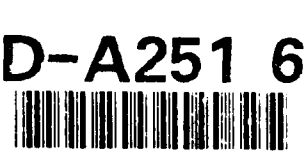

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A new reduction method for the preparation of the molybdenum halides $MoCl_3(THF)_3$ and $MoCl_4(THF)_2$ in high yield and with high purity directly from $MoCl_5$ is described. The preparation of pure starting materials is crucial to the success of the subsequent chemical reduction. Reduction of $MoCl_3(THF)_3$, $MoCl_4(THF)_2$ or $WCl_4$ in THF with $LiBEt_3H$ at room temperature did not result in formation of Mo and W as anticipated but instead resulted in formation of nanophase $M_2C$ M = Mo and W binary metal carbides. These species were characterized by SEM, TEM, energy dispersive spectroscopy, electron diffraction, elemental analysis, thermogravimetric analysis and X-ray diffraction. These techniques showed the black solids were crystalline and comprised 1-2 nm sized crystallites which could be grown by heating to higher temperatures (450 - 500°C). The solids isolated from these experiments could be redispersed in THF to form colloidal black solutions.

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# FORMATION OF HIGHLY DISPERSED METAL CARBIDES, $M_2C$ (M=Mo,W) VIA CHEMICAL REDUCTION METHODS

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## ABSTRACT

A new reduction method for the preparation of the molybdenum halides $MoCl_3(THF)_3$ and $MoCl_4(THF)_2$ in high yield and with high purity directly from $MoCl_5$ is described. The preparation of pure starting materials is crucial to the success of the subsequent chemical reduction. Reduction of $MoCl_3(THF)_3$, $MoCl_4(THF)_2$ or $WCl_4$ in THF with $LiBEt_3H$ at room temperature did not result in formation of Mo and W as anticipated but instead resulted in formation of nanophase $M_2C$ M = Mo and W binary metal carbides. These species were characterized by SEM, TEM, energy dispersive spectroscopy, electron diffraction, elemental analysis, thermogravimetric analysis and X-ray diffraction techniques. These techniques showed the black solids were crystalline and comprised 1-2 nm sized crystallites which could be grown by heating to higher temperatures (450 - 500°C). The solids isolated from these experiments could be redispersed in THF to form colloidal black solutions.

## INTRODUCTION

In the previous paper, the chemical reduction of a rhodium(I) compound to form 2 nm sized crystalline rhodium(0) colloids was described. This result is consistent with that described in the literature for the general reduction of metal salts with $LiBEt_3H$, where Bonnemann et al.[1,2] have shown that trialkylborohydride reducing agents can be used to reduce a variety of metal complexes to form the corresponding metal colloids. The metals are reasonably pure (70% - 98%), the particle size was approximately 10-100nm and generally crystalline materials were formed depending on the specific system as determined by X-ray diffraction. In this work, we report the reduction of $MoCl_3(THF)_3$, $MoCl_4(THF)_2$ and $WCl_4$ in THF with $LiBEt_3H$, which does not result in the formation of the corresponding metal particles as anticipated but rather resulted in the formation of the nanophase binary metal carbides $M_2C$, M = Mo, W. These materials comprise a class of interstitial metal carbides which are generally prepared under much more forcing conditions including high temperature ( > 1200°C) reduction of the corresponding metal oxide[3-6] or halide[7] or ball-milling mixtures of elemental powders for extended periods at lower

temperatures.[8,9] The method described here represents a high yield, low-temperature alternative that results in formation of crystalline particles smaller than those prepared by any other technique.

## RESULTS AND DISCUSSION

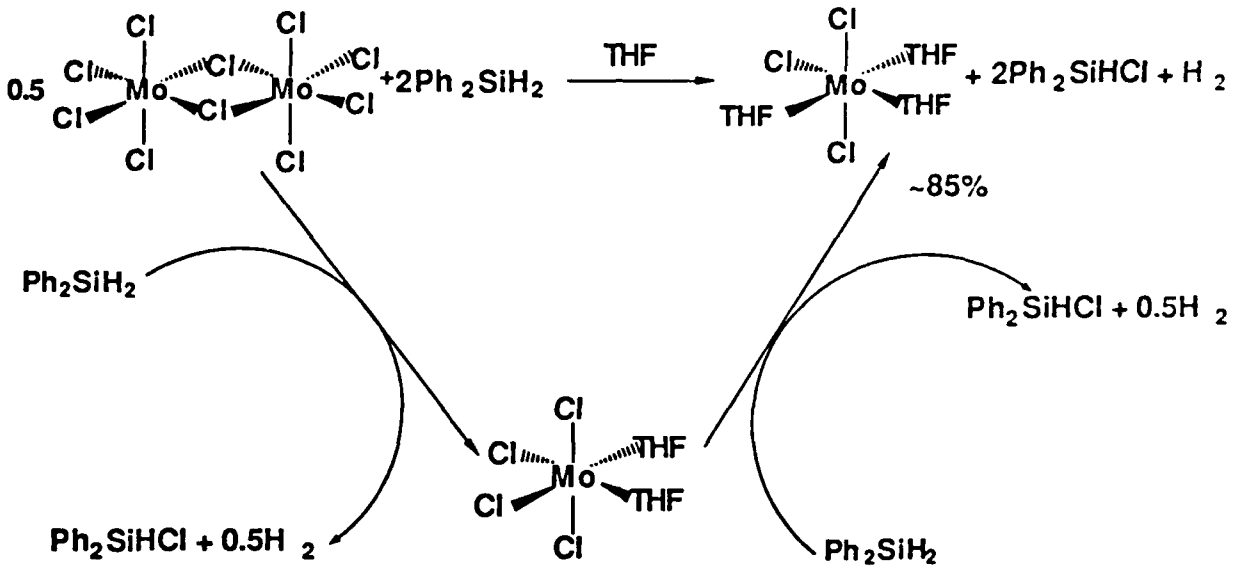
Initial studies focused on the development of new high yield routes for the preparation of high purity $MoCl_3(THF)_3$ as a precursor for the reduction with $LiBEt_3H$. We have found that the literature methods for the formation of this species, which involve the tin reduction of $MoCl_4(THF)_2$ result in contamination of the final product (after $LiBEt_3H$ reduction) with tin.[10] Direct reduction of $MoCl_5$ with diphenylsilane in THF produced $MoCl_3(THF)_3$ in high yield (85%) based on $MoCl_5$ as described by equation 1.[11]

$$MoCl_5 + 2\ Ph_2SiH_2 \text{ --THF--> } MoCl_3(THF)_3 + 2\ Ph_2SiHCl + H_2 \qquad (1)$$

The $MoCl_3(THF)_3$ formed was separated by filtration and purified by washing with THF to remove all the silicon containing by-products. The silicon products were isolated by evaporating the solvents from the washings *in vacuo*. Both $^1H$ NMR and $^{29}Si$ NMR show that $Ph_2SiHCl$ is the main silicon component. During this experiment, a yellow solid was observed as an intermediate during the early stages of the reaction. An IR spectrum of this yellow solid, showed a strong absorption at 810 $cm^{-1}$, consistent with formation of $MoCl_4(THF)_2$. An experiment in which one equivalent of $Ph_2SiH_2$ was reacted with $MoCl_5$ resulted in formation of $MoCl_4(THF)_2$, as shown in equation 2 below.

$$MoCl_5 + Ph_2SiH_2 \text{ --THF--> } MoCl_4(THF)_2 + Ph_2SiHCl + 1/2\ H_2 \qquad (2)$$

The yellow product formed was easily separated by filtration and washed with THF. The identity of $MoCl_4(THF)_2$ was confirmed by IR spectroscopy and elemental analysis. The silicon containing products were analyzed by $^1H$ and $^{29}Si$ NMR spectroscopy and revealed the presence of $Ph_2SiHCl$ as the only by-product. The reactions are summarized in Scheme 1.




Scheme 1

The reduction of THF suspensions of $MoCl_4(thf)_2$, $MoCl_3(THF)_3$ and $WCl_4$ at -10°C with a slight excess of the stoichiometric amount of $LiBEt_3H$ resulted in the formation of a black solution accompanied by gas evolution. After stirring for 24hr., the colloidal solutions generally aggregated and black powders could be isolated by centrifugation. Under some conditions, the black powders could be isolated and redispersed in THF to give black colloidal solutions. For $WCl_4$, the black powder isolated had a particle size of approximately 1-2μm (SEM) and contained only W by energy dispersive spectroscopy. Closer examination by transmission electron microscopy revealed that the 1-2μm sized particles were agglomerates of smaller, 2nm sized particles. Energy dispersive spectroscopy revealed only W and electron diffraction revealed a diffuse ring at a d-spacing corresponding to ~2.3Å, consistent with the very broad peak observed for the same sample by X-ray powder diffraction. The broadening observed by X-ray diffraction is consistent with the particle size observed by TEM. Unfortunately, due to the broadness of the X-ray diffraction peak and the similarity between the crystal structures of W and $W_2C$, a distinction between these species could not be made at this stage. To distinguish these two possibilities, the sample was sintered at a number of different temperatures, *in vacuo*, to increase the size of the crystallites. On heating to 450°C, the X-ray diffraction pattern sharpened and corresponded to that of $W_2C$. No evidence for W was observed. Similar observations were made for the formation of $Mo_2C$ from $MoCl_3(THF)_3$ and $MoCl_4(THF)_2$. The X-ray diffraction data for as-prepared $Mo_2C$ at room temperature and after heating to 500°C *in vacuo* are presented in Figure 1.

Higher temperature (750°C) sintering of $Mo_2C$ at $10^{-2}$ torr resulted in partial oxidation to form traces of crystalline Mo, $MoO_2$, as determined by X-ray diffraction, and presumably $CO_2$. Thermogravimetric analysis in air quantitatively confirmed this oxidation to $MoO_2$ via an observed weight gain of 25% (calculated, 26%) as shown in Figure 2.

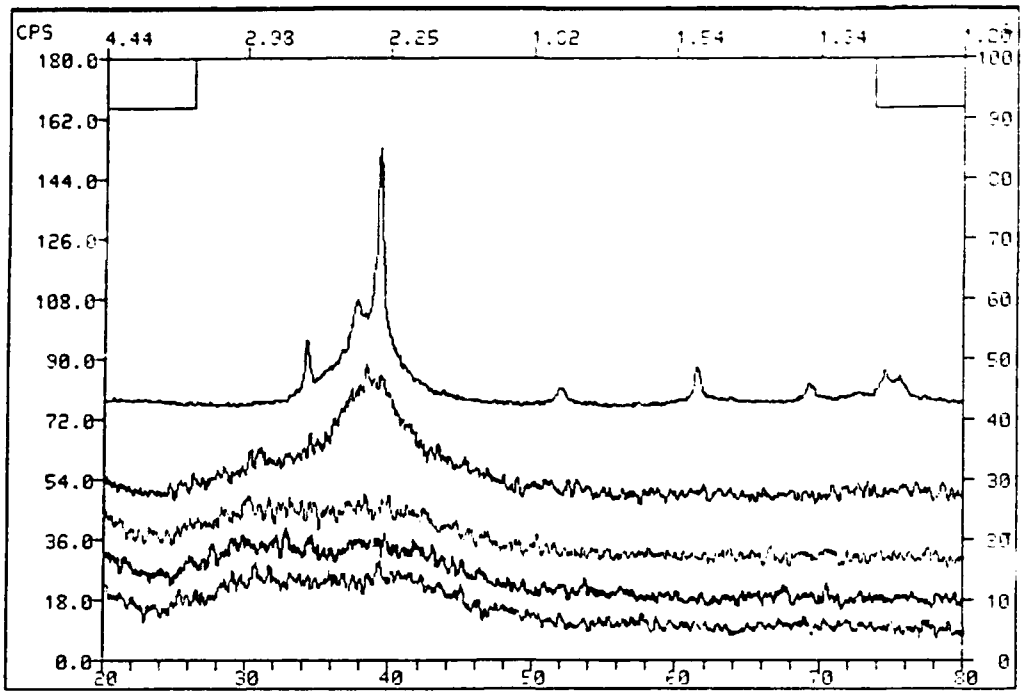



Figure 1: Variable temperature X-ray diffraction data showing the crystallization behavior of $Mo_2C$. From bottom to top, 100°C, 200°C, 300°C, 400°C, 500°C.

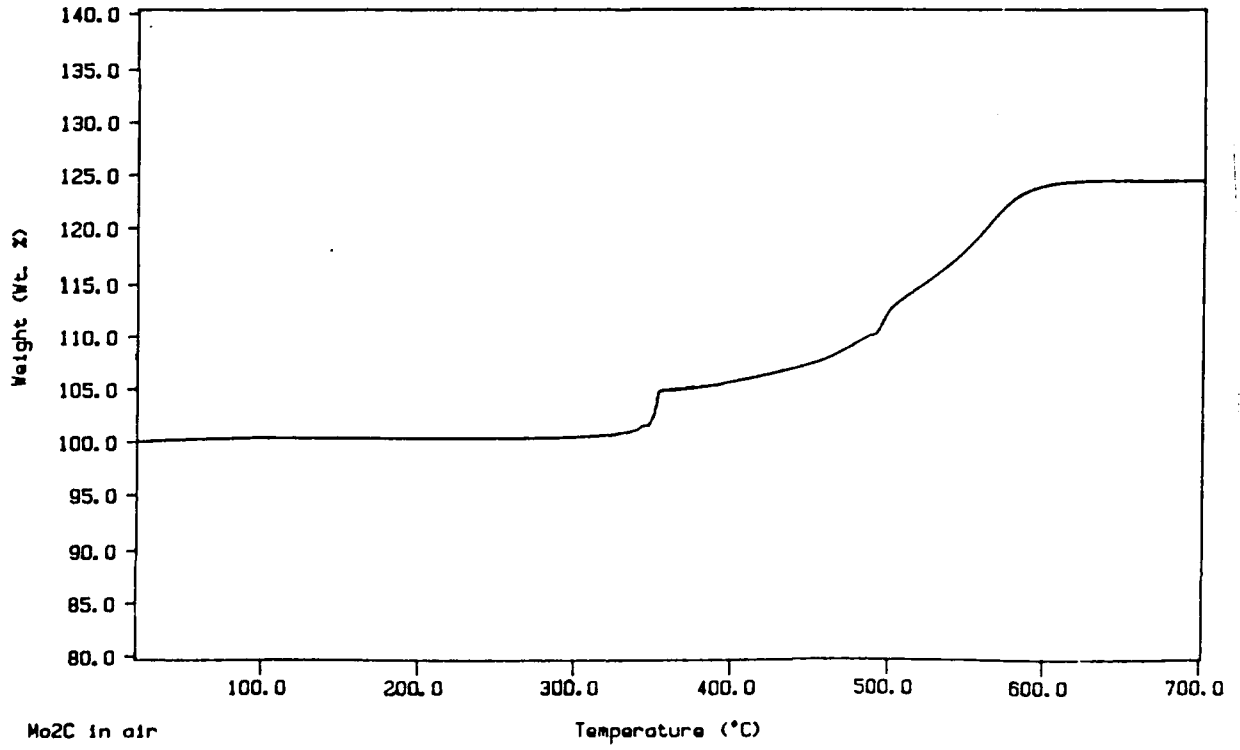



Figure 2: Thermogravimetric analysis of $Mo_2C$ showing a weight increase corresponding to the formation of $MoO_2$ and $CO_2$.

## CONCLUSIONS

These data show that crystalline metal carbide phases can be formed by chemical reduction of molybdenum and tungsten halides, $MoCl_4(THF)_2$, $MoCl_3(THF)_3$ and $WCl_4$ at room temperature with $LiBEt_3H$ in THF solution. The origin of the carbide is not known at this stage, but we speculate that it is more likely to be derived from the reducing agent than from the solvent. Further studies are in progress to investigate the generality of these reactions.

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