J. Am. Chem. Soc. **1995,** *117,* 2096–2097

Communications to the Editor

Laser-Induced Fluorescence of Gaseous Vanadium Methylidyne, VCH: A Triatomic Organometallic Molecule

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Received November 9, 1994

The first transition metal complexes containing a formal metal–carbon triple bond were synthesized in 1973 by Fischer et al.;[1] their general formula was

$$\text{X–M(CO)}_4\text{≡CR} \qquad [\text{M} = \text{Cr, Mo, W; X} = \text{F, Cl, Br, I; R} = \text{Me, Ph}]$$

To date, most of the compounds of this type that have been prepared are octahedral complexes of the group 6 metals (Cr, Mo, W), although some four- and five-coordinated structures also exist. X-ray and neutron diffraction measurements show that the M≡C bond lengths are typically 1.65–1.75 Å for first row transition metals (Cr, Mn, Fe), and 1.75–1.90 Å for second (Mo) and third row transition metals (Ta, W, Os).

We have recently identified an example of the simplest possible type of metal carbyne complex, a linear triatomic molecule consisting of a transition metal atom bonded to a CH group. The gas-phase electronic spectrum of the transient radical VCH has been recorded in the 600–800 nm region following the reaction of laser-ablated vanadium atoms with methane. Only two other triatomic transition metal containing molecules, CuOH[2] and YNH,[3] have been definitely identified by their gas-phase electronic spectra; VCH is the first carbyne. Its molecular structure has been determined by isotope substitution, and two of its three vibrational frequencies have been measured.

The experimental apparatus follows the design of Simard et al.[4] Briefly, a rotating vanadium rod (Goodfellow 99.8%+) was ablated with 900 μJ/pulse of 532 nm radiation from a Nd:YAG laser. The V atoms were entrained in a pulse of high-pressure "oxidant" gas (80 psi of He containing 5–10% CH_4) and expanded into the vacuum of the apparatus, forming a supersonic jet-cooled molecular beam. A tunable probe laser beam, ~5 cm downstream, excited molecular fluorescence, which was passed through a monochromator (to eliminate emission from unwanted impurities) and recorded with a cooled photomultiplier tube. Survey spectra were obtained using a Lumonics HD500 tunable pulsed dye laser, pumped by a second Nd:YAG laser; high-resolution spectra, with a line width of about 90 MHz, were recorded with a Coherent Inc. Model 899-21 ring laser, pumped by an Ar^+ laser.

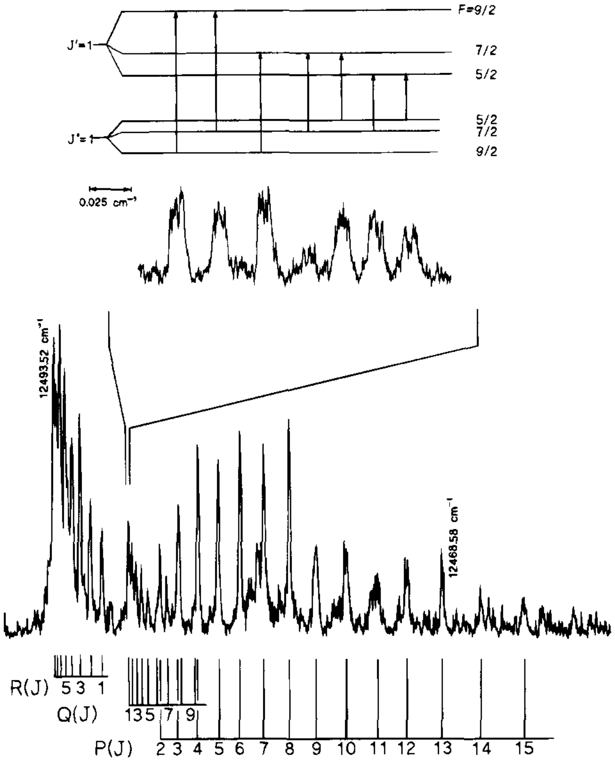

Figure 1. Medium-resolution spectrum (0.1 cm^{-1} line width) of the $^3\Delta_1 - X^3\Delta_1$ sub-band of VCH at 800.5 nm. The hyperfine structure of the Q(1) line, recorded at high resolution (0.003 cm^{-1} line width), is shown above. The energy level diagram illustrates the splittings given by the vanadium nucleus and their quantum number assignments; the doubling caused by the proton is only resolved for the longest wavelength component.

Representative spectra are given in Figure 1. The figure shows the longest wavelength band of VCH that we have found, near 800 nm, together with the nuclear hyperfine structure of the first Q branch line, Q(1). The hyperfine patterns, which are characteristic for a nucleus with spin $I = {}^7/_2$, prove that the carrier contains a vanadium atom; the presence of hydrogen is proved by experiments with CD_4, which give the corresponding bands of VCD. The linear molecule sub-band structure, the integer rotational quantum numbers (indicating an even number of unpaired electrons), and the derived rotational constants leave no doubt that the carrier is VCH. The lower state has projection quantum number $\Omega = 1$, which, by comparison with the isoelectronic VN molecule,[5] indicates that the ground state of VCH is $^3\Delta_1$.

Figure 2 illustrates the pattern of wavelength-resolved fluorescence given by a band of VCD near 760 nm; most bands give very complex patterns, but this one is particularly simple. Ground-state levels appearing prominently in the spectra lie at 139, 564, 838, 1120, and 1425 cm^{-1} for VCH, and at 139, 442, 813, 892, and 1245 cm^{-1} for VCD. The isotope-independent interval of 139 cm^{-1} is assigned as the ground-state spin–orbit splitting between $^3\Delta_2$ and $^3\Delta_1$, by analogy with VN. The vibrational fundamentals obey the isotope rules[6] very well and are unambiguously assigned as ν_3 (VC stretch) = 838 (813) cm^{-1} and ν_2 (bend) = 564 (442) cm^{-1} for VCH (VCD). The bending fundamental is forbidden to appear in the emission

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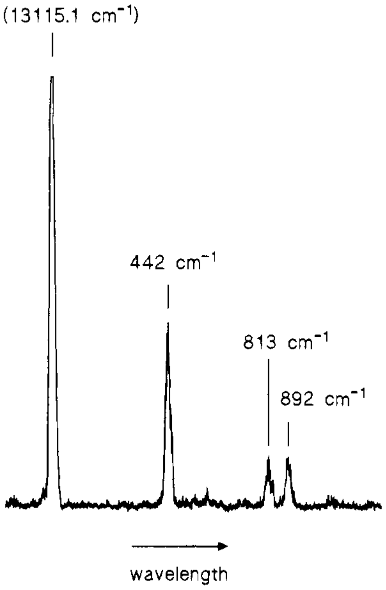

Figure 2. Wavelength-resolved laser-induced fluorescence spectrum given by the 762.5 nm band of VCD. The peaks to the red of the scatter from the exciting laser line at 13 115.1 cm^{-1} represent emission to the ground-state levels ν_2 (442 cm^{-1}), ν_3 (813 cm^{-1}), and $2\nu_2$ (892 cm^{-1}).

spectrum by the strict vibrational selection rules, but is seen in Figure 2 as a result of vibronic coupling; at high dispersion it is found to have different rotational selection rules from the other bands, indicating that it is non totally symmetric. The other levels appearing in the spectra can be assigned as overtones, combinations, or spin–orbit intervals. No bands attributable to the CH (CD) stretching fundamental have yet been observed.

A least squares fit to the rotational combination differences from the high-resolution spectra gives the ground-state rotational constants,

$$B_0(\text{VCH}) = 0.493\,69\ \text{cm}^{-1};\quad B_0(\text{VCD}) = 0.422\,02\ \text{cm}^{-1}$$

from which the substitution structure can be derived:

$$r_s(\text{VC}) = 1.702_5\ \text{Å};\quad r_s(\text{CH}) = 1.080\ \text{Å}$$

The CH bond length is midway between those in HCN (1.064 Å[7]) and C_2H_4 (1.090 Å[8]); the VC bond is almost 10% longer than that in free VN (1.567 Å[5]), consistent with values found from crystal structure determinations of larger organometallic complexes containing metal–carbyne and metal–nitrido bonds[9].

Nuclear hyperfine structure is observed throughout the high-resolution spectra. The pattern shown in Figure 1 shows both vanadium and hydrogen splittings, though in most of the bands the hydrogen splitting is too small to be resolved. The vanadium splittings can be interpreted in terms of a parameter h, defined as $a\Lambda + (b + c)\Sigma$. Since the lower state of all the bands observed is the $^3\Delta_1$ spin component of the ground state, which has $\Sigma = -1$, we determine the combination

$$h = 2a - (b + c) = -0.008\,29(3)\ \text{cm}^{-1}$$

The negative value shows that the contact parameter b is the dominant contributor, which is consistent with the expected electron configuration (V, 4sσ)^1 (V, 3dδ)^1. The observed value of h is less than half of that found in the ground state of VN.

The electronic spectra of VCH and VCD each consist of about 30 bands in the region 600–800 nm. From the first lines of the branches in the high-resolution spectra it can be shown that there are three overlapping electronic transitions present, with upper states $^3\Delta$ (see Figure 1), $^3\Phi$ (750 nm), and $^3\Pi$ (680 nm). The upper states are very strongly perturbed, with a rotational line often being split into several close-lying components; in addition, there is extensive vibronic coupling between the $^3\Delta$ and $^3\Phi$ excited electronic states through the bending vibration.

In conclusion, the free VCH molecule has been identified following reaction of vanadium atoms with methane, under conditions similar to those recently used to obtain mass spectra[10] of the carbohedrene V_8C_{12}. The vibrational bands seen in the emission spectrum show clearly that the V≡C stretching frequency is 838 cm^{-1}, not up near 1300 cm^{-1} as has been proposed for some metal carbyne complexes.[9,11] Very recently, we have discovered similar band systems of TiCH and TiCD in ablation experiments using titanium metal; these have not yet been analyzed rotationally.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

JA943650+

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