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$(dmpe)_2Cl$], indicates that the first step in the formation of **5** and **6** is oxidative addition of HX. This step would then be followed by protiolysis of the trimethylsilyl groups, yielding the final product.

It has also been discovered in these studies that the disiloxyacetylene ligand in [Ta(t-$BuMe_2SiOCCOSiMe_2$-t-Bu)$(dmpe)_2Cl$] (**8**) can be removed from the metal center with the C–C bond intact via hydrogenation by using hydrogen or synthesis gas in the presence of either 5% palladium on carbon or Wilkinson's catalyst. The resulting alkene, (t-$BuMe_2SiO$)CHCH($OSiMe_2$-t-Bu) (**9**), has been characterized by proton and carbon NMR spectroscopy along with comparison to an authentic sample. Compound **9** appears to adopt a cis stereochemistry, which is consistent with this type of hydrogenation reaction. While the chemistry of **9** has not yet been explored further, it may be a potential precursor to useful organic substrates. Investigations of the possibility of catalytic reductive coupling followed by hydrogenation are currently in progress.[36]

Acknowledgment. This work was supported by a grant from the National Science Foundation. FAB mass spectra were obtained with the assistance of Dr. C. Costello at the facility supported by NIH Grant RR 00317 (Principal Investigator, Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources. We also thank Prof. R. West for helpful comments.

Supplementary Material Available: Tables S1, S2, S4, and S5, reporting non-hydrogen atom thermal parameters and hydrogen atom positional and thermal parameters for [TaH(HOCCOH)$(dmpe)_2Cl$]Cl and [TaH($Me_3SiOCCOBF_3$)$(dmpe)_2Cl$]·$C_6H_5CH_3$ (5 pages); Tables S3 and S6, giving observed and calculated structure factors for the two compounds (65 pages). Ordering information is given on any current masthead page.

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[36] Note added in proof: Extension of this work to vanadium has led to the isolation and full characterization of the complexes [V($Me_3SiOC{\equiv}COSiMe_3$)$(dmpe)_2X$] and [V($Me_3SiOC{\equiv}COSiMe_3$)$(dmpe)_2$]X, which react directly with H_2 in the absence of an external catalyst to form *cis*-bis(trimethylsiloxy)ethylene (Protasiewicz, J. D.; Lippard, S. J. Submitted for publication).

(η^5-Cyclopentadienyl)(η^7-cyclooctatrienyl)vanadium: Synthesis via Stereoselective Protonation of the (η^5-Cyclopentadienyl)(cyclooctatetraene)vanadate Anion. NMR and ESR Properties and Evidence for Metal-Assisted H-Migration

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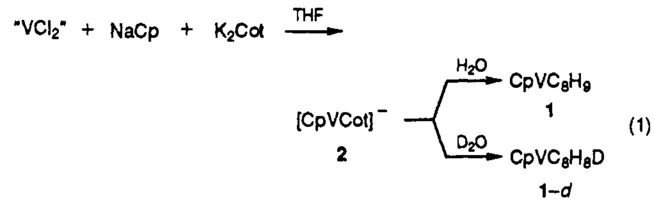
(η^5-Cyclopentadienyl)(η^7-cyclooctatrienyl)vanadium (**1**) can be obtained by a one-pot reaction in THF by starting from VCl_2, NaCp (Cp = cyclopentadienyl), and K_2Cot (Cot = cyclooctatetraene) as simple educts and with subsequent hydrolysis. The monodeuterated derivative **1**-*d* is obtained on hydrolysis of the reaction mixture with D_2O. EPR data for **1** show a paramagnetic V(d^5) mixed sandwich compound with a nondegenerate doublet ground state. By means of ^1H and ^2H NMR spectroscopy strong evidence is found for a stereoselective exo addition of D^+ to the $[CpVCot]^-$ anion and a subsequent metal-assisted H-migration.

Protonation of a metal-coordinated cyclooctatetraene (Cot) can occur stereoselectively via an exo or an endo attack with respect to the metal center. For both pathways some examples have been described previously.[1-3] However, in these examples no migration of hydrogen within the Cot ligand was reported. We wish to give an account of a stereoselective protonation of the anionic Cot complex $[CpVCot]^-$ to $CpVC_8H_9$ (**1**) followed by a metal-assisted hydrogen migration.

Results and Discussion

The paramagnetic cyclooctatrienyl complex $CpVC_8H_9$ (**1**) was first prepared by the "isopropyl Grignard" method.[4] We found a simpler way to synthesize the highly oxygen sensitive complex **1** in good yield in a one-pot reaction (1). For (1) the vanadium(II) chloride, which is obtained by the reduction of VCl_3 by Zn, can be used directly without further purification. The advantage of this reaction is the facile one-pot synthesis of **1** from simply prepared starting



(1)

"VCl_2" = $^1/_4[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$[5] or $^1/_2[V_2(\mu\text{-}Cl)_3(THF)_6][AlCl_2Et_2]$[6]

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[‡] Universiteit Nijmegen.

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Table I. EPR Data for d^5 Vanadium Sandwich Complexes

	g values[a]			^{51}V hyperfine coupling[b]			
	g_{iso}	$g_\perp$	$g_\parallel$	a_{iso}	$A_\perp$	$A_\parallel$	ref
1	1.981[c]	1.973,[d] 1.976[d]	2.004[d]	7.90	10.67,[d] 9.57[d]	0.49[d]	this work
$CpVC_7H_7$	1.987	1.978	2.005	7.41	10.41	1.49	8
$V(C_6H_6)_2$	1.987	1.979	2.001	6.35	9.20	0.65	7

[a] ±0.001. [b] ±0.05 mT. [c] Determined with respect to second-order effects. [d] Obtained from the calculated spectrum with 1.5 mT line width.

Table II. ^{1}H NMR Data for Paramagnetic d^5 Sandwich Complexes of Vanadium and Chromium

	T, K	δ(Cp)	$\nu_{1/2}$,[a] kHz	δ(others)	$\nu_{1/2}$,[a] kHz	ref
1[b]	318	127 (2)	15.0	58 (1) (1 H)	4.3	this work
				−63 (1) (1 H)	5.0	
$CpVC_7H_7$[c]	305	130 (5)	12	310 (10) (7 H)	15	8
$CpCr(\eta^6$-Cot)[b]	323	130 (2)	21.8	−36.2 (2) (2 H)	1.4	13
$CpCrC_6H_6$[c]	300	172 (5)	7.4	340 (5) (6 H)		12

[a] Line width. [b] Toluene solution. [c] Powder sample.

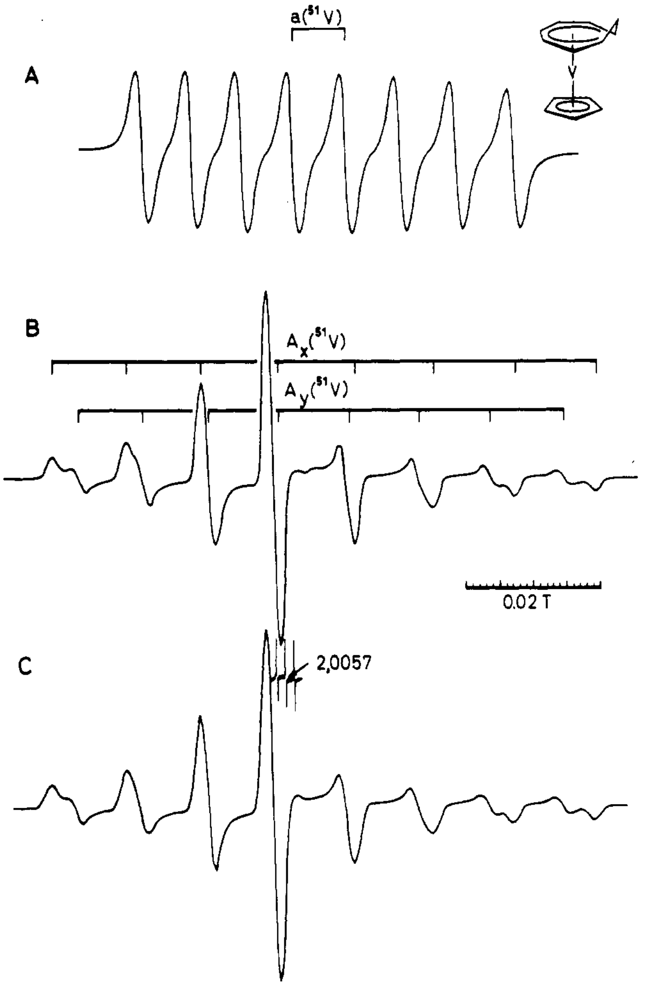

Figure 1. X-Band EPR spectra of 1 dissolved in toluene: (A) fluid solution, 300 K; (B) solid solution, 130 K; (C) calculated spectrum of (B).

materials. The key step of reaction 1 is the hydrolysis. The use of D_2O in place of H_2O yields the monodeuterated complex $CpVC_8H_8D$ (1-*d*), as indicated by EI-MS and paramagnetic ^{2}H NMR spectroscopy. These preparative results confirm that the anion $[CpVCot]^-$ (2) is formed as a stable intermediate.

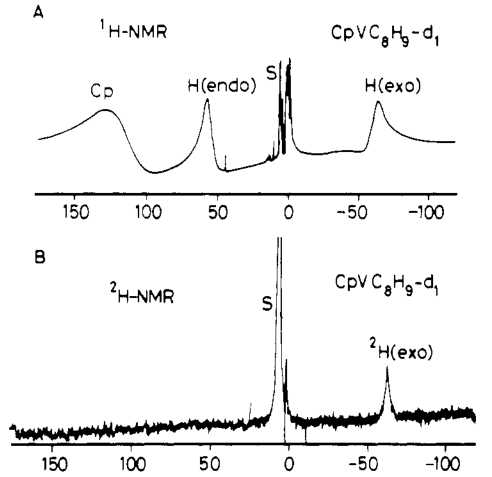

Figure 2. (A) ^{1}H NMR spectrum of 1 (in toluene-d_8; s = solvent) at 318 K. (B) ^{2}H NMR spectrum of 1-d (in toluene + benzene-d_6; s = solvent) at 318 K.

The 17-valence-electron (ve) complex 1 shows a well-resolved fluid-solution EPR spectrum (Figure 1A) containing eight lines due to the hyperfine coupling (hfc) of the unpaired electron with the V center ($I(^{51}V) = ^7/_2$). The isotropic ^{51}V hfc constant $a(^{51}V)$ for 1 is almost equal to those of other V(d^5) sandwich compounds as well as the isotropic g value g_{iso} (see Table I).

From the solid-solution spectrum of 1 three different g and corresponding $A(^{51}V)$ values can be determined by calculation of the experimental spectrum (g_1 = 1.973, g_2 = 1.976, g_3 = 2.004, A_1 = 1.067 mT, A_2 = 0.957 mT, and A_3 = 0.49 mT; see Figure 1B,C and Table I), but two of them are only slightly different from each other. Hence, only a small deviation from axiality of the **g** and **A** tensors of 1 must be assumed. However, the hfc constants as well as g values are in good harmony with other 17-ve V sandwich compounds such as $V(C_6H_6)_2$[7] and $CpVC_7H_7$.[8] Conclusively the semioccupied molecular orbital in 1 must be predominately a V(d_{z^2}) orbital.[9] To our knowledge 1 is the first example of a V(d^5) sandwich compound with a slight perturbation of the tetragonal **g** and hf tensors caused by a π-ligand.

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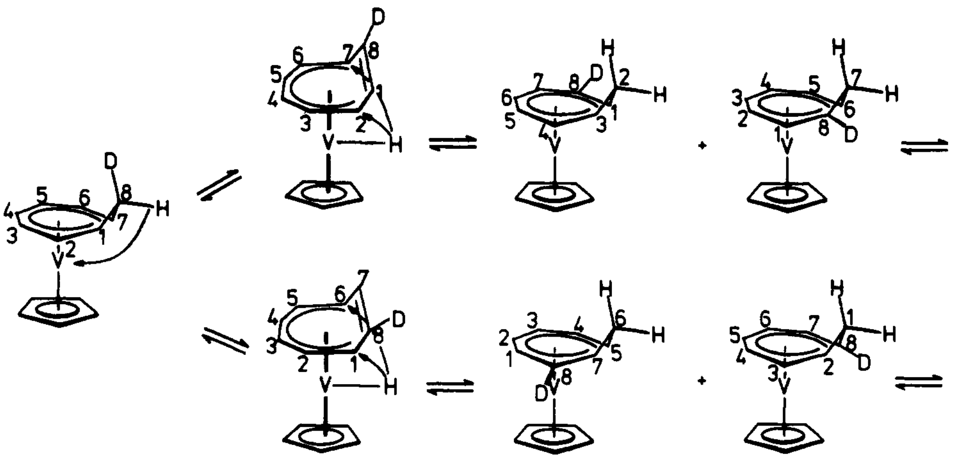
Scheme I



The ^{1}H NMR spectrum of the toluene solution of 1 (Figure 2A, Table II) shows three different signals of considerably broad line width, which of course lie far away from the normal diamagnetic shift range.[10] The dependence of the chemical shifts of the three signals on $1/T$ is linear, and the reduced shifts $\Theta = \delta_{para}T/298$ are almost temperature-independent (Figure 3), indicating the Curie behavior of the paramagnetism of 1.[11] From the rough integrals and especially from its chemical shift the signal at δ(318 K) = 127 ppm is assigned to the Cp protons. Similar shifts of Cp resonance signals are found for other paramagnetic (η^5-cyclopentadienyl)metal(d^5) radical complexes such as $CpCrC_6H_6$ and CpCr(η^6-Cot) (Table II).[12,13] Since the anisotropy of the **g** tensor of 1 is small (see Table I), the chemical shift is governed by the contact shift $(\Delta\nu/\nu)_c = \delta_{para} = g_{iso}[a(^1H)](11.06 \times 10^{-4}/T)$,[13] from which the hfc coupling of the Cp protons can be calculated as $a(^1H)$ = 0.211 (5) mT. This is in good accordance with $a(^1H)_{Cp}$ values obtained from other paramagnetic (η^5-cyclopentadienyl)metal(d^5) complexes, e.g., $CpVC_7H_7$.[8]

The resonance signals δ(318 K) = 58 and −63 ppm must be assigned to the protons of the CH_2 group of the cyclooctatrienyl ring. In principle, these protons are in β-positions with respect to the coordinated part of the C_8 ring. Normally, for β-protons in d^5 sandwich complexes with the unpaired electron in a d_{z^2} metal orbital ($^2A_{1g}$ ground state) a high-field shift is expected. This high-field shift is due to a conformationally independent through-bond spin polarization and a conformationally dependent hyperconjugation as delineated recently, calling forth a negative spin density on β-protons (Figure 4).[14,15] The unusually low field shift of the signal of one methylene proton must be caused by a very special position of this proton with respect to the paramagnetic metal center. This position has to allow a direct spin delocalization onto the proton, resulting at last in a positive spin density that induces a low-field shift (Figure 2). Direct metal–proton interactions are described in several π-ligand transition-metal complexes, showing an interaction between an endo proton and the metal center that can induce metal-assisted hydrogen migrations.[16,17] Therefore, the low-field-shifted signal at δ = 58 ppm is attributed to the endo proton of the methylene group.[18]

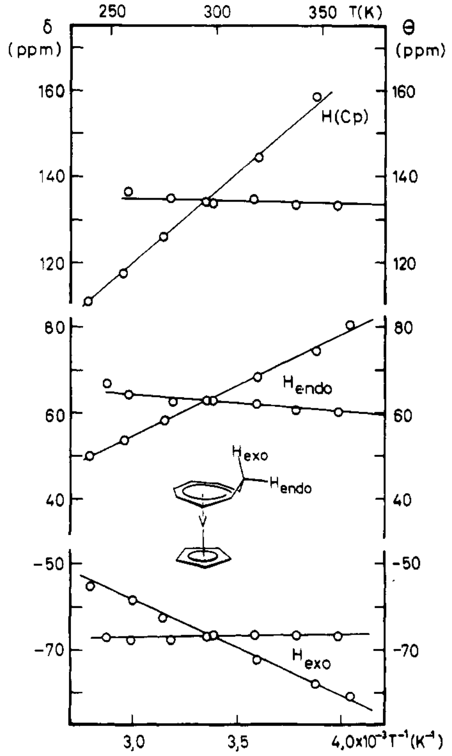


Figure 3. Temperature dependence of the chemical shifts δ as well as the reduced chemical shifts Θ of the Cp and methylene proton signals in 1.

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[10] Corresponding to the convention of NMR spectroscopy, here the low-field shifts are defined as positive, whereas the high-field shifts are negative.

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[18] The α-proton resonance signals of the coordinated part of the cyclooctatrienyl ligand cannot be seen in the ^{1}H NMR spectrum because of the dependence of the line width on the square of the proton hfc constant.[19] Assuming an $a(^1H)$ value for the α-protons similar to those of the C_7 and C_8 ligands of $CpCrC_7H_8$[20] and CpCrCot,[13] respectively, the line widths of the signals of the α-protons increase to about 80–160 kHz, which is too large to be detected.

[19] Swift, T. J. In *NMR of Paramagnetic Molecules, Principles and Applications*; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; p 53 ff.

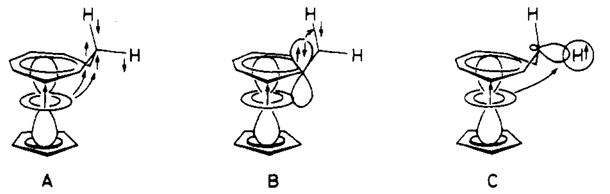

Figure 4. Qualitative picture of electron spin transfer in 1: (A) conformationally independent through-bond spin polarization; (B) conformationally dependent hyperconjugation between π-orbitals of the organic ligand and the C–H bond; (C) direct spin delocalization.

Surprisingly, the same ^1H NMR spectrum is obtained for the monodeuterated derivative 1-*d*, confirming the occupation of the endo as well as the exo position of the methylene group by protons. This result is corroborated by two aliphatic C–H stretching vibrations ($\tilde{\nu}$ = 2918 and 2853 cm^{-1}) found for 1 as well as for 1-*d* in IR studies. However, a ^2H NMR study shows the deuterium only to be in the exo position of the cyclooctatrienyl ligand (Figure 2B). This seeming contradiction that in 1-*d* protons can be in the exo as well as in the endo position whereas a deuterium only occupies the exo position is explained by a hydrogen migration. Considering a stereospecific exo attack of D^+ at the cyclooctatrienyl ligand, the proton at the sp^3 carbon attains the endo position. This special position allows the endo proton to have a metal-assisted migration around the C_8 ring, in the course of which this proton remains in the endo position. Successively D^+ occupies the positions of the coordinated part of the cyclooctatrienyl ligand. Unfortunately, the corresponding ^2H NMR signals could not be observed because of the line width.[18,21] When the endo proton accidentally passes the D-substituted carbon atom, the deuterium always flips in the exo position (see Scheme I).

Although exo additions of protons to coordinated cyclic oligoolefinic ligands of transition-metal complexes are well-known, no hints of a hydrogen migration have been reported in these examples,[1,3,17b] even when the protonated products are moderately heated.[22,23]

Experimental Section

All manipulations were carried out under a N_2 atmosphere and with N_2-saturated solvents. Tetrahydrofuran (THF), toluene, and hexane were freshly distilled from the appropriate alkali metal or metal alloy. The EPR spectra were recorded on a Varian EE 12 X-band spectrometer and the NMR spectra on a Bruker WH 400 spectrometer. The ESR and NMR sample tubes were sealed under high vacuum.

Preparation of $CpVC_8H_9$. A 43.8-mL amount of a 0.3 M K_2Cot solution in THF is added to a cooled solution (−78 °C) of 5.25 g (6.56 mmol) of $[V_2Cl_3(THF)_6][AlCl_2Et_2]$[6,24] in 100 mL of THF. After the mixture is stirred for 1 h, 10 mL of THF containing 13.13 mmol of NaCp is added dropwise. The reaction solution is warmed overnight and is quenched with 1 mL of oxygen-free water. The solvent is stripped under vacuum, and the residue is extracted with hexane. The dark green hexane extract is concentrated to 40 mL, and the products are separated by column chromatography (alumina/5% H_2O, hexane, length 30 cm, diameter 3 cm). As a first fraction the blue-violet solution of vanadocene is obtained, and from the second fraction 870 mg (3.94 mmol) of 1 (30%) is isolated.

The monodeuterated derivative 1-*d* is prepared in the same manner as described above for 1. For the hydrolysis oxygen-free D_2O is used. EI-MS (*m/e*; 1, 1-*d*, %): 222 (13.8, 100), 221 (100, 16.5), 220 (13.8, 20.4), 219 (24.7, 64.1), 218 (72.2, 26.0), 194 (6.9, 20.2), 193 (28.8, 11.5), 154 (1.5, 6.8), 153 (10.2, 4.6), 116 (57.3, 60.4), 51 (15.6, 13.7). IR and C,H analytical data for 1 and 1-*d* are in accordance with published data.[4]

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie (FRG), and we are greatly indebted to the BASF for the donation of Cot.

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(21) A ^2H-ENDOR study of 1-*d* is in progress in order to obtain information about deuterium in α-positions.

(22) Salzer, A.; Bigler, P. *Inorg. Chim. Acta* **1981**, *48*, 199.

(23) A H-migration from the metal of a hydride compound to the Cot ligand, forming a cyclooctatrienyl compex, has been found just recently for Cp*Zr(Cot)H: Cp*Zr(η^8-Cot)H $\rightleftharpoons$ Cp*Zr(η^7-C_8H_9). This reaction is reversible, and both compounds have been characterized by means of X-ray structure determination: Teuben, J. H.; Sinnema, P.-J. Personal communication. These results agree very well with the metal-assisted H-migration outlined in Scheme I.

(24) In place of the THF-soluble "VCl_2" it is also possible to use $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$,[5] which is only very slightly THF-soluble.