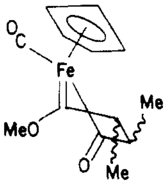
6 would be favored over 8. Consistent with this prediction was an observed NOE effect between Cp and OCH_3 and the absence of such an effect between Cp and either methyl.[23,24]



8

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 metallocycles 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 I is probably correct in view of the known photobehavior of Fp-alkyl complexes[28] as well as our successful isolation of the primary rearrangement product (corresponding to 4) from rearrangement of cyclobutyl[29] and cyclobutenyl[30] complexes. These results as well as anticipated mechanisms studies on the rearrangement of 2 to 6 will be provided in future papers.

Acknowledgment. This work was partially supported by the National Science Foundation to whom we are grateful. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. High-field NMR spectra were obtained on a Nicolet NT-300 spectrometer, operating at a field of 7 T; therefore acknowledgment is made to the Instrument Program, Chemistry Division, National Science Foundation, for financial assistance in the purchase of the instrument. We are also grateful to W. R. Winchester for providing the aforementioned EHMO calculations.

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

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Summary: Reaction of $CpVCl_2(PMe_3)_2$ with MeLi and PhMgBr yields $CpVMe_2(PMe_3)_2$ and $CpVPh_2(PMe_3)_2$, respectively. Conproportionation of $CpVCl_2(PMe_3)_2$ and $CpVMe_2(PMe_3)_2$ gives selective conversion to $CpVMe(Cl)(PMe_3)_2$. These paramagnetic compounds show isotropic ^1H NMR shifts of the P–Me protons. $CpVMe_2(PMe_3)_2$ reacts rapidly with CO to give acetone and *diag*-$CpV(CO)_2(PMe_3)_2$. Borohydride converts $CpVCl(Me_2PCH_2CH_2PMe_2)$ to $CpV(\eta^2\text{-}BH_4)(dmpe)$, shown to have one unpaired electron, two less than its chloride precursor. Conversion of this monochloride to CpVR(dmpe) occurs with MeLi and PhMgBr. The monomethyl compound has a low VC–H stretching frequency (2750 cm^{-1}), but the crystal structure shows no agostic 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 $P2_12_12_1$.

Complexes of the early transition metals containing one $\eta^5\text{-}C_5H_5$ ligand are currently under study[1-6] since they are less sterically encumbered and offer more metal orbitals for transformations of coordinated ligands than do their bis($\eta^5\text{-}C_5H_5$) 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 CpV^{2+} compounds, although d^2, contain two unpaired electrons.[7,8] We report here the synthesis of methyl and phenyl compounds of the CpV^{2+} and CpV^+ fragments, as well as their characterization by selected physical methods and reactivity studies.

As summarized in eq 1a, purple-blue $CpVCl_2(PMe_3)_2$ can be converted, in Et_2O at −30 °C, to red $CpVR_2(PMe_3)_2$, R = Me and Ph.[9] Both air-sensitive compounds can be

$$CpVCl_2(PMe_3)_2 \xrightarrow[\text{(a)}]{\text{RM}} CpVR_2(PMe_3)_2 \xrightarrow[\text{(b)}]{\text{CO}} CpV(CO)_2(PMe_3)_2 + R^2CO \quad (1)$$

$$\text{RM} = \text{MeLi, PhMgBr}$$

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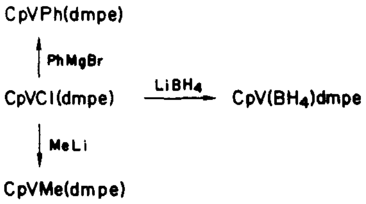
Scheme I



manipulated in hydrocarbon solvents under N_2 at 25 °C. 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 ^1H NMR to demonstrate that the reaction in eq 2

$$\mathrm{CpVCl_2(PMe_3)_2 + CpVMe_2(PMe_3)_2 \rightarrow 2CpVMeCl(PMe_3)_2} \quad (2)$$

occurs (<12 h) at 25 °C in Et_2O *not* statistically, but essentially to completion. The mixed methyl chloro complex[10] isolated from eq 2 is also paramagnetic and is not accessible from the 1:1 reaction of $CpVCl_2(PMe_3)_2$ with MeLi at −20 °C (followed by prompt workup); instead at 50% yield of $CpVMe_2(PMe_3)_2$ results. A thermodynamic bias for dispersing π-donor ligands (e.g., Cl, OR) has been observed before for Ti(IV) complexes.[11] Equation 2 is not rapid on the isotropically shifted ^1H NMR time scale, nor have we observed rapid exchange of $CpVMe_2(PMe_3)_2$ 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(I) carbonyl $CpV(CO)_2(PMe_3)_2$,[12] isolated as the *diagonal* isomer.

An attempt to form a borohydride derivative of $CpVCl_2(PMe_3)_2$ using 1 mol of $LiBH_4$ yielded $CpVCl(PMe_3)_2$[8] (i.e., V(II)). Consequently, efforts were concentrated on direct preparation of a V(II) borohydride complex (Scheme I). CpVCl(dmpe),[7] with three unpaired electrons,[8] is readily converted into $CpV(BH_4)(dmpe)$,[13] whose ^1H NMR appears to show only one dmpe CH_2 chemical shift (13 ppm, fwhm 256 Hz),[14] 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 (2380 (s), 2345 (s), 2255 (s), 1855 (m, br) cm^{-1}) not clearly conforming to the proposed guidelines[15] for η^1-, η^2-, or η^3-BH_4^- binding. The preliminary results of a single-crystal diffraction study on a twinned crystal show η^5-C_5H_5, η^2-BH_4 and η^2-dmpe coordination. If we count η^5-Cp as utilizing three orbitals on vanadium and η^n-BH_4 as requiring n orbitals on vanadium, it is predicted that the seven orbitals required to bind η^5-Cp, η^2-dmpe, and η^2-BH_4 will force spin pairing among the three d electrons in $CpV(BH_4)(dmpe)$.

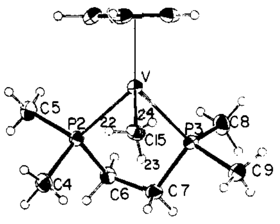


Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)VCH_3(Me_2PCH_2CH_2PMe_2)$. Hydrogens on methyl group bound to vanadium are indicated by small numbers only. Selected structural parameters: V–P(2) = 2.4626 (12) Å, V–P(3) = 2.4709 (12) Å, V–C(15) = 2.219 (4) Å; ∠P(2)–V–P(3) = 81.11 (4)°, ∠P(2)–V–C(15) = 92.67 (12)°, ∠P(3)–V–C(15) = 90.83 (12)°.

This agrees with the measured solution magnetic moment,[16] 1.6 μ_B at 25 °C, while the "high-spin" compound CpVMe(dmpe) has the expected moment of 3.6 μ_B. this "orbital counting" formalism also correctly explains the one unpaired electron observed for $CoH(\eta^2\text{-}BH_4)(PCy_3)_2$[17] and predicts diamagnetism for $Cp_2V(\eta^2\text{-}BH_4)$ (magnetic susceptibility not reported).[18]

Preparation of two cyclopentadienylvanadium(II) hydrocarbyls proceeds as in Scheme I. Each compound[19] 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 $CpVMe_2(PMe_3)_2$ (2795 cm^{-1}), Cp_2TiMe_2,[20] BMe_3,[21] Al_2Me_6,[22] or any of the high-valent metal/methyl complexes synthesized by the Wilkinson group.[23] With little prospect of settling this problem by ^{13}C or ^1H NMR studies of paramagnetic CpVMe(dmpe), we have determined its crystal structure[24] (Figure 1). The molecule is a monomeric three-legged piano stool, and the V–CH_3 unit shows no evidence of an agostic[25] hydrogen; the V–C–H angles are 105 (4)°, 122 (3)°, and 105 (5)°, with internal H–C–H angles being 105 (5)°, 117 (6)°, and 104 (6)°. 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) Å) is difficult. This distance is considerably longer than V–C found in V(III) complexes such as $Cp_2V(C{\equiv}C\text{-}t\text{-}Bu)$, 2.075 (5) Å,[26] or $V(C_6Me_3H_2)_3\cdot THF$, 2.116 (7)/2.099 (6)/2.113 (7) Å[27] but similar to those in the vanadocene adduct $Cp_2V(EtO_2CCH{=}CHCO_2Et)$, 2.186/2.213 (12) Å.[28] Also, com-

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[9] For red $CpVMe_2(PMe_3)_2$, crystallized from pentane (C and H elemental analysis): ^1H NMR (360 MHz, C_6D_6, 20 °C, shifts relative to Me_4Si (δ 0), downfield shifts positive) PMe at −3.9 (940) ppm. The compound is paramagnetic with μ_{eff} = 2.74 μ_B (solid sample, 80–300 K, Faraday method). For brown-red $CpVPh_2(PMe_3)_2$, crystallized from Et_2O (C, H, and V elemental analysis): ^1H NMR (360 MHz, C_6D_6, 20 °C) PMe at −10.8 (1200) ppm. Full-width at half maximum, in Hz, is given in parentheses after the chemical shift.

[10] For dark brown $CpVMeCl(PMe_3)_2$, crystallized from Et_2O: ν_{VC-H} 2805 cm^{-1}; ^1H NMR (360 MHz, C_6D_6, 21 °C) PMe at −9.5 (1620).

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[14] For comparison, the 360-MHz ^1H NMR of CpVCl(dmpe) at 25 °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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[19] For black CpVMe(dmpe), crystallized from Et_2O/pentane (C, H, V elemental analysis): ^1H NMR (200 MHz, C_6D_6) Cp at +243 (4000) ppm, PMe at +19 (440) and −14 (400) ppm, and CH_2 at +34 and +31.8 ppm. For black CpVPh(dmpe): ^1H NMR (360 MHz, C_6D_6, 21 °C) PMe at −11.25 (630) and +9.1 (570) ppm and CH_2 at +33 (570) with a shoulder at +35 ppm.

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[24] Crystals grown from Et_2O/pentane assume space group $P2_12_12_1$ with (−158 °C) a = 12.526 (3) Å, b = 9.285 (2) Å, c = 12.772 (3) Å, and Z = 4. $R(F)$ = 3.2% for 1797 reflections. All hydrogens were refined isotropically. A complete tabulation of crystallographic parameters and bond lengths and angles is available as supplementary material.

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parison to the Ti–C_2H_5 distance involving the inherently larger Ti(O) in (η^7-C_7H_7)Ti(C_2H_5)(dmpe), 2.211 (5) Å,[29] permits the conclusion that CpVMe(dmpe) contains a somewhat long V–CH_3 bond.

The distinctly low V–Me C–H stretching frequency in CpVMe(dmpe) thus finds no explanation in the X-ray study. We suggest that one of the half-filled orbitals is not only metal localized but also V–C and C–H antibonding. This would account for the IR anomaly, the lack of observation of the V–CH_3 proton resonance, and also the long V–C distance.

Acknowledgment. This work was supported by the U.S. National Science Foundation (Grant CHE-8305281) and by NATO (NATO Research Grant No. 070-82).

Supplementary Material Available: Tables of atomic positional parameters and bond lengths and angles for (C_5H_5)$VCH_3(Me_2PCH_2CH_2PMe_2)$, a listing of F_o and F_c for CpVMe(dmpe), and tables of elemental analyses and magnetic susceptibility data (18 pages). Ordering information is given on any current masthead page.

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

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Summary: (1,4-Diaza-1,3-diene)tricarbonyliron complexes react with electron-deficient alkynes under an atmosphere of CO to give a thermally labile, bicyclic intermediate which rearranges to a (1,5-dihydropyrrol-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.[3,4] The reaction of (dad)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-dihydropyrrol-2-ones (e.g., 3, see Scheme I) suggests that this is not the case.[1] This is supported by the observation of a thermally labile mononuclear intermediate 2a. In view of the importance of this reaction,[5] we decided to investigate the structure of 2a. The ^{13}C 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,[6] a compound with very similar spectroscopic properties to 2a was isolated.[7]

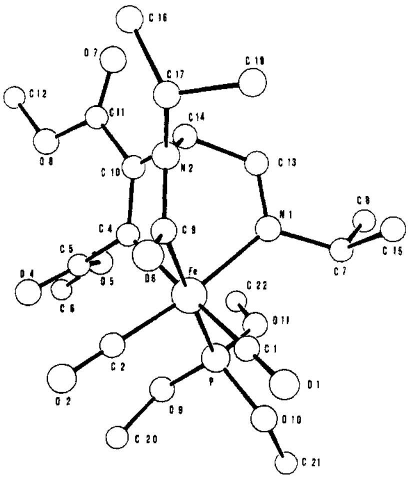
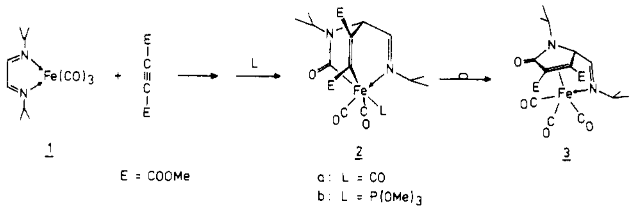


Figure 1. The molecular structure of 2b. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe–C(4) = 2.023 (3), Fe–C(9) = 2.023 (3), Fe–N(1) = 2.030 (2), Fe–C(1) = 1.808 (3), Fe–C(2) = 1.767 (3), Fe–P = 2.260 (1), C(4)–C(10) = 1.337 (4), C(9)–N(2) = 1.362 (4), 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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[6] Preparation of 2b: A solution of 0.67 g (2.4 mmol) of (glyoxalbis(isopropylimine))tricarbonyliron 1[12] in ca. 20 mL of tetrahydrofuran (THF) was cooled to −15 °C. Then 0.283 mL (298 mg, 2.4 mmol) of trimethyl phosphite (z. Synth.; E. Merck, Darmstadt) was added, followed slowly from a dropping funnel by a solution of 341 mg (2.4 mmol) of dimethyl acetylenedicarboxylate in 30 mL of THF, keeping the reaction temperature below −5 °C. After removal of the solvent in vacuo, the vesicular residue was redissolved in 25 mL of methanol at 0 °C. After the mixture was slowly cooled to −78 °C, 0.65 g of a light yellow crystalline powder was precipitated. It was dried in vacuo. The concentrated mother liquor yielded an additional 0.11 g: total yield 0.76 g (58%).

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