot nH_2O$ dissolved in ethylene glycol in a three necked flask at 110 °C for 3–4 h a mixture of tri- and di-carbonyl ruthenium(II) species, probably of the kind [$Ru(CO)_3$-Cl_2(ethylene glycol)] and [$Ru(CO)_2Cl_2$(ethylene glycol)$_x$] ($x = 1, 2$), [5,8] is formed. Addition of K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1) followed by CO (1 atm) bubbling at 160 °C for 8 h, affords a dark red solution which infrared spectrum shows carbonyl stretching bands at $\nu_{CO} = 2034$ (vw), 1977 (vs), 1953 (vw, sh), 1917 (w) cm^{-1}, typical for [$Ru_6C(CO)_{16}$]$^{2-}$. Repeated extraction of this anion under N_2 with a solution of [NBu$_4$]I in CH_2Cl_2 affords [NBu$_4$]$_2$[$Ru_6C(CO)_{16}$] in 80–84% yields (working on a high preparative scale), similar to the yields obtained starting from [$Ru(CO)_3Cl_2$]$_2$ dissolved in ethylene glycol [5] or on the silica surface starting from

$RuCl_3 \cdot nH_2O$ via $[Ru(CO)_3Cl_2(HOSi\equiv)]$ that requires a much longer reaction time (ca. 5 days) [1].

In conclusion, by a spring of inspiration from silica-mediated syntheses, we found a new convenient two-step methodology to prepare $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, and $[Ru_6C(CO)_{16}]^{2-}$ rapidly, in high yields and under mild conditions by controlled reduction of a simple starting material such as $RuCl_3 \cdot nH_2O$ dissolved in ethylene glycol. These new syntheses in solution are reproducible and much more convenient than those previously reported either in solution [5] or on the silica surface as reaction medium [1].

3. Experimental

3.1. General comments

$RuCl_3 \cdot nH_2O$ (40.82–42.68 wt.% Ru) was purchased from Engelhard. The exact content of water was determined before each reaction by thermogravimetric analysis. All the reactions were monitored by infrared spectroscopy in the carbonyl region. Reaction products were identified by infrared, ^{1}H-NMR (when appropriate), and mass spectroscopies, their spectra being compared with those of pure samples. Their purity was controlled by thin-layer chromatography (when possible) and by elemental analysis.

3.2. Synthesis of [Ru_3(CO)_12]

$RuCl_3 \cdot nH_2O$ (40.82 wt.% Ru; 0.231 g, 0.933 mmol) was dissolved in ethylene glycol (60 ml) in a three necked flask equipped with a condenser and thermometer. CO (1 atm) was bubbled through the resulting dark brown solution for 5 min and than was allowed to flow only on the top of the condenser. The reaction mixture was heated under CO at 110 °C for 2 h. After cooling to 25 °C, Na_2CO_3 (0.147 g, 1.389 mmol; molar ratio Na_2CO_3:Ru = 3:2) was added and CO (1 atm) was allowed to flow on the top of the condenser. Thermal treatment at 80 °C for 7 h afforded an orange material ($[Ru_3(CO)_{12}]$) which precipitated in the reaction flask whereas, in parallel, some $[Ru_3(CO)_{12}]$ sublimed on the cold walls of the condenser. Extraction of the sublimate and reaction mixture with dichloromethane (4 × 50 ml) at room temperature (r.t.), followed by evaporation to dryness of the dichloromethane phase, gave an orange solid residue which was washed twice with water (2 × 5 ml) and then pentane (2 × 5 ml), in order to eliminate traces of ethylene glycol, affording spectroscopically pure $[Ru_3(CO)_{12}]$ (0.181 mg; 0.283 mmol; 91% yield).

Starting from a higher amount of $RuCl_3 \cdot nH_2O$ (40.88 wt.% Ru; 2.173 g, 8.790 mmol) dissolved in ethylene glycol (600 ml) the first (without base) and second (with base) reductive steps were carried out for 5 and 15 h,

respectively. During the second step some brown powder (still unidentified complex, characterized by v_{CO} at 1998 (vs) and 1975 (sh) cm^{-1} in Nujol, which is insoluble in organic solvents, donor solvents and even aqueous 37% HCl) precipitated along with orange $[Ru_3(CO)_{12}]$. The work-up was carried out as follows. Dichloromethane (ca. 150 ml) was added under stirring to the reaction mixture, left to stand and separated in order to extract $[Ru_3(CO)_{12}]$. This treatment was repeated several times until no more $[Ru_3(CO)_{12}]$ was present in the CH_2Cl_2 phase. The CH_2Cl_2 phase was then filtered in order to eliminate the brown powder and then dried to give $[Ru_3(CO)_{12}]$ which was washed with water (3 × 10 ml) and then pentane (3 × 10 ml), in order to eliminate traces of ethylene glycol, affording spectroscopically pure $[Ru_3(CO)_{12}]$ (1.145 g; 1.790 mmol; 61% yield). Extraction of the brown ethylene glycol solution with a solution of $[NBu_4]I$ in CH_2Cl_2 afforded a mixture of anionic carbonyl clusters such as $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_6(CO)_{18}]^-$ as identified by infrared and ^{1}H-NMR spectroscopies [1].

3.3. Synthesis of [H_4Ru_4(CO)_12]

$RuCl_3 \cdot nH_2O$ (40.88 wt.% Ru; 0.998 g, 4.038 mmol) was dissolved in ethylene glycol (250 ml) in a three necked flask equipped with a condenser and thermometer. CO (1 atm) was bubbled through the resulting dark brown solution for 5 min and than was allowed to flow only on the top of the condenser. The reaction mixture was heated under CO at 110 °C for 5 h. After cooling to 25 °C, Na_2CO_3 (0.639 g, 6.031 mmol; molar ratio Na_2CO_3:Ru = 3:2) was added and a mixture of $CO + H_2$ (molar ratio = 1:3; 1 atm) was allowed to flow on the top of the condenser. The solution was heated at 95 °C for 6–7 h. During the reaction a yellow precipitate of $[H_4Ru_4(CO)_{12}]$ was formed whereas, in parallel, some $[H_4Ru_4(CO)_{12}]$ sublimed on the cold walls of the condenser. Besides, in the ethylene glycol solution some $[H_3Ru_4(CO)_{12}]^-$ was present as confirmed by infrared spectroscopy. After 7 h, acidification of the ethylene glycol solution with aqueous (aq.) H_2SO_4 (up to pH = 1; ca. 5 ml) led to the precipitation of more $[H_4Ru_4(CO)_{12}]$. Successive extraction of the sublimate and the reaction mixture with dichloromethane (4 × 80 ml) at r.t., followed by evaporation to dryness of the dichloromethane phase, gave a yellow solid residue which was washed twice with water (2 × 10 ml) and then pentane (4 × 5 ml) affording spectroscopically pure $[H_4Ru_4(CO)_{12}]$ (0.550 g; 0.738 mmol; 73% yield).

3.4. Synthesis of [Ru_6C(CO)_16]^{2-}

$RuCl_3 \cdot nH_2O$ (41.2 wt.% Ru; 2.01 g, 8.17 mmol) was dissolved in ethylene glycol (550 ml) in a three necked flask equipped with a condenser and thermometer. CO

(1 atm) was bubbled through the resulting dark brown solution and the reaction mixture was heated under CO at 110 °C for 4 h. After cooling to r.t., K_2CO_3 (11.29 g, 81.73 mmol; molar ratio K_2CO_3:Ru = 10:1) was added and CO (1 atm) was bubbled through the resulting mixture. The solution was heated under CO at 160 °C for 8 h, then cooled to r.t. Repeated extraction under N_2 with a solution (3 × 200 ml) of [NBu$_4$]I (2.22 g, 6.03 mmol) in CH_2Cl_2 (600 ml) gave a dark red solution. A further extraction was carried out, till the CH_2Cl_2 phase was no longer colored, with 2 × 50 ml of [NBu$_4$]I (0.952 g, 2.58 mmol) in CH_2Cl_2 (100 ml). Evaporation of the combined CH_2Cl_2 solutions afforded an oily slurry that was washed with H_2O (3 × 50 ml) and pentane (2 × 20 ml) in order to obtain spectroscopically pure [NBu$_4$]$_2$[Ru$_6$C(CO)$_{16}$] as a red powder (1.73 g, 1.11 mmol, 82% yield). Yields vary slightly from preparation to preparation and are typically in the range 80–84%. Lower yields were obtained by working with higher concentrations.

Acknowledgements

References

[1] D. Roberto, E. Cariati, E. Lucenti, M. Respini, R. Ugo, Organometallics 16 (1997) 4531.

[2] D. Roberto, E. Cariati, R. Psaro, R. Ugo, Organometallics 13 (1994) 734.

[3] D. Roberto, E. Cariati, R. Ugo, R. Psaro, Inorg. Chem. 35 (1996) 2311.

[4] D. Roberto, R. Psaro, R. Ugo, Organometallics 12 (1993) 2292.

[5] C. Roveda, E. Cariati, E. Lucenti, D. Roberto, J. Organomet. Chem. 580 (1999) 117 (and references therein).

[6] E. Lucenti, D. Roberto, C. Roveda, R. Ugo, E. Cariati, J. Cluster Sci. 12 (2001) 113.

[7] Professor Peter Maitlis and Dr. Aurora Castro found that our previously reported synthesis in ethylene glycol of [Ru$_6$C(CO)$_{16}$]$^{2-}$ starting from RuCl$_3 \cdot n$H$_2$O was not reproducible and we confirmed the non-reproducibility of the synthesis not only of this anionic cluster but also that of [Ru$_3$(CO)$_{12}$] and [H$_4$Ru$_4$(CO)$_{12}$].

[8] D. Roberto, R. Psaro, R. Ugo, J. Organomet. Chem. 451 (1993) 123 (and references therein).

[9] (a) M. Faure, L. Maurette, B. Donnadieu, G. Lavigne, Angew. Chem. Int. Ed. 38 (1999) 518;
(b) A.F. Hill, Angew. Chem. Int. Ed. 39 (2000) 130.

[10] G. Lavigne, personal communication.