A minor product in the reaction between W₂(NMe₂)₆ and neopentanol in hydrocarbon solvents has been isolated and characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy and a single crystal X-ray study. At -174°C, a = 11.669(1) Å, b = 25.801(5) Å, c = 24.345(4) Å, β = 100.91(1)°, Z = 4, dcalc = 1.60 g cm⁻³, and space group P2₁/c. The compound is formulated as W₄(µ₄-C)(NMe)(OCH₂Bu')₁₁(H). There is a W₄-butterfly and the carbido group is cradled between the wing-tip and back-bone W atoms with W-C = 1.90-1.96 and 2.20-2.26 Å, respectively. The five W-W bonding distances span a narrow range 2.74-2.84 Å. The structure of this molecule resembles that previously reported for W₄(µ₄-C)(NMe)(OPr')₁₂ where one OPr' ligand bonded to a backbone W atom is replaced by a hydride ligand. The hydride was not located crystallographically but is implicated by (i) a void at one W atom, (ii) its trans-influence as determined by the W-O bond distance of the group trans to the void, and (iii) electron counting which requires the presence of a W₄(µ₄-C)⁴⁺ rather than a W₄(µ₄-C)³⁺ moiety in order to account for the observed diamagnetism. The present finding is compared with the previous preparations and characterizations of W₄(µ₄-C)⁴⁺ alkoxide supported clusters.

KEY WORDS: Alkoxide; tungsten; cluster; carbide; hydride.

INTRODUCTION

We have recently reported the preparation of a series of tetranuclear tungsten carbido clusters based on the cleavage of carbon monoxide...
In some instances, an intermolecular oxo-for-alkoxide exchange reaction occurs leading to the isolation of carbido compounds of formula $W_4(\mu_4-C)(OR)_{14}$, e.g., for $R = \text{CH}_2\text{Pr}'$, c-pentyl, c-hexyl. These represent the first series of molecular carbides of tungsten and they share a common $W_4(\mu_4-C)^{14+}$ core. However, the first example of a carbido tungsten cluster, namely $W_4(\mu_4-C)(\text{NMe})(\text{OPr}')_{12}$ [2], was isolated as a minor product from the reaction between $W_2(\text{NMe}_2)_6$ and excess Pr'OH. We report here on a closely related reaction involving $W_2(\text{NMe}_2)_6$ that yields yet another $W_4(\mu_4-C)$ containing compound which we propose contains a hydride ligand in place of one of the OPr' ligands in $W_4(\mu_4-C)(\text{NMe})(\text{OPr}')_{12}$.

RESULTS AND DISCUSSION

Synthesis

The title compound is prepared in the reaction between $W_2(\text{NMe}_2)_6$, pyridine and neopentanol in hydrocarbon solvents at room temperature. The main product at short reaction times is $W_2(\text{OCH}_2\text{Bu'})_6(\text{py})_2$ and the title compound is formed in ca. 10% yield. The two are readily separable by their different solubilities. Dark green crystals of $W_4(\mu_4-C)(\text{NMe})(\text{OCH}_2\text{Bu'})_{11}(\text{H})$, suitable for the X-ray study, were grown from dimethoxyethane (DME).

The compound is air-sensitive, hydrocarbon soluble, and thermally stable (inert) in the solid-state when stored under N$_2$ at room temperature.

The $^1H$ and $^{13}C$ NMR spectra are complex but are consistent with a non-fluxional molecule having no element of symmetry and 11 OCH$_2$Bu' ligands. The $^1H$ and $^{13}C$ NMR data for the NMe group are virtually identical with that seen for $W_4(\mu_4-C)(\text{NMe})(\text{OPr}')_{12}$ as is the carbido carbon resonance at $\delta$ 367 [2].

The hydride ligand was not seen in the $^1H$ NMR spectrum—quite possibly it is obscured by the other multitudinous resonances.

The mechanism of the formation of this compound is not known but, as discussed before, is believed to arise from degradation of a NMe$_2$ ligand during the act of alcoholysis. A compound with a $W_2(\mu-\eta^2-\text{CH}_2\text{NMe})$ ligand derived from a NMe$_2$ ligand by H atom transfer has been previously characterized [3]. Cleavage of the $\mu-\eta^2-\text{CH}_2\text{NMe}$ ligand to imido, NMe and methylene ligands is easy to envisage. Degradation of alkylidenes to