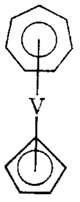
Magnetic Resonance and Mass Spectrum of π-Cyclopentadienyl-π-cycloheptatrienylvanadium. Mass Spectral Rearrangement to Bis(benzene)vanadium

Michael F. Rettig, Charles D. Stout, Anthony Klug, and Paul Farnham

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received March 30, 1970*

Abstract: Vanadium and hydrogen hyperfine constants have been determined for π-cyclopentadienyl-π-cycloheptatrienylvanadium (cpVtr) by means of wide-line nmr and esr experiments. Assignments were made by partial deuteration of the five-membered ring. All of the observed parameters are consistent with MO calculations done by the extended Hückel method. The dominant means of electron delocalization in cpVtr involves interaction of an unpaired d_{z^2} electron with an in-plane σ orbital in either of the rings. The d_{z^2} interaction with the seven-membered ring is about three times that with the five-membered ring. The results are compared with earlier data for vanadocene and bis(benzene)vanadium. Analysis of the mass spectrum of partially deuterated cpVtr gives conclusive proof that a facile intramolecular rearrangement to bis(benzene)vanadium follows electron impact.

King and Stone, who first prepared π-cyclopentadienyl-π-cycloheptatrienylvanadium (I, abbreviated cpVtr) in 1959,[1] reported the compound to be paramagnetic with one unpaired electron. The crystal structure of cpVtr was reported in preliminary form by Engebretson and Rundle,[2] who confirmed the π-sandwich structure for the molecule. The perpendicular distance from vanadium to the five-membered ring was found to be 1.90 Å, while the corresponding distance to the seven-membered ring was 1.50 Å. All the metal–carbon distances were equal within experimental error.[2] In 1967, Gulick and Geske reported that cpVtr could be electrochemically oxidized in acetonitrile to an unstable cation, and they recorded electronic spectra of both the neutral molecule and the cationic species.[3] The mass spectrum of cpVtr was recorded by Müller and Göser,[4] who also obtained ionization potentials for the molecular and certain fragment ions, as well as the gaseous heat of formation. Later, Müller, Göser, and Laubereau[5] isolated and characterized a triiodide salt of cpVtr, $[cpVtr]I_3$, obtained by reaction of cpVtr with iodine in benzene or ether. Aside from an inconclusive discussion[6] of the infrared spectrum of cpVtr, no further mention of this material has appeared in the literature, to the best of our knowledge.


I

In view of the considerable current interest[7–16] in the magnetic properties of π-sandwich compounds, we decided to undertake for the first time a magnetic resonance investigation of a *mixed* sandwich species, namely cpVtr. Previous nmr and esr investigations of symmetrical vanadocene and bis(benzene)vanadium have led to some definite conclusions concerning the ground states and modes of electron delocalization, and it was therefore of interest to compare with these the properties of the unsymmetrical cpVtr. We have succeeded in obtaining good quality wide-line proton nmr spectra of cpVtr, as well as esr spectra in liquid and glassy solution. Both proton and vanadium hyperfine structure were observed in the glassy solution spectrum. Extended Hückel molecular orbital calculations have also been carried out for cpVtr, and the results are in agreement with the observed vanadium and proton hyperfine coupling constants. In the course of this work we also recorded the mass spectrum of a partially deuterated sample of cpVtr, and we have come to conclusions different from those of the previous workers[4] regarding the mode of fragmentation of the molecular ion. Specifically, rearrangement of the molecular ion to bis(benzene)vanadium has been demonstrated to occur, and this had been specifically ruled out.[4]

Experimental Section

Nmr spectra were obtained at 100 MHz, using a Varian HA-100 spectrometer operating at 305°K, or at 60 MHz using a Varian DP-60 spectrometer operating in HR and wide-line modes. The field was swept using the Varian precession field scanning unit. The spectra were calibrated using the side-band technique. Esr spectra were determined near 9 GHz (X-band) using a Varian V-4502 esr spectrometer. Spectra were calibrated using external DPPH, and by direct reading of the Mark II Field-Dial. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-9D

---

(1) R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, **81**, 5263 (1959).

(2) G. Engebretson and R. E. Rundle, *ibid.*, **85**, 481 (1963).

(3) W. M. Gulick and D. H. Geske, *Inorg. Chem.*, **6**, 1320 (1967).

(4) J. Müller and P. Göser, *J. Organometal. Chem.*, **12**, 163 (1968).

(5) J. Müller, P. Göser, and P. Laubereau, *ibid.*, **14**, 7 (1968).

(6) H. Fritz and R. Schneider, *Chem. Ber.*, **93**, 1171 (1960).

(7) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 1361 (1969).

(8) M. F. Rettig and R. S. Drago, *ibid.*, **91**, 3432 (1969).

(9) M. F. Rettig and R. S. Drago, *Chem. Commun.*, 891 (1966).

(10) R. Prins, *J. Chem. Phys.*, **50**, 4804 (1969).

(11) J. H. Schachtschneider, R. Prins, and P. Ras, *Inorg. Chim. Acta*, **1**, 462 (1967).

(12) R. Prins and F. J. Reinders, *Chem. Phys. Lett.*, **3**, 45 (1969).

(13) R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, **91**, 4929 (1969).

(14) S. E. Anderson and R. S. Drago, *ibid.*, **91**, 3656 (1969).

(15) H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *Z. Naturforsch. B*, **22**, 891 (1967).

(16) H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *ibid.*, *B*, **23**, 298 (1968).

double-focusing mass spectrometer. The direct insertion (solid inlet) system was used, with a sample temperature of about 80°.

2-Methyltetrahydrofuran and toluene (for esr experiments) were distilled, deoxygenated, and handled only in a Vacuum Atmospheres Dri-Lab–Dri-Train under nitrogen.

Molecular orbital calculations were carried out by means of the extended Hückel method previously described,[8] using an IBM 7040 computer. Bond distances were taken from the X-ray data.[2] The overlap matrix was computed from a multiexponential basis set, as previously described for vanadocene.[8] The coordinate system was chosen so that the z axis passes through the center of the two rings, with the x and y axes in the plane of the vanadium between the two rings. The vanadium position was taken as the origin.

Syntheses of Compounds. 1. $[(\pi\text{-}C_5H_5)(\pi\text{-}C_7H_7)V]$. This was prepared according to the method in ref 17. The compound was identified by its mass spectrum.

2. Partially Deuterated cpVtr. This was prepared as above, using partially deuterated cyclopentadiene in the synthesis of π-cyclopentadienylvanadium tetracarbonyl. The cyclopentadiene was deuterated as follows. A mixture of 1.95 g of KOD, 100 ml of D_2O, and 22 g of freshly distilled (cracked) cyclopentadiene was rapidly agitated under nitrogen for 3.5 hr using a magnetic stirrer. The aqueous layer was saturated with NaCl, and the organic layer was separated using a separatory funnel. Without drying, the deuterated cyclopentadiene was quickly distilled through a 20-cm Vigreux column. The nmr spectrum of the product (about 10 g) showed no water and a trace of dicyclopentadiene. On comparison with the nmr of undeuterated cyclopentadiene, the treated sample was found to be about 62% deuterated.

Results

Nuclear Magnetic Resonance. The nmr spectrum of solid cpVtr contained in a 5-mm o.d. tube was determined using the HR mode of the HA-100 spectrometer. Two very broad but easily observed resonances were observed downfield of external water. The peaks overlapped somewhat but were otherwise symmetric. Despite repeated observation with different instrumental parameters, the intensity ratio of the peaks could not be assessed accurately enough to assign the spectrum. However, the spectrum of the sample deuterated at the five-membered ring left no doubt that the farther downfield resonance arises from the seven-membered ring. The two resonances are assigned as follows (relative to external water): -310 ± 10 ppm (line width about 15,000 Hz) for the C_7H_7 ring, -130 ± 5 ppm (line width about 12,000 Hz) for the C_5H_5 ring. The spectrum of the solid was also observed at 60 MHz. The peaks overlapped to a greater extent, but otherwise the results were the same. The observed contact shifts were converted to hyperfine coupling constants by means of eq 1, where the symbols have

$$\frac{\Delta\nu}{\nu} = -A\left(\frac{\gamma_e g\beta S(S+1)}{\gamma_H 3kT}\right) \qquad (1)$$

their familiar meanings. In eq 1 we used the isotropic g value, 1.987, obtained from solution esr experiments described below. The calculated coupling constant, A, for the five-membered ring is 1.8 ± 0.1 G, and that for the seven-membered ring is 4.3 ± 0.2 G.

Electron Spin Resonance. The isotropic ^{51}V hyperfine splitting and the isotropic g value were determined at room temperature from an undeuterated sample of cpVtr dissolved in 2-methyltetrahydrofuran. The isotropic splitting and g value, both corrected for second-order shifts of the hyperfine lines,[18,19] are, respectively, 68.7 G and 1.987. This same solution solidified to a glass at liquid nitrogen temperature, again giving an eight-line spectrum with intensity distribution characteristic of a glass. We believe (see below) that the spectrum observed in the glass arises from molecules having their symmetry axis perpendicular to the field direction. The observed $|A_\perp|$ and $g_\perp$ (corrected for second-order shifts) are 96.1 G and 1.978.

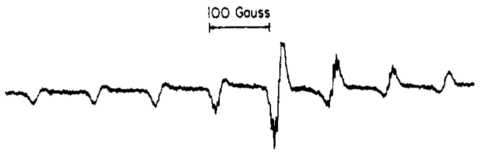


Figure 1. Esr spectrum of partially deuterated (C_5 ring only) cpVtr in glassy toluene at liquid nitrogen temperature. The magnetic field increases from right to left.

Finally, a glassy toluene solution of partially deuterated cpVtr at liquid nitrogen temperature was found to exhibit extra hyperfine structure due to the protons of the undeuterated seven-membered ring (see Figure 1). Although one cannot unambiguously count the expected eight lines in the first-derivative spectrum, the second-derivative spectrum of the third peak from lowest field clearly shows the eight proton hyperfine lines with approximately correct intensity ratios. From the second-derivative spectrum, the proton coupling constant, $A_H{}^7$, was found to be 4.8 ± 0.3 G, consistent with the value obtained from the nmr experiment. The proton hyperfine structure appears only in the deuterated sample, and must be observable by virtue of the absence of hyperfine broadening due to the five-membered ring.

Mass Spectrum. The mass spectrum of cpVtr (undeuterated) has been reported.[4] Our interest lies mainly in the origin of the peak assigned to $(VC_6H_6)^+$, and we discuss here only the regions of the spectrum relevant to the $(VC_6H_6)^+$ fragment. To this end, some peak locations, intensities, and assignments are given in Table I. From the relative intensities in the m/e 207–212 region, we find that the five-membered ring is, on the average, 62% deuterated, in agreement with the nmr result. The metastable peaks near m/e 79 and

Table I. Partial Listing of Mass Spectrum of Deuterated cpVtr

m/e	Fragment of process	Relative intensity[a]
212	$(C_5D_5)V(C_7H_7)^+$	33
211	$(C_5HD_4)V(C_7H_7)^+$	87
210	$(C_5H_2D_3)V(C_7H_7)^+$	100
209	$(C_5H_3D_2)V(C_7H_7)^+$	72
208	$(C_5H_4D)V(C_7H_7)^+$	22
207	$(C_5H_5)V(C_7H_7)^+$	6
134	$V(C_6HD_5)^+$	5
133	$V(C_6H_2D_4)^+$	13
132	$V(C_6H_3D_3)^+$	15
131	$V(C_6H_4D_2)^+$	10
130	$V(C_6H_5D)^+$	3
129	$V(C_6H_6)^+$	42
83	$V(C_{12}H_{7+x}D_y)^+ \rightarrow (C_6H_{x+1}D_y)V^+ + C_6H_8$ (metastable)	
79	$V(C_{12}H_{7+x}D_y)^+ \rightarrow V(C_6H_6)^+ + C_6H_{x+1}D_y$ (metastable)	

[a] Intensities are corrected for natural abundance ^{13}C.

---

(17) R. B. King, *Organometal. Syn.*, 1, 140 (1965).

(18) B. Bleaney, *Phil. Mag.*, 42, 441 (1951).

(19) B. R. McGarvey, "Transition Metal Chemistry," Vol. 3, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1966, p 125.

83 were assigned by means of eq 2, where m^* is the

$$m^* = \frac{(m_2)^2}{m_1} \quad (2)$$

mass number of the observed metastable peak, m_2 is the mass of the product ion, and m_1 is the mass of the parent ion ($m_1 \rightarrow m_2$ + neutral). In our case, m_1 was taken to be 210, the center of the mass envelope for the molecular ion. m_2 was either 132 or 129, corresponding to the fragment ions indicated in Table I.

Molecular Orbital Calculations. Calculations were carried out for two relative orientations of the rings, and the results of the two choices of geometry were nearly identical. We report here only results for the conformation having two carbon atoms eclipsed, as was found in the crystal structure determination.[2] The molecular orbital calculation predicts that the unpaired electron occupies the nearly nonbonding d_{z^2} orbital (the coefficient of d_{z^2} in this orbital is 1.0179). The calculated energy of this half-filled MO is −8.29 eV, nearly 2 eV higher than the degenerate MO's derived from d_{xy} and $d_{x^2-y^2}$ (found at −10.05 ev). The d_{xz}, d_{yz} antibonding MO's are found at −6.00 eV. Thus the d orbitals are widely separated and there is little chance for accidental degeneracy.

The unpaired electron distribution in vanadium AO's is as follows: d_{z^2}, 0.90 unpaired electron; 4s, 0.017. The MO coefficients for the hydrogens in the half-filled MO are −0.0652 for the hydrogen bound to the seven-membered ring and −0.0385 for the hydrogen bound to the five-membered ring. Using the previously described procedure,[8] the hydrogen coupling constants calculated from these coefficients are $A_{\mathrm{H}}{}^7$, calcd = 3.78 and $A_{\mathrm{H}}{}^5$, calcd = 1.62 G.

The calculated charges are: vanadium, +0.648; C_7 carbon, −0.0058; C_7 hydrogen, −0.039; C_5 carbon, −0.032; C_5 hydrogen, −0.035.

Discussion

Magnetic Resonance Results and MO Calculations. The nearness of the observed g values to the free-electron value and the fact that the esr spectrum of cpVtr is easily observable at room temperature (implying long electronic relaxation time) both strongly suggest a nondegenerate ground state. The only configuration leading to a nondegenerate ground state in axial symmetry is $(d_{z^2})^1$. The experimental conclusions are supported by the MO calculations, which clearly predict this ground state. We further make the reasonable assumption that the glassy solution spectrum arises from molecules with z axes perpendicular to the applied field, and this is also consistent with a d_{z^2} ground state. With $g_{\mathrm{iso}} = 1.987$ and $g_\perp = 1.978$, the relation $g_{\mathrm{iso}} = (g_\parallel + 2g_\perp)/3$ gives $g_\parallel = 2.005$. These g values are nearly identical with the isoelectronic $\mathrm{Cr(C_6H_6)_2}$, which was shown by Prins and Reinders[12] to have a nondegenerate d_{z^2} ground state.

The ^{51}V hyperfine structure may be analyzed as follows: with $|A_{\mathrm{iso}}| = 68.7$ G and $|A_\perp| = 96.1$ G (from the glass), we find that $|A_\parallel| = 13.9$ or 398.3 G, from $A_{\mathrm{iso}} = (A_\parallel + 2A_\perp)/3$. The anisotropic hyperfine splitting may also be calculated[20] from eq 3 and 4, where

$$A_\parallel = A_{\mathrm{iso}} + 4/7\alpha^2P - 1/7(g_\perp - -2.0023)P \quad (3)$$

$$A_\perp = A_{\mathrm{iso}} - 2/7\alpha^2P + 15/14(g_\perp - 2.0023)P \quad (4)$$

α^2 is the fractional occupation of d_{z^2} by the unpaired electron and $P = g_e g_{^{51}\mathrm{V}} \beta_e \beta_{^{51}\mathrm{V}} \langle r^{-3} \rangle d_{z^2}$. It turns out that with the physically reasonable values $P \approx 100$ G and $\alpha^2 \approx 1$, the only solutions of (3) and (4) which agree with the experimental hyperfine splittings require A_{iso} to be negative. This then leads to negative $A_\parallel$ and $A_\perp$ as well. We now take the position that the least well known quantity in (3) and (4) is P, and we will solve for P and $A_\parallel$ using $\alpha^2 = 0.90$ (from the MO results), $A_{\mathrm{iso}} = -68.7$ G, and $A_\perp = -96.1$ G. Solving eq 4 first, we find $P = 118$ G. Substituting this into eq 3 gives $A_\parallel = -14$ G. Thus the experimentally observed hyperfine splittings, together with the MO result for α^2, require P and $A_\parallel$ to be 118 and −14 G, respectively. We now inquire into the reasonableness of these calculated results. The $A_\parallel$ result suggests that we might observe a parallel spectrum in the glass centered at $g = 2.005$ with a small hyperfine splitting. This spectrum is expected to be weak or absent because of the low probability of molecules aligning with their z axes parallel to the applied field. We do not observe a discrete parallel spectrum, but it is likely that it is hidden in the most intense perpendicular hyperfine component (see Figure 1). This peak is centered at $g = 2.016$ and extends over the range $g = 2.003$–2.027 (from left to right, Figure 1). Since $\langle r^{-3} \rangle d_{z^2}$ varies as the charge and electron configuration of vanadium vary, we do not know exactly what to expect for a calculated value of P. Our calculated result (118 G) does lie between the values reported by McGarvey:[20] V^0, $P = 91.8$ G and V^{2+}, $P = 137$ G. A linear interpolation between these two extremes implies that the charge on vanadium in cpVtr is +1.15, which is a physically quite reasonable result. This charge does not agree particularly well with that computed by the Mulliken population analysis (0.648), but in view of the uncertainties involved in transferring atomic $\langle r^{-3} \rangle$ values to molecular problems, and in view of the somewhat arbitrary nature of the Mulliken population analysis, the agreement of the two calculated charges is satisfactory. We should observe that a larger value of α^2 would ultimately lead to a lower calculated vanadium charge, but we believe that the MO result for α^2 (0.90) is reliable because of our earlier successes with MO calculations of this type.[8]

The ^{51}V hyperfine results and principal g values are therefore indicative of and quite consistent with a d_{z^2} ground state with a fractional d_{z^2} occupation of about 0.9. The charge on vanadium appears to be near 1+.

We now turn our attention to the proton hyperfine results. These results are particularly interesting in view of our recent work with bis-π-cyclopentadienylvanadium (vanadocene)[7,8] and allied work with bis(benzene)vanadium[14] and bis(benzene)chromium cation.[12] As mentioned above, the proton hyperfine coupling constants were calculated from the MO coefficients using the method described earlier for the related metallocenes.[8]

The calculated results ($A_{\mathrm{H}}{}^5 = 1.62$ G, $A_{\mathrm{H}}{}^7 = 3.78$ G) are in surprisingly good agreement with the experimental values of 1.8 ± 0.1 G (nmr, five-membered ring) and 4.5 ± 0.3 G (nmr–esr, seven-membered ring). These calculations do not include possible dipolar (pseudocontact) contributions to the observed shifts, but such contributions are expected to be quite

---

(20) B. R. McGarvey, *J. Phys. Chem.*, 71, 51 (1967).

small. An anisotropy in the proton hyperfine of about 0.5 G was observed[12] for $Cr(C_6H_6)_2^+$, and we expect nothing larger for cpVtr since both compounds have the same ground states, similar g values, and similar metal–hydrogen geometric relationships. The disagreement of the calculated and observed proton coupling constants may be partially due to dipolar coupling, but the small disagreement more likely reflects inadequacies in the calculation.

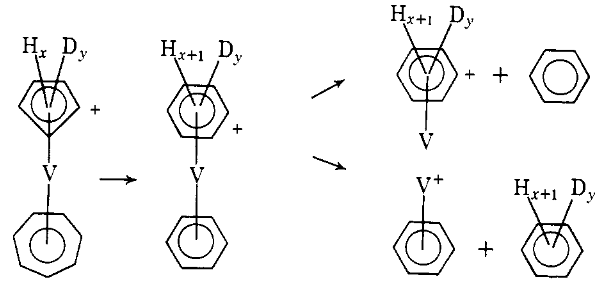
The molecular orbital wholly responsible for the proton hyperfine is the highest occupied MO, which is almost entirely d_{z^2} in character. This MO has nonzero coefficients from all the AO's on the rings, with the main contributions coming from hydrogen 1s, carbon 2s, $2p_x$, and $2p_y$ orbitals. Thus the electron–proton hyperfine coupling appears to be accomplished through d_{z^2} interacting (weakly) with carbon hybrid orbitals which lie in the plane of the ring, as was found earlier for vanadocene.[8] The electron–proton coupling in the five-membered ring found here is about twice as large as was found earlier in vanadocene.[7,8] The observed vanadocene result[7] (0.83 G) was shown[8] to be almost entirely due to delocalization of the unpaired d_{z^2} electron. It seems reasonable that the coupling in cpVtr is considerably larger than in cp_2V because of the lower metal charge in the former case. If C_5H_5 is coordinated as an anion, and C_7H_7 as a cation, the formal charge on V in cpVtr is zero, and the corresponding charge on V in cp_2V is 2+. Such a situation is bound to lead to less delocalization in cp_2V. The formal charges are not attained, of course, and there is a redistribution of charge in the molecule on complex formation.

The cpVtr coupling constants may also be compared to the electron–proton coupling constant in $V(C_6H_6)_2$, which is also known to have an $S = {}^1/_2$, d_{z^2} ground state. The bis(benzene)vanadium result is $+4.0 \pm 0.1$ G,[14] which lies between our results of 1.8 (C_5) and 4.5 G (C_7). Thus there appears to be a correlation between ring size and hyperfine coupling, with the larger rings experiencing the larger coupling constants. We originally believed that this effect must be due to greater metal–carbon overlap as the ring size increases, since the rings move closer to the metal as they get larger. However, the metal–carbon distances are nearly invariant, and explicit calculation of d_{z^2}–$2p_x$ overlap integrals for the five-, six-, and seven-membered rings at the bonding distances shows that this overlap is nearly constant. The d_{z^2}–2s overlap does change significantly with ring size: it is 0.1106 for the five-membered ring, 0.0743 for the six membered ring, and 0.0395 for the seven-membered ring. This trend in *overlap* is counter to the observed trend in hyperfine coupling, and suggests that the *energy* of the delocalized σ molecular orbital is the determining factor in its mixing with d_{z^2}. Unfortunately, our calculations do not yield the energy levels for the starting ligand molecular orbitals, and it would be especially difficult to arrange this when the ligand carries nonintegral charge as it does in the molecule.

We conclude that the extent of delocalization of d_{z^2} electron density from vanadium to a five-membered ring depends strongly on the formal charge on vanadium, decreasing as the formal charge increases. We further conclude that the extent of delocalization increases as the size of the coordinated ring increases, and that this is probably a result of σ MO energy level variations in the ligand, since overlap integrals show either no trend or a counter trend.

Mass Spectrum of cpVtr. The most interesting feature of the mass spectrum of cpVtr is the appearance of an intense peak due to the fragment $(VC_6H_6)^+$. This was observed and discussed earlier by Müller and Göser.[4] The present work shows that their conclusions concerning the origin of the $(VC_6H_6)^+$ fragment are incorrect.

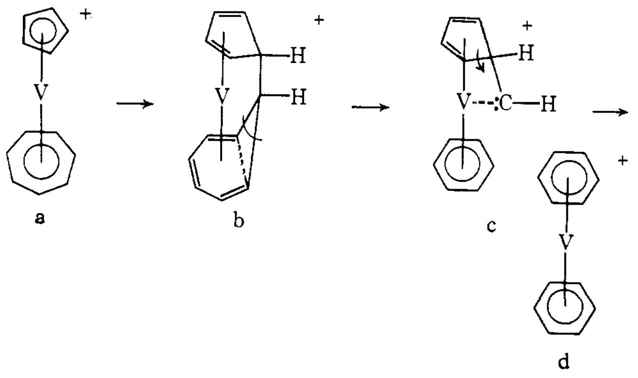
Inspection of the *m/e* 134–129 data in Table I shows clearly that VC_6^+ fragments containing deuterium are produced even though the deuterium was only introduced into the five-membered ring in the starting cpVtr (see the Experimental Section). One also observes that $(VC_6H_6)^+$ is produced which has *no* deuterium. We are forced to the conclusion that the VC_6^+ fragment may arise either from the C_5 or the C_7 ring. It is also apparent from Table I that the total probability of producing deuterated VC_6^+ fragments is almost exactly the same as the probability of producing undeuterated VC_6^+ fragments (certainly within our experimental error). This result strongly suggests that the VC_6^+ fragment arises exclusively from dissociation of symmetrical bis(benzene)vanadium, which itself arises from rearrangement of cpVtr after excitation by electron impact



Further, metastable peaks for dissociation of labeled or unlabeled benzene are observed at *m/e* 70 and 83, respectively.

Although the earlier suggestion[4] that the $(VC_6H_6)^+$ fragment is not due to $(C_5H_5VCH)^+$ is certainly correct, the conclusion that bis(benzene)vanadium is not implicated[4] is incorrect. The earlier workers' strongest argument against bis(benzene)vanadium intervention was that the $VC_6H_6^+$ fragment from cpVtr had a different appearance potential than the $VC_6H_6^+$ fragment from $(C_6H_6)_2V$. However, their error limits do not warrant such a conclusion.

We suggest that a reasonable pathway for this interesting rearrangement is as follows



In c the postulated carbene may or may not be coordinated to vanadium. The c → d conversion requires a vinyl migration, which is normally not a favorable process for alkylcarbenes (hydrogen migration to yield a coordinated fulvene would have been more in line with alkyl carbene chemistry).[21] However, alkyl migrations have been observed, as in the ring expansion of cyclopropylcarbene to cyclobutene.[22] The presence of vanadium and the details of the postulated cyclopentadienylcarbene coordination may favor the vinyl migration over hydrogen migration in the present case. We also recognize the possibility of formation of (fulvene)vanadium(benzene), which could then rearrange to vanadiumbis(benzene), but we favor the vinyl migration because of its simplicity. We also note the similarity of this rearrangement to that occurring in the reaction of $(C_7H_7)Cr(CO)_3^+$ with $C_5H_5^-$, the products being $C_6H_6Cr(CO)_3$ and an unknown C_6 fragment.[23] This reaction apparently proceeds by attack of $C_5H_5^-$ on the coordinated C_7H_7 (compare b above). leading to isolable $(C_{12}H_{12})Cr(CO)_3$. The $C_{12}H_{12}Cr(CO)_3$ is converted to $C_6H_6Cr(CO)_3$ on treatment with excess $C_5H_5^-$, and the other C_6 fragment was postulated to be fulvene.

Finally, we were able to observe no rearrangement of either cpVtr or cpVtr$^+$ (prepared as in ref 5) upon heating dilute solutions to 200° in either THF or toluene for days. Evidently, considerable vibrational or electronic excitation of cpVtr$^+$ is required for production of $V(C_6H_6)_2^+$. Such an excitation may be easily accomplished by electron impact.[24]

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of California Intramural Fund for support of this research. C. D. S. and A. K. were NSF Undergraduate Research Participants for the summers of 1968 and 1969, respectively.

---

(21) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 47–64.

(22) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960).

(23) J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3479 (1961).

(24) NOTE ADDED IN PROOF. H. O. van Oven and H. J. de Liefde Meijer, *J. Organometal. Chem.*, 23, 159 (1970), have recently reported the preparation, properties, and mass spectral fragmentation of cpTitr. The Ti compound also gives rise to an important $(TiC_6H_6)^+$ fragment, although these workers did no labeling studies. Our results make it likely that the Ti fragmentation involves $Ti(C_6H_6)_2^+$, which, to the best of our knowledge, is unknown, as is the neutral $Ti(C_6H_6)_2$. Curiously, it appears that fragmentation to $M(C_6H_6)^+$ is favored in the order Ti > V ≫ Cr, which probably reflects the instability order of the parent $M(C_5H_5)(C_7H_7)^+$ or the derived $M(C_6H_6)_2^+$.

Carbonate Ligand Exchange Studies of *cis*- and *trans*-Carbonatodiammineethylenediamine Complexes of Cobalt(III). A Revised General Mechanism for Chelated Carbonate Ligand Exchange Reactions in Basic Aqueous Solution

R. J. Dobbins[1] and G. M. Harris[2]

Contribution from the State University of New York at Buffalo,
Buffalo, New York 14214. Received March 24, 1970

Abstract: A comprehensive set of new data on the carbonate exchange reaction of *cis*-$Co(NH_3)_2enCO_3^+$ is correlated with recently accrued results of other types of studies of the chemistry of the chelated carbonato complexes of formula $CoN_4CO_3^+$ (where N_4 represents the four coordinated nitrogen atoms of the nonexchanging NH_3 or amine ligands). At 25° and $7.5 < pH < 9.5$, only about 0.1% of the complex is in the ring-opened form produced by reaction of water with the chelated parent compound. Three monodentate carbonato species are in an equilibrium represented by

$$CoN_4(H_2O)(CO_3H)^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} CoN_4(OH)(CO_3H)^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} CoN_4(OH)(CO_3)$$

for which the first and second pK values are approximately 5.3 and 8.7 at 25°. Carbonate exchange results from a combination of the two dissociative decarboxylations of the type $R'CO_3H \rightleftarrows R'OH + CO_2$, and the two associative carboxylations of the type $R''OH + CO_2 \rightleftarrows R''CO_3H$. The four rate constants for the *cis*-$(NH_3)_2$en species have values of 0.4 sec^{-1}, 2.5×10^{-3} sec^{-1}, 15 M^{-1} sec^{-1}, and 50 M^{-1} sec^{-1}, respectively, in good agreement with expectations based on independent data. The new mechanism is shown to offer a very satisfactory interpretation of results of analogous exchange studies extending back to 1952, and a number of the earlier discrepancies are now resolved. Comparative studies of the carbonate exchanges of the ions *cis*-$Co(NH_3)_2enCO_3^+$, *trans*-$Co(NH_3)_2enCO_3^+$, and *trans*-$Co(NH_3)_2tnCO_3^+$ (en = ethylenediamine, tn = trimethylenediamine) throw new light on some previously noted stereochemical influences of the amine ligands on carbonato ligand reactivity.

Our previous paper in this series[3] reported details of a study of the carbonate exchange reactions of the complex ion carbonatobis(propylenediamine)cobalt(III). On the basis of the evidence then available, a rational mechanism was proposed for the various chelated carbonatotetraminecobalt(III) exchanges[4,5]

---

(1) Work done as part of the Ph.D. requirement of the State University of New York at Buffalo, and presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. Complete dissertation available from University Microfilms, Ann Arbor, Mich.

(2) To whom correspondence concerning this paper should be addressed.

(3) G. Lapidus and G. M. Harris, *J. Amer. Chem. Soc.*, **85**, 1223 (1963).