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Preliminary communication

NEW SYNTHESIS OF HEXAMETHYLTUNGSTEN(VI); HEXAMETHYLRHENIUM(VI) AND DIOXOTRIMETHYLRHENIUM(VII)

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Summary

A new synthesis of hexamethyltungsten involves the reaction of WCl_6 and $AlMe_3$, while interaction of $AlMe_3$ and $ReOMe_4$ gives $ReMe_6$; a dioxorhenium(VII) methyl, ReO_2Me_3, is reported.

The synthesis of hexamethyltungsten [1] by the interaction of methyllithium and tungsten hexachloride in diethyl ether involves a complex series of reactions. We understand that other workers have experienced considerable difficulty in repeating this preparation; we are not surprised as it appears that adventitious oxygen is required.

We can now make the compound in multigram quantities by the interaction of tungsten hexachloride and trimethylaluminium in petroleum ether at —70° (eqn. 1).

$$WCl_6 + 6Me_3Al \rightarrow WMe_6 + 6Me_2ClAl \qquad (1)$$

The separation of WMe_6 from Me_2ClAl is difficult due to the relative instability of the former, but the latter can be removed by treatment with trimethylamine, quinoline or similar bases. After removal of the aluminium complexes and solvent, WMe_6 can be purified by vacuum sublimation.

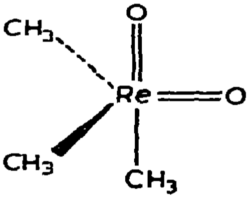
CAUTION: *Hexamethyltungsten must be handled with very great care and must be treated as potentially explosive.* We have had several unexplained explosions with the compound that caused serious damage.

The synthesis of large quantities of WMe_6 has allowed spectroscopic properties and reactions of the compound to be studied in more detail than was possible previously when amounts of only a few hundred milligrams could normally be obtained; these will be described elsewhere.

The failure to obtain WMe_6 by use of excess methyllithium was attributed to the formation of a lithium tungsten methylate salt [1]. The latter has now been isolated from interaction of LiMe and WMe_6 in diethyl ether as its dioxanate and shown to be $Li_2[WMe_8]\cdot 2C_4H_8O_2$ by elemental analysis, NMR and acid decomposition to give methane.

The use of trimethylaluminium has also allowed us to prepare hexamethylrhenium by interaction with oxotetramethylrhenium, $ReOMe_4$ [2]. In this case, the excess alkylaluminium can be removed by careful treatment with water. The green, crystalline, volatile $ReMe_6$ is paramagnetic, d^1, and is reasonably stable at 25° (mass spectrum, $ReMe_6^+$ (M^+), 275, 277).

Interaction of oxotetramethylrhenium(VI) with nitric oxide produces a yellow, crystalline solid, m.p. ca. 10°, shown to be *cis*-dioxotrimethylrhenium(I), the first example of a Re^{VII} alkyl. The compound is diamagnetic and five-coordinate.



(I)

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References

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2 K. Mertis and G. Wilkinson, Chem. Commun., (1974) 93.