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Registry No. I, 36333-76-3; II, 36333-78-5; $CrCl_3(THF)_3$, 10170-68-0; $TiCl_4(THF)_2$, 31011-57-1; 1-norbornyllithium, 930-81-4; 1-chloronorbornane, 765-67-3; 1,2′-binorbornyl, 18313-42-3.

EPR Spectra of $V(CO)_5$ and $V(CO)_4$ in a Krypton Matrix†

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The free radical carbonyls $V(CO)_4$ and $V(CO)_5$ have been detected by EPR spectroscopy at 20 K in a γ-irradiated sample of $V(CO)_6$ in krypton. $V(CO)_4$ is in a high-spin d^5 configuration ($^6A_1$ in T_d), whereas $V(CO)_5$ appears to have a $^2B_2$ ground state in C_{2v} symmetry (distorted trigonal bipyramid).

Introduction

In recent years we have been studying the EPR spectra of free radical carbonyls centered on transition metals of the first row (V–Ni). Our early experiments involved the dissolution of stable carbonyls, for example, $V(CO)_6$[1] or $Fe(CO)_5$,[2,3] in single crystals of chromium hexacarbonyl followed by generation of paramagnetic derivatives through UV or γ irradiation. This technique was limited by the poor solvent properties of $Cr(CO)_6$, and we were eventually obliged to seek other hosts. Promising results have been obtained with a krypton matrix.[4] Solid krypton is a surprisingly good solvent for transition-metal carbonyls, and EPR spectra observed therein are unusually sharp. On the whole these advantages over $Cr(CO)_6$ outweigh the disadvantages, which are the following: first, liquid helium capability is a prerequisite, and second, the spectra are those of a powder, not a single crystal. The last is a grave disadvantage as it means that principal values of ligand hyperfine interactions are often impossible to obtain, as we shall see. Furthermore, heavy reliance must be placed on computer simulation, a technique which does not always lead to a unique solution.

We had modest success with $V(CO)_6$ dissolved in $Cr(CO)_6$: the spectra of $OV(CO)_{4or5}{}^{2+}$ and $V(CO)_6$ itself were obtained and analyzed.[1] This paper is a discussion of the results obtained from the $V(CO)_6$–krypton system; the spectra of $V(CO)_4$ and $V(CO)_5$ will be described and analyzed.

Experimental Section

The bis(diglyme) complex of $NaV(CO)_6$ was obtained from Alfa Inorganics Inc. and dissolved in sodium-dry tetrahydrofuran. It was then treated with anhydrous H_3PO_4 to liberate the volatile $V(CO)_6$. In order to enrich the $V(CO)_6$ in the isotope ^{13}C, the solution of the vanadium salt was placed under ^{13}CO (Merck, 99.8%) at a pressure of ca. 30 kP in a Pyrex vessel and irradiated with a 100-W high-pressure Hg lamp for 15 h. After the spent CO was removed and replaced twice with fresh ^{13}CO, the solution was treated with H_3PO_4 to liberate the ^{13}C-enriched $V(CO)_6$. An enrichment in excess of 98% was obtained by this method. Appropriate proportions (ca. 1:1000) of $V(CO)_6$ and krypton were mixed in the gas phase and then condensed into a 4-mm o.d. Suprasil sample tube and sealed off at 77 K.

The samples were γ irradiated at 77 K in a 19000 Ci ^{60}Co γ cell to a total dose of approximately 0.2 Mrad. Alternatively, they were exposed to the full light of a high-pressure Hg–Xe lamp (λ > 254 nm) at 4 K. They were subsequently examined with a Varian E12 EPR spectrometer equipped with an Oxford Instruments ESR 9 liquid-helium cryostat.

Table I. Principal *g* Factors and ^{51}V, ^{13}C Hyperfine Interactions for $V(CO)_5$ in Krypton

axis	*g*	a_V/G	a_C/G
x	1.9877	95.2	2 at 3.3, 2 at 12.8
y	2.0559	35.9	2 at 4.8, 2 at 9.0
z	2.0898	38.2	too weak

Results

The EPR spectrum of $V(CO)_6$ in $Cr(CO)_6$ and other matrices has been discussed elsewhere. Although krypton is known to be a good solvent for transition-metal carbonyls and in general yields splendid EPR spectra, we have never been able to generate a well-resolved spectrum of $V(CO)_6$ in krypton. This fact continues to be a source of considerable frustration and mystification. Suffice to say that unirradiated and irradiated samples of $V(CO)_6$–Kr contained a broad (100 G maximum slope width) derivative-shaped line centered at $g = 2.066$.

The spectrum of irradiated $V(CO)_6$–Kr (natural abundance of ^{13}C) at 20 K is shown in Figure 1a. It is evidently the spectrum of a ^{51}V ($I = {}^7/_2$) centered species having low symmetry, since three distinct manifolds (labeled *x*, *y*, and *z*) of ^{51}V hyperfine structure are apparent. The 24 lines that constitute this spectrum were measured as accurately as possible and, taking $\pm m_I$ pairs, were used to compute principal *g* factors and ^{51}V hyperfine interactions. The usual method of diagonalization of the spin matrix was used.[5] The agreement between the four sets of m_I pairs was ±0.0002 in *g* and ±0.5 G in the ^{51}V hyperfine interaction. The averages of these parameters over the four m_I pairs for *x*, *y*, and *z* are given in Table I.

In Figure 1b a computer simulation obtained by using these parameters is shown.[6] The agreement between the

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† NRCC No. 23341.

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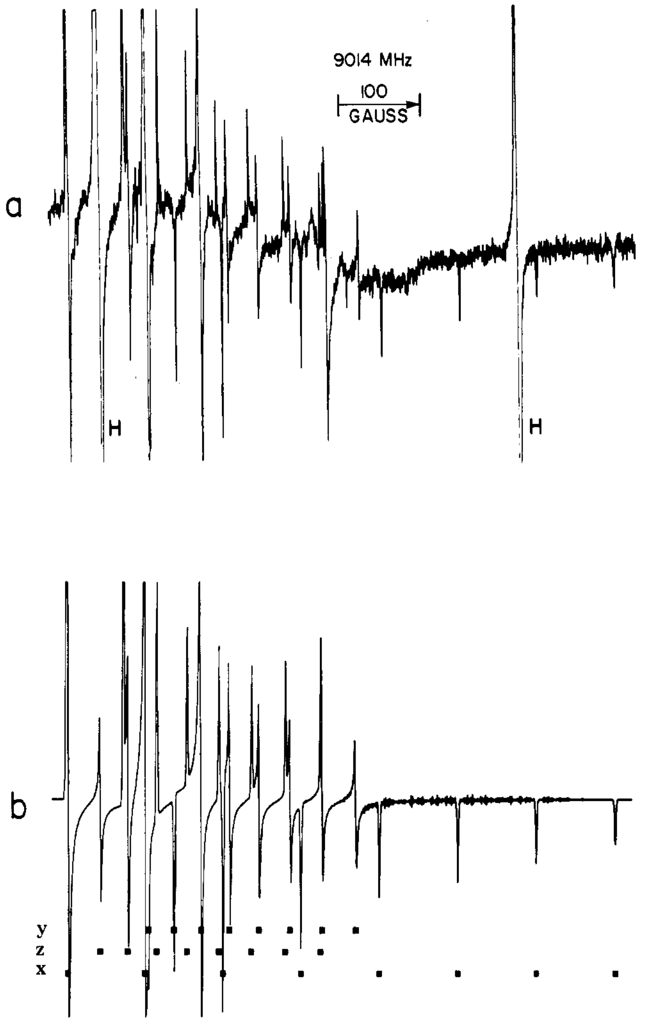

Figure 1. (a) The EPR spectrum of $V(CO)_5$ in a krypton matrix at 20 K. (b) A computer simulation of (a) using the spectral parameters (g, a_V) given in Table I.

real spectrum and the simulation is sufficient to confirm the correctness of the analysis.

Using a sample containing 98% ^{13}C, the x axis line for $m_I = +^5/_2$ had the ^{13}C hyperfine structure shown in Figure 2a, and the y axis line for $m_I = +^3/_2$ had the structure shown in Figure 2b. Both of these patterns indicate the presence of two pairs of carbon atoms. Their hyperfine interactions are included in Table I.

A second spectrum was sometimes present in irradiated $V(CO)_6$–Kr samples. In nonenriched samples it was a single, derivative-shaped line at $g = 1.9583 \pm 0.0001$. In 98% ^{13}C-enriched samples the ^{13}C hyperfine structure was that of four equivalent ^{13}C nuclei having a hyperfine interaction of 7.6 G. No ^{51}V hyperfine was apparent. This second spectrum was readily distinguished from the first by the fact that it was strongest at 5 K, 20 mW, whereas the spectrum shown in Figure 1a was best at 20 K, 2 mW.

Discussion

We identify the carrier of Figure 1a as $V(CO)_5$ for the following reasons: It contains at least four carbon atoms and probably is uncharged since it was produced by near-UV photolysis. The carrier is therefore $V(CO)_n$, where n = 4, 5, or 6. By analogy with the isoelectronic $Cr(CO)_4^+$,[7] we would expect $V(CO)_4$ to be in a high-spin $^6A_1$ state whose spectrum (in a powdered matrix) would show hyperfine structure with four equivalent ^{13}C nuclei, not two pairs of ^{13}C nuclei as in the present instance. The other possibility, $V(CO)_6$, has already been detected in a single crystal of $Cr(CO)_6$[1] and has quite different **g** and ^{51}V hyperfine tensors from those presently reported. In a Kr matrix, it probably gives rise to the broad feature at g = 2.066. Thus, discounting the possibility of doubly charged species, we are obliged to conclude that the carrier of Figure 1a is $V(CO)_5$.

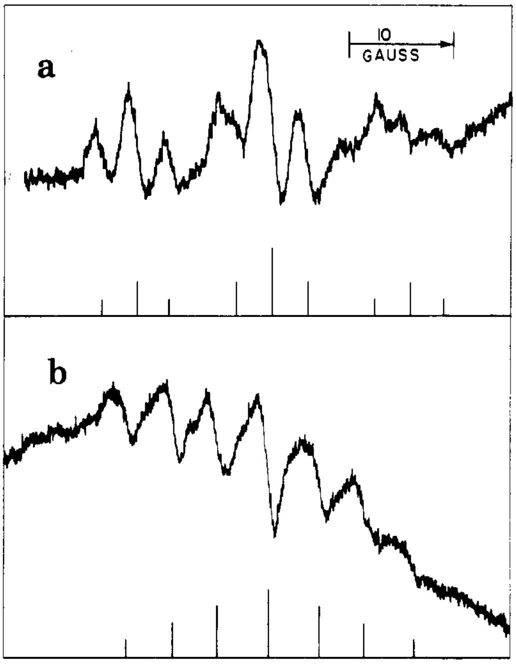

Figure 2. The EPR spectrum of a $V(CO)_5$–Kr sample containing ^{13}C enriched to 98%: (a) the x axis, $m_I = +^5/_2$ line; (b) the y axis, $m_I = +^3/_2$ line.

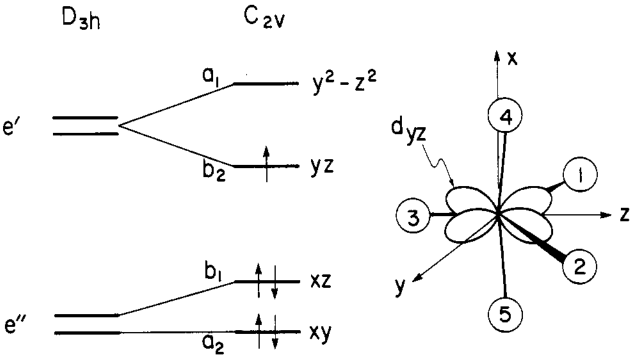

Figure 3. Energy level diagram for the distortion of a trigonal-bipyramidal $V(CO)_5$ toward C_{2v} symmetry.

Rossi and Hoffmann,[8] in their discussion of transition-metal pentacoordination, describe the energy changes along a Berry pseudorotation coordinate connecting D_{3h} and C_{4v} symmetries. The intermediate (C_{2v}) symmetry has the energy level scheme shown in Figure 3 in which a slight departure from D_{3h} symmetry is envisaged. The molecule $V(CO)_5$ is a d^5 species, and in D_{3h} symmetry the fifth electron would enter the e′ orbital. The $^2E'$ state so formed would be subject to a Jahn–Teller distortion with the formation of a $^2B_2$ state in C_{2v} symmetry.

The experimental data are certainly consistent with this hypothesis. The unpaired electron is in a molecular orbital of the B_2 representation to which V $3d_{yz}$ makes an important contribution. We would therefore expect x to be the direction of largest (negative) ^{51}V hyperfine interaction

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and negative g shift. The latter is due to spin–orbit interaction between the ground $^2B_2$ state and the excited $^2A_1$ state ($A_1 \times B_2$ transforms as R_x in C_{2v}). In Table I we see that there is a principal direction corresponding to large ^{51}V hyperfine interaction and negative g shift; it is according labeled x.

The hypothesis of $V(CO)_5$, $^2B_2$ in C_{2v}, also requires the y and z axes to be directions of small hyperfine interaction and positive g shift ($B_1 \times B_2$ and $A_2 \times B_2$ transform as R_z and R_y, respectively). Again, in Table I, we see that the hypothesis is in accord with the experimental data. In other words, the conclusion that the carrier of Figure 1a is $V(CO)_5$ can be accommodated by current structural theories.

Spin population in V $3d_{yz}$ can be estimated by the usual method[9] to be 0.42, assuming the two small principal values of the ^{51}V hyperfine tensor are positive, the other negative.

As regards the ^{13}C hyperfine interactions, we must use caution in any discussion since the values reported in Table I are not principal values of the ^{13}C hyperfine tensors. They are merely the ^{13}C hyperfine interactions along the principal directions of the **g** tensor. In fact, the line width variation across the spectra shown in Figure 2 is diagnostic of nonparallel **g** and hyperfine tensors. In a powder, as opposed to a single crystal, principal values of ligand hyperfine interactions are often not determinable. Association of the measured ^{13}C hyperfine interactions with the carbons of the C_{2v} structure (Figure 3) is thus impossible. We can, however, unambiguously assign the unique carbon that shows no resolvable interaction along x or y to the equatorial position 3.

We turn now to the second signal observed in $V(CO)_6$–Kr samples: a derivative-shaped line at $g = 1.9583$ without ^{51}V hyperfine structure, but showing hyperfine interactions of 7.6 G with four equivalent ^{13}C nuclei on enrichment. We suspect that this species is $V(CO)_4$, $^6A_1$ in T_d symmetry. The analogy with $Cr(CO)_4{}^+$–Kr leads us to expect a low g signal with almost isotropic ^{13}C hyperfine interactions.[7] The signal observed is due to the $|m_S = {}^1/_2\rangle \leftarrow |m_S = -{}^1/_2\rangle$ transition which, in a powder, is the only one detectable.[10] This transition, being isotropic, generates a relatively strong signal with full derivative line shape, as observed. The absence of ^{51}V hyperfine structure is disconcerting, but examination of $Fe(CO)_5$ or $Ni(CO)_4$ in krypton under similar conditions failed to reproduce the spectrum and convinced us that it was not due to an Fe- or Ni-containing impurity.

The observed isotropic hyperfine interaction for the metal nucleus in the $^6A_1$ state is due to a net s orbital unpaired spin density arising from three separate contributions: a direct, positive component from valence s orbital participation in the wave function, a negative component due to core polarization, and a positive contribution due to bond polarization.[11] The last term is often ignored in treating transition-metal ions but cannot be dismissed in cases such as metal carbonyls, where the ligands are covalently bound. In $V(CO)_4$ it would appear that the three terms cancel, whereas in $Cr(CO)_4{}^+$ a net Cr 4s spin density of ~0.06 is indicated.[7] This difference may be attributed to an enhanced metal–carbon bond strength in $Cr(CO)_4{}^+$ and a concomitant reduction in the bond polarization term. The anticipated stronger interaction of metal 3d and CO σ orbitals in $Cr(CO)_4{}^+$ will also result in a greater separation of the molecular antibonding orbitals and a reduced g shift from free spin vis-à-vis $V(CO)_4$.

We note that our ground-state assignment of $^6A_1$ in T_d for $V(CO)_4$ is in accord with the observation[12] of a single ν(CO) stretching mode for that species. Our finding of a C_{2v} structure for $V(CO)_5$, however, conflicts with the D_{3h} assignment deduced[12,13] from infrared spectroscopic data. It would appear, therefore, that certain CO stretching modes observed in the V–CO deposition experiments were misassigned.

Since both of the carriers exhibited hyperfine interactions with four carbon nuclei, we naturally considered the possibility that they were isomers of $V(CO)_4$, viz., a high-spin tetrahedral form and a low-spin distorted tetrahedral form. However, Cotton and Wilkinson's[14] strongly expressed arguments against the existence of low-spin tetrahedral d^5 species make us extremely reluctant to associate the spectrum of Figure 1a with low-spin $V(CO)_4$.

Registry No. $V(CoO)_4$, 59982-53-5; $V(CO)_5$, 59982-54-6; $V(CO)_6$, 14024-00-1.

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