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New insight into a convenient base-promoted synthesis of $Ru_3(CO)_{12}$†

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The addition of two equivalents of KOH per Ru under 1 atm CO at 75 °C to a mixture of $[Ru(CO)_2Cl_2]_n$ and $[Ru(CO)_3Cl_2]_2$ generated *in situ* by carbonylation of 5 grams of $RuCl_3\cdot 3H_2O$ in 2-ethoxyethanol, triggers a reaction cascade producing $Ru_3(CO)_{12}$ in yields exceeding 90% within 45 minutes.

During the past 30 years, zinc has been used as a common reducing agent in one of the most widely developed low pressure synthetic routes to $Ru_3(CO)_{12}$.[1]

Thus, our report, in 1999,[2] that the same reaction could be performed much more rapidly and efficiently with KOH as the only "reducing" agent represented a significant conceptual advance.[3] The reaction was rationalized in terms of a reductive elimination of HCl from an elusive hydrido complex produced *via* de-carboxylation of the initial hydroxy-carbonyl adduct.[2]

Independently, interesting reports by Roberto and co-workers,[4] directly inspired by surface-mediated reactions,[5] indicated that a related reduction, albeit conducted on very small quantities of salt and requiring longer reaction times, could be obtained in ethylene glycol in the presence of alkali carbonates.

In our original procedure,[2] the need to use a very fast CO stream for efficiently releasing HCl was neither fully satisfactory from an ecological point of view, nor easy to obtain experimentally, thus sometimes requiring slightly more than one equivalent of base.[6]

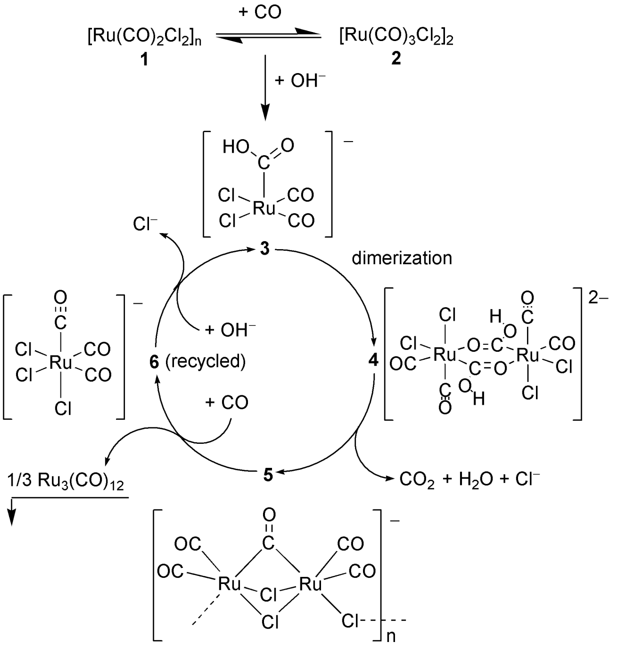
Later on,[7] it was found that under specific mild conditions, the incipient hydroxy-carbonyl adduct is spontaneously converted into a polymeric Ru(I) poly-anion whose CO-induced disproportionation ultimately produces equimolar amounts of Ru(II) and Ru(0) at 25 °C.[7] Clearly, the latter observation was revealing the existence of *a particularly low activation energy pathway*, possibly exploitable for producing $Ru_3(CO)_{12}$. This led us to develop the present modified synthesis, working within a lower temperature range than the previous one, and scaled up to convert 5 g of $RuCl_3\cdot 3H_2O$ into $Ru_3(CO)_{12}$ in 90% yield within less than 4 hours. As shown below, this new preparation follows a clear mechanistic pathway which can be fully rationalized in terms of elementary equations.

The first step of this one-pot synthesis involves minor modifications of the "classical" reduction of $RuCl_3\cdot 3H_2O$ in 2-ethoxyethanol under CO (1 atm) (eqn. 1).[8]

$$\mathrm{RuCl_3\cdot \mathit{n}H_2O} \xrightarrow[\text{2-ethoxyethanol}]{\text{CO}} \underset{\mathbf{1}}{[\mathrm{Ru(CO)_2Cl_2}]_n} \overset{\text{CO}}{\rightleftharpoons} \underset{\mathbf{2}}{[\mathrm{Ru(CO)_3Cl_2}]_2} \qquad (1)$$

In our new procedure requiring no specific precaution against moisture, the incidental formation of undesirable aqua monocarbonyl Ru species is systematically avoided in a simple way by performing the initial carbonylation step at moderate temperature (80 °C)[9] during the first hour, giving a dark blood red color that turns yellow within the next 45 minutes after the temperature is subsequently brought to reflux (135 °C).

Major modifications are found in the second step: the reaction cascade shown in Scheme 1 is triggered by direct addition of two equivalents of KOH pellets to the above solution kept at a working temperature strictly maintained at 75 °C under CO bubbling.



Scheme 1 Proposed mechanistic pathway for the production of $Ru_3(CO)_{12}$ at 75 °C in the presence of hydroxide ions.

We enter the cycle *via* instantaneous generation of a spectroscopically detectable 16e− hydroxyl-carbonyl adduct $[Ru(CO)_2Cl_2\{C(O)OH\}]^-$ (**3**) in equilibrium with a dimeric form $[Ru(CO)_2Cl_2\{C(O)OH\}]_2^{2-}$ (**4**) of unknown structure,[10] which rapidly de-carboxylates to give the previously isolated polymeric $Ru^{(I)}$ polyanion $\{[Ru_2(CO)_5Cl_3]^-\}_n$ (**5**) according to the global eqn. 2. Significantly, under such conditions, only *one* mole of CO_2 per dimeric Ru unit is produced.[7,11]

$$\underset{\mathbf{2}}{[\mathrm{Ru(CO)_3Cl_2}]_2} + 2\,\mathrm{OH^-} \longrightarrow \underset{\mathbf{5}}{[\mathrm{Ru_2(CO)_5Cl_3}]^-} + \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Cl^-} \qquad (2)$$

Then, a CO-induced disproportionation of the incipient $Ru^{(I)}$ species (eqn. 3) gives equimolar amounts of $Ru^{(II)}$, obtained exclusively under the form of the soluble anionic complex $[Ru(CO)_3Cl_3]^-$ (**6**) (detected by IR monitoring) and $Ru^{(0)}$, recovered as $Ru_3(CO)_{12}$, which readily precipitates.

$$\underset{\mathbf{5}}{[\mathrm{Ru_2(CO)_5Cl_3}]^-} + 2\,\mathrm{CO} \longrightarrow \underset{\mathbf{6}}{[\mathrm{Ru(CO)_3Cl_3}]^-} + 1/3\ \mathrm{Ru_3(CO)_{12}} \qquad (3)$$

The disproportionation occurring here is reminiscent of that observed by Fachinetti and co-workers for closely related Ru(I)

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† Electronic supplementary information (ESI) available: full details of the synthesis. See http://www.rsc.org/suppdata/cc/b3/b303884j/

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complexes $[Ru_2X_2(CO)_6]$ (X = CF_3COO^-) in the presence of an excess of trifluoroacetate.[12]

The anionic Ru(II) complex $[Ru(CO)_3Cl_3]^-$ (**6**) appearing in eqn. 3 is automatically recycled upon reaction with the second equivalent of hydroxide (Scheme 1), thus entering a new reduction–disproportionation cycle until total consumption of the base. The most spectacular point is that after reaction completion, the final solution is limpid and almost colorless, containing only KCl, whereas crystals of $Ru_3(CO)_{12}$ are deposited at the bottom of the flask.

In principle, the presence of an excess of hydroxide ions might be problematic if we consider that $Ru_3(CO)_{12}$ is also susceptible to being attacked according to eqn. 4.[13]

$$Ru_3(CO)_{12} + OH^- \rightarrow [Ru_3(\mu\text{-}H)(CO)_{11}]^- + CO_2 \qquad (4)$$

In reality, OH^- ions undergo highly preferential nucleophilic attack onto the electrophilic carbonyls of $K[Ru(CO)_3Cl_3]$ even in the presence of $Ru_3(CO)_{12}$ *below a critical temperature of 80 °C* (such a net discrimination is also favoured by the insolubility of $Ru_3(CO)_{12}$ in 2-ethoxyethanol), thus allowing the reaction to proceed cleanly to completion. Of course, any excess of OH^- that would be still present after total consumption of $Ru^{(II)}$ is susceptible to re-solubilize $Ru_3(CO)_{12}$ to produce the anionic complex $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ (characteristic violet colour). By chance, even in cases where this incidentally happens, recovery of $Ru_3(CO)_{12}$ is still possible. Indeed, $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ is a hydride transfer agent whose reaction with water in the presence of CO leads back to $Ru_3(CO)_{12}$ according to the water gas shift reaction (eqn. 5).[14]

$$[Ru_3(\mu\text{-}H)(CO)_{11}]^- + H_2O + CO \rightarrow Ru_3(CO)_{12} + H_2 + OH^- \qquad (5)$$

As shown in Scheme 1, water is inevitably present in the second reaction step since it is produced during the reduction of Ru(II) to Ru(I) (eqn. 2), thereby allowing the above reaction (eqn. 5) to take place, albeit at slower rate. Effectively, dark violet solutions incidentally obtained at the end of the above preparation due to an excess of base (and reflecting the presence of $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$) were seen to become clearer upon overnight treatment with CO at 25 °C, with concomitant recovery of $Ru_3(CO)_{12}$.

In conclusion, and in light of previous reports,[2,4,7] there is evidence to suggest that two mechanistic pathways are operative in the base-promoted reduction of carbonyl chlororuthenium(II) complexes, depending on the reaction conditions. If the thermally induced de-carboxylation of a mono-nuclear hydroxy-carbonyl intermediate is made to occur at relatively high temperature (>85 °C) and with one equivalent of base, further reductive elimination of HCl leads directly to $Ru^{(0)}$, as experimentally established earlier.[2] By contrast, at moderate temperature, dimerization of the hydroxy-carbonyl intermediate takes place prior to the de-carboxylation step, and then follows the reduction–disproportionation sequence described here, obviously requiring a second equivalent of base to recycle $Ru^{(II)}$.

While the performances of the present procedure are matching those of our original synthetic route[2] in terms of rapidity (both methods are much faster than high pressure methods[15]), this new synthetic strategy is more reliable and more efficient in practice than the previous one due to its technical simplicity and also to the fact that it works cleanly under unprecedented mild conditions, at which only a limited number of intermediate species are involved.

Successful attempts to extend the present observations to the reduction of carbonylchlororuthenium(II) complexes in the presence of ancillary ligands other than CO are underway.

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