Some Acetylene Complexes of Vanadium*

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It was previously reported[1] that π-dicyclopentadienyl-vanadium causes the catalytic polymerization of various acetylenes. Much attention was then drawn to a possible isolation of acetylene complexes of vanadium in an effort to elucidate the catalysis of the vanadium complex, which seems to be different from that of such nickel compounds as $(PPh_3)_2Ni(CO)_2$[2] and $NiCl_2 \cdot 2PPh_3$[3] in the catalytic polymerization of acetylenes. We will now report on the preparation, some properties and a proposed structure of some new acetylene complexes of vanadium, such as π-$C_5H_5(RC_2H)V(CO)_2$, prepared from the reactions of π-cyclopentadienyl-vanadium tetracarbonyl[4] with several acetylenes. The infrared and nuclear magnetic resonance spectra of the acetylene complexes are used as the basis of discussion of their structure and of the type of bonding by which the acetylenes may be bonded to metal. Regarding the bonding of the acetylenes to vanadium, the acetylene complexes described here are probably related to an intermediate in the catalytic polymerization mentioned above. Although a wide variety of acetylene complexes of such transition metals as manganese,[5,6] iron,[7] cobalt,[7-9] nickel,[7,9,10] tungsten,[11] and platinum[6,12,13] have been reported, some acetylene complexes described here are the first examples of vanadium.

Preparation and Properties

π-Cyclopentadienyl-vanadium tetracarbonyl[4] (I) reacted with pressured acetylene in benzene near room temperature under the influence of the irradiation of light from a tungsten lamp. The reaction solution turned from orange to green to form an acetylene complex. Similar photochemical reactions of I with an excess of such 1-alkynes as 1-pentyne, 1-hexyne and *t*-butylacetylene proceeded with the evolution of approximately 2 mol. of carbon monoxide per atom of vanadium present and gave green acetylene complexes. On the other hand, in the interactions of an excess of I with 1-alkynes 2 mol. of carbon monoxide per mole of the alkynes present were evolved, and also the corresponding acetylene complexes were obtained. It is, therefore, reasonable to assume from these facts and from the results of the elemental and spectroscopic analyses to be described later, that the resulting compounds are acetylene complexes of vanadium (II) in which two carbonyl groups of the starting material, I, have been replaced by the corresponding acetylene molecule by the following reaction:

$$\underset{\text{(I)}}{\pi\text{-}C_5H_5V(CO)_4} + RC{\equiv}CH \xrightarrow{h\nu} \underset{\text{(II)}}{\pi\text{-}C_5H_5(RC_2H)V(CO)_2} + 2CO$$

$(R{=}H,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9 \text{ and } (CH_3)_3C)$

Acetylene complexes of vanadium II were purified through chromatography over alumina, followed by vacuum distillation. They are either viscous oils or low melting solids which crystallize spontaneously on cooling. All of them are quite sensitive to air, so they must be handled under oxygen-free nitrogen. These properties make it difficult to obtain satisfying values from the elemental analyses. The acetylene complexes II are easily soluble in most organic solvents. Their infrared and nuclear magnetic resonance spectra are shown in the Experimental section and in Table I respectively, together with some assignments.

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TABLE I. NMR SPECTRA OF ACETYLENE COMPLEXES OF VANADIUM II[a)]

Compound[b)]	Solvent	Band position (τ)[c,d)]				
		π-C_5H_5-	HC_2-	-C_2CH_2-	-CH_2-	-CH_3
M(HC_2H)	CCl_4	4.46(s)[e)]	4.92(s)			
	C_6H_6	4.88(s)	5.63(s)			
M($HC_2C_3H_7$)	$CHCl_3$	4.50(s)	4.93(s)	6.61(t)[e)]	8.18(m)[e)]	9.01(t)
M($HC_2C_4H_9$)	C_6H_6	4.78(s)	5.60(s)	6.46(t)	8.37(m)	9.01(t)
M(HC_2CMe_3)	CCl_4	4.48(s)	4.90(s)			8.76(s)
	$CHCl_3$	4.45(s)	4.90(s)			8.73(s)

a) Measured at 60 Mc./sec. at room temperature.
b) M = π-$C_5H_5V(CO)_2$.
c) Relative to $SiMe_4$ (τ = 10) as the internal standard.
d) The relative intensities were essentially consistent with those to be expected from the assigned structure. The decomposition during the measurements sometimes also showed complex spectra containing absorptions of free acetylene molecules.
e) (s), (t) and (m) indicate multiplicity, singlet, triplet and complex multiplets respectively.

Attempts to make the complex I interact with phenylacetylene and tolane were made in order to obtain more stable and higher melting acetylene complexes than the complex II itself. The reactions occurred with the evolution of carbon monoxide and presumably formed the corresponding acetylene complexes of vanadium, but their isolation was unsuccessful because of the great difficulty of purifying them. Seeking to obtain a more stable and crystalline acetylene complex, we have investigated the preparation of a complex in which at least one of the two remaining carbonyl groups of the acetylene complexes II obtained above is replaced by triphenylphosphine.

The photochemical reaction of the carbonyl compound I with triphenylphosphine in a benzene solution at room temperature proceeded quantitatively, with the evolution of a mole of carbon monoxide equal to the mole of the vanadium compound present, and it gave orange crystals of a mono-substituted product (III) by the following reaction:

$$\pi\text{-}C_5H_5V(CO)_4 + PPh_3 \xrightarrow{h\nu} \pi\text{-}C_5H_5V(PPh_3)(CO)_3 + CO$$

(III)

The phosphine derivative III is completely air-stable in the solid state, and it is only slowly oxidized by air in solutions; these characteristics indicate that the stability of the new compound III is higher than that of I. It is fairly soluble in hot benzene and carbon tetrachloride, but poorly soluble in *n*-hexane, ethers and alcohols.

The reaction between III and tolane gave yellow crystals of the expected acetylene complex (IV):

$$\pi\text{-}C_5H_5V(PPh_3)(CO)_3 + PhC{\equiv}CPh \xrightarrow{h\nu} \pi\text{-}C_5H_5(PhC_2Ph)V(PPh_3)(CO) + 2CO$$

(IV)

The tolane complex IV could be recrystallized from *n*-hexane in a careful operation, though it is still sensitive to air. It is easily soluble in most organic solvents in the same manner as is II.

Discussion

In general, acetylenes are known[14)] to give many kinds of organometallic complexes upon reaction with transition metal carbonyl compounds. On the basis of the chemical and physical properties of the acetylene complexes of vanadium reported here, it is clear that they are monomeric compounds obtained through the replacement of two carbonyl groups in the complex I by the acetylene, and that the acetylene molecule is bonded to a single vanadium atom as a bidentate ligand. On the other hand, there are some examples of the π-bonding of acetylenes as monodentate ligands through a single electron pair of their triple bond to a metal, for instance, in such manganese complexes as π-$C_5H_5(PhC_2Ph)Mn(CO)_2$,[5)] which is prepared from the reaction of π-cyclopentadienyl-manganese tricarbonyl with tolane. It is very interesting that the bonding of acetylenes to the vanadium atom is assumed to be different from that in the manganese complexes even though the same types of acetylene complexes are derived from the similar reaction of π-cyclopentadienyl-metal carbonyl compounds with acetylenes.

The infrared spectra of all of the acetylene complexes II indicate that the wave numbers of the two carbonyl bands are a little smaller than those in the original compound, I, as a result of the replacement of two carbonyl groups in I by the acetylene. The infrared

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14) M. A. Bennet, *Chem. Revs.*, **62**, 611 (1962); R. G. Guy and B. L. Shaw, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 4, Academic Press Inc., New York (1962), p. 78.

spectra of the alkyne complexes II (R=alkyl) showed no absorptions in the region of 3300 $\mathrm{cm^{-1}}$ due to the presence of the acetylenic hydrogen atoms and of the band at 2100 $\mathrm{cm^{-1}}$ arising from the stretching vibrations of the terminal triple bonds. The lack of the characteristic absorptions of 1-alkynes suggests that their triple bond nature is weakened in the acetylene complexes. The stretching absorptions of the coordinated acetylenic bond are reported to be situated at 1919 $\mathrm{cm^{-1}}$ in the manganese complex, π-$C_5H_5(CF_3C_2CF_3)Mn(CO)_2$,⁶⁾ in which the acetylene is merely acting as a donor. In contrast, they have been found in the 1700 $\mathrm{cm^{-1}}$ region in such complexes of platinum, rhenium and tungsten as $(RC_2R)Pt(PPh_3)_2$,¹²⁾ $(PhC_2H)_2ReCl$,¹⁵⁾ and $(RC_2R)_3W(CO)$¹¹⁾ respectively, in which the acetylenes are considered to be σ-bonded or doubly π-bonded to the metal, apparently as a bidentate ligand. In the vanadium compounds II, however, it was impossible to assign any band to the stretching vibration of the coordinated multiple bond with certainty. The two broad, strong absorptions of the carbonyls could also be presumed to cover the absorption band in question.

The nuclear magnetic resonance spectra of the acetylene complexes II given in Table I indicate what the property of the coordinated acetylenic bond might be. All of the compounds II possess essentially the same chemical shifts for the acetylenic hydrogens, at τ 4.9 in carbon tetrachloride and chloroform or at τ 5.6 in benzene. In carbon tetrachloride and chloroform, the spectra of the acetylenic protons of the coordinated acetylenes are shifted about τ 2.7 toward the lower-magnetic field than those of the corresponding free acetylenes; they are thus located in the region of olefinic protons. As a result of the coordination of the acetylenes to vanadium metal, the chemical shift of the acetylenic hydrogens is expected to be mainly influenced by a diamagnetic effect due to d-electrons of the metal on the one hand, and, on the other hand, by a paramagnetic effect which is brought about through the loss of the diamagnetic anisotropy of the triple bond. In this case, the great paramagnetic shift observed might be presumed to result from the more remarkable effect of the latter than the former.

These facts, consistent with the results of the infrared spectra described above, suggest that the triple bond of the acetylenes in II may be reduced effectively to a double bond by their bonding to vanadium metal. The higher shielding of the acetylenic protons in benzene than that in the other chlorinated hydrocarbons may be considered to result from a solvent effect due to the remarkable diamagnetic anisotropy and plane form of the benzene molecule. Such a shielding due to the solvent effect of benzene is seen also in the chemical shifts of the cyclopentadienyl ring protons, though it is not so great as in those of the acetylenic hydrogens. A comparison of the spectra in the different solvents tested indicates that of all kinds of hydrogens present in the acetylene complexes II, the acetylenic protons are affected by solvents most sensitively.

On the basis of these experimental results, various possible structures of the acetylene complexes of vanadium II might be considered: The structure formulated in Fig. 1(A), in which the acetylene is π-bonded to the metal by only a single π-electron pair, as in the above-mentioned complexes⁵,⁶⁾ of manganese; the structure presented in Fig. 1(B), in which the acetylenic carbon atoms are substantially rehybridized toward the sp^2 configuration and the acetylene is bonded to the metal through two σ-bondings, as in the above-described complexes of platinum¹²⁾ and rhenium¹⁵⁾, and a possible intermediate structure, one between structures A and B.

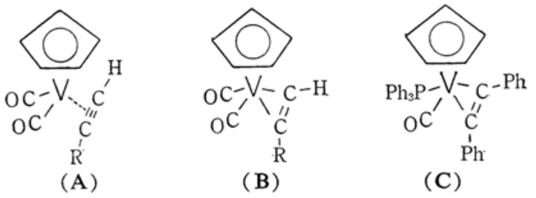

Fig. 1. Acetylene complexes of vanadium.

It may be concluded from the experimental evidence that the most probable structure of the vanadium complexes II is consistent with, or at least near, structure B, even if it may be intermediate between structures A and B. The tolane complex IV prepared from the phosphine derivative III is presumed in the same way to have the structure given in Fig. 1(C).

In the catalysis of dicyclopentadienyl-vanadium for the polymerization of acetylenes, it appears reasonable to assume that the polymerization proceeds through the initial formation of an acetylene complex in which the acetylene molecule is bonded to a vanadium atom by a bonding similar to that in the structure B of the isolated complexes II.

Further investigation has led to the successful preparation of a few acetylene complexes in which an acetylene molecule is probably σ-bonded to a vanadium metal, one simultaneously having two coordinated cyclopentadienyl

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15) R. Colton, R. Levitus and G. Wilkinson, *Nature*, **186**, 233 (1960).

rings. The findings on such acetylene complexes will be soon presented elsewhere.

Experimental

All preparations, chromatographic separations, distillations and analytical measurements were carried out under an atmosphere of dry, oxygen-free nitrogen or in a vacuum. Solvents were distilled and saturated with nitrogen before use. All melting points are uncorrected.

Preparation. —*π-Cyclopentadienyl - acetylene - vanadium Dicarbonyl.*—In a 70ml. glass autoclave acetylene was pressured into a solution of 0.58 g. (2.5 mmol.) of π-cyclopentadienyl-vanadium tetracarbonyl[4] (I) in 30 ml. of benzene up to about 5 kg./cm^2. The resultant orange solution was irradiated with a 500 W. tungsten lamp for ca. 4 hr. while being cooled with running water; it thus turned dark green and had an evolution of small bubbles from the bottom of the vessel. After the solvent had been removed at room temperature, the oily residue was chromatographed over alumina which had been treated with nitrogen before use. The elution of the column with benzene gave, at first, a light orange solution of the unchanged material I and then a clear green solution. When the green fraction was concentrated in vacuo at room temperature, a green oil was left; this was then distilled in 0.1 mmHg at ca. 70°C. The resulting green viscous distillate crystallized spontaneously upon being cooled, yielding 0.10 g. of green crystals, m. p. 27—30°C.

Found: C, 55.7; H, 3.7; mol. wt. (cryoscopic in benzene), 183. Calcd. for $C_9H_7O_2V$: C, 54.6; H, 3.6%; mol. wt., 198.

The yield of the isolation procedure virtually depended upon the decomposition of the product during the manipulations. The discrepancy in the elemental analysis for the acetylene complex may be due to the instability of the complex, which could not be purified by recrystallization.

π-Cyclopentadienyl-(1-pentyne)-vanadium Dicarbonyl. —Into a 100 ml. flask connected to a gas-measuring vessel a solution of 0.815 g. (3.57 mmol.) of I in 30 ml. of benzene and 2.0 ml. of 1-pentyne was placed. The reaction system was then magnetically stirred and irradiated with a tungsten lamp while being cooled with running water. The color of the solution gradually turned from orange to green, and was a gas evolved. Irradiation was continued for 8 hr., until the evolution of the gas had ceased. The carbon monoxide evolved amounted to approximately 165 ml. (7.05 mmol.). The reaction mixture was then chromatographed and distilled as has been described above, yielding 0.35 g. of a green oil.

Found: C, 61.0; H, 5.6. Calcd. for $C_{12}H_{13}O_2V$: C, 60.0; H, 5.5%.

π-Cyclopentadienyl-(1-hexyne)-vanadium Dicarbonyl and π-Cyclopentadienyl-(t-butylacetylene)-vanadium Dicarbonyl.—A mixture of I and the 1-alkyne in benzene was treated in the manner described for the pentyne complex.

Hexyne gave a green oil of the acetylene complex.

Found: C, 62.1; H, 6.3. Calcd. for $C_{13}H_{15}O_2V$: C, 61.4; H, 6.0%.

Tertiary butylacetylene gave green crystals of the acetylene complex, m. p. 31—32°C.

Found: C, 62.0; H, 5.9; CO, 21.7. Calcd. for $C_{13}H_{15}O_2V$: C, 61.4; H, 6.0; CO, 22.0%.

π-Cyclopentadienyl-triphenylphosphine-vanadium Tricarbonyl.—A mixture of 5.85 g. (25.5 mmol.) of I and 7.02 g. (26.8 mmol.) of triphenylphosphine, dissolved in 80 ml. of benzene, was photochemically treated in a manner similar to that described above. A gas evolved smoothly, and fine orange crystals separated. Irradiation was then continued for about 15 hr., until the evolution of the gas almost ceased. The carbon monoxide evolved amounted to 570 ml. (24.4 mmol.). The reaction mixture was then filtered, and the precipitate washed well with cold benzene and dried under reduced pressure to yield 9.40 g. (87.8%) of orange crystals of a mono-substituted product III, m. p. 160—161°C.

Found: C, 67.38; H, 4.53; V, 11.23. Calcd. for $C_{26}H_{29}O_3PV$: C, 67.55; H, 4.36; V, 11.02%.

Furthermore, 0.50 g. of III was recovered by recrystallization from the orange filtrate.

π-Cyclopentadienyl - tolane - triphenylphosphine - vanadium Carbonyl.—A mixture of 0.658 g. (1.42 mmol.) of III and 0.267 g. (1.49 mmol.) of tolane in 50 ml. of benzene was worked up in the same way. The carbon monoxide evolved amounted to 50 ml. (2.14 mmol.), though there was a slower evolution of the gas. The reaction mixture was then evacuated and chromatographed over alumina with benzene, and the resulting yellow-green eluate was evaporated to dryness under reduced pressure. The residue was recrystallized from *n*-hexane at the temperature of dry ice to yield 0.25 g. of a yellow crystalline powder, m. p. 35—37°C.

Found: C, 78.02; H, 5.35; mol. wt. (cryoscopic in benzene), 559. Calcd. for $C_{38}H_{30}OPV$: C, 78.08; H, 5.17%; mol. wt., 584.

Infrared Spectra. — Measurements were made with a Hitachi EPI-2 spectrophotometer. The spectra and some assignments are shown below:

$\pi\text{-}C_5H_5(HC_2H)V(CO)_2$[a]: 3100 w[c] 2940 w 2860 w 1996 vs[d] 1925 vs[d] 1528 w 1434 m[e] 1363 vw 1009 m[e] 950 m 810 s[e] 787 sh 695 m.

$\pi\text{-}C_5H_5(HC_2C_3H_7)V(CO)_2$[b]: 3120 vw[c] 2960 m[f] 2932 sh[f] 2875 w[f] 1985 vs[d] 1905 vs[d] 1635 vw 1520 vw 1460 w 1431 w[e] 1378 vw 1098 w 1063 w 1010 m[e] 980 vw 953 w 895 vw 866 vw 806 s[e] 700 sh.

$\pi\text{-}C_5H_5(HC_2C_4H_9)V(CO)_2$[b]: 1990 vs[d] 1910 vs[d]

$\pi\text{-}C_5H_5(HC_2CMe_3)V(CO)_2$[a]: 3130 vw[c] 3060 vw 2970 s[f] 2910 sh[f] 2880 m[f] 1994 vs[d] 1920 vs[d] 1632 w 1474 sh 1458 m 1435 w[e] 1389 w 1361 s 1227 m 1205 sh 1116 vw 1060 vw 1030 vw 1010 m[e] 955 w 931 w 885 vw 857 vw 805 s[e] 772 vw 750 vw 718 vw

$\pi\text{-}C_5H_5V(PPh_3)(CO)_3$[a]: 3060 vw[c] 1950 vs[d] 1855 vs[d] 1840 vs[d] 1587 vw 1473 m 1435 s[e] 1307 w 1183 m 1160 w 1119 vw 1090 s 1071 w 1025 w 1013 m[e] 996 m 969 vw 920 vw 909 vw 833 m 819 s[e] 750 sh 744 s[g] 718 vw 700 sh 688 s[g].

$\pi\text{-}C_5H_5(PhC_2Ph)V(PPh_3)\ (CO)$[a]: 1825 vs[d]

a) measured in Nujol and hexachlorobutadiene; b) measured as thin films of the pure oil; c) a C–H stretch of π-C_5H_5; d) a C≡O stretch; e) π-C_5H_5 frequencies; f) a C–H stretch of alkyl groups; g) phenyl absorptions.

Nuclear Magnetic Resonance Spectra.—Measurements were made on a Varian A 60 spectrometer. The spectra and conditions of measurements are given in Table I.

Summary

Some acetylene complexes of vanadium of the π-$C_5H_5(RC_2H)V(CO)_2$ (R=H, n-C_3H_7, n-C_4H_9 and $(CH_3)_3C$) and π-$C_5H_5(PhC_2Ph)V(PPh_3)(CO)$ types have been prepared by the photochemical reaction of the corresponding acetylene with π-cyclopentadienyl-vanadium tetracarbonyl and its phosphine derivative respectively. It has been proposed, on the basis of their infrared and nuclear magnetic resonance spectra, that the acetylene complexes of vanadium have a structure in which the acetylene molecule is bonded via two σ-bondings to a vanadium atom.

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