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An Improved Reaction Vessel for the Synthesis of $[Rh(CO)_2Cl]_2$

Di-μ-chlorotetracarbonyl dirhodium has been used frequently in the preparation of oxide-supported rhodium heterogeneous catalysts. Although the rhodium carbonyl dimer is commercially available, many researchers, because of cost or availability considerations, continue to synthesize the compound from $RhCl_3 \cdot XH_2O$ ($X = 3$–4) according to the reaction:

$$2RhCl_3 \cdot XH_2O + 6CO \xrightarrow[100°C]{1\ atm} [Rh(CO)_2Cl]_2 + 2XH_2O + 2COCl_2.$$

The apparatus described by McCleverty and Wilkinson (*1*) for the reductive carbonylation of $RhCl_3 \cdot XH_2O$ is shown in Fig. 1a. In this simple design, the water released during the reaction condenses at the upper end of the vessel. Failure to periodically remove the condensation allows the water to flow down the reaction vessel and decompose the nascent dimer, resulting in poor yields and impure product. However, this water removal can be tedious and time consuming. As a benefit to other catalysis researchers utilizing this important compound, we report here a modification to the basic design which alleviates this problem.

The modified vessel, shown in Fig. 1b, includes an interior enclosure which traps the subliming dimer, fosters its crystal growth, and excludes condensed water. The procedure for the use of the modified apparatus is as follows.

The solid crystalline $RhCl_3 \cdot XH_2O$ is introduced through the restricted mouth of the interior enclosure with the aid of a long-stem powder funnel. The crystals are distributed evenly over the surface of the medium fritted disk (D) by gently tapping the sides of the apparatus. The vessel is lowered into a carefully regulated 100°C oil bath, such that the liquid level reaches the ring seal (C). The flow rate of the carbon monoxide, introduced at (A), is adjusted during the initial phase of the synthesis to allow the $[Rh(CO)_2Cl]_2$ formed to sublime and condense within the interior enclosure. With an ideal flow rate established, beautiful red needles of the dimer will grow at the shoulder (E). The water liberated in the reaction condenses near the base of the \$ 45/50 joint. If it runs down the interior of the vessel, it is rendered innocuous, as it is trapped between the exterior wall of the inner enclosure and the interior wall of the outer enclosure (F). Any water remaining in the vessel can be conveniently removed after completion of the reaction. As with the apparatus suggested by McCleverty and Wilkinson, the effluvium from the reaction, containing phosgene and unreacted CO, is carried out of the vessel from (B) to a bub-

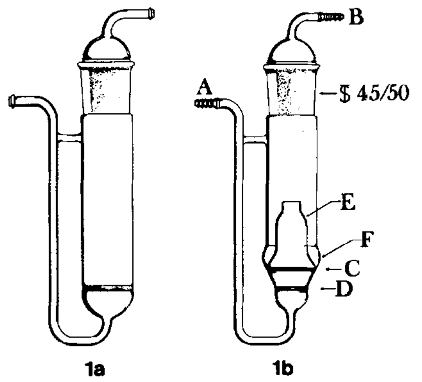

FIG. 1. (a) Apparatus designed by McCleverty and Wilkinson for the reductive carbonylation of $RhCl_3 \cdot XH_2O$. (b) An improved reaction vessel for the synthesis of $[Rh(CO)_2Cl]_2$. The apparatus is drawn to scale with the medium fritted disk diameter equal to 30 mm.

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bler and subsequently discharged into an exhaust system. Upon completion of the reaction, the dimer can be collected as dark-red needles and any residue retrieved by dissolution. A solvent such as *n*-hexane, introduced through a long-stem funnel into the interior enclosure, will dissolve the residual dimer to the exclusion of unreactive anhydrous $RhCl_3$, which is usually present. The solution can then be forced through the fritted glass filter, with CO or N_2 introduced from the top, and collected at the end of the gas delivery tube (A).

With frequent periodic removal of the condensed water, with absorbent cotton, from the upper section of the earlier-design vessel, a 96% yield was obtained by McCleverty and Wilkinson. However, utilizing their procedure and apparatus, our yields were usually lower (~90%), and we found the potential water contamination bothersome. With the modified vessel, quantitative yields are routine and its principal advantages are convenience in use and improved crystal growth and purity.

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