that neighboring (d_{xz} or d_{xy}) participation as in IV cannot be significant.[23]

The significance of these results to other ferrocene reactions and the possible structure of α-ferrocenylcarbonium ions will be discussed in the full report.

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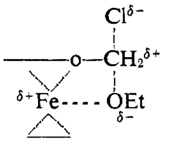
[23] The similarity in the ratios of the S_N1 and S_N2 (7.6 *vs.* 8.6) reactions seems to indicate that the ethoxide must attack preferentially from the hindered side[24] or else suffer the *endo*/*exo* deceleration of 0.5 log (2500) = 1.7, or about 50-fold. That our S_N2 reaction is "too fast" does not detract from the argument unless these results are obtained with, *e.g.*, chloride exchange. What this result possibly suggests is a small contribution from "merged" S_N2-E2 mechanism.[25]



β-Metalloalkyl derivatives seem to us excellent substrates for such mechanisms because more charge will be developed on metals than on hydrogen.

[24] We previously suggested the possibility of steric hindrance contributing to the stereospecificity in solvolyses of metallocenylmethyl derivatives. However, the microscopic reverse of our proposed "elimination" must give the same stereospecificity as the elimination itself. Thus, any addition which is the microscopic reverse of E2 elimination will give high (E2-like) stereospecificity. The steric effect probably contributes only 5–10 to the *exo*/*endo* product ratio.

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Valency Tautomerism in Metal–Olefin Complexes. Cyclooctatetraenemolybdenum, -chromium, and -iron Tricarbonyls[1]

Sir:

Several π-bonded cyclic olefin complexes of transition metals are known in which the free ligand has π electrons to offer in excess of the electronic requirements of the metal. In some of these complexes, part or all of the "excess" π electrons of the free olefin are diverted into C–C σ bonding, giving rise to a bicyclic ligand as in bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl[2a,b] or bicyclo[5.1.0]octa-2,4-dieniumiron tricarbonyl [from protonation of $C_8H_8Fe(CO)_3$].[2c,3a] A second possibility is that the metal takes up a coordination position relative to two or three of the available olefinic groups, leaving the others geometrically isolated as observed with $C_8H_8Fe(CO)_3$ in the crystal.[4a] A still conceivable third possibility is that the metal is simultaneously and symmetrically attached to all the olefinic carbon atoms with only a fraction of the olefinic π electrons involved in bonding.[5]

Several compounds have been reported which display single sharp proton resonance for the olefinic group containing "excess" π electrons, most notably $C_8H_8Fe(CO)_3$ (I),[2a] $C_7H_7Mo(CO)_2(C_5H_5)$ (II),[6a] $C_7H_7Co(CO)_3$ (III),[6a] $C_7H_7{}^+Fe(CO)_3$ (IV),[7] $C_7H_7{}^+Fe_2(CO)_6$ (V),[7] $C_8H_8Fe_2(CO)_6$ (VI),[7c] and, most recently, $C_8H_8Mo(CO)_3$ (VII).[3a] As we have already indicated,[3a] VII is the first complex in this group whose proton nmr was observed to change from a single line at high temperatures to a multiplet pattern at low temperature. In this complex, therefore, the metal is involved in bonding with only six π electrons on six carbon atoms (6π6C) at any one time, and over a time average all eight carbon atoms of the ring become equivalent owing to valency tautomerism. The infrared spectrum of $C_8H_8Mo(CO)_3$, with three carbonyl stretching absorptions and a band attributable to an uncoordinated C=C, is in agreement with this interpretation. Metal–carbon valency tautomerism was suspected for the other compounds listed above which display single sharp resonances for the olefin groups containing "excess" π electrons; however, this can be proved only by the demonstration of temperature variation of the nmr or with other evidence obtained from a faster "camera" such as infrared spectroscopy.

Since our earlier report[3a] on VII, the temperature dependence of the nuclear magnetic resonance of the C_7H_7 protons in II has also been demonstrated.[6b] We now report on the temperature dependence of the nmr spectrum of VII and that of the analogous complex $C_8H_8Cr(CO)_3$ (VIII) which we have synthesized for the first time. Also, a reinvestigation of $C_8H_8Fe(CO)_3$ (I) has confirmed previous unpublished reports that the nmr spectrum remains essentially a single sharp line down to very low temperatures (*ca.* −100°). However, by using still lower temperatures, −140 to −150°, we have now been able to observe the nmr spectrum of the "frozen" complex.

The new compound $C_8H_8Cr(CO)_3$ (VIII) is obtained as red-brown crystals in 20% yield by stirring cyclooctatetraene with $(NH_3)_3Cr(CO)_3$[8] in refluxing *n*-hexane for 65 hr.

Anal. Calcd for $C_{11}H_8CrO_3$: C, 55.01; H, 3.36; Cr, 21.65. Found: C, 54.74; H, 3.62; Cr, 21.74, 21.89.

Three characteristic strong absorptions were noted for the metal carbonyls in the infrared for VIII (1996, 1940, and 1912 cm^{-1}; cyclohexane solution, LiF prism), analogous to but not superimposable on those (2006, 1945, and 1916 cm^{-1}) found for VII. A recognizable absorption at 1675 cm^{-1} for VII and 1668 cm^{-1} for VIII denotes the presence of an uncoordinated double bond. This excludes with certainty a complex containing the bicyclic[4.2.0] valency tautomer of C_8H_8.

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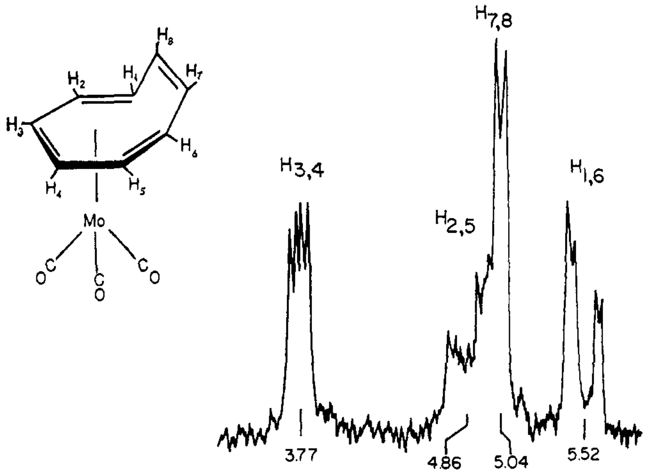

Figure 1. Nmr spectrum of $C_8H_8Mo(CO)_3$ (VII) at −40° in $CDCl_3$; tetramethylsilane internal reference; chemical shifts given in τ values.

The nmr spectrum of VIII was temperature dependent, like that of VII. Both compounds show single resonances at +80° with broadening and finally full development of a multiplet pattern at lower temperatures, shown in Figure 1 for VII. From these spectral changes, rates of rearrangement and free energies of activation may be estimated: VII, $k \approx 25$ sec^{-1} at 10°, $\Delta F^* = 14.8$ kcal/mole; VIII, $k \approx 25$ sec^{-1} at 20°, $\Delta F^* = 15.4$ kcal/mole.

The weighted average (τ 4.80 for VII, 4.76 for VIII) of the resonances at lower temperature is, within experimental error, at the same position as the single line (τ 4.82 for VII,[9] 4.78 for VIII) observed at higher temperatures. This indicates that the frozen forms are the same as the rapidly equilibrating forms at higher temperatures.

The "frozen" nmr spectra of VII and VIII at −40° are very similar and can be interpreted readily in terms of the model shown in Figure 1. Chemical shift values for VII are shown in Figure 1, and the corresponding values for VIII are τ 3.74, 4.82, 5.08, and 5.38. Thus VII and VIII must have very similar structures. The assignments for the resonances shown in Figure 1 for protons $H_{3,4}$ and $H_{2,5}$ are based on the strong resemblance with similarly assigned resonances in the nmr spectrum of 1,3,5-cyclooctatrienemolybdenum tricarbonyl.[6c] The other assignments follow quite reasonably. The protons of the uncoordinated double bond $H_{7,8}$ (τ 5.04) are shifted by approximately 0.7 ppm to higher field from their position in free cyclooctatetraene (τ 4.30).[10]

The single line in the nmr spectrum of $C_8H_8Fe(CO)_3$ broadened rapidly below −100° and separated into two bands below −118°. The spectrum at −130° consisted of two bands (width at half-height, *ca.* 20 cps) separated by about 80 cps. This behavior was observed in a number of solvents (Me_2O, CH_3CHO–$CDCl_3$, and $CHCl_2F$–$CBrF_3$). In the Freon mixture, where a temperature of −150° could be reached, the two bands were found to be unsymmetrical and independent of temperature in the range of −140 to −150°; this was particularly apparent in the upfield band (Figure 2), which was well clear of the solvent peaks. From these changes we calculate $k_{(\text{rearrangement})} \approx 200$ sec^{-1} at −120° and $\Delta F^* = 7.2$ kcal/mole.

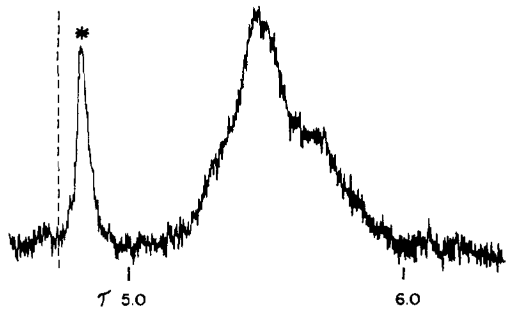

Figure 2. The upfield band of the nmr spectrum of $C_8H_8Fe(CO)_3$ in $CHCl_2F$–$CBrF_3$ (5:1) at −145°. The dashed line indicates the position of the single band obtained above the coalescence temperature. The sharp peak indicated by an asterisk is a ^{13}C satellite of $CHCl_2F$.

The nmr spectra as well as the other available evidence strongly favor the 1,3-diene-bonded model for $C_8H_8Fe(CO)_3$ like that found in the crystal.[4a] This model would require an $A_2B_2M_2N_2$ pattern for the nmr which is consistent with the unsymmetrical spectrum at low temperatures. The high-field band is presumably due to the four-coordinated 1,3-diene protons. The temperature dependence of the nmr rules out a "planar symmetrical" model,[5] and the appearance of the bands in the frozen nmr spectrum rules out a tub 1,5-bonded model (which requires two sharp lines).[10] Furthermore, in those complexes containing C_8H_8 coordinated in the tub form,[10] namely, $C_8H_8CoC_5H_5$, $C_8H_8RhC_5H_5$, and the most recently reported $C_8H_8Mo(CO)_4$,[3b] none gives evidence for rapid valency tautomerism. The nmr spectra do not fit well with a bicyclic[4.2.0] tautomer; this structure is further ruled out by the absence of any bands in the infrared and Raman spectra[4b] near 1650 cm^{-1} required by an uncoordinated cyclobutene double bond. In any case, the bicyclic form would not be expected to partake in very rapid valency tautomerism. A further argument in favor of the 1,3-diene-bonded model for this complex in solution is the recent infrared and Raman studies[4b] which indicate identical structures in the solution and solid states.

In the metal complexes I, VII, and VIII in which valency tautomerism is now proved, the rearrangements must involve a deformation of the ring system and movement of the metal to coordinate to new and detach from old carbon atoms. In part, these processes are related to ring inversion and bond change in cyclooctatetraene,[11] and thus it is interesting to compare their energetics. The nmr experiments indicate the following order of increasing difficulty for rearrangement: $C_8H_8Fe(CO)_3 \ll C_8H_8 < C_8H_8$-$Mo(CO)_3 < C_8H_8Cr(CO)_3$.

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