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Rapid and mild synthesis of $[Re_2(CO)_{10}]$ by reduction of $[NH_4][ReO_4]$ at atmospheric CO pressure†

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With a view to accessing radiopharmaceuticals based on ^{186}Re and ^{188}Re, a simple, efficient and rapid synthesis at low CO pressure of the key complex $[Re_2(CO)_{10}]$ from $[NH_4][ReO_4]$ using $(Me_2CHCH_2)_2AlH$ in toluene as reducing agent has been obtained.

Owing to the nearly ideal properties of certain of their isotopes, the chemistry of chelates of technetium(v) and rhenium(v) is of considerable current interest with respect to accessing selective inorganic radiopharmaceuticals for use in imaging and therapy.[1]

Recently,[2] it has been suggested that organometallic complexes of rhenium(i) could provide valuable alternatives for use as radiopharmaceutical species. The key intermediate for the synthesis of organometallic radiopharmaceuticals is $[M_2(CO)_{10}]$ (M = Tc or Re). For example, $[Re_2(CO)_{10}]$ provides easy access to $[ReX(CO)_5]$ and $[Re(CO)_3(C_5H_5)]$ in good yields.[3] Unfortunately, all reported syntheses of $[Re_2(CO)_{10}]$ or $[Tc_2(CO)_{10}]$ from ammonium pertechnetate or perrhenate require elevated temperatures, long reaction times (up to 2 d) and potentially dangerous elevated pressures, of CO (100–300 atm).[4] Owing to the unsuitability of these methods for accessing organometallic radiopharmaceuticals, it is thus necessary to re-examine the synthesis of $[Re_2(CO)_{10}]$ (Tc chemistry is in general similar to that of Re) with three aims: high yield, low pressures of CO for safety reasons and ease of operation, and short reaction times for compatibility with the use of the radioactive products. Moreover, the procedure must be adaptable to a scale of milligrams or even less.

We have found a new reaction which satisfies all these aims, namely the reduction of ammonium perrhenate by diisobutylaluminium hydride in the presence of gaseous carbon monoxide, equation (1).‡

$$[NH_4][ReO_4] \xrightarrow[\substack{(Me_2CHCH_2)_2AlH,\ C_6H_5Me \\ 70\text{–}80\ ^\circ C}]{CO\ (1\ atm)} \underset{62\%}{\tfrac{1}{2}[Re_2(CO)_{10}]} \qquad (1)$$

The choice of $[NH_4][ReO_4]$ as substrate is dictated because of its availability in both 'cold' and radioactive forms. We have found that in this three-phase reaction (solid, liquid, gas) $[Re_2(CO)_{10}]$ can be prepared with a yield of 62% isolated product. Optimisation of reaction conditions, which involves three reacting species in three different phases, is crucial. Nevertheless, the reaction is perfectly reproducible if the following points are taken into account. (*a*) The choice of solvent is important. It must have a significant solubility for CO and the boiling point must allow heating for both activation and easy removal of solvent at the end of the reaction. Toluene is an excellent choice; the solubility of CO at 1 atm at 25 °C is 7.59×10^{-3} mol l^{-1} and its boiling point is 111 °C. (*b*) The best temperature is 70–80 °C. To optimise contact between the three phases, a CO circulation pump is used with a gas bubbler immersed in the solution. It is also necessary to saturate the solvent with CO before reaction and to finely powder the $[NH_4][ReO_4]$. Addition of the reducing agent must be slow. After work-up, $[Re_2(CO)_{10}]$ is recovered in 62% yield by recrystallisation. Small quantities of clusters such as $[Re_3H_3(CO)_{12}]$ may also be detected in the crude reaction product.

The reaction may be reduced in scale to 10 mg of $[NH_4][ReO_4]$ with an increased yield of $[Re_2(CO)_{10}]$ (72%). Furthermore, the photochemical reaction of $[Re_2(CO)_{10}]$ with cyclopentadiene leads rapidly (2 h) to $[Re(CO)_3(C_5H_5)]$ in 98% yield. It is also possible, by using the known thermal reaction,[3b] to prepare $[Re(CO)_3(C_5H_5)]$ in a one-pot synthesis in 58% yield starting from $[NH_4][ReO_4]$. The complex $[ReBr(CO)_5]$ may be similarly prepared by addition of Br_2 to the crude reaction product.

We thus have available a rapid, efficient and mild synthesis of an important organometallic complex of Re^0 of general interest, derived from a Re^{VII} precursor which is easily accessible in radioactive form. We hope that this reaction, which should be easily extended to the Tc series, will greatly enhance progress in the area of organometallic radiopharmaceuticals.

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† *Non-SI unit employed:* atm = 101 325 Pa.

‡ Synthesis of $[Re_2(CO)_{10}]$. Finely powdered $[NH_4][ReO_4]$ (0.134 g, 0.5 mmol) was placed in a Schlenk tube equipped with a dropping funnel and a gas bubbler linked to a circulation pump and connected to a gas reservoir. Dry toluene (17 cm^3) was added and the mixture heated at 70–80 °C for 1 h with magnetic stirring. The pump was started 30 min after heating began to circulate CO and to saturate the solution. Diisobutylaluminium hydride (5 cm^3 of a 1 mol dm^{-3} solution in toluene) was added dropwise (1 drop every 30–50 s). After complete addition, the dark brown solution was stirred for 1–2 h at 70–80 °C. After cooling, the CO was removed by flushing with argon, methanol (5 cm^3) was added to neutralise the excess reducing agent, and toluene was removed under vacuum. The crude product was dissolved in diethyl ether, filtered through a layer of silica gel and evaporated to dryness. The infrared spectrum in CH_2Cl_2 shows the presence of $[Re_2(CO)_{10}]$ (three strong bands at 2069, 2011 and 1969 cm^{-1}) as the major product as well as a small quantity of $[Re_3H_3(CO)_{12}]$. The complex $[Re_2(CO)_{10}]$ was extracted from the crude product with hot pentane. White crystals of $[Re_2(CO)_{10}]$ were obtained by slow evaporation of the clear yellow solution in air. The mother-liquor was chromatographed on a silica gel plate using pentane as eluent to recover the remaining $[Re_2(CO)_{10}]$. A total yield of 101 mg of $[Re_2(CO)_{10}]$ was obtained (62%, m.p. 177 °C). Physical characteristics were identical with those previously reported.

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