Acetylene Complexes of Dicyclopentadienyl-vanadium

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Previous work has demonstrated a catalytic polymerization⁽¹⁾ of acetylenes with dicyclopentadienyl-vanadium⁽²⁾ (I) and the preparation⁽³⁾ of a series of acetylene complexes of vanadium, such as π-$C_5H_5(HC_2H)V(CO)_2$. The present communication will deal with the preparation of a few acetylene complexes of I as a model substance of an intermediate in the polymerization of acetylene with I. Although a great variety of transition metal-acetylene complexes are known,⁽⁴⁾ the acetylene complexes described here may be the first examples of compounds in which the acetylenic bond is directly bonded to the metal coordinated by two π-cyclopentadienyl rings.

To a stirred, violet solution of 2.79 g. of I in 60 ml. of benzene, 2.40 g. of dimethyl acetylenedicarboxylate (II) was added drop by drop at a room temperature under nitrogen. The reaction solution almost instantaneously turned dark green, with a slight evolution of heat, and some dark-colored crystals precipitated spontaneously. After having been stirred at 50°C for 1 hr., the resulting reaction mixture was evaporated to dryness under reduced pressure. The residue was then recrystallized from toluene to yield 4.20 g. (84.5% yield) of air-sensitive, dark green crystals (III); m. p., 146—147°C (decomp.) (Found: C, 59.33; H, 4.99;

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1) R. Tsumura and N. Hagihara, This Bulletin, **37**, 1889 (1964).

2) E. O. Fischer and S. Vigoureux, *Chem. Ber.*, **91**, 2205 (1958).

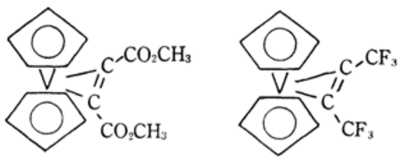
3) R. Tsumura and N. Hagihara, presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964; This Bulletin, to be published.

4) M. A. Bennet, *Chem. Revs.*, **62**, 611 (1962).

mol. wt. (cryoscopic in benzene), 314. Calcd. for $C_{16}H_{16}O_4V$: C, 59.45; H, 4.99%; mol. wt., 323).

The elemental analysis and molecular weight determination indicated a mononuclear vanadium complex with the composition: $(C_5H_5)_2VC_2(CO_2CH_3)_2$. The complex III is paramagnetic, and its electron paramagnetic resonance spectrum showed a *g*-factor of 1.9976 and a hyperfine splitting of 44.0 gauss. The treatment of III with chlorine in carbon tetrachloride gave the original acetylene II and dicyclopentadienyl-vanadium dichloride in 37 and 68% yields respectively. The reduction of III with a large excess of lithium aluminum hydride gave the starting complex I in a 6% yield. These facts suggest that, in the acetylene complex III, both of the π-cyclopentadienyl rings are left coordinated to vanadium, to which also the acetylene II itself is bonded.

The infrared spectrum of III showed a strong absorption at 1821 cm^{-1}; this is probably to be assigned to a carbon-carbon stretching vibration of a multiple bond of the acetylene. This absorption is shifted toward a lower frequency by the coordination of II to vanadium in a cis-type and is increased in intensity through conjugation with two adjacent keto-carbonyls of the esters groups. It may thus reasonably be concluded, in comparison with a proposed structure of the above-mentioned complex π-$C_5H_5(HC_2H)V(CO)_2$, that the new acetylene complex III has the structure represented in Fig. 1 (III), in which the acetylene is bonded via two σ-bondings to vanadium, simultaneously having two π-cyclopentadienyl rings.



(III) (IV)

Fig. 1. Acetylene complexes of dicyclopentadienyl-vanadium.

A similar reaction of I with perfluoro-2-butyne also gave air-sensitive, brown crystals of the corresponding acetylene complex (IV); m. p., 124—126°C (decomp.) (from *n*-hexane and toluene); yield; 87.0% (Found: C, 48.89; H, 3.07; mol. wt. (cryoscopic in benzene), 332. Calcd. for $C_{14}H_{10}F_6V$: C, 49.00; H, 2.94%; mol. wt., 343). The complex IV gave a paramagnetic resonance spectrum with a *g*-factor of 1.9971 and a hyperfine splitting of 46.0 gauss. The infrared spectrum of IV showed a strong absorption near 1800 cm^{-1}. This absorption may reasonably be assigned to the stretching vibration of the acetylenic bond, this assignment is consistent with its assignment in the case of the complex III. These facts suggest that the acetylene complex IV also possesses a structure similar to that of III, as is shown in Fig. 1 (IV).

The acetylene complexes III and IV are therefore presumed to reveal a model structure of an initial intermediate in the catalytic polymerization of acetylenes with I.

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