

side-bonded dinitrogen species with increased coordination is unknown, side-bonded complexes could produce the anomalous frequency trend observed for this system.

Side bonding can also be used to explain the apparent anomalous behavior observed in nitrogen matrices. It is reasonable to assume that because of steric effects, $\text{Cr}(\text{N}_2)_4$ is the highest coordinated side-bonded chromium-dinitrogen complex which can be formed and that this complex could be formed in nitrogen matrices using "normal" deposition conditions. However, if this complex is metastable, it could be converted to the thermodynamically more stable end-bonded $\text{Cr}(\text{N}_2)_6$ by providing sufficient energy to convert side-bonded $\text{Cr}(\text{N}_2)_4$ to end-bonded $\text{Cr}(\text{N}_2)_4$, which can then react with free nitrogen in the matrix to form $\text{Cr}(\text{N}_2)_6$. The lamps used to photolyze the nitrogen matrix provided this energy.

Even if the type of bonding is established, the matrix structures may not be the most stable structures of the free species. There is growing evidence of quasi-stable compounds formed from the interaction between the trapped species and the matrix gas. For example, the electronic spectrum of vanadium atoms trapped in argon matrices¹⁶ was shown to be quite similar to the electronic spectrum expected for the hypothetical molecule $\text{V}(\text{Ar})_6$. Thus solvation effects could influence the structures of the intermediate complexes. In fact, Kundig and Ozin¹⁷ have recently suggested the structure of free $\text{Cr}(\text{CO})_5$ is trigonal bipyramidal (D_{3h}) rather than the square-pyramidal (C_{4v}) structure reported by Graham et al.¹⁸ They suggested the C_{4v} complex is actually $\text{Cr}(\text{CO})_5\text{S}$, where S = solvent. From the variation found in the visible absorption spectrum of $\text{Cr}(\text{CO})_5$ in mixed rare gas matrices, Perutz and Turner¹⁹ have also concluded that $\text{Cr}(\text{CO})_5\text{S}$ may be a better representation of the complex. However, they expressed doubt that the solvation effect was strong enough to influence the structure of the complex.

Conclusion

The binary dinitrogen complexes of chromium with from one to six coordinated dinitrogen ligands per metal atom have been identified from their infrared spectra in N_2/Ar mixtures at 10 K. Tentative structures, which are consistent with the infrared spectra, have been determined for each complex.

Unfortunately, in several cases, more than one possible structure was found to be consistent with the infrared data.

The uv spectrum of $\text{Cr}(\text{N}_2)_6$ was observed in a N_2 matrix and found to be qualitatively similar to the previously observed electronic spectrum of $\text{Cr}(\text{CO})_6$. Although the magnitude of the d-d splitting parameter in the hexakis(dinitrogen) complex is slightly less than the magnitude of the d-d splitting parameter found for the hexacarbonyl, it clearly establishes that N_2 is a strong-field ligand with a field strength comparable to CN^- .

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Registry No. $\text{Cr}(\text{N}_2)$, 32376-71-9; $\text{Cr}(\text{N}_2)_2$, 58815-27-3; $\text{Cr}(\text{N}_2)_3$, 58815-28-4; $\text{Cr}(\text{N}_2)_4$, 58815-29-5; $\text{Cr}(\text{N}_2)_5$, 58815-30-8; $\text{Cr}(\text{N}_2)_6$, 28042-66-2.

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Synthesis of Dodecacarbonyldivanadium in Low-Temperature Matrices¹

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The products of the cocondensation of V atoms with CO at 10 K have been investigated using ir and uv spectroscopy. Two vanadium carbonyl complexes, $\text{V}(\text{CO})_6$ and $\text{V}_2(\text{CO})_{12}$, have been identified and the structure of each complex was determined from the analysis of the ir spectrum. In addition, the electronic spectrum of $\text{V}(\text{CO})_6$ has been analyzed.

Introduction

Vanadium hexacarbonyl ($\text{V}(\text{CO})_6$) has been investigated by a number of techniques including infrared and ultraviolet spectroscopy,^{2a} photoelectron spectroscopy,^{2b} electron spin resonance spectroscopy,³ and magnetic measurements.^{4,5} These studies indicate that at room temperature $\text{V}(\text{CO})_6$ has one unpaired electron and virtual octahedral geometry producing an effective $^2T_{2g}$ ground state. According to the Jahn-Teller theorem, this structure should undergo some distortion which will remove the orbital degeneracy. In fact, there is strong experimental evidence of a dynamic Jahn-Teller

distortion at room temperature.^{2a} At ~ 66 K, both ESR³ and magnetic measurements^{4,5} indicate the dynamic distorted structure is transformed into a statically distorted structure, which is thought to have one unpaired electron and D_{4h} symmetry producing a $^2B_{2g}$ ground state. Since D_{4h} $\text{V}(\text{CO})_6$ had not been previously observed spectroscopically, the technique of matrix isolation was used to investigate this molecule spectroscopically.

During this study several additional bands were observed in the infrared spectrum of vanadium isolated in CO matrices. An investigation of these bands indicated that they arose from

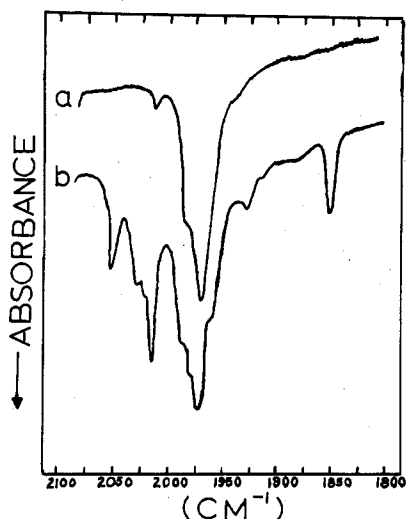


Figure 1. Infrared spectra of the vanadium carbonyl complexes observed in a CO matrix. Trace a is prior to annealing; trace b is after annealing.

a dimeric vanadium carbonyl species, most likely $V_2(CO)_{12}$. This dimeric species was investigated and a tentative structure has been proposed.

Experimental Section

The apparatus used in this study has been described previously.⁶ $V(CO)_6$ was produced in situ by codepositing vanadium metal atoms with CO or with 1–8 mol % CO/Ar mixtures on a NaCl optical window at 8–15 K and annealing the matrix. The metal atoms were produced by vaporizing vanadium metal (99.95% pure) in a resistively heated tungsten wire basket purchased from Ladd Research, Inc. The furnace temperature was adjusted to give metal atom pressures between 0.005 and 0.015 Torr. The rate of deposition of the matrix gas was typically 0.15 mmol of matrix gas/min for 25 min.

Matheson research grades Ar and CO were used in this study. All spectra were taken at 8 K using a Beckman IR-7 instrument in the infrared region and a Cary 14 recording spectrometer in the uv-visible region. The continuum for the Cary 14 instrument was provided by a high-intensity tungsten lamp in the visible region and by a hydrogen discharge lamp in the ultraviolet region. The infrared band positions were calibrated using atmospheric H_2O bands and are estimated to be accurate to ± 2 cm^{-1} . The uv bands were calibrated from matrix-isolated vanadium bands and are estimated to be accurate to ± 0.3 nm for the sharper bands.

Results and Discussion

The infrared spectra obtained from two experiments in which vanadium atoms were codeposited with CO are shown in Figure 1. In addition, all spectra contained intense bands at 2138 and 2092 cm^{-1} due to ^{12}CO and ^{13}CO , respectively, which are not shown. If conditions favoring good isolation were used, the infrared spectrum contained two strong bands at 1972 and 1980 cm^{-1} and a rather weak band at 2014 cm^{-1} (Figure 1a). However, if the matrix is deposited at a faster rate, a condition which increases the probability of surface diffusion during the deposition process, the spectrum shown in Figure 1b was obtained. In addition to the bands observed in Figure 1a, new bands were observed at 1852, 1927, 1958, 1987, 2021, 2030, and 2046 cm^{-1} , and the band at 2014 cm^{-1} had markedly increased in intensity.

In order to establish better the origin of these bands, the species produced by carefully codepositing vanadium atoms with CO/Ar mixtures were examined. The spectra obtained from one annealing experiment using 5% CO/Ar are shown in Figure 2. Prior to annealing, ir bands were observed at 1874, 1896, 1910, 1922, 1948, 1955, 1963, 1975, 1981, 2014, and 2030 cm^{-1} . Upon annealing (Figure 2b and c), the bands at 1874, 1896, 1910, and 1948 cm^{-1} disappeared and the bands at 1922, 1955, and 1963 cm^{-1} decreased in intensity. With

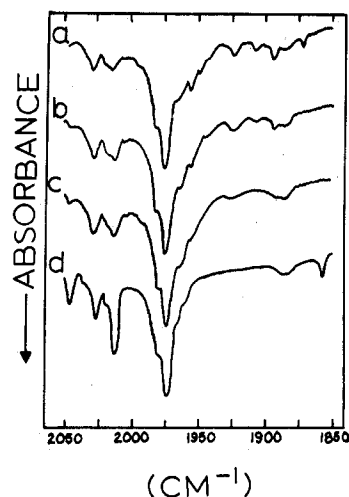


Figure 2. Infrared spectra of the vanadium carbonyl complexes in 5% CO/Ar. Trace a is prior to annealing; traces b–d are after warming the matrix to 30 K for several minutes.

Table I. Secular Equations for the Infrared-Active Modes for $D_{4h} V(CO)_6$ ^a

m_x	m_y	m_z	G	Sym	F matrix
0	0	2	1	A_{2u}	$K_a - K_p$
2	2	0	1	E_u	$K_e - K_t$

^a Notation from ref 7.

Table II. Comparison of the Observed and Calculated Ir Spectrum of $D_{4h} V(CO)_6$ ^a

Sym	Obsd		Calcd	
	Freq, ^b cm^{-1}	Intens ^b	Freq, ^c cm^{-1}	Intens ^c
A_{2u}	1980	~2	1981	~2
E_u	1972	4	1975	4

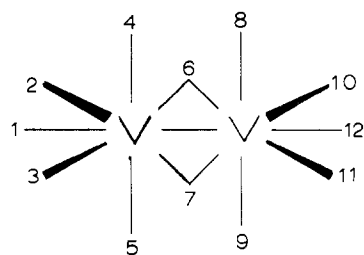
^a $K_a - K_p = 15.79$ mdyn/A; $K_e - K_t = 15.68$ mdyn/A. ^b CO matrix. ^c Ar matrix.

further annealing, the bands at 1922, 1955, and 1963 cm^{-1} disappeared, the band at 2014 cm^{-1} increased in intensity, and new bands were observed at 1858, 2021, and 2046 cm^{-1} .

The bands at 1975 and 1981 cm^{-1} appear to arise from the same species. Since this species is apparently a product upon annealing and is a product from the codeposition of vanadium atoms with CO and the frequencies are in good agreement with the reported CO stretching frequency for solid $V(CO)_6$, this species has been assigned as $V(CO)_6$. The observation of two ir bands for $V(CO)_6$ in both Ar and CO matrices suggests that at low temperatures $V(CO)_6$ has D_{4h} symmetry.

An attempt was made to verify that this splitting resulted from a true molecular distortion and did not originate from matrix effects by calculating the ir spectrum expected for $D_{4h} V(CO)_6$ using the method of Haas and Sheline⁷ and comparing the calculated spectrum with the observed spectrum. The secular equations needed for this calculation are given in Table I. Although the extensive overlap of the bands in the observed spectrum prevented an accurate determination of the relative intensities, the agreement between the observed spectrum and the spectrum calculated using the observed Cotton-Kraihanzel force constants is quite good as shown in Table II and supports the hypothesis that the bands arise from a true molecular distortion rather than from a matrix effect.

Since the intensity of the bands at 1874, 1896, 1910, 1922, 1948, 1955, and 1963 cm^{-1} decreased rapidly upon annealing, these bands are believed to arise from partially coordinated species. The bands at 1922, 1955, and 1963 cm^{-1} appear to arise from the same species. Since these frequencies are in

Figure 3. Tentative structure for $V_2(CO)_{12}$.Table III. Secular Equations for the Infrared-Active Modes of $V_2(CO)_{12}$ Assuming D_{2h} Symmetry^a

m_x, m_y, m_z	G	Sym	F matrix
2 0 0	1	B_{1u}	K_b $2^{1/2}K_y$
4 0 0	1	B_{1u}	$K_e - K_t + K_n - K_o$
0 0 2	1	B_{2u}	$2^{1/2}K_v$
0 0 0	1	B_{2u}	$K_e + K_t - K_n$ $2(K_c - K_s)$
0 0 0	1	B_{2u}	$-K_d$ $K_e + K_t - K_n$
0 4 0	1	B_{3u}	$K_e - K_t + K_n - K_d$

^a $K_a = f_1^1$; $K_b = f_6^6 - f_6^7$; $K_c = f_2^4$; $K_d = f_2^{11}$; $K_e = f_2^2$; $K_n = f_2^{10}$; $K_p = f_1^{12}$; $K_s = f_2^3$; $K_t = f_2^3$; $K_v = f_1^2 - f_1^8$; $K_y = f_4^6 - f_4^7$.

reasonably good agreement with the frequencies reported by Kundig et al. for $V(CO)_5$,⁸ this species has been assigned as $V(CO)_5$. The assignments for the 1874-, 1896-, 1910-, and 1948- cm^{-1} bands have not been established. However, the observed behavior of these bands upon annealing and the similarity of these frequencies reported by DeKock⁹ for the partially coordinated tantalum carbonyls suggest these bands may arise from $V(CO)$, $V(CO)_2$, $V(CO)_3$, and $V(CO)_4$, respectively.

The bands at 1852, 2014, 2021, and 2045 cm^{-1} , which increase in intensity upon annealing after the partially coordinated species could no longer be observed in the spectrum, are believed to arise from a single dimeric vanadium carbonyl. Since $V_2(CO)_{12}$ would satisfy the 18-electron rule, this species is thought to be $V_2(CO)_{12}$. Since the band at 1852 cm^{-1} indicates the presence of at least one bridging group in the dimer and the small number of observed ir bands suggests that the molecule has an inversion center, $V_2(CO)_{12}$ is most likely structurally similar to the double-bridged structure shown in Figure 3. To determine if this assignment and structure are reasonable, the infrared spectrum for this species was calculated using the method of Haas and Sheline and the calculated spectrum was compared to the observed infrared spectra. The secular equations needed to reproduce this calculation are given in Table III. Since an insufficient number of frequencies was available to calculate all of the force constants, the interaction force constants between two linear CO groups have been assumed to be equal to the interaction force constants calculated by Haas and Sheline for $Mn_2(CO)_{10}$. As shown in Table IV the agreement between the observed spectra and the spectra calculated using this model with the observed Cotton-Kraihenzel force constants is quite good, which supports the proposed structure of $V_2(CO)_{12}$.

The origin of the 2030- cm^{-1} band is still in doubt. However, it also most likely arises from a dimeric species.

The electronic spectrum of $V(CO)_6$ in a CO matrix is shown in Figure 4a. Although the spectrum is badly overlapped, a compilation of several scans reveals some fine structure which is shown in Figure 4b. While the spectrum undoubtedly contains considerable vibronic structure, it is not totally unreasonable to assume that only the strongest band from each electronic transition was resolved, and the spectrum has been analyzed using this assumption. The lowest doublet energy states for d^5 ions in a strong tetragonally distorted octahedral ligand field in terms of crystal field and Racah parameters

Table IV. Comparison of the Observed and the Calculated Ir Spectrum of $D_{2h} V_2(CO)_{12}$ ^a

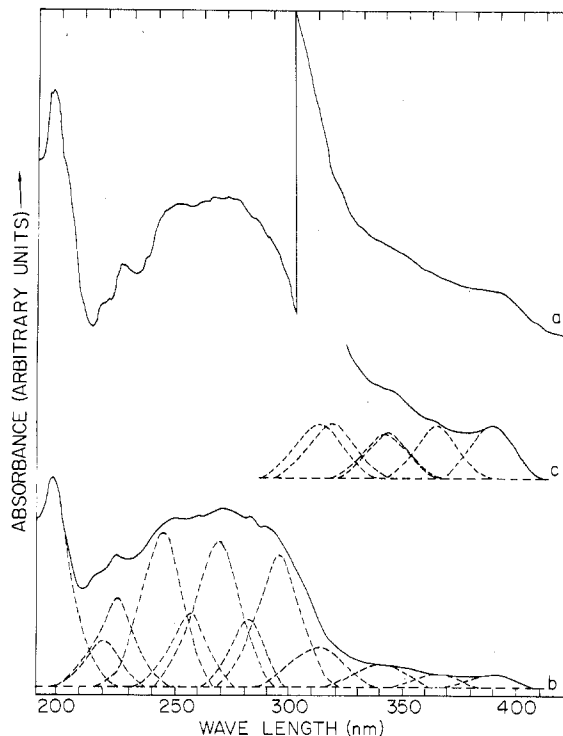
Sym	Obsd		Calcd	
	Freq, ^b cm^{-1}	Intens ^b	Freq, ^c cm^{-1}	Intens ^c
B_{1u}	1852	1.8	1858	1.4
B_{1u}	2014	3.6	2014	4.3
B_{2u}	1987	0.4		0.0
B_{2u}	2021	0.4	2021	0.2
B_{2u}	2046	1.8	2046	2.1
B_{3u}	2014	4.0	2014	4.0

^a $K_a = 16.10$ mdyn/Å; $K_b = 13.84$ mdyn/Å; $K_c = 0.20$ mdyn/Å; $K_d = 0.07$ mdyn/Å; $K_e = 16.53$ mdyn/Å; $K_n = 0.27$ mdyn/Å; $K_p = 0.08$ mdyn/Å; $K_s = 0.13$ mdyn/Å; $K_t = 0.39$ mdyn/Å; $K_v = 0.16$ mdyn/Å; $K_y = -0.21$ mdyn/Å. ^b CO matrix. ^c Ar matrix.

Table V. Lowest Spin Doublet Energy States for d^5 Ions in a Strong Crystal Field with D_{4h} Symmetry

Electron confign	Designation	Total orbital energy ^a	Racah energy (+10A)
$e_g^4 t_{2g}^2$	$^2B_{2g}$	$5\epsilon_0 - 20Dq - 2Ds + 15Dt$	$-20B + 10C$
$e_g^3 b_{2g}^2$	$^2E_g(1)$	$5\epsilon_0 - 20Dq + Ds + 10Dt$	$-20B + 20C$
$e_g^4 a_{1g}$	$^2A_{1g}$	$5\epsilon_0 - 10Dq - 6Ds + 10Dt$	$+10C$
$e_g^3 b_{2g} a_{1g}$	$^2E_g(2)$	$5\epsilon_0 - 10Dq - 3Ds + 5Dt$	$-13B + 9C$
	$^2E_g(3)$	$5\epsilon_0 - 10Dq = 3Ds + 5Dt$	$-9B + 9C$
$e_g^4 b_{1g}$	$^2B_{1g}$	$5\epsilon_0 - 10Dq - 2Ds + 15Dt$	$-20B + 10C$
$e_g^3 b_{2g} b_{1g}$	$^2E_g(4)$	$5\epsilon_0 - 10Dq + Ds + 10Dt$	$-20B + 9C$
	$^2E_g(5)$	$5\epsilon_0 - 10Dq + Ds + 10Dt$	$-14B + 9C$

^a The one-electron orbital energies are $E(b_{1g}) = \epsilon_0 + 6Dq + 2Ds - Dt$, $E(a_{1g}) = \epsilon_0 + 6Dq - 2Ds - 6Dt$, $E(b_{2g}) = \epsilon_0 - 4Dq + 2Ds - Dt$, and $E(d) = \epsilon_0 - 4Dq - Ds + 4Dt$.

Figure 4. Electronic spectrum of $V(CO)_6$ in a CO matrix. Trace a is the observed spectrum; trace b is an approximate Gaussian resolution of the spectrum; trace c is the calculated d-d spectrum for $V(CO)_6$.

are given in Table V. Ds and Dt are parameters which represent the distortion from O_h symmetry. A value greater than zero for Dt , a parameter directly related to the tetragonal distortion, corresponds to a lengthening of the bond along the fourfold axis. If C is assumed to be approximately equal to $4B$, crystal field and Racah parameters can be calculated from the four lowest energy bands of $V(CO)_6$.

Table VI. Crystal Field and Racah Parameters for $V(CO)_6$ (cm^{-1})

$10Dq$	Ds	Dt	B	C^a
29 300	1215	365	450	1800

^a Estimated value.Table VII. States Expected for the Charge-Transfer Bands from the e_g and $b_{2g} \pi^*$ Orbitals to the a_{2u} and $e_u \sigma^*$ Orbitals

Electron Confign	Designation
$e_g^4 a_{2u}$	$^2A_{2u}$
$e_g^3 b_{2g} a_{2u}$	$^2E_u(1)$
$e_g^4 e_u$	$^2E_u(2)$
$e_g^3 b_{2g} e_u$	$^2A_{1u}, ^2A_{2u}, ^2B_{1u}, ^2B_{2u}$

Table VIII. Tentative Assignments for the Electronic Spectrum of $V(CO)_6$

Transition	λ , nm	$\bar{\nu}$, cm^{-1}	Transition	λ , nm	$\bar{\nu}$, cm^{-1}
$^2E_g(2) \leftarrow ^2B_{2g}$	388.2	25 758	$^2A_{2u} \leftarrow ^2B_{2g}$	283.0	35 336
$^2E_g(3) \leftarrow ^2B_{2g}$	363.0	27 546	$^2E_u(2) \leftarrow ^2B_{2g}$	269.2	37 147
$^2B_{1g} \leftarrow ^2B_{2g}$	341.6	29 274	$^2B_{2u} \leftarrow ^2B_{2g}$	260.0	38 462
$^2E_g(4) \leftarrow ^2B_{2g}$	341.0 ^a	29 317 ^a	$^2B_{1u} \leftarrow ^2B_{2g}$	242.5	41 237
$^2A_{1g} \leftarrow ^2B_{2g}$	317.2	31 526	$^2A_{2u} \leftarrow ^2B_{2g}$	226.0	44 248
$^2E_g(5) \leftarrow ^2B_{2g}$	312.5	32 000	$^2A_{1u} \leftarrow ^2B_{2g}$	220.0	45 455
$^2E_u(1) \leftarrow ^2B_{2g}$	295.4	33 852			

^a Calculated value.

From a first-order analysis of the ESR spectrum, Pratt and Meyers³ have calculated that $10Dq \leq 36\,200\,cm^{-1}$ and $3Ds - 5Dt \leq 1880\,cm^{-1}$. The proposed assignments were permuted until the calculated crystal field parameters satisfied these limits. These parameters were then tested by calculating the expected d-d spectrum and comparing it to the observed d-d spectrum. The parameters listed in Table VI reproduced the observed spectrum quite well as shown in Figure 4c and satisfied both upper limits for the crystal field parameters. Consequently, these parameters were used to assign the observed d-d spectrum.

Since the photoelectron spectrum of $V(CO)_6$ indicates the ligand bonding molecular orbitals are at least 5 eV lower in energy than are the metallike d orbitals,^{2b} the charge-transfer bands are most likely transitions from the b_{2g} and $e_g \pi^*$ orbitals to the a_{2u} and $e_u \sigma^*$ orbitals. The states expected for these one-electron transitions are listed in Table VII. Since only the two 2E_u states and the $^2B_{1u}$ states are electronic dipole allowed, these transitions are expected to give rise to the three strongest bands observed in the spectrum. Using this and the calculated d-orbital energies, tentative assignments for the charge-transfer spectrum have been made. The assignments for all of the observed electronic transitions of $V(CO)_6$ are given in Table VIII.

Conclusions

As expected from previous studies, $V(CO)_6$ was found to have D_{4h} symmetry in matrices at low temperatures. The electronic spectrum of $V(CO)_6$ in a CO matrix was examined and tentative assignments have been made for the bands contained in the spectrum. Approximate crystal field and Racah parameters have been determined.

$V_2(CO)_{12}$ has been identified from the ir spectrum, and a tentative structure has been proposed for this molecule.

Registry No. $V(CO)_6$, 14024-00-1; $V_2(CO)_{12}$, 58815-50-2.

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Pulsed Nuclear Magnetic Resonance Study of the Molecular Dynamics of Fluxional Organometallic Molecules in the Solid State.

1. Complexes Containing Cyclooctatetraene Ligands

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Motion of the cyclooctatetraene moiety in the series of fluxional organometallic molecules $C_8H_8Fe(CO)_3$, $C_8H_8Fe_2(CO)_5$, and $(C_8H_8)_2Ru_3(CO)_4$ in the solid state is confirmed by measurements of T_1 , the spin-lattice relaxation time, and $T_{1\rho}$, the spin-lattice relaxation time in the rotating frame, and accurate values obtained for the activation energies. The results are discussed in relation to the structure and bonding in the compounds and to the results from high-resolution NMR measurements in solution as well as the results from continuous-wave NMR and x-ray crystallographic investigations in the solid state.

Introduction

The structure and bonding of fluxional organometallic compounds has been extensively investigated in recent years.²

In these compounds, the bonding between the metal atom and the ligand is localized at some point in the latter, as shown by x-ray diffraction studies in the solid, but the bonding in solution is of a dynamic nature, the point of attachment continually changing and the static structure being observed only at low temperatures. In this light, the properties of I,

$C_8H_8Fe(CO)_3$, II, $C_8H_8Fe_2(CO)_6$, III, $C_8H_8Fe_2(CO)_5$, and IV, $(C_8H_8)_2Ru_3(CO)_4$, have been extensively investigated.³⁻¹⁶ The structure of each compound has been determined by x-ray diffraction. The compounds I, III, and IV are fluxional; a single proton resonance peak is observed in solution at room temperature, indicating that the point of attachment of metal to ring is continually changing. After some dispute, it has been concluded² that the rearrangement mechanism in I (cyclooctatetraeneiron tricarbonyl) is by a series of 1,2 shifts