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

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Electronic supplementary information.

Experimental procedure:

Chemicals: $RuCl_3$. $3H_2O$ (5 g; ca.19.1 mmol) (Johnson Matthey) - 250 mL of 2-ethoxyethanol (Fluka) taken directly from the bottle - KOH pellets (2.4 g. corresponding to 38.2 mmol, taking into account the fact that weighted KOH pellets commonly contain at least 10 % water) (RIEDEL, or any other label) - CO gas cylinder (Air Liquide, N20 grade).

Apparatus: Heating magnetic stirrer and oil bath - large (olive shaped) magnetic stirbar - three-necked round-bottomed 500 mL flask equipped with a reflux condenser the upper part of which is connected to a gas bubbler and a hose sending toxic vapors to the top of the hood. One lateral neck of the flask is equipped with a CO gas inlet consisting of a glass bubbler (steel needles are not convenient) of sufficiently large diameter (2-3 mm) to avoid clogging by accumulation of solid $Ru_3(CO)_{12}$. The second lateral neck is used to introduce KOH pellets in the second reaction step (vide infra).

Step I . Reduction of $Ru^{(III)}$ to $Ru^{(II)}$

5 g of $RuCl_3$, $3H_2O$, and 250 mL of 2-ethoxyethanol are introduced into the flask. The solution is first simply de-aerated by bubbling nitrogen or by stirring under reduced atmosphere for a few minutes. The flask is then connected to the reflux condenser, whereupon the CO gas inlet is introduced. A fast CO stream (ca. 2 bubbles per second) and a vigorous agitation are needed in this first reduction step. The temperature is first raised to 80°C for 45 minutes, during which the colour progressively turns blood red. It is then increased up to 135°C (reflux) for 30/45 minutes, until a perfectly limpid *golden yellow solution* is obtained. At that stage, the temperature of the bath is allowed to cool down to 75°C and regulated prior to the beginning of the second step.

Note: The yellow solution exhibits a three band pattern ν(CO) = 2135.5 m, 2063.6 s, 1992.9 m, cm^{-1} corresponding to the overlap of the characteristic bands of the polymeric $[Ru(CO)_2Cl_2]_n$ (IR ν (CO) = 2063s; 1993s) and dimeric $[Ru(CO)_3Cl_2]_2$ (IR ν (CO) = 2135s; 2065s). The equilibrium cannot be displaced toward the formation of the tri-carbonyl at high temperature (total conversion to the latter is observed only after prolonged (overnight) treatment with CO at room temperature). However, this is not required in the present preparation since CO uptake by the di-carbonyl species becomes very fast as soon as the hydroxide ions are added (in step II below).

Step II: Overall reduction of $Ru^{(II)}$ to $Ru^{(0)}$.

A strict temperature control is required here: the temperature of the bath should be stabilized around 75-80°C, and should remain below 85°C to avoid (i) competing de-carboxylation from the mononuclear hydroxyl-carbonyl (see main text) and (ii) further attack of hydroxide onto $Ru_3(CO)_{12}$. The rate of CO bubbling may be reduced to ca. 1 bubble per second. KOH pellets (2.4 g) are then added directly into the solution (at 75°C) via the lateral neck of the flask (cautiously opened under the hood for just a few seconds). A progressive darkening of the solution is then observed over the next 15 minutes after which the orange crystalline $Ru_3(CO)_{12}$ begins to appear on the walls of the glassware. After a total time of 45 minutes, the heater is stopped, but CO bubbling and a moderate magnetic stirring are maintained. Keeping the flask in the oil bath at that stage allows to ensure a very slow cooling down to room temperature during the crystallization of $Ru_3(CO)_{12}$, which occurs particularly efficiently between 70 and 50°C and is accompanied by a significant lightening of the initial brown colour. A limpid and *almost colourless* solution is obtained at the end.

Since $Ru_3(CO)_{12}$ is totally insoluble in 2-ethoxyethanol, its characteristic IR absorption bands (ν (CO) = 2060 vs, 2030 s, 2011w cm^{-1}) neither appear at intermediate stage nor in the final solution spectrum, which generally shows only small amounts of the residual anionic $Ru^{(II)}$ complex $[Ru(CO)_3Cl_3]^-$ (ν (CO) = 2126 m; 2048 s cm^{-1}) and possibly also trace amounts of a soluble minor complex, previously identified as the known di-anionic $Ru^{(I)}$ oxo derivative $[Ru_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4(CO)_{10}]^{2-}$ (ν (CO) = 2014s; 1939m, 1733 w cm^{-1}) reflecting the presence of traces of water.

Crystals of $Ru_3(CO)_{12}$ are perfectly air stable. They can be easily recovered by filtration on a frit after venting cautiously the solution under nitrogen for a few minutes to evacuate CO. They generally need to be washed with alcohol and/or water to remove traces of KCl, the only side product of this reaction. Alternatively, a rapid chromatographic workup of the crude product $Ru_3(CO)_{12}$ (solubilized in 300-400 mL of dichloromethane) on a silicagel column, using dichloromethane as the eluent, is the best way to eliminate KCl, which is retained at the top of the column. After solvent evaporation under reduced pressure, the crystals are subsequently dried under vacuum and weighted (ca. 3.9 g; 6.1 mmol; 96 %).

Safety precautions: CO gas and phosgene (the latter may be formed as a volatile by-product in the first step) are highly toxic ! Caution must be exercised and all manipulations must be carried out in a highly efficient fume cupboard.