

## Preliminary communication

### Synthesis and ESR spectrum of tetrabenzylvanadium

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Very little is known about the nature of vanadium(IV)—carbon  $\sigma$ -bonds because they are unstable. Such compounds that have been isolated<sup>1</sup> tend to be those in which extra stabilisation has been achieved by a combination of  $\pi$ -coordination and steric factors such as in  $(\pi\text{-C}_5\text{H}_5)_2\text{V}^{\text{IV}}(\text{C}\equiv\text{C}\cdot\text{C}_6\text{H}_5)_2$ . Dimethyl- and diethylvanadium dichloride have also been reported<sup>2</sup>.

We report the synthesis and isolation of tetrabenzylvanadium, the first example of a vanadium(IV) compound with four V—C  $\sigma$ -bonds. We have found that dibenzylmagnesium<sup>3</sup>, reported to be a good benzylating agent, reacts quite readily in the presence of a little diethyl ether, with vanadium tetrachloride in pentane at  $-20^\circ$  to give a green complex. The complex dissolves readily in pentane to give a deep-green colouration which progressively darkens to a brown colour on prolonged exposure to light at room temperature. It is very unstable to air and moisture. Under nitrogen, and in toluene, the compound can be heated to  $60^\circ$  without appreciable change in colouration.

Analysis of the pentane solution shows it to be practically free of magnesium. (Analytical data of a typical sample were as follows: V = 2.25 mg/ml; Mg = 0.016 mg/ml). A GLC analysis of the products formed on treatment with methanol shows that four moles of toluene are formed for each g-atom of vanadium. The infrared spectrum of the pentane solution is very similar to that of tetrabenzyltitanium<sup>4</sup> with the characteristic absorption bands of a monosubstituted aromatic ring.

Evidence for the presence of a vanadium(IV) species containing four benzyl ligands was obtained by ESR. The pentane solution of the complex at room temperature gave the well-resolved ESR spectrum shown in Fig. 1. The eight lines are due to interaction with a <sup>51</sup>V nucleus, having a splitting of 57G, with  $g = 1.993$ . Under higher resolution each line is further split into an odd number of lines of approximately 3G separation. This fine structure, seen on one of the vanadium lines in Fig. 2, arises from coupling to eight equivalent protons. For comparison, Fig. 3 shows a computer simulated spectrum of eight equivalent protons, with a half-line width equal to twice the line separation. It is a reasonable assumption that the eight equivalent protons are the eight methylene protons on four benzyl ligands.

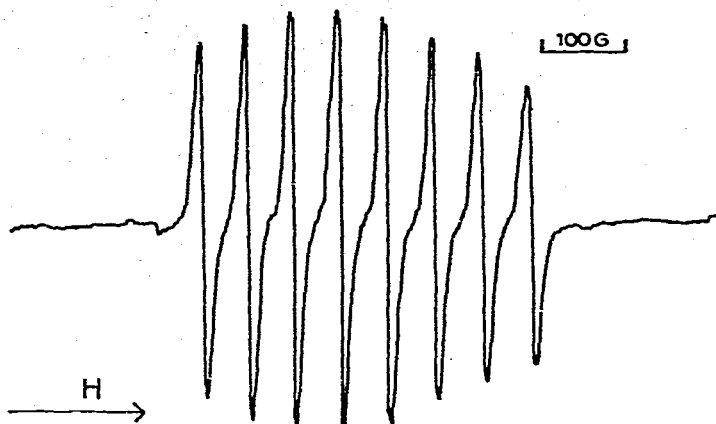


Fig. 1.

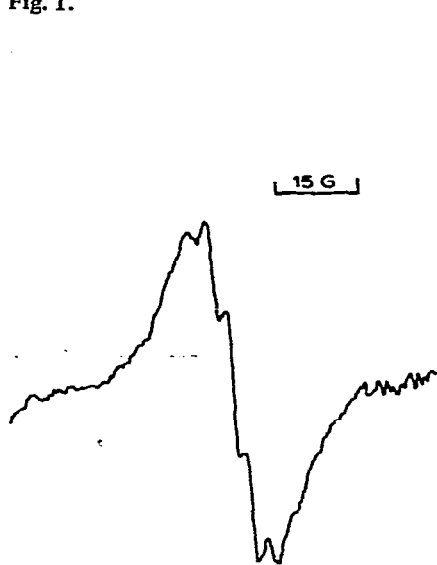


Fig. 2.

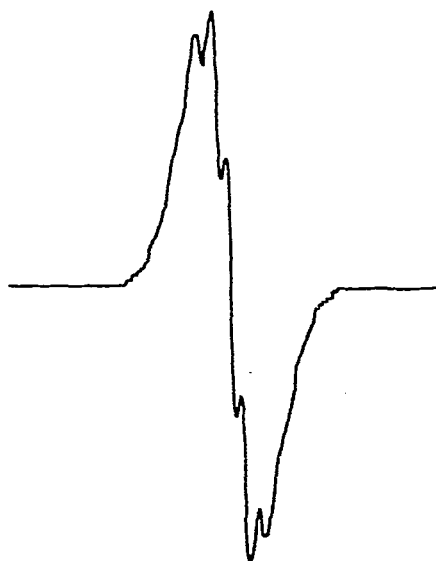


Fig. 3.

To show a well-resolved ESR spectrum of a vanadium(IV) system at room temperature, it is necessary that the complex should be of low symmetry. Tetrahedral vanadium(IV) has little separation between the ground state and the next higher state, thus producing short spin-lattice relaxation times and broad absorption lines at most temperatures. For instance, the ESR spectrum of tetrahedral vanadium tetrachloride has only been observed<sup>5</sup> at temperatures below 50 K. It is likely, therefore, that tetrabenzylvanadium has a distorted tetrahedral structure, similar to that recently observed for tetrabenzylzirconium<sup>6</sup>.

From these data we conclude that the green complex has the formula  $V(\text{CH}_2 \cdot \text{C}_6\text{H}_5)_4$  with four V-C  $\sigma$ -bonds.

Our earlier attempts to obtain tetrabenzylvanadium by reacting vanadium tetrachloride with benzylmagnesium chloride were unsuccessful. We obtained instead, large quantities of vanadium trichloride as a purple solid. The successful synthesis of tetrabenzylvanadium using dibenzylmagnesium as the benzylating agent confirms the observation<sup>3</sup> that magnesium halides in Grignard reactions probably behave as Lewis acid sites and are important in promoting reduction in the oxidation state of the metal. The increased stability of tetrabenzyl vanadium when compared with the alkyl or aryl analogues is in part due to the absence a  $\beta$ -hydrogen<sup>7,8</sup> which would promote an elimination process.

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