6 would be favored over 8. Consistent with this prediction was an observed NOE effect between Cp and OCH₃ and the absence of such an effect between Cp and either methyl.²³,²⁴

The facility of the rearrangement of 2 to 6 is striking and probably results from a combination of methoxy acceleration and relief of strain. Thus, the methoxy must favor this reaction since its position on saturated carbon can do little to stabilize 2 while conjugation with the p orbital in the carbene should have a significant impact on the energy of 4. It is more difficult to assess the contribution of strain relief to this reaction because even though there would be little question that ring strain on the cyclopropane side of the equilibrium is about 25 kcal/mol,²⁵ the strain on the metallacyclobutene side is not known. Were the rearrangement to a carbocycle, strain would slightly favor the cyclopropane; however, small ring metalloccycles are probably much less strained than their carbocyclic analogues.²⁶ However, it is unlikely that relief of ring strain, alone, is sufficient to induce the rearrangement since photolysis of cyclopropyl σ-complexes with α-hydrogens showed no reaction.²⁷

Attempts to obtain evidence for the intermediacy of 3 in the rearrangement sequence by studying the effect of added CO on the rate of rearrangement were inconclusive due to the photoinduced decomposition of 6 which was retarded by the presence of CO. However, the mechanism in Scheme 1 is probably correct in view of the known photobehavior of Fe-alkyl complexes²⁸ as well as our successful isolation of the primary rearrangement product (corresponding to 4) from rearrangement of cyclobutyl²⁹ and cyclobutenylyl complexes. These results as well as anticipated mechanisms studies on the rearrangement of 2 to 6 will be provided in future papers.

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Cyclopentadienylationium(III) and -vanadium(II) Methyl, Phenyl, and Borohydride Compounds

Bart Hessen and Jan H. Teuben*  
Department of Inorganic Chemistry, University of Groningen  
9747 AG Groningen, The Netherlands

Timothy H. Lemmen, John C. Huffman, and  
Kenneth G. Caulton*  
Department of Chemistry and Molecular Structure Center  
Indiana University, Bloomington, Indiana 47405

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Summary: Reaction of CpVCl₂(PMe₃)₂ with MeLi and PhMgBr yields CpVMe₃(PMe₃)₂ and CpVPh₃(PMe₃)₂, respectively. Conproportionation of CpVCl₂(PMe₃)₂ and CpVMe₂(PMe₃)₂ gives selective conversion to CpVMe(CO)(PMe₃)₂. These paramagnetic compounds show isotropic ¹H NMR shifts of the P–Me protons. CpVMe₂(PMe₃)₂ reacts rapidly with CO to give acetone and diazocyclopentadiene(CO)₃(PMe₃)₂. Borohydride converts CpVCl₂(Me₂PCH₂CH₂PMe₃) to CpV(P₆-BH)₂(dmpe), shown to have one unpaired electron, two less than its chloride precursor. Conversion of this monochloride to CpV(dmpe) occurs with MeLi and PhMgBr. The mononuclear compound has a low VC=H stretching frequency (2750 cm⁻¹), but the crystal structure shows no agnostic hydrogen to be involved. Crystal data (−158 °C): a = 12.526 (3) Å, b = 9.285 (2) Å, c = 12.772 (3) Å, Z = 4 in space group P2₁2₁2₁.

Complexes of the early transition metals containing one n⁵-C₅H₅ ligand are currently under study since they are less sterically encumbered and offer more metal orbitals for transformations of coordinated ligands than do their bis(n⁵-C₅H₅) relatives. Among early transition metals, representatives of the first transition series are particularly interesting since they offer a situation atypical in organometallic chemistry, that of isolable paramagnetic compounds. For example, all monomeric CpV²⁺ compounds, although d⁵, contain two unpaired electrons.⁷,⁸ We report here the synthesis of methyl and phenyl compounds of the CpV²⁺ and CpV³⁺ fragments, as well as their characterization by selected physical methods and reactivity studies.

As summarized in eq 1a, purple-blue CpVCl₂(PMe₃)₂ can be converted, in Et₂O at −30 °C, to red CpVR₂(PMe₃)₂, R = Me and Ph.⁹ Both air-sensitive compounds can be

\[
\text{CpVCl}_2(P\text{Me}_3)_2 \xrightarrow{\text{RM}} \text{CpVR}_2(P\text{Me}_3)_2 \xrightarrow{\text{CO}} \text{CpV(CO)}_2(P\text{Me}_3)_2 + R^2\text{CO} \tag{1}
\]

where RM = MeLi, PhMgBr.

(2) Wolczanski, P. T.; Berca, J. E. Organometallics 1982, 1, 798 and references therein.  
Both compounds are paramagnetic, and the isotropic shifts of the resonances of the phosphine methyl hydrogens serve as useful spectroscopic probes. For example, it is possible to use $^1$H NMR to demonstrate that the reaction in eq 2

$$\text{CpVCl}(\text{PMe}_3)_2 + \text{CpVMeCl}(\text{PMe}_3)_2 \rightarrow 2\text{CpVMeCl}(\text{PMe}_3)_2$$  (2)

occurs ($<12$ h) at $25^\circ$C in Et$_2$O not statistically, but essentially to completion. The mixed methyl chlorocomplex isolated from eq 2 is also paramagnetic and is not accessible from the 1:1 reaction of CpVCl(\text{PMe}_3)_2 with MeLi at $-20^\circ$C (followed by prompt workup); instead at $50\%$ yield of CpVMe(\text{PMe}_3)_2 results. A thermodynamic bias for dispersing $\pi$-donor ligands (e.g., Cl, OR) has been observed before for Ti(IV) complexes.\(^1\) Equation 2 is not rapid on the isotropically shifted $^1$H NMR time scale, nor have we observed rapid exchange of CpVMe(\text{PMe}_3)_2 with free PMe$_3$.

Both the dimethyl and the diphenyl compounds react rapidly (eq 1b) with 1 atm CO to eliminate the corresponding ketones and produce the same (V) carboxyl CpV(CO)$_2$(\text{PMe}_3)$_2$\(^1\) isolated as the diagonal isomer.

An attempt to form a borohydride derivative of CpVCl(\text{PMe}_3)$_2$ using 1 mol of LiBH$_4$ yielded CpVCl(\text{PMe}_3)$_2$(\text{BH}_4)$^-$ (i.e., VIII). Consequently, efforts were concentrated on direct preparation of a V(II) borohydride complex (Scheme I). CpVCl(dmpe)$^5$ with three unpaired electrons,\(^5\) is readily converted into CpV(BH$_4$)(dmpe)$^6$,\(^5\) whose $^1$H NMR appears to show only one dmpe CH$_2$ chemical shift (13 ppm, fwhm 256 Hz),\(^5\) and a dmpe methyl chemical shift ($-12.9$ ppm, fwhm 600 Hz) with a shoulder on the downfield side. The infrared spectrum (Nujol, KBr) is equally problematic, exhibiting a pattern (2980 (s), 2345 (s), 2255 (s), 1585 (m, br) cm$^{-1}$) not clearly conforming to the proposed guidelines for $\pi^*$-$\sigma^*$, or \(\pi^*\)-BH$_4^-$ binding. The preliminary results of a single-crystal diffraction study on a twinned crystal show \(\eta^5\)-C$_5$H$_5$, \(\eta^2\)-BH$_4^-$, and \(\eta^2\)-dmpe coordination. If we count $\eta^5$-Cp as utilizing three orbitals on vanadium and \(\eta^2\)-BH$_4$ as requiring $\pi$ and $\sigma$-dmpe coordination. The preliminary results of a single-crystal diffraction study on a twinned crystal show \(\eta^5\)-C$_5$H$_5$, \(\eta^2\)-BH$_4^-$, and \(\eta^2\)-dmpe coordination. If we count $\eta^5$-Cp as utilizing three orbitals on vanadium and \(\eta^2\)-BH$_4$ as requiring $\pi$ and $\sigma$-dmpe coordination.

This agrees with the measured solution magnetic moment,\(^1\) $1.6 \mu_B$ at $25^\circ$C, while the "high-spin" compound CpV(dmpe) has the expected moment of $3.6 \mu_B$, this "orbital counting" formalism also correctly explains the one unpaired electron observed for CpH($\pi^*\)-BH$_4^-$)(PCy$_3$)$_2$\(^7\), and predicts diamagnetism for CpV($\eta^*\)-BH$_4^-$) (magnetic susceptibility not reported).\(^1\)

Preparation of two cyclopentadienylnanadium(II) dihydrocarbonyls proceeds as in Scheme I. Each compound\(^1\) exhibits isotropically shifted dmpe proton signals indicative of two methyl and two methylene environments. Particularly puzzling is the observation that the methyl group bound to vanadium in CpVMe(dmpe) exhibits a C-H stretching frequency of 2750 cm$^{-1}$, which is lower than that in CpVMe(\text{PMe}_3)$_2$ (2795 cm$^{-1}$). CpVClMe\(^2\)\(^2\) BMe$_2$,\(^2\) AlMe$_2$,\(^2\) or any of the high-valent metal/methyl complexes synthesized by the Wilkinson group,\(^2\)\(^3\) with little prospect of settling this problem by X-ray or $^1$H NMR studies of paramagnetic CpV(dmpe), we have determined its crystal structure (Figure 1). The molecule is a monomeric three-legged piano stool, and the V--CH$_3$ unit shows no evidence of an agostic\(^2\) hydrogen; the V--C--H angles are 105 (4)$^\circ$, 122 (3)$^\circ$, and 105 (5)$^\circ$, with internal H--C--H being 105 (5)$^\circ$, 117 (6)$^\circ$, and 104 (6)$^\circ$. Since this is the first V(II) methyl compound synthesized and structurally characterized, evaluation of the significance of the V--C distance (2.219 (4) A) is difficult. This distance is considerably longer than V--C found in V(III) complexes such as Cp$_2$V(C=C-t-Bu)$_2$THF, 2.075 (5) A,\(^2\) or V(\text{CMe}_5)$_2$(\text{THF}), 2.219 (5)$^\circ$. The preliminary results of a single-crystal diffraction study on a twinned crystal show \(\eta^5\)-C$_5$H$_5$, \(\eta^2\)-BH$_4^-$, and \(\eta^2\)-dmpe coordination.

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(19) For black CpV(dmpe) isolated from Et$_2$O/pentane (C, H, and V elemental analysis): $^1$H NMR (360 MHz, CD$_2$Cl$_2$, 20 $^\circ$C) ppm at $-10.8$ (1200) ppm. Full-width at half maximum, in Hz, is given in parentheses after the chemical shift.
(20) For dark brown CpVCl(dmpe)$^2$ crystallized from Et$_2$O: \(^{\text{ORFTP}}\) 2805 cm$^{-1}$; $^1$H NMR (360 MHz, CD$_2$Cl$_2$, 21 $^\circ$C) ppm at $-9.5$ (1620).
(23) The E1 mass spectrum shows a parent ion.
(24) For comparison, the 360-MHz $^1$H NMR of CpV(dmpe) at $25^\circ$C shows Cp at 243 (6000) ppm, methyl resonances at 2.4 (460) and $-25.5$ (520) ppm, and methylene resonances at 16.8 (560) and 8.9 (720) ppm.

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$^{\text{ORTFP}}$ =< --158$^\circ$ C $\approx$ 12.526 (3) $\AA$, $b$ $\approx$ 9.285 (2) $\AA$, $c$ $\approx$ 1585 (5, br) cm$^{-1}$ not clearly conforming to the proposed guidelines for $\pi^*$-$\sigma^*$, or \(\pi^*\)-BH$_4^-$ binding.

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1,5-Dihydopyrrol-2-ones from (1,4-Diaza-1,3-diene)tricarbonyliron and Alkyne. 2.
Structure of a [2.2.2] Bicyclic Intermediate with Iron at the Bridgehead Position

Hans-Werner Frühauf, Frank Seils, Richard J. Goddard, and Marla J. Romão

FB 6, Organische Chemie der Universität-Gesamthochschule Duisburg, 4000 Duisburg 1, West Germany
Max-Planck-Institut für Strahlenchemie and Max-Planck-Institut für Kohlenforschung D-4330 Mülheim, West Germany

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Summary: (1,4-Diaza-1,3-diene)tricarbonyliron complexes react with electron-deficient alkenes under an atmosphere of CO to give a thermally labile, bicyclic intermediate which rearranges to a (1,5-dihydopyrrol-2-one)tricarbonyliron complex. With trimethyl phosphite instead of CO, the intermediate is stabilized, and it has been possible to determine its structure by X-ray crystallography.

Until recently it was thought that C-C bond-forming reactions of 1,4-diaza-1,3-dienes (dad) in the coordination sphere of transition metals were only feasible in binuclear complexes with the dad coordinated to both metal centers in an unsymmetrical six-electron mode, involving the π-electrons of one C==N moiety. The reaction of (dad)-

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Figure 1. The molecular structure of 2b. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe-C(4) = 2.023 (3), Fe-C(9) = 2.023 (3), Fe-N(1) = 2.030 (2), Fe-C(1) = 1.808 (3), Fe-C(2) = 1.767 (3), Fe-P = 2.260 (1), C(4)-C(10) = 1.397 (4), C(9)-N(2) = 1.362 (4), N(1)-C(13) = 1.269 (4), C(9)-Fe-P = 178.8 (1), C(1)-Fe-C(4) = 173.7 (1), C(2)-Fe-N(1) = 170.8 (1), C(4)-Fe-C(9) = 87.6 (1).

Scheme I

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tricarbonyliron complexes 1, in which the dad is coordinated in the chelating 4-electron mode through the nitrogen lone pairs only, with dimethyl acetylenedicarboxylate under an atmosphere of CO, finally yielding tricarbonyliron complexes of 1,5-dihydopyrrol-2-ones (e.g., 3, see Scheme I) suggests that this is not the case. This is supported by the observation of a thermally labile mononuclear intermediate 2a. In view of the importance of this reaction, we decided to investigate the structure of 2a. The 13C NMR resonances of this intermediate could be fully assigned from the proton-coupled spectra and revealed shift differences of up to 125.5 ppm with respect to the isomerized product 3 (cf. Figure 2), consistent with a [2.2.2] bicyclic structure. Unfortunately, the structure of this intermediate could not be determined by X-ray methods. However, when the reaction was performed in the presence of trimethyl phosphite, a compound with very similar spectroscopic properties to 2a was isolated.