Vanadium–Carbon Bonds in Paramagnetic Bent Vanadocene Derivatives[1]

Frank H. Köhler,*[2a] Peter Hofmann,[2b] and Wolfram Prössdorf[2a]

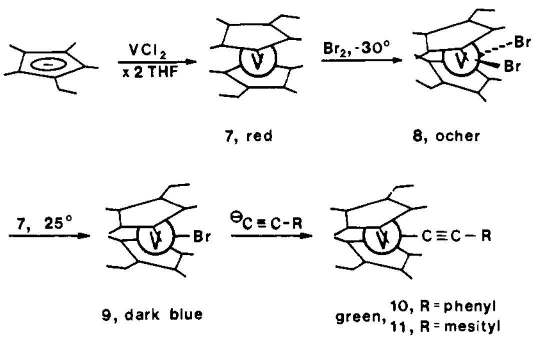
Contribution from the Anorganisch-chemisches Institut, Technische Universität München, D-8046 Garching, and the Institut für Organische Chemie, Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany. *Received December 29, 1980*

Abstract: The thermally labile compounds Cp_2V-R (Cp = cyclopentadienyl) have been studied by ^1H and ^{13}C NMR partly at low temperatures. Stabilization of the η^1 bond is achieved by peralkylation of the Cp ring yielding the new compounds $(R'_5C_5)_2V-R$ with R = $C{\equiv}CC_6H_5$ and $C{\equiv}CC_6H_2(CH_3)_3$. The NMR signals of the paramagnetic compounds appear over wide ranges (^1H, 730 ppm; ^{13}C, 300 ppm) and allow detailed structural determinations. For R = $(C{\equiv}C)_nC_6H_5$ the phenyl is locked between the Cp rings of Cp_2V-R if $n = 0$ while it is rotating if $n = 1$. This is supported by temperature-dependent ^1H NMR spectra. Even the V-alkyl bond has a considerable π contribution which is detected via unusually large and varying shifts of the protons nearest to the metal. Extended Hückel calculations have been carried out for Cp_2V-R with R = C_6H_5, $C{\equiv}CC_6H_5$, and CH_3. They provide a general understanding of the magnetism, the different molecular geometries, the nature of the vanadium–carbon bond, the electron spin distribution, and the NMR shifts.

Vanadocene is an electronically and coordinatively unsaturated molecule which is able to bind various ligands L in either a η^1 or a η^2 manner. This is accompanied by a structural change from the sandwich to a bent arrangement of the Cp rings which is found in compounds of the type $Cp_2V(\eta^1\text{-L})$, $Cp_2V(\eta^1\text{-L})_2$, and $Cp_2V(\eta^2\text{-L})$. Within the field of transition metal–carbon bonds, which still is under intensive investigation in many laboratories,[3] we are interested in ligands forming vanadium–carbon bonds. Besides $Cp_2V(\eta^1\text{-R})_2$[4a] and $Cp_2V(\eta^2\text{-R})$[4b] the chemistry of $Cp_2V(\eta^1\text{-R})$ has been studied with varying success.[4a,5] Two basic difficulties arose: the vanadium–carbon bond is rather thermolabile, and due to the lack of systematic NMR or ESR investigations (see, however, ref 5c,g), little structural information exists about this type of compound. Especially, there is no agreement concerning the magnetism: two unpaired electrons per molecule[5c,d,f] as well as diamagnetism[4a,5e] have been claimed for Cp_2V-R.[6]

The results of our NMR investigation of paramagnetic vanadocene halides[7] as well as a ^1H NMR study of uranium–alkyl and -aryl compounds[8] encouraged us to investigate the utility of NMR spectroscopy for structural examinations of organo transition-metal radicals with metal–carbon σ bonds. Simultaneously, we tried to stabilize the V–C bond.[9] We report herein the synthesis of new vanadocene derivatives, the ^{13}C and ^1H paramagnetic NMR spectra of vanadocene–alkyl compounds, their application for detailed structural information, and extended Hückel calculations which allow a general understanding of the experimental findings.

Scheme I



Results

A. Synthesis and Properties of Vanadocenes with V–C Bonds. Vanadocene dihalides Cp_2VX_2 as well as monohalides Cp_2VX (X = Cl, Br) react with metalated hydrocarbons RM (M = Li, Na, MgBr) to form V–C bonds.[5b,c] Cp_2VCl_2 is by far the most stable starting material; however, 1 equiv of RM is consumed for its reduction. Often RM compounds are difficult to prepare, and their oxidation products seriously complicate the isolation of the desired compounds. We therefore allowed Cp_2VCl to react with RM to obtain Cp_2V-R (R = CH_3, **1**; $n\text{-}C_4H_9$, **2**; $CH_2Si(CH_3)_3$, **3**; $CH_2(C_6H_5)$, **4**; C_6H_5, **5**; $C{\equiv}CC_6H_5$, **6**). The extremely air-sensitive compounds, which are green to grayish blue in solution, have been synthesized before by using a somewhat different method.[5b,d,f] We can confirm most of the reported properties; however, satisfactory elemental analysis results could be obtained only for **1**, **3**, **4**, and **5**. We attribute this to the thermal lability of the V–C bond, which has been previously underestimated.[5f] Even in analytically pure samples we were able to detect small amounts of vanadocene by ^1H NMR. Critical examinations showed the error of elemental analysis of such sensitive compounds to be up to ±1%.[10,11] This also complicates physical measurements which are based on the sample weight, e.g., magnetic measurements.

Stabilization of the V–C bond is possible by peralkylation[12,13] of the Cp rings. We chose ethyltetramethylcyclopentadiene as the starting material which can be metalated with KH or n-BuLi in THF. The further synthesis of the vanadium acetylene de-

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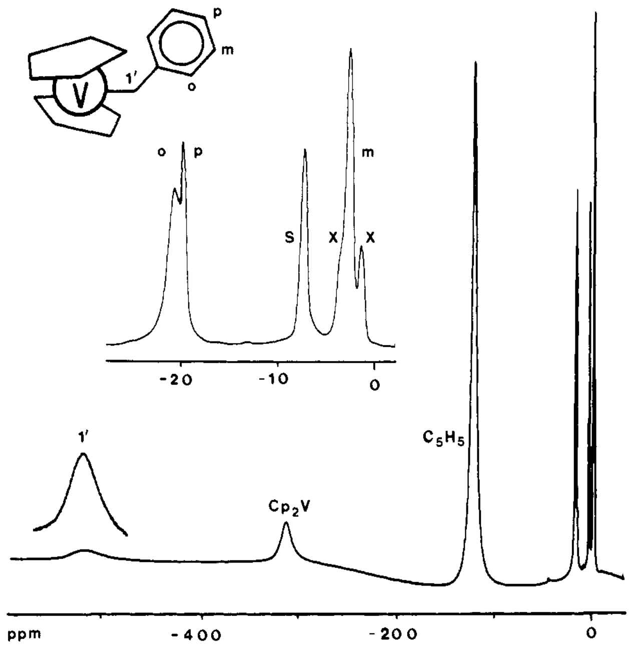

Figure 1. 200-MHz ^1H NMR spectrum of $(C_5H_5)_2V-CH_2(C_6H_5)$ (**4**) dissolved in C_6D_6, after several days kept at 305 K (X = impurity).

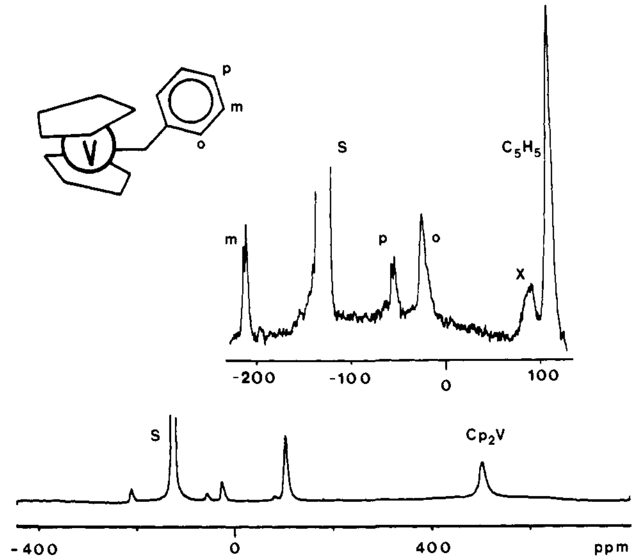

Figure 2. 50.3-MHz ^{13}C NMR spectra of $(C_5H_5)_2V-CH_2(C_6H_5)$ (**4**) dissolved in C_6H_6 at 340 K: bottom, $^{13}C\{^1H\}$; top, ^{13}C (X = impurity (CpVCl)).

Table I

compd	solvent	alkylating agent	% yield
Cp_2V-CH_3 (**1**)	THF	CH_3Li	51
$Cp_2V-n\text{-}C_4H_9$ (**2**)	pentane	$n\text{-}C_4H_9MgBr$	48
$Cp_2V-CH_2Si(CH_3)_3$ (**3**)	pentane	$(CH_3)_3SiCH_2MgCl$	57
$Cp_2V-CH_2C_6H_5$ (**4**)	THF	$C_6H_5CH_2MgBr$	45
$Cp_2V-C_6H_5$ (**5**)	THF	C_6H_5MgBr	54
$Cp_2V-C{\equiv}C-C_6H_5$ (**6**)	ether	$C_6H_5-C{\equiv}CNa$	29

rivatives **10** and **11** proceeds according to Scheme I. As we have shown for simpler vanadocenes,[14] yields are considerably higher when $VCl_2{\cdot}2THF$ is used instead of VCl_3. In this way **7** was obtained in more than 50% yield. Reaction of **7** with bromine at low temperatures gave the dibromide **8**, which need not be isolated; it reacts at room temperature with a second equivalent of **7** to form **9**. Compounds **7** and **9** yield ^{13}C and ^1H NMR spectra which we will report together with the spectra of other paramagnetic peralkyl metallocenes.

After the title compounds were dissolved in THF or benzene at room temperature most of them, in particular **6**, soon change color from green to brown and eventually to violet. This indicates the formation of vanadocenes. Compounds **10** and **11** are substantially more stable: they remain green for weeks as a solid as well as in solution and melt without decomposition. The color of toluene solutions does not change during several hours of reflux. This stability also allowed us to perform an X-ray structure analysis.[9,15]

B. ^1H and ^{13}C NMR Investigations. All Cp_2V-R compounds give ^1H NMR spectra with a signal for each nonequivalent nucleus. At room temperature, the signals cover a range of about 750 ppm, which is exceptionally large even for paramagnetic compounds. No proton-proton couplings are observed since for all line widths Δ^{exptl} we find 50 Hz < Δ^{exptl} < 6500 Hz. However, there is a favorable ratio of spectral range to line widths, so that impurities can easily be detected. This is most important for paramagnetic decomposition products. Figure 1 shows a typical example. Besides the signals of **4**, an additional peak near −300 ppm appears when the sample is kept at room temperature for several days. Its isotropic shift corresponds to that of the Cp protons of vanadocene.[16] In fact, after thermolysis of $Cp_2V-C_6H_5$, vanadocene has been isolated.[17] Paramagnetically shifted signals are observable by ^{13}C NMR as well. Since protons of the V-R fragment which are separated from the vanadium atom by two bonds exhibit large shifts (compare H1' in Figure 1), we were particularly interested in the shift of C1' which is directly bound to the vanadium atom. However, in all of the Cp_2V-R compounds investigated, signals for neither C1' nor for the adjacent C2' have so far been detected. These resonances must have line widths Δ^{exptl} and/or shifts δ^{para} considerably larger than the extreme values (δ^{para} > 1500; Δ^{exptl} > 5000 Hz) which we have recently established for nickelocenes.[18] For carbons in other positions even the $^1J(^{13}C-^1H)$ couplings can be observed, if the line widths of the corresponding ^1H and ^{13}C signals are narrow enough. A typical example is the ^{13}C spectrum shown in Figure 2: in contrast to meta-C and para-C, $^1J(^{13}C-^1H)$ for ortho-C is completely quenched due to the shorter distance from the paramagnetic center. As in the ^1H NMR spectrum the thermolysis product vanadocene can be identified by its characteristic signal.[16]

The assignment of the NMR signals needs some comment. For the protons of unsubstituted Cp rings it follows from the signal intensity, for H1', from comparison of **1**–**4**, and for H2'–H4' of **2**, from the intensities and the fact that the shifts should decrease sharply along the chain. Identification of ortho-, meta-, and para-H of **4**, **6**, **10**, and **11** is possible by the signal intensities and by the fact that the shifts have different signs. In contrast all phenyl protons of **5** appear at high field; ortho-H and meta-H are distinguished by the assumption that the ortho-H, which is closer to vanadium experiences the larger shift. This is confirmed by an NMR investigation of bridged vanadocenes.[19] The alkyl protons of the peralkylated Cp rings of **10** and **11** are identified by comparison with **9** and by signal integration. The assignment of α-H2/5 and α-H3/4 follows our arguments for $(RC_5H_4)_2V-X$,[7] although the inverse assignment cannot be ruled out strictly.

As far as ^{13}C signals are obtained the assignment is straightforward. The Cp signals all appear in a region known from vanadocene halides;[7] they are further identified by their signal

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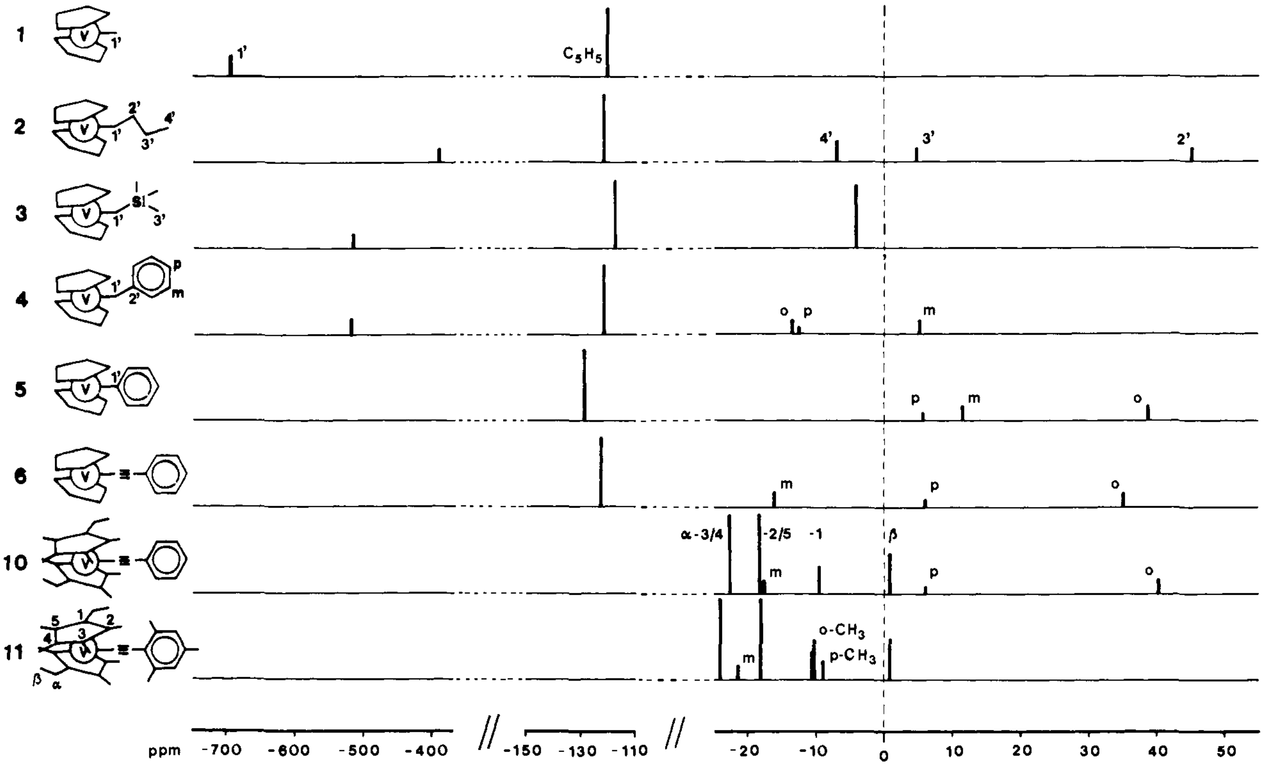

Figure 3. Systematic representation of the paramagnetic ^{1}H shifts. For numerical values see Table II in the Experimental Section.

intensities. The benzyl carbon assignment of **4** follows from integration and from the alternation of the shift signs which should be opposite to those of the neighboring protons. The only detected carbons of **5** have an integral ratio of 2/1 so that the smaller signal must be para-C. Since in the whole series no carbon is found which is separated from vanadium by less than three bonds the bigger signal should be meta-C. This is confirmed by the bridged analogue Cp_2V-C_6H_4-VCp_2 where no phenyl carbons appear.[19]

The NMR results are summarized in Figure 3; numerical values are given in Table II (Experimental Section) as $\delta_{298}{}^{para}$, i.e., paramagnetic (isotropic) shifts in parts per million at 298 K with negative sign to low field. Details concerning reference signals and error limits are given in the Experimental Section. **5** and **11** have been studied at variable temperatures. Their δ^{para} are linear with $1/T$, the standard least-squares deviation being $r^2 > 0.999$. Whether there is Curie behavior or not may most easily be decided by plotting the reduced shifts[20] $\vartheta = \delta^{para}T/298$ K vs. T. Figure 4 shows that a considerable deviation from the expected constant value is found for **5**, while in the case of **11** it hardly exceeds the error limits.

Discussion

The results unequivocally identify Cp_2V–R as paramagnetic compounds. This is in contrast to the statements of Razuvaev et al.[4a,5e] and confirms de Liefde Meijer's solid-state magnetic measurements.[5d] Possible errors caused by paramagnetic byproducts like vanadocene, which is easily generated due to the thermolability of the V–C bond, are excluded by the NMR method presented in this paper.

A characteristic feature of the ^{1}H NMR spectra of **1**–**6** are the Cp signals, which all appear near −120 ppm, where we have previously found the analogous signals of vanadocene monohalides.[7] Such a shift appears to be characteristic for bent monomeric vanadocene derivatives Cp_2VX with two unpaired electrons, where X can be any η^1 ligand. The ^{13}C signals of the Cp rings also lie in a typical range. As an advantage over ^{1}H NMR, however, these ^{13}C shifts are quite sensitive to the change of ligands X. This is expected to be a useful probe for ligand influences: for electronic and steric reasons X changes the energy of the Cp_2VX orbitals (vide infra) and consequently influences the spin delocalization in the Cp rings.

A second characteristic feature are the signals of protons H1′. They span a range of ca. 300 ppm and appear almost as low as −700 ppm, which makes them unique. We attribute these extreme shifts to hyperconjugation, which selectively transfers unpaired spin from vanadium to nuclei separated by two bonds (vide infra). Accordingly, we have so far been unable to locate ^{13}C signals for C2′ of **4** and ortho-C of **5**. Several unfavorable conditions accumulate in this case: the large δ^{para} (the experimental line width Δ^{exptl} is proportional to $(\delta^{para})^2$[21]), the poor NMR receptivity of ^{13}C, and the required low temperatures ($1/\Delta^{exptl}$ decreases with T). We assume that similar reasons are responsible for the absence of a signal for C1′, except that now another difficulty should arise from the short distance r to vanadium since $\Delta^{exptl} \sim r^{-6}$.

Unlike the proton H1′ the butyl protons H2′ of **2** do not interact strongly with the metal as can be seen from the shifts in Figure 3. NMR results therefore suggest that β elimination is not an important mechanism for the ready[5h] fission of the V–C bond.

Another remarkable feature of the spectra is that the phenyl proton shifts of **4**, **6**, and **10** change sign on going from ortho- to meta- and to para-H. For **5**, however, they are all at high field. Alternating shift signs are usually taken as evidence that the π mechanism dominates electron spin delocalization.[22] Compound **4** is a particularly good example, providing additional information about the signs of ortho-, meta-, and para-C and H1′; Figure 5 summarizes spin directions. The dotted arrows on C1′ and C2′, which were not observed, follow from the sign alternance. We thus expect C1′ at high field and C2′ at low field. Moreover, Figure 5 shows spin delocalization onto the Cp rings. In case of **5**, where the phenyl is directly bound to vanadium, the equal sign

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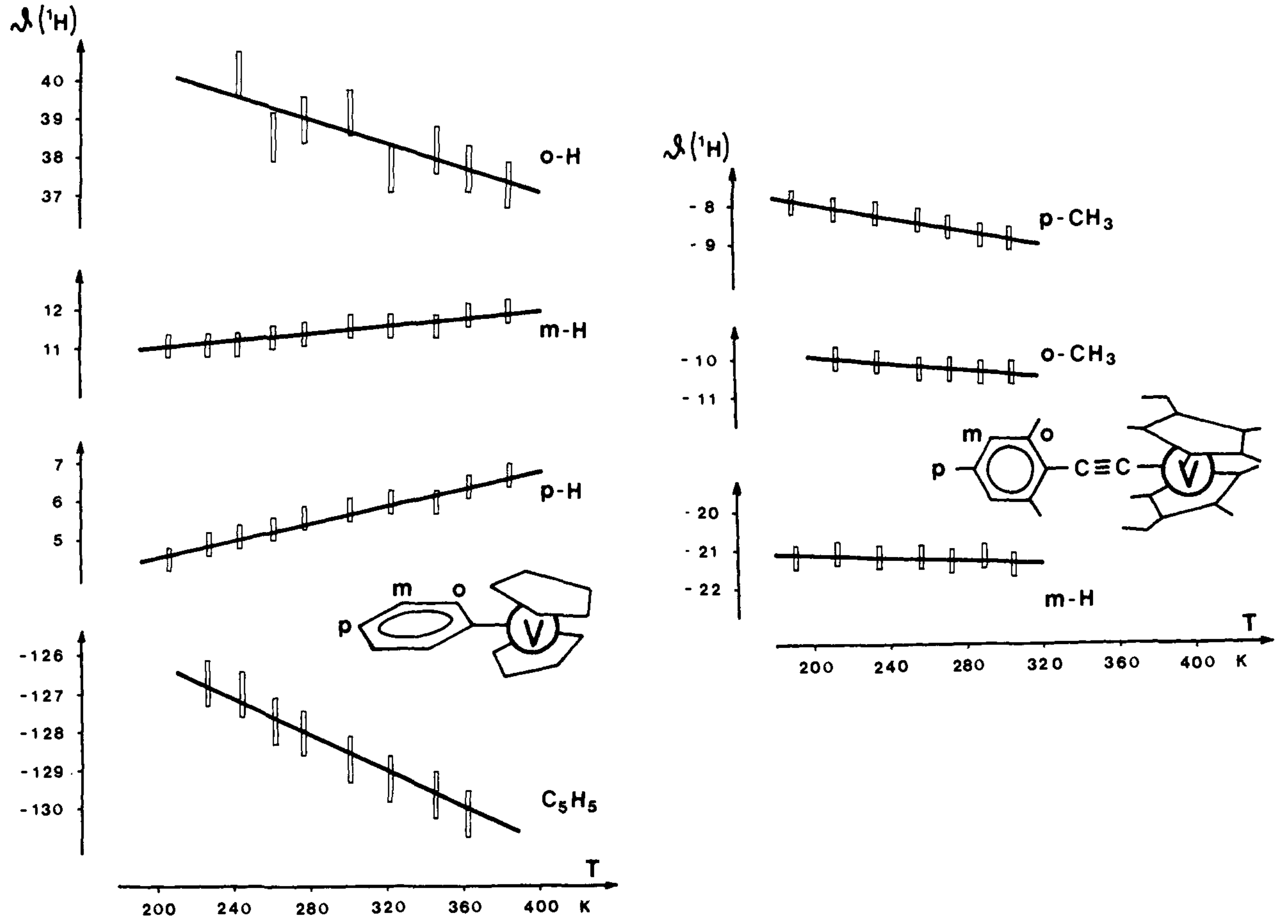


Figure 4. Temperature dependence of the reduced shifts of $(C_5H_5)_2V{-}C_6H_5$ (**5**) and $[(C_2H_5)(CH_3)_4C_5]_2V{-}C_2[C_6H_2(CH_3)_3]$ (**11**).

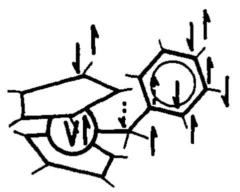


Figure 5. Polarization of the unpaired electron spin in $(C_5H_5)_2V{-}CH_2{-}(C_6H_5)$ (**4**).

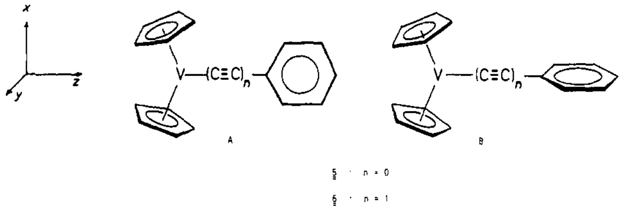
of the δ^{para} of ortho-, meta-, and para-H indicates the predominance of σ delocalization.

C. Extended Hückel Calculations. In order to provide qualitative understanding of the results above, we have carried out MO calculations, combining them with perturbation theory arguments. A reliable theoretical evaluation of paramagnetic ^1H and ^{13}C shifts in molecules as complex as $Cp_2V{-}R$ does not appear to be feasible today.

Our analysis is based on the valence orbitals of a bent Cp_2M fragment which has been described in detail by Lauher and Hoffmann.[23] Such a fragment is obtained if $Cp_2V{-}R$ is constructed from the d^2-system Cp_2V^+ and R^-. Figure 6 shows the important frontier orbitals, $1a_1$ and b_2 are nearly degenerate and accommodate two electrons. This corresponds to the paramagnetism of $Cp_2V{-}R$ and has similarly been shown for Cp_2VCl.[24]

Relative to a symmetrical R^- two Cp_2V^+ orbitals, $1a_1$ and $2a_1$, have σ character. From the nodal properties of $1a_1$ and its predominant metal d_{y^2} character its overlap with the σ-donor function of R^- is much less important than for $2a_1$. In addition, V–R π interaction is possible between b_2 (a combination of d_{yz} and p_y) and ligand orbitals of suitable symmetry. This interaction strongly depends on the conformational arrangement of the "single-faced" π-donor or π-acceptor ligand. We thus have a stereochemical control of π- and σ-spin delocalization. Ligands R^- may be distinguished with respect to having rotational symmetry or not.

η^1 Ligands without Rotational Symmetry. Phenyl. For a phenyl group which is directly bound to vanadium as in **5** the following two extreme conformations A, shown in I, must be considered: A, with maximum, and B, with minimum conjugation between b_2 and the benzene π orbitals. Hence A should be energetically favored with a rotational barrier around the $V{-}C_{sp^2}$ axis. Another factor influencing the relative stability of A and B of course is steric repulsion between the phenyl ortho positions and the Cp rings. With increasing substitution at these sites and decreasing distance between V and phenyl C1′ conformation B rather than A should be favored. In fact, our MO calculations on $Cp_2V{-}C_6H_5$ show that B is the much more stable conformation for steric reasons. This agrees well with X-ray structural results, which we obtained from the corresponding bridged compound.[19]



I

Figure 6 describes the electronic structure of **5** in the sterically accessible conformation B. Among the relevant MO's of $C_6H_5^-$, symmetry selects only three which interact with Cp_2V^+: the σ-donor orbital (n, lone pair at C1′) with $1a_1$ and $2a_1$ and the benzene σ orbitals $1\sigma_a$ and $2\sigma_a$ interact with b_2. While n slightly

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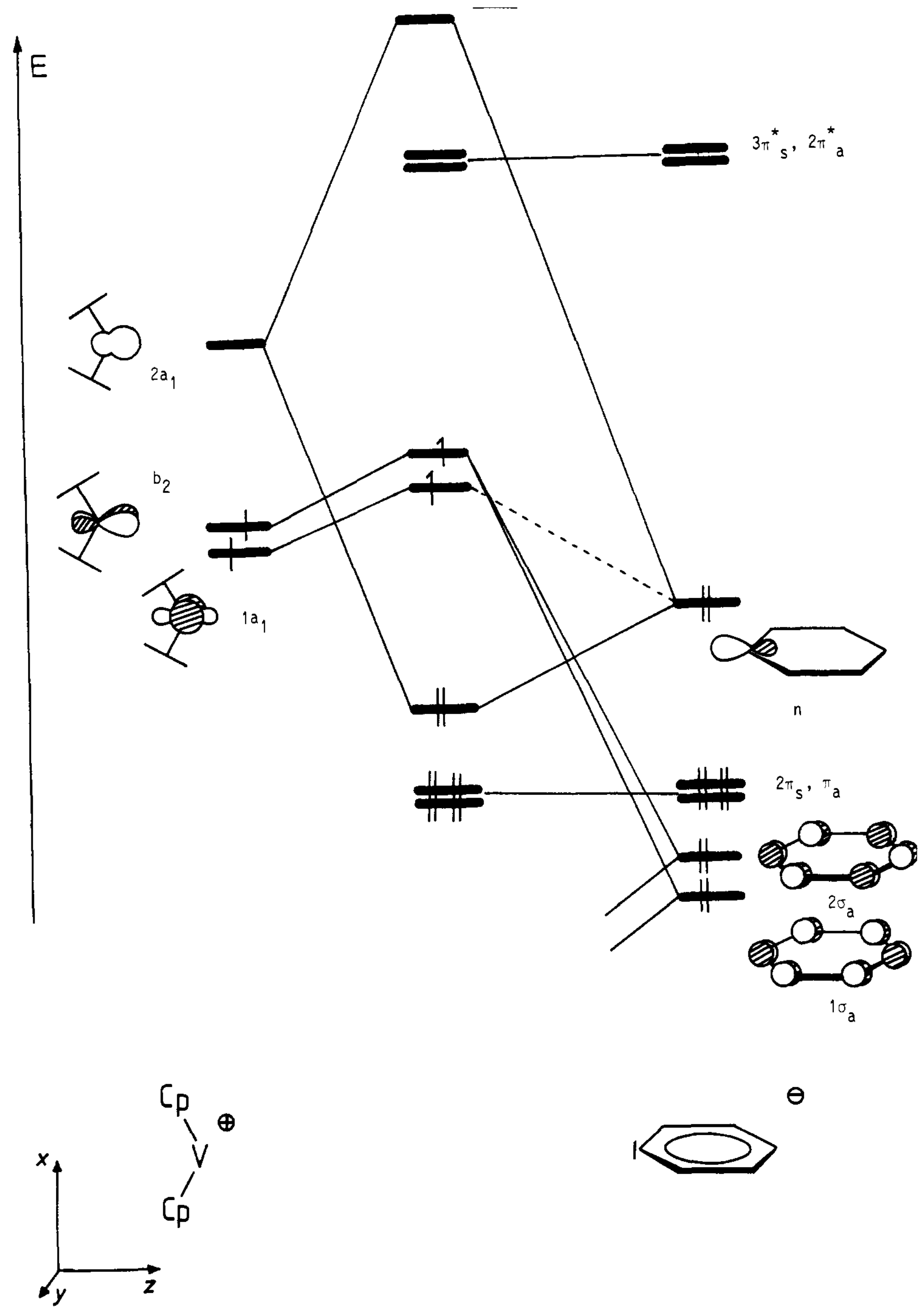
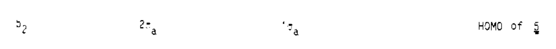


Figure 6. Simplified interaction diagram for $Cp_2V\text{-}C_6H_5$ (**5**) in conformation B. Only energy levels relevant for our discussion are given.

destabilizes $1a_1$, the most important bonding contribution results from the linear combination of n and $2a_1$, giving a V–C σ bond. The one-electron levels derived from $1a_1$ and b_2 are separated by only 0.2 eV. Within the spin-free formalism of our EH calculations this clearly indicates that $Cp_2V\text{-}C_6H_5$ has to be a high-spin d^2 system.

It is easily seen from Figure 6 that the phenyl ring receives electron spin density only via its σ orbitals. Actually, the higher of the two singly occupied MO's results from an antibonding mixing of the two phenyl σ orbitals into the Cp_2V^+ b_2 orbital, as shown below in II, with mixing signs following from perturbation theory. According to the resulting wave function (HOMO of **5**) the spin density is mainly transferred to C1′ and ortho-C with a dramatic drop on going to para-C. An alternative view would be that hyperconjugation between b_2 and the C1′–ortho-C bonds selectively places electron spin onto these carbons. The overall delocalization onto C_6H_5 is small; we calculate 72% of the wave function on vanadium and 24% on the Cp rings.



II

The spin density on C_6H_5 is further influenced by the second unpaired electron. Its MO corresponds to the Cp_2V^+ $1a_1$ orbital which is destabilized by the phenyl n orbital; the metal and Cp ring contributions are 84% and 12% in our calculations. Here σ delocalization leads to spin accumulation essentially on C1′.

Comparison with the NMR data of **5** in Figure 3 yields good qualitative agreement. The MO results show the uniform signs of the phenyl ^1H shifts to be due to σ delocalization and reproduce their attenuation. The failure to detect C1′ and the ortho-carbons corresponds to the high spin density which is expected at these carbons according to II. Finally the temperature dependence of

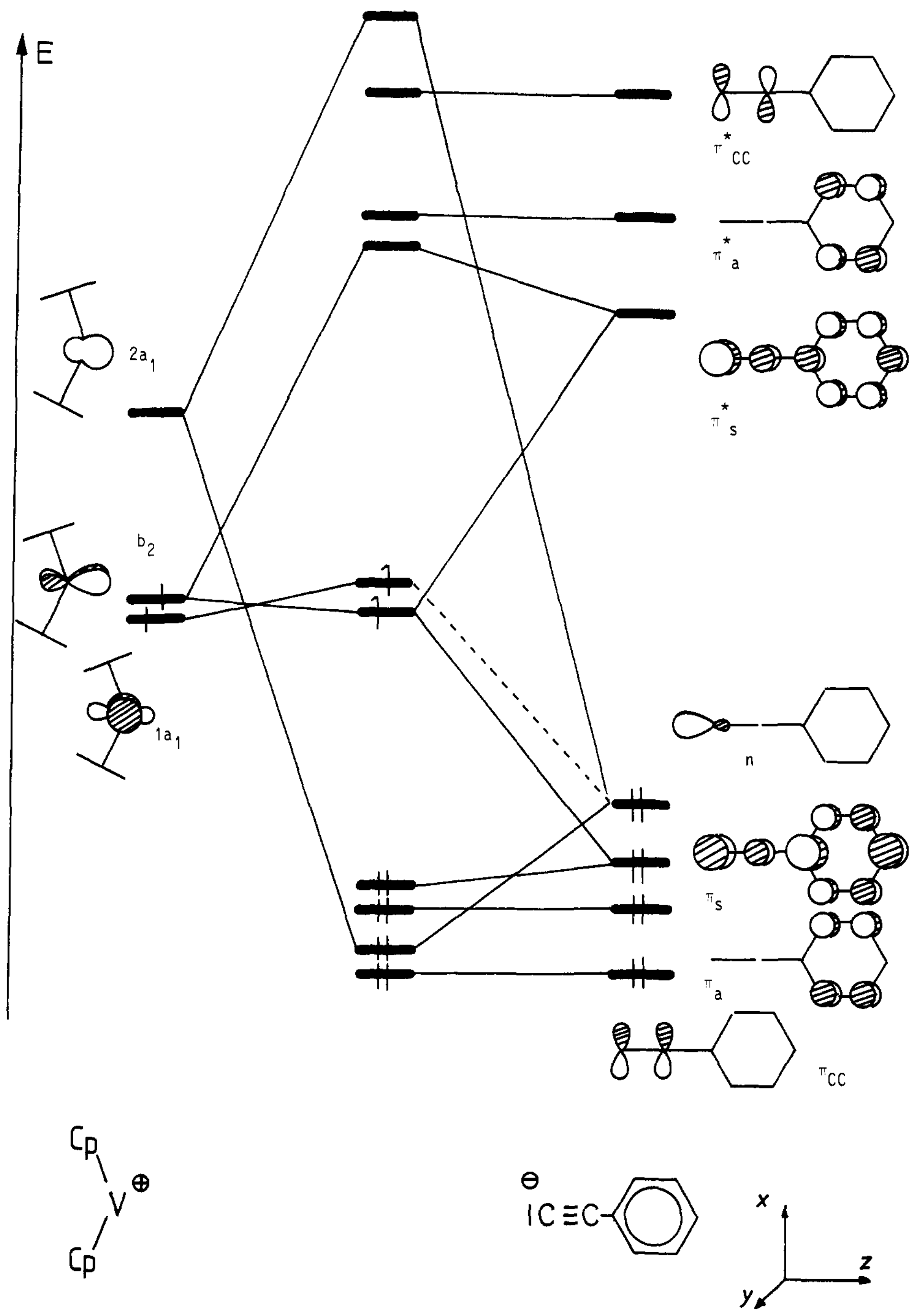


Figure 7. Interaction diagram for the construction of the important MO's of **6** in configuration A.

the $\delta^{para}(^1H)$ (Figure 4) may be understood as arising from a twisting vibration which makes partial π delocalization thermally accessible (rigid rotation is excluded by too close steric contacts between phenyl and the two Cp rings). Interestingly, another rotational barrier is established experimentally for the Cp rings in Figure 4. It is most probably due to the angular dependence of the metal–Cp bond which is introduced by the splitting of the two singly occupied frontier orbitals. Details based on shift signs are not borne out here. Nevertheless, the rare example of σ-exchange polarization,[25] which brings the phenyl resonances to high field rather than to low field as observed with usual σ delocalization,[27] becomes plausible from Figure 6. It should be noted that, like in Cp_2VCl,[7] polarization is mainly responsible for the ^1H and ^{13}C shift signs of the Cp rings.

η^1 Ligands without Rotational Symmetry. Phenylethynyl. If the phenyl is no longer bound directly to vanadium as in **5** but separated by a C≡C moiety as in **6**, **10**, and **11**, the same conformations I, A, and B must be considered. As an important difference, our calculations on **6** show that now A is about 10 kJ mol^{-1} more stable than B. Thus, steric hindrance no longer dominates the conformational choice A ⇌ B but rather conjugation between the metal and C_6H_5.

The interaction between Cp_2V^+ and the phenylacetylide ligand in configuration A is shown in Figure 7. Again two almost degenerate frontier orbitals leading to the triplet state of **6** are obtained (similar results are found for configuration B). One of

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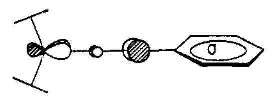
(25) The unpaired electrons on the metal polarize the relevant paired phenyl σ electrons: close to the metal they are aligned parallel to the unpaired spin; this is compensated by antiparallel spin on the phenyl. Such a polarization is well-known for π delocalization, e.g., in vanadocenes and chromocenes.[16] σ polarization has been observed by La Mar et al.[26]

(26) La Mar, G. N.; Van Hecke, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3442–3450.

(27) Doddrell, D.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 6839–6844 and references cited therein.

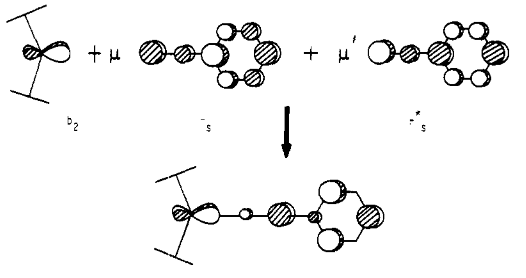
the two orthogonal sets π and π^* of the triple bond mixes with suitable π and π^* orbitals of the benzene. This yields the π_s and π^*_s orbitals of Figure 7 which are easily recognized as linear combination of alkyne and benzene orbitals. For symmetry reasons the corresponding π_a and π^*_a are pure benzene π orbitals. The orthogonal π system of the triple bond (π_{CC} and π^*_{CC}) contains only small contributions with σ character in the benzene ring; they are not shown in Figure 7 for simplicity. The highest occupied MO of the ligand $C_6H_5C_2^-$ is the lone pair at the acetylide carbon (n).

In both geometries A and B one of the two unpaired electrons resides in an MO with essentially $1a_1$ character, somewhat destabilized by n. This is similar to **5** (vide supra) and means that the MO is localized at the metal with small contributions in the Cp_2 system and at C1′. While this orbital (and the corresponding electron spin density distribution) is invariant to phenyl rotation, the character of the second singly occupied MO depends on the conformation. Its composition in geometry B (unlike Figure 7) is shown in III. The antibonding linear combination of b_2 and π_{CC}[28] mixes with π^*_{CC}; this decreases the coefficient of the wave function at C1′, increases it at C2′, and causes a minor delocalization into the benzene σ system. The fragment V–C1′–C2′ looks like the nonbonding π-MO of an allylic system although in our case it is localized mainly on the metal.



III

In geometry A the second singly occupied MO (cf. Figure 7) results from the overlap of the Cp_2V^+ orbital and π_s as well as π^*_s. This is illustrated in IV: b_2 is destabilized by antibonding mixing with π_s whereas a bonding interaction with respect to b_2 occurs between the resulting wave function and π^*_s. The net effect is a localization not only at C2′ but also at the ortho and para positions of the benzene π system. Similarity this time exists to the nonbonding π-MO of the phenylallyl skeleton. The fact that conformation A is more stable than B is caused by the relative energy separations between b_2 and π^*_s compared to b_2 and π^*_{CC} (cf. Figure 7); in A the phenylacetylide LUMO π^*_s is a better π acceptor toward b_2 than π^*_{CC} in conformation B and this makes the b_2-type MO about 10 kJ mol^{-1} more stable than in B.



IV

The small energy difference between A and B means almost free phenyl rotation in solution, so that the unpaired electron in the b_2-type MO experiences both σ and π delocalization. However, the π mechanism should dominate since the phenyl contribution in the b_2-type wave function is calculated to be larger in A (π delocalization) than in B (σ delocalization). This agrees well with the alternating NMR shift signs of **6** in Figure 3. The high spin density at C1′ and C2′ (following from III and IV, for C1′ from the additional $1a_1$–n interaction) explains that we were unable to detect these ^{13}C signals. With the above-mentioned low rotational barrier in mind it is clear that we find almost no deviation from the Curie law down to −82 °C (cf. Figure 4).[29] On the other hand a 10-kJ mol^{-1} barrier is usually exceeded by lattice energies so that our X-ray results,[9,15] which show geometry B for the highly substituted derivative **11**, are not surprising.

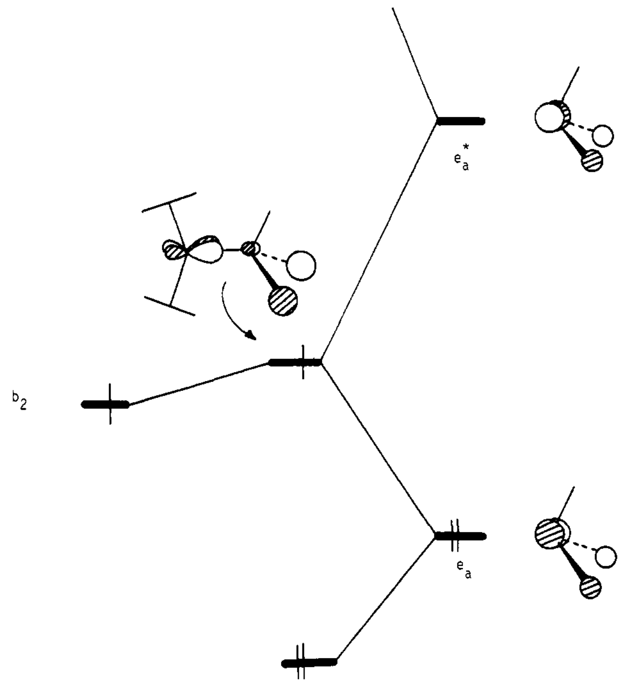


Figure 8. Spin transmission to methyl hydrogens **1**–**4** by interaction of Cp_2V^+ and methyl orbitals (qualitatively).

η^1 Ligands with Rotational Symmetry. Such a ligand is represented by CH_3^-. Its σ interaction with the CpV^+ $1a_1$ and $2a_1$ orbitals resembles the previous examples. A difference arises from the bonding and antibonding C–H orbitals e and e*,[30] one component of which is shown in Figure 8. They overlap with the Cp_2V^+ b_2 orbital, giving an identical result for each rotamer. Figure 8 selects one conformation and the interaction of b_2 with e_a and e_a^*.[31] This three-orbital interaction decreases the wave function on carbon and increases it at the hydrogens. Accordingly the spin density on H1′ is very high, leading to the enormous proton shift.

Introduction of a substituent yields the CH_2R groups in **2**–**4** where we expect hindered rotation with an energy minimum when R is situated between the Cp rings. In this conformation the methylene protons experience less unpaired spin transferred from b_2. Since the rotational barriers and the equilibrium conformations depend strongly on R the unusual variation of δ^{para} (H1′) in Figure 3 is found. This phenomenon is related to ESR results on aromatic radicals showing first-order hyperconjugation and to the spin transmission in the organic part of nickel chelate complexes.[20a] A detailed study is in progress.

Conclusions

Our results provide new possibilities to study transition-metal η^1-carbon bonds in great detail and with high accuracy. If unpaired electrons with short relaxation times exist in the molecule, a labile M–C bond may be examined by NMR either at low temperatures or, after chemically stabilizing the molecule, at elevated temperatures. Structural information like the number of unpaired electrons, the number of nonequivalent nuclei, and static as well as dynamic stereochemistry information are obtained.

Apart from the metal–carbon π bond to cyclopentadienyls the Cp_2V—R series includes examples for V—C_{sp}, V—C_{sp^2}, and

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(28) That b_2 and π_{CC} have the same symmetry for conformation B may be seen after rotating π_{CC} in Figure 7 by 90°.

(29) For sake of computer time calculations were carried out only on C_5H_5 derivatives. We feel justified in applying the qualitative arguments also to peralkylated analogues since corresponding nuclei of **6**, **10**, and **11** give similar NMR shifts.

(30) Jorgensen, W. L.; Salem, L. "The Organic Chemists Book of Orbitals"; Academic Press: New York/London, 1973; pp 8–10.

(31) After a 30° rotation of the CH_3 group the other component of the two e sets would replace e_a and e_a^*.

Table II. Isotropic ^{13}C and ^{1}H Shifts (ppm) at 298 K

				other positions						
compd	solvent	nucleus	five-ring position	1′	2′	3′	4′	ortho	meta	para
1	C_6D_6	^1H	−120	−686						
	THF	^{13}C	193.8	*a*						
2	THF-d_8	^1H	−121	−389	45.2	4.8	−6.9			
3	C_6D_6	^1H	−117	−530		−4.2				
	C_6D_6	^{13}C	176.3	*a*		−50.1				
4	C_6D_6	^1H	−122	−534				−13.6	5.2	−12.7
	C_6D_6	^{13}C	169.2	*a*	*a*			103.4	−85.1	69.9
5	C_7D_8	^1H	−128					38.7	11.5	5.7
	THF	^{13}C	196.5	*a*				*a*	−40.8	−101.5
6	C_7D_8	^1H	−122					35.2	−16.2	6.0
	C_7D_8	^{13}C	189.2						113.1^d	
10	C_6D_6	^1H	α-2/5, 3/4, 1, −18.1, −22.5,^{b} −9.6; β, 0.8					40.2	−17.6	6.0
	C_6H_6	^{13}C	2/5, 3/4, 1, 233, 250, 240						129.7^d	
			α-2/5 + 3/4, 1, −398, −356; β, −120.7							
11	C_7D_8	^1H	α-2/5, 3/4, 1, −18.2, −23.9, −10.5;^{c} β, 0.7					−10.4 (ortho-CH_3)	−21.3	−8.8 (para-CH_3)

^{a} Not observed. ^{b} ± 0.5 ppm due to overlap with *m*-H. ^{c} ± 1 ppm due to overlap with *o*-CH_3 and *p*-CH_3. ^{d} Tentative assignment derived from ^1J(CH), relative intensity and sign; no other signal could be observed.

$V—C_{sp^3}$ bonds. It is however more advantageous to classify η^1 ligands as having rotational symmetry or not since most M—C bonds have σ and π contributions (an exception is $Cp_2V—C_6H_5$ with a pure σ bond at low temperatures). The now widely accepted frontier orbital approach yields a good (at least) qualitative understanding of the NMR results; a more rigorous treatment of course has to include electron repulsion and electron spin. The η^1 ligands in $Cp_2V—R$ may be classified as free radicals R· having a reduced spin density. Thus, there is reasonable agreement between the hyperfine coupling constants of $C_6H_5—C{\equiv}C\cdot$[32] $C_6H_5—CH_2\cdot$, and $C_6H_5\cdot$[33] and our NMR shifts of the corresponding $Cp_2V—R$ derivatives. NMR more easily obtains ^{13}C and sign information; it may be advantageous when R· is very unstable. Severe limitations arise, however, if the mechanisms which delocalize the unpaired electron on R differ. This especially influences nuclei close to the spin source.

Experimental Section

General Remarks. All metal organic compounds were handled under dry oxygen-free argon by using the Schlenk technique. As far as mentioned standard cooling baths were used; frits were equipped with jackets and could be kept at −20 °C. Solvents were dried with sodium (THF, toluene, pentane) or magnesium (alcohols) and distilled under argon before use. Melting points were determined in capillaries sealed under argon. Elemental analyses were performed by the microanalytical laboratory of this institute.

Preparation of Vanadocene Derivatives Cp_2VR. General Procedure. This procedure follows ref 5b,d,f with slight changes. A solution or suspension of Cp_2VCl (2.2 g, 10 mmol) in 50 mL of the solvent given in Table I was cooled to −20 °C, and 1 equiv of the alkylating agent was added. After 2 h stirring at 0 °C, the solvent, if not pentane, was removed and the residue extracted with pentane. The green to grayish blue pentane solutions were separated by filtration and cooled to −78 °C to give the crude products as black crystals. They were purified by repeated recrystallization from pentane.

Preparation of Peralkylvanadocene Derivatives (η^5-$C_5Me_4Et)_2VR$. (η^5-$C_5Me_4Et)_2V$ (7). A solution of 3-ethyl-1,2,4,5-tetramethylcyclopentadiene[37] (16.2 g, 108 mmol) in THF (100 mL) was cooled to −10 °C, and a 2.15 M solution of *n*-butyllithium in hexane (50.2 mL, 108 mmol) was added with vigorous stirring. A white suspension formed which was stirred at room temperature for 1 h and then added to a solution of $VCl_2\cdot 2THF$, prepared from VCl_3 (8.6 g, 54.7 mmol) in THF (100 mL) according to ref 14. After the mixture was stirred at room temperature for 4 days, the solvent was removed and the brown-red oily residue extracted with pentane and filtered. After evaporation of the solvent, the product was purified by recrystallization from boiling methanol (four times). Large red crystals of 7 (9.8 g, 52%) were isolated, melting at 144–146 °C.

Anal. Calcd for $C_{22}H_{34}V$: C, 75.62; H, 9.81. Found: C, 75.73; H, 9.81.

(η^5-$C_5Me_4Et)_2VBr$ (9). A solution of 7 (6.7 g, 19.3 mmol) in ether (50 mL) was cooled to −30 °C. Bromine (1.54 g, 9.6 mmol), dissolved in ether (20 mL) precooled to −30 °C, was added with stirring. Yellow-brown (η^5-$C_5Me_4Et)_2VBr_2$ (8) precipitated. When this was warmed to room temperature, the solid disappeared, leading to a dark blue solution. After the solution was stirred for 3 h, the solvent was removed. The crude product was purified by recrystallization from pentane at −78 °C (three times), yielding blue crystals of 9 (7.45 g, 90%), mp 116–117 °C.

Anal. Calcd for $C_{22}H_{34}BrV$: C, 61.54; H, 7.98. Found: C, 61.58; H, 7.99.

(η^5-$C_5Me_4Et)_2V—C{\equiv}C—C_6H_5$ (10). To a solution of 9 (1.60 g, 3.7 mmol) in ether (50 mL) was added sodium phenylacetylide[38] (0.46 g, 3.7 mmol). The mixture was stirred at room temperature for 3 days to give an olive green solution. The ether was removed; the residue was extracted with pentane and filtered. The extract was treated with ethanol (30 mL) and the pentane removed under reduced pressure. The product crystallized from the ethanol solution at −78 °C. Recrystallization from ethanol (two times) and from pentane (three times) gave black crystals of **10** (1.15 g, 69%), melting at 70–71 °C.

Anal. Calcd for $C_{30}H_{39}V$: C, 79.97; H, 8.72. Found: C, 80.07; H, 8.41. IR: 2040 cm^{-1} ($\nu_{C\equiv C}$).

(η^5-$C_5Me_4Et)_2V—C{\equiv}C—C_6H_2Me_3$ (11). This compound was prepared and purified in the same way as **10**. Compound **9** (1.45 g, 3.4 mmol) and sodium mesitylacetylide[38,39] (0.58 g, 3.5 mmol) gave **11** as black crystals (0.35 g, 21%), melting at 83–84 °C.

Anal. Calcd for $C_{33}H_{45}V$: C, 80.45; H, 9.21. Found: C, 80.40; H, 9.17. Mass spectrum [70 eV, 75 °C; ion (relative intensity)]: M^+ (32), $[M + 1]^+$ (12), $[M - (C_2C_6H_2Me_3)]^+$ (72), $[M + 2 - (C_5Me_4Et)]^+$ (100), $[M - (C_5Me_4Et)]^+$ (44), $[M - 2(C_5Me_4Et)]^+$ (20).

Physical Measurements. The mass spectrum was obtained by using a Varian MAT 311A spectrometer with the assistance of Dr. F. R. Kreissl. The IR spectrum was recorded on a Beckman IR 10 instrument as halocarbon mull.

The NMR spectra were obtained from concentrated solutions of the compounds. Table II summarizes our results. NMR tubes (10 mm for ^{13}C and 5 mm for ^1H) were equipped with ground-glass joints and stoppers to assure long term exclusion of oxygen. ^{13}C spectra (and some ^1H spectra) were recorded with a Bruker CXP 200 spectrometer with B-ST 100/700 temperature unit. Typical parameters for ^{13}C (^1H) were pulse width, 8 μs (4 μs), number of accumulations, 20K (2K), and data collection time, 28 min (3 min). Other parameters varied with signal

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spread. Some ^{1}H spectra were recorded with a JEOL C 60 HL spectrometer with JNM-VT temperature unit; the technique has been described earlier.[34] Temperatures at thermal equilibrium were measured before and after an experiment with a Lauda R 42 resistance thermometer, the sensor being positioned in an NMR tube filled with solvent only.

Experimental signal shifts, δ^{exptl}, were determined relative to solvent signals; for $\delta(^{13}C)$ we took the data of ref 35, for protons: benzene δ 7.3, toluene $\delta(CH_3)$ 2.3, THF $\delta(CH_2\text{-}\beta)$ 1.9. Calculation of δ^{exptl} relative to isostructural diamagnetic molecules gave the isotropic shifts of Table II with negative shifts to low field. All isotropic shifts were referenced to 298 K either by temperature-dependent measurements (^{1}H for **5** and **10**) or on the basis of the Curie law. Errors due to deviations from Curie behavior are believed to be small. An approximation was necessary for diamagnetic reference signals. Appropriate molecules would be $(C_5H_5)_2Re\text{–}R$.[36] However, their NMR data are not complete. On the other hand, $\delta(^1H)$ for $(C_5H_5)_2Re\text{–}R$ are similar to those of $(C_5H_5)_2Fe$. We therefore used $\delta(C_5H_5)$ 4.1 and for protons of the peralkylated cyclopentadienyls $\delta(\alpha\text{-}1)$ 2.1, $\delta(\alpha\text{-}2\text{–}5)$ 1.6, and $\delta(\beta)$ 0.9.[37] Mean values of δ 1.0 were taken for aliphatic protons in positions 1′ to 4′, δ 7.3 for phenylprotons, and δ 2.3 for CH_3 in mesitylene. Since ^{13}C data for diamagnetic molecules of the type $(C_5H_5)_2M\text{–}R$ do not appear to exist, we tentatively used ferrocene (δ 67.8) and benzene (δ 128.0) as mean values for all phenyl carbons and TMS for the $Si(CH_3)_3$ group; for introduced errors cf. ref 7. The accuracy of δ^{exptl} (^{1}H) depended on the shift range: $\delta < 50, \pm 0.1$; $\delta < 300, \pm 1$; $\delta > 300, \pm 5$; all δ^{exptl} (^{13}C), ±1.

MO Calculations. Extended Hückel type calculations were carried out according to ref [40]. The following parameters, adapted from the X-ray results on **11**,[9,15] were used for the model calculations on **1**, **5**, and **6**: Cp_2V fragment (C_s symmetry), C–C in Cp = 1.42 Å, C–H = 1.08 Å, V–Cp(center) = 1.975 Å, ∠Cp(center)–V–Cp(center) = 150°; phenyl, C–C = 1.40 Å, C–H = 1.08 Å. Compound **5**: V–C1′ = 2.03 Å. Compound **6**: V–C1′ = 2.03 Å, C1′–C2′ = 1.234 Å, C2′–ipso–C = 1.447 Å. Compound **1**: V–C1′ = 2.0 Å, C1′–H1′ = 1.09 Å, tetrahedral symmetry at C1′.

The atomic parameters for vanadium are[41]

orbital	H_{ii}, eV	ζ_1[a]	ζ_2[a]
4s	−9.17	1.60	
4p	−5.46	1.60	
3d	−10.48	4.75 (0.4558)	1.50 (0.7516)

[a] Slater exponents; the coefficients of the double-ξ-3d functions are given in parentheses.

The parameters for C and H are standard values,[40] and a modified Wolfsberg–Helmholz formula[42] was used.

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Supplementary Material Available: Listing of experimental ^{13}C and ^{1}H NMR shifts (1 page). Ordering information is given on any current masthead page.

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Synthesis of [1.1]Ferrocenophanes via 1,1′-Bis(6-fulvenyl)ferrocene

A. Cassens,[1] P. Eilbracht,[2] A. Nazzal, W. Prössdorf,[3] and U. T. Mueller-Westerhoff*

Contribution from the Physical Science Department, IBM Research Laboratory, San Jose, California 95193. Received January 26, 1981

Abstract: An efficient and practical synthesis of [1.1]ferrocenophane is described. The sequence of reactions starts with 1,1′-dilithioferrocene, which is added to 6-dimethylaminofulvene, producing, after hydrolysis, the previously unknown 1,1′-bis(6-fulvenyl)ferrocene in better than 80% yield. Other procedures for the preparation of the compound are also given. The fulvene is reduced with lithium tri(*sec*-butyl)borohydride in THF to the 1,1′-bis(cyclopentadienylmethyl)ferrocene dianion, from which the [1.1]ferrocenophane is obtained by reaction with ferrous chloride in THF in average yield of 35 to 45% after purification. Thus, the ferrocenophane is available for the first time through a satisfactory preparative method in large enough quantities to investigate its chemistry. From the intermediates used in this synthesis, substituted ferrocenophanes can also be obtained.

The compound [1.1]ferrocenophane (**1**), in which two ferrocenes are linked together by two bridging methylene groups, shows several very unusual properties, which are based on the relative proximity of the two metallocenes and a high degree of rotational flexibility around the bridging methylene groups. Dissolution of **1** in aqueous acidic media appears to produce hydrogen[4] and the dication of **1**. It is believed that initial protonation at the iron atoms is followed by rapid elimination of hydrogen, a process which is facilitated by the proximity of the hydrogens in an appropriate conformation as well as the possibility of **1** forming a stable dication. Nothing is known about this dication of **1**, except that it can be reduced quantitatively to the neutral species. This reversibility, however, makes **1** an interesting candidate for the modification of semiconductor surfaces in solar energy systems for the production of hydrogen from water.[5] Oxidation of **1** leads to a monocation[6,7] of the mixed-valence type, which was claimed[6] to be in equilibrium with an average valence species. The dimethyl derivative **2** of [1.1]ferrocenophane has been oxidized to a mono- and a dication.[6] The diamagnetism of the dication was taken as evidence for a strong intramolecular interaction, supposedly due to the proximity of the ferrocenes rather than a coupling through the saturated bridges. However, there also exists a possibility that

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