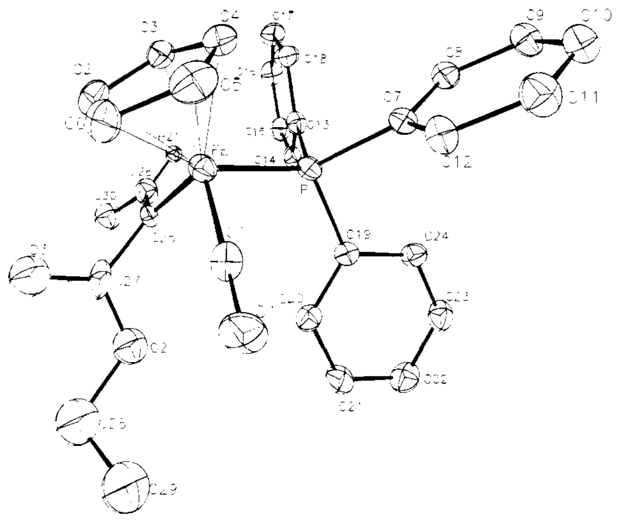
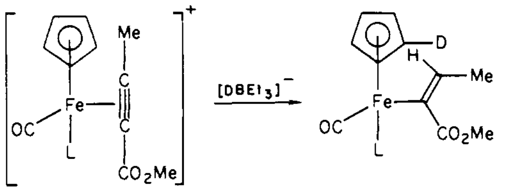


**Figure 1.** ORTEP plot of the molecular structure of $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)(\eta^1\text{-}(E)\text{-}C(CO_2Et){=}C(H)Me)$.

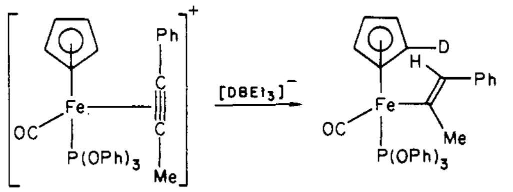
normal and quite similar to those for **2**. Most notably, the Fe–C(alkenyl) distance of 2.02 (1) Å is that expected for a single bond and is similar to the 2.030 (2) Å distance found in **2**.

Insight into how hydride adds cis is demonstrated by reactions 2 and 3. A combination of $^1H$, $^{13}C$ and $^2H$ NMR spectroscopy



(2)

L = PPh$_3$, P(OPh)$_3$

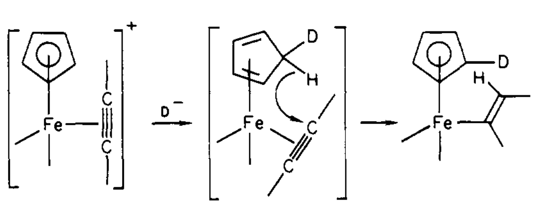


(3)

has been used to show that the added deuteride is in the Cp ring for each case. First, careful integration of the $^1H$ spectra shows a 3:4 ratio for the Me group(s) resonance vs. the Cp ring resonance. Also, the vinyl methyl group resonance in the product of reaction 2 is a normal doublet ($J = 7$ Hz) showing that H, not D, is geminal to it. Second, $^2H$ NMR spectra show a single resonance at the location expected for the Cp resonance from the $^1H$ NMR spectra. Again, integration vs. the natural abundance solvent resonance shows approximately one deuterium per ring. Finally, $^{13}C$ NMR spectra show that there is one deuterium in *each* Cp ring for all three cases. Although, we have been unable to observe the C–D carbon atom resonance in the proton decoupled spectra,[8] the remaining C–H ring carbon atoms appear as two equal-intensity resonances separated by ca. 0.1 ppm. This is what would be expected for a $\beta$-deuterium isotope shift in a $C_5H_4D$ ring.[9]

Scheme I shows a reasonable course for these reactions. The first step, exo nucleophilic addition to an $\eta^5\text{-}C_5H_5$ ring, is a well-documented reaction.[10] The second step, transfer of an endo $\eta^4\text{-}C_5H_6$ hydrogen atom to an auxiliary ligand appears to be unique. Metal orbitals could potentially be involved in the transfer

Scheme I



(or even a formyl type intermediate), but generation of a discrete $(\eta^5\text{-}C_5H_5)Fe(L)(\eta^2\text{-alkyne})H$ intermediate (a ligand, either CO or L, needs to dissociate in order to have an 18-electron species) seems unlikely. We note that cis addition of hydride to the 16-electron complex $[(\eta^5\text{-}C_5H_5)Mo[P(OMe)_3](\eta^2\text{-}HC{\equiv}C\text{-}t\text{-}Bu)]^+$ has been reported.[11] In contrast to our results presented above, a deuterium label (from $[BD_4]^-$) was shown to be incorporated exclusively at the $\beta$-alkenyl carbon atom.

**Acknowledgment** is made to the National Science Foundation for its support of this research through Grant CHE-8019513 (D.L.R.) and Grant CHE-8205871 (J.L.A.).

**Registry No. 1**, 86563-30-6; **2**, 80485-08-1; $CpFeCO(P(OPh)_3)(\eta^1\text{-}(E)\text{-}C(CO_2CH_3){=}C(H)CH_3)$, 86563-31-7; $(CpFeCO(P(OPh)_3(\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Ph)$, 86563-32-8; $[(\eta^5\text{-}C_5H_5)FeCO(PPh_3)B]^+$ (B = ethyl 2-butynoate), 80501-95-7; $[(\eta^5\text{-}C_5H_5)FeCO(PPh_3)B]^3$ (B = methyl 2-butynoate), 86563-34-0; $[(\eta^5\text{-}C_5H_5)FeCO(P(OPh)_3)B]^+$ (B = methyl 2-butynoate), 86563-35-1; $[(\eta^5\text{-}C_5H_5)FeCO(P(OPh)_3)B]^+$ (B = 1-phenyl-1-propyne), 83096-11-1; $[HB(sec\text{-}Bu)_3]^-$, 86563-33-9; $[DBEt_3]^-$, 86563-36-2.

**Supplementary Material Available:** Characterization of new $\eta^1$-complexes, additional structural information, tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[8] A C–D carbon atom resonance would be split into a triplet ($^2H$ has $s = 1$), line broadened due to the $^2H$ quadrupole and significantly lose intensity because of the loss of NOE.[9] They are generally not observed.

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# Contribution of Intrinsic Volume Change of the Reactants to the Pressure Effect on Outer-Sphere and Intramolecular Electron-Transfer Reactions Involving Cobalt(III) to Cobalt(II) Reduction

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Activation volume has been used extensively for elucidating the mechanism of ligand substitution and isomerization reactions of metal complexes in solution.[1-5] On the other hand, much less study has been carried out on the electron-transfer reactions.[1,6-8]

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Table I. Activation Volumes for Some Electron-Transfer Reactions in Aqueous Solution

| reaction | oxidant | reductant | $\Delta V_T^{\ddagger}$, cm$^3$ mol$^{-1}$ | $\Delta V_{OS}$, cm$^3$ mol$^{-1}$ | $\Delta V_e^{\ddagger}$, cm$^3$ mol$^{-1}$ | temp, °C | $I$, M | ref |
|---|---|---|---|---|---|---|---|---|
| 4 | $[Co^{III}(en)_3]^{3+}$ | $[Co^{II}(en)_3]^{2+}$ | −19.8 ± 1.5 | | | 65 | 0.5 | 1 |
| 5 | $[Fe^{III}(H_2O)_6]^{3+}$ | $[Fe^{II}(H_2O)_6]^{2+}$ | −12.2 ± 1.5 | | | 2 | | 1 |
| 6 | $Tl^{3+}$ | $Tl^+$ | −13.2 ± 1.0 | | | 30 | 1.1 | 1 |
| 7 | $[Ir^{IV}Cl_6]^{2-}$ | $[Mo^V{}_2O_4(OH)(hedta)]^{2-\,f}$ | −12.3 ± 1.4 | | | 25.0 | 0.1 | 14 |
| 2$^c$ | $[Co^{III}(edta)]^-$ | $[Fe^{II}(CN)_6]^{4-}$ | +13.4 ± 0.5 | | | 25.0 | 1.0 | *b* |
| 8 | $[Co^{III}{}_2(\mu\text{-}O_2{}^{(-)},NH_2)(en)_4]^{4+}$ | $[Mo^V{}_2O_4(OH)(hedta)]^{2-\,f}$ | +19.6 ± 4.5 | +7.8 ± 3.7 | +11.8 ± 0.8 | 25.0 | 0.1 | 14 |
| 9 | $[Co^{III}{}_2(\mu\text{-}O_2{}^{(-)})(NH_3)_{10}]^{5+}$ | $[Mo^V{}_2O_4(edta)]^{2-}$ | +35.8 ± 4.9 | +23.7 ± 3.0 | +12.1 ± 1.9 | 41.1 | 0.1 | 6 |
| 1$^d$ | $[Co^{III}(NH_3)_5py]^{3+}$ | $[Fe^{II}(CN)_6]^{4-}$ | +47.3 ± 4.3 | +23.4 ± 3.3 | +23.9 ± 1.0 | 25.0 | 1.0 | *b* |
| 3$^e$ | $[Co^{III}{}_2(\mu\text{-}O_2{}^{(2-)})(en)_4(NH_3)_2]^{4+\,a}$ | | +23.8 ± 0.3 | | | 20.0 | 0.1 | *b* |
| | $[Co^{III}{}_2(\mu\text{-}O_2{}^{(2-)})(dien)_2(en)_2]^{4+\,a}$ | | +18.8 ± 0.3 | | | 45.0 | 0.1 | *b* |
| | $[Co^{III}{}_2(\mu\text{-}O_2{}^{(2-)})(dien)_2(R\text{-}pn)_2]^{4+\,a}$ | | +21.3 ± 0.6 | | | 45.0 | 0.1 | *b* |

[a] Unimolecular redox decompositon to Co$^{II}$ and $O_2$. [b] This work. [c] $[Fe^{II}] = (2.01–12.4) \times 10^{-3}$ M; $[Co^{III}] = (7.01–15.1) \times 10^{-4}$ M; [ascorbic acid] = $(4.5–9.0) \times 10^{-3}$ M; pH 4.4 (acetate buffer); $\Delta\beta_T^{\ddagger}$ (compressibility of activation) = $(-2.5 \pm 1.4) \times 10^{-2}$ cm$^3$ mol$^{-1}$ MPa$^{-1}$. [d] $[Fe^{II}] = (2.43–8.52) \times 10^{-3}$ M; $[Co^{III}] = (1.09–2.26) \times 10^{-4}$ M; [diethylenetriaminepentaacetic acid] = $2.48 \times 10^{-4}$ M; pH 5.6–6.5 (acetate buffer); $\Delta\beta_{OS} = (+8.8 \pm 3.3) \times 10^{-2}$ cm$^3$ mol$^{-1}$ MPa$^{-1}$; $\Delta\beta_e^{\ddagger} = \sim 0$ cm$^3$ mol$^{-1}$ MPa$^{-1}$. [e] $[Co^{III}]$ = ca. $1.4 \times 10^{-4}$ M; [HCl] = 0.01 M. [f] $H_3$hedta = *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid.

In the case of outer-sphere electron-transfer reactions, activation volume has been believed to be governed mainly by rearrangement in the solvation sphere, since no bond formation or cleavage is involved. We recently reported the activation volume for the electron transfer within an ion pair ($\Delta V_e^{\ddagger}$) (reaction 9 in Table I.[6] The $\Delta V_e^{\ddagger}$ value (+12 cm$^3$ mol$^{-1}$) may manifest the volume change of the reacting species on going to the transition state accompanied by the change in bond lengths and/or angles, but did not allow further discussion because of complicated structure of the reactants.

We have recently measured the activation volume (obtained in the range 1–294 MPa) of two outer-sphere electron-transfer reactions (1[10] and 2[11]) and of three internal redox reactions 3[12,13]

$$[Co^{III}(NH_3)_2py]^{3+} + [Fe^{II}(CN)_6]^{4-} \rightarrow [Co^{II}(NH_3)_5py]^{2+} + [Fe^{III}(CN)_6]^{3-} \quad (1)$$

$$[Co^{III}(edta)]^- + [Fe^{II}(CN)_6]^{4-} \rightarrow [Co^{II}(edta)]^{2-} + [Fe^{III}(CN)_6]^{3-} \quad (2)$$

$$[(N)_5Co^{III}(O_2{}^{(2-)})Co^{III}(N)_5]^{4+} \rightarrow 2[Co^{II}(N)_5(H_2O)]^{2+} + O_2{}^{(2-)} \quad (3)$$

$$(N)_5 = (en)_2NH_3,\ (en)\ (dien),\ (R\text{-}pn)\ (dien)^9$$

(Table I)[9] and wish to show that the contribution of the volume change of the reactants themselves to the $\Delta V^{\ddagger}$ is indeed significant. All these reactions involve the change of oxidation state of cobalt from III to II and are expected to involve relatively large changes in the metal–ligand bond distances. Reactions were monitored at appropriate wavelengths by the usual method with a Hitachi 330 spectrophotometer equipped with a high-pressure cell compartment. First-order plots with respect to the Co$^{III}$ complex (reactions 1 and 2) and the binuclear species gave straight lines at least up to 2 half-lives and mostly beyond 3 half-lives, at each pressure employed.

Outer-sphere redox reactions proceed through rapid preequilibrium to form encounter complexes and the electron-transfer takes place within them. Reaction 1 enables individual evaluation of the encounter complex formation constant ($K_{OS}$) and of the net electron-transfer rate constant ($k_e$) within the encounter complex,[10] since $K_{OS}[Fe^{II}]$ is comparable with unity in the rate law 4. Hence the volume change due to encounter complex

$$k_{obsd} = K_{OS}k_e[Fe^{II}]/(1 + K_{OS}[Fe^{II}]) \quad (4)$$

formation ($\Delta V_{OS}$) and the activation volume accompanied by the electron-transfer ($\Delta V_e^{\ddagger}$) are individually obtained. In reaction 2, $k_{obsd}$ equals $K_{OS}k_e[Fe^{II}]$ since $K_{OS}[Fe^{II}]$ is negligible to unity, and the observed $\Delta V_T^{\ddagger}$ is the sum of $\Delta V_{OS}$ and $\Delta V_e^{\ddagger}$.

Negative $\Delta V_T^{\ddagger}$ values for reactions 4–7 in the table are best explained by invoking a major contribution from the negative $\Delta V_{OS}$, which is due to the increase in the electrostriction by charge concentration on encounter complex formation. The positive $\Delta V_T^{\ddagger}$ value for reaction 2 is understood only by considering that the $\Delta V_e^{\ddagger}$ is highly positive and overwhelms the negative $\Delta V_{OS}$.[15] The $\Delta V_e^{\ddagger}$ value of reaction 1 is considerably more positive than those of reactions 8 and 9. The solvent rearrangement on going to the transition state within the encounter complex would not give a large volume change because the charge redistribution should be much smaller than that on the encounter complex formation. Thus the high positive $\Delta V_e^{\ddagger}$ values for reactions 1 and 2 should be due to the volume change of the reactants, particularly of the cobalt complexes. The reductant, $[Fe^{II}(CN)_6]^{4-}$, requires only a small change in volume on oxidation to $[Fe^{III}(CN)_6]^{3-}$.[16]

The rate-determining step for reaction 3 is claimed to be the electron-transfer from the bridging $O_2{}^{2-}$ to Co$^{III}$. Outer-sphere association need not be considered. Since the rate and activation volume are insensitive to pH (2–10), ionic strength $I$ (0.01–1.0 M) (M = mol dm$^{-3}$), and the kind of electrolyte added for adjusting the ionic strength, the state of second sphere does not seem important.[17] The $\Delta V^{\ddagger}$'s should be governed by the volume change of the complex ion itself, mainly by the increase in volume of one of the cobalt ions on intramolecular electron transfer.[18]

The change in volume of the cobalt species was evaluated by use of the Co–N distances, 1.96 and 2.16 Å, for $[Co^{III}(NH_3)_6]^{3+}$[19] and $[Co^{II}(NH_3)_6]^{2+}$,[20] respectively. These values are reckoned,

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(15) The activation volume, $\Delta V_T^{\ddagger}$, of reaction 2 at $I$ = 0.1 M is almost identical with that at $I$ = 1.0 M, indicating that the $\Delta V_T^{\ddagger}$ is intrinsic and does not reflect the change of "salt effect" with pressure.

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(18) If the rate-determining step for reaction 3 were the bond cleavage, $k_2$, rather than $k_1$ of eq 5, the activation volume should be the sum of volume

$$Co^{III}\text{–}O_2{}^{(2-)}\text{–}Co^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co^{II}\text{–}O_2{}^{(-)}\text{–}Co^{III} \xrightarrow{k_2} Co^{II} + Co^{III}\text{–}O_2{}^{(-)} \quad (5)$$

change on rapid preequilibrium ($K_1 = k_1/k_{-1}$) and the activation volume on the bond cleavage. Available $\Delta V^{\ddagger}$ values for some ligand substitution reactions of cobalt(II) complexes are in the range +5–+8 cm$^3$ mol$^{-1}$.[1] Thus the volume change accompanied by the electron transfer should be ca. +12 cm$^3$ mol$^{-1}$, which is still considerably positive.

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as first approximation, to represent the difference in coordination bond lengths between $Co^{III}$ and $Co^{II}$ complexes. The change in volume of the $Co^{III}$ complexes within the van der Waals region on going to $Co^{II}$ species is estimated to be +19.7 and +29.8 $cm^3$ $mol^{-1}$, for reactions 1 and 2, respectively. These values are regarded as maximum, since the bond distances at the transition state should be somewhere between those of $Co^{III}$ and $Co^{II}$. The observed values are close to the above values, suggesting that the transition state would be closer to $Co^{II}$ than to $Co^{III}$ with respect to the bond distances.

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**Registry No.** $[Ir^{IV}Cl_6]^{2-}$, 16918-91-5; $[Co^{III}(edta)]^-$, 15136-66-0; $[Fe^{II}(CN)_6]^{4-}$, 13408-63-4; $[Co_2{}^{III}(\mu\text{-}O_2{}^{(-)})(\mu\text{-}NH_2)(en)_4]^{4+}$, 12387-59-6; $[Co^{III}(NH_3)_5Py]^{3+}$, 31011-67-3; $[Co_2{}^{III}(\mu\text{-}O_2{}^{(2-)})(en)_4(NH_3)_2]^{4+}$, 47178-28-9; $[Co_2{}^{III}(\mu\text{-}O_2{}^{(2-)})(dien)_2(en)_2]^{4+}$, 22386-10-3; $[Co_2{}^{III}(\mu\text{-}O_2{}^{(2-)})(dien)_2(R\text{-}pn)_2]^{4+}$, 86561-36-6.

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# Carbon-13 NMR Study on Liquid Crystal Solutions. Chemical Shift Tensors in Benzonitrile

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Carbon-13 chemical shifts have been widely used in the study of molecular structure, motion, and properties. The components of the chemical shift tensor are a more sensitive probe into molecular structure than the trace alone.[1] The most straightforward way of determining the chemical shift tensor is to perform a line-shape analysis of the proton-decoupled carbon-13 NMR spectrum of a polycrystalline solid. When there are overlapping signals, they can be resolved by using magic angle spinning, and the anisotropic patterns of individual signals can be reconstructed from the spinning sidebands[2-4] or by using pulses synchronized with the rotation of the spinner.[5-7] Chemical shift tensors for individual carbons can also be obtained by analyzing the spectra obtained from single crystals oriented at various angles.[8-10]

Another approach to measuring the chemical shift tensor is to study the NMR spectra of molecules in liquid crystal solutions.[11,12] In the past, this has been limited to the investigation of very simple molecules, and compounds with carbon-13 enrichment were often used for carbon-13 NMR study. This is mainly due to problems in solvent interference and insufficient decoupling power in spectrometers designed for studying liquid samples. We have recently shown[13] that the first problem can be solved by using a simple spin-echo sequence of 90°–$\tau$–180°–2$\tau$–180°–$\tau$– acquisition, and the second problem can be solved or at least reduced by using phase-alternated broad-band decoupling.[14-21] Here we report the determination of carbon-13 chemical shift tensors of all carbon atoms in benzonitrile by this approach.

The proton-decoupled $^{13}C$ spectra of benzonitrile in deuteriochloroform and in three liquid crystal solutions are shown in Figure 1. The assignment of the peaks in the isotropic spectrum is straightforward.[22,23] The assignment of the peaks in the spectra

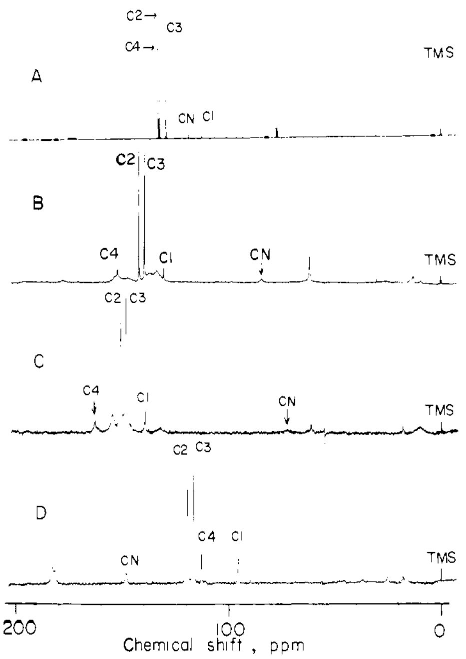

**Figure 1.** Carbon-13 NMR spectra at 75.43 MHz and 298 K of benzonitrile (ca. 7%) and tetramethylsilane (ca. 1%) in (A) $CDCl_3$, (B) EBBA, (C) NP 1565 TNC, and (D) ZLI 1167. The unmarked peaks in the spectra of the liquid crystal solutions are residual solvent peaks and were identified by comparing these spectra with those with other solutes. The spectra were obtained with a Varian XL-300 spectrometer. A 90°–$\tau$–180°–2$\tau$–180°–$\tau$–acquisition pulse sequence with $\tau$ = 0.3 ms and a phase alternated broad-band decoupling scheme (MLEV-64, ref 15) were used in obtaining spectra B–D, with 1000 scans in 33 min for each spectrum.

Table I. Ordering Factors of Benzonitrile (ca. 7% with ca. 1% $Me_4Si$) in Three Liquid Crystal Solutions at 298 K[a]

| solvent | $S_{zz}$ | $S_{xx} - S_{yy}$ | $S_{zz}/(S_{xx} - S_{yy})$ |
|---|---|---|---|
| EBBA | 0.1696 ± 0.0002 | 0.0592 ± 0.0005 | 2.865 |
| NP 1565 TNC | 0.2313 ± 0.0001 | 0.1614 ± 0.0004 | 1.433 |
| ZLI 1167 | −0.1494 ± 0.0003 | −0.1078 ± 0.0007 | 1.386 |

[a] The $z$ axis is the CN-bond axis, and the $y$ axis is perpendicular to the ring.

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