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An Improved and Convenient Synthesis of the Osmium(II) Carbonyl Chlorides $Os(CO)_4Cl_2$ and $[Os(CO)_3Cl_2]_2$

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Metal carbonyl halides are convenient starting materials for the synthesis of a series of metal complexes with a great variety of different ligands. Although convenient and high-yield syntheses of carbonyl halides of the majority of transition metals are known [1], the synthesis of Os(II) carbonyl halides (*e.g.* $Os(CO)_4X_2$ and $[Os(CO)_3X_2]_2$, where X = halogen) are not so well reported in the literature.

Early works described the direct carbonylation of osmium halides, under different conditions of pressures and at different temperatures [2, 3]. More recently Hales and Irving re-investigated the direct carbonylation under pressure of $OsCl_3 \cdot nH_2O$ [4, 5]: they reported that the only compound which could be isolated in good yields was the dimer $[Os(CO)_3Cl_2]_2$. The related monomeric *cis*-$Os(CO)_4Cl_2$ compound was obtained in high yields only by reaction at room temperature of CCl_4 with $H_2Os(CO)_4$; this latter bis hydrido complex is produced under rather difficult conditions [6].

We report here an easy, convenient and reproducible synthesis of *cis*-$Os(CO)_4Cl_2$ and its quantitative conversion to $[Os(CO)_3Cl_2]_2$.

Experimental

Osmium trichloride (anhydrous) was purchased from Aldrich. The infrared spectra were recorded on a Nicolet MX-1 spectrophotometer, operating in the F.T. mode.

The high pressure reactions were carried out in a 200-ml stainless steel autoclave heated in a thermostatted oven.

Cis-*Dichlorotetracarbonylosmium*

(a) Anhydrous osmium trichloride (422 mg, 1.142 mmol) was introduced into the autoclave, which was evacuated and carbon monoxide (65 atmospheres) was pumped in. The temperature was then raised to 155 °C and this temperature was maintained for 22 hours. After cooling at room temperature, the gases were vented and a white crystalline powder corresponding to $Os(CO)_4Cl_2$, containing some traces of a black powder, was recovered.

This sample was usually sufficiently pure for further reactions, but a complete purification may be carried out by sublimation at 110 °C under vacuum (10^{-2} mmHg). The yield of the sublimed compound is usually about 60% (310 mg, 0.835 mmol).

Elemental analysis, mass and infrared spectra (see Table I) are in agreement with the formulation as *cis*-dichlorotetracarbonylosmium either before or after sublimation. *Anal.*: Calcd. for $Os(CO)_4Cl_2$ C, 12.88; H, 0.00. Found: C, 12.95; H, 0.00.

b) In another experiment, osmium trichloride was carbonylated with carbon monoxide (80 atmospheres) at 165 °C for 24 hours. The yields are increased to about 80% but the product is not so pure, since it contains a small percentage (10–15%) of the dimeric complex $[Os(CO)_3Cl_2]_2$, as confirmed by elemental analysis, mass and infrared spectra. The purification by sublimation at 110 °C under vacuum gives the more volatile, pure monomeric complex.

TABLE I. Infrared Absorption Frequencies (cm^{-1}) of *cis*-$Os(CO)_4Cl_2$.

$\nu(CO)^a$	$\nu(Os–C)$ and $\delta(Os–C–O)^{b,c}$	$\nu(Os–Cl)^b$	Ref.
2184 w, 2118 vs, 2091 s, 2051 vs	619 sh, 595 s, 567 s, 548 ms, 502 m, 494 m, 471 w, 453 m, 402 m	327 s 303 s	This work
2187 w, 2119 vs, 2092 s, 2051 s	–	–	[6]
–	452 m	328 m 298 m	[9]

$^a CCl_4$ solution. ^{b}Polythene pellet (this work), nujol mull between polythene discs (ref. 9). ^{c}This is the time in which these stretching frequencies are fully reported.

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Bis-Dichlorotricarbonylosmium

Dichlorotetracarbonylosmium (240 mg, 0.643 mmol), prepared according to procedure (a), was dissolved in chloroform and the solution was heated under reflux. The conversion reaction was followed by infrared spectroscopy. After 1–2 hours the monomeric complex was quantitatively transformed into the dimeric complex; the same reaction occurs more slowly at room temperature.

From the chloroform solution, the pure white compound $[Os(CO)_3Cl_2]_2$ (0.216 mg, 0.312 mmol) was obtained by crystallization with n-pentane; the yields are usually in the range 90–97%. The compound was characterised by mass and infrared spectra.

Results and Discussion

Our work clarifies the contradictory results of some early reports since for the direct carbonylation under pressure of $OsCl_3$ different groups reported the formation of a mixture of *cis*-$Os(CO)_4Cl_2$ and $[Os(CO)_3Cl_2]_2$ [2, 3] or the synthesis of pure $[Os(CO)_3Cl_2]_2$ [4, 5]. We have defined reaction conditions at which only *cis*-$Os(CO)_4Cl_2$ is formed; the dimer begins to be produced as a secondary product only under more drastic conditions. Moreover our yields are higher than those previously reported by other authors.

In addition we have found that *cis*-$Os(CO)_4Cl_2$ can easily be separated from $[Os(CO)_3Cl_2]_2$ by simple sublimation under well-defined conditions at which we did not observe relevant thermal transformation of $Os(CO)_4Cl_2$ into $[Os(CO)_3Cl_2]_2$.

Our method of synthesis of *cis*-$Os(CO)_4Cl_2$ is not only simpler but also more convenient than the previous method, which requires $H_2Os(CO)_4$ as starting material [6].

Finally the facile transformation of *cis*-$Os(CO)_4Cl_2$ into $[Os(CO)_3Cl_2]_2$, that we have reported here, gives a very convenient method of preparation of this dimeric product. Earlier syntheses were based on the carbonylation with formic acid in solution of $OsCl_3$ (low yields) [7] or the reaction in a sealed tube, heated at 170 °C for 40 hours, of a mixture of $Os_3(CO)_{12}$ and HCl dissolved in cyclohexane (yields about 80% after purification) [8]. Obviously our method of synthesis gives not only higher yields but is considerably more simple than alternative methods.

In conclusion we have reported synthetic methods which make easily available Os(II) carbonyl chlorides, which can be useful starting materials for the synthesis of many osmium compounds, some of which have not yet been investigated [10].

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