would not *a priori* expect ML_2^+ to eliminate a radical fragment. However, a peak corresponding to $ML(L-CF_3)^+$ is observed for both iron and cobalt. Since a metastable peak corresponding to $ML_2^+ \rightarrow ML(L-CF_3)^+$ is seen for hfa complexes of both metals, it appears most reasonable to assign the reduction of the metal to this step, *e.g.*, $M^{III}L_2^+ \rightarrow M^{II}L_2\cdot^+ \rightarrow M^{II}L(L-CF_3)^+$. Thus the CF_3 radical is in effect eliminated from an odd-electron ion. This assignment is strengthened by noting that only even-electron fragments are eliminated during the rest of the reaction sequence (Figure 1).

While the elimination of neutral iron and cobalt difluorides has been observed previously in the mass spectra of fluorinated complexes,[8,9] we believe this is the first time neutral iron fluorides of different stoichiometry have been observed to result from the same parent compound. Further, the elimination of the metal trifluorides, CrF_3 and FeF_3, have not been noted earlier.

CrL_3, FeL_3, and CoL_3 were prepared by published methods[10-12] and were purified by sublimation just prior to use. Mass spectra were recorded on a Hitachi RMU-6E single-focusing mass spectrometer using a 70-V electron beam. Samples were introduced through a heated inlet. Inlet and source temperatures were held at less than 60° to prevent thermal decomposition.

(8) R. D. King, *J. Am. Chem. Soc.*, **89**, 6368 (1967).

(9) R. D. King, *ibid.*, **90**, 1429 (1968).

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(12) M. L. Morris and D. A. Aikens, *Nature*, **207**, 631 (1965).

(13) (a) NASA Predoctoral Fellow. (b) On leave to the National Science Foundation, 1968–1969.

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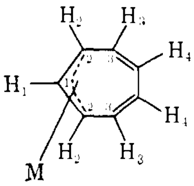
Variable-Temperature Proton Resonance Spectra of *Trihapto*cycloheptatrienylmetal Complexes

Sir:

It is generally assumed that the seven-membered ring in the complexes $\pi-C_5H_5Mo(CO)_2C_7H_7$ (**1**)[1,2] and $C_7H_7-Co(CO)_3$ (**2**)[2] is attached to the metal *via* a π-allylic (three π-electron) bond[3] and that the remaining four π electrons are not formally involved in metal–ring bonding (I). This allows the metals to achieve the favored 18-electron configuration. At room temperature, both complexes show only one resonance due to the C_7H_7 protons and, although the C_7H_7 resonance of **1** broadens on cooling to $-60°$,[4,5] previous studies have failed to reveal multiplet structure. On this basis, it has been suggested that **1** and **2** are fluxional molecules.[6] We now report a variable-temperature nmr study of **1** and **2**, which provides good evidence for the previously assumed formulation and for the fluxional character of the complexes.



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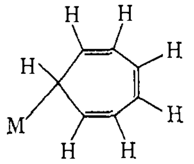

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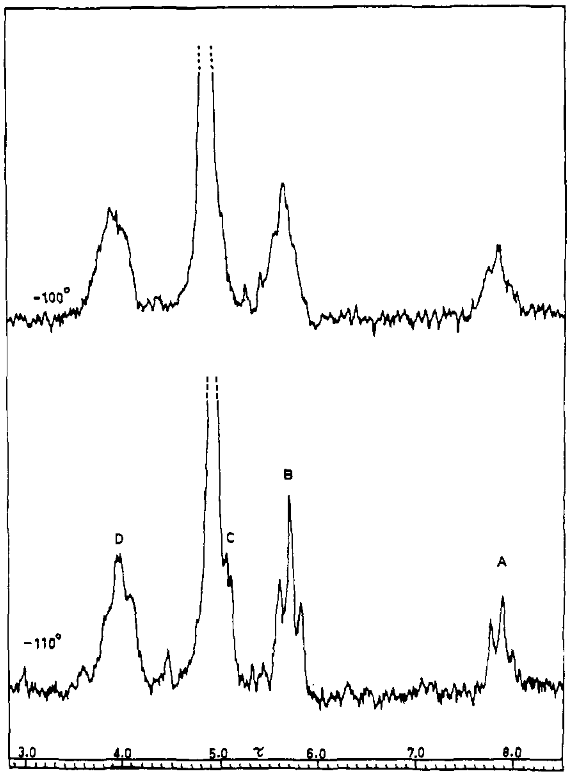

Figure 1. Proton resonance spectra of $h^5-C_5H_5Mo(CO)_2-h^3-C_7H_7$ in 1:2 $CFCl_3-CS_2$ (~10 mg/0.5 ml) at −100 and −110°.

The nmr spectrum of **1** in 1:2 $CFCl_3-CS_2$ at $-100°$ shows a broad peak superimposed on the sharp C_5H_5 resonance, and in the range -100 to $-110°$ the spectrum is as shown in Figure 1; peak positions and multiplicities are in Table I. Attempts to observe spectra below $-110°$ have been frustrated by the onset of crystallization, but the appearance of sharp multiplets in peaks A, B, and C due to spin–spin coupling suggests that we are close to the limiting spectrum.

The nmr spectrum of **2** in CF_2Cl_2 at -130 and $-140°$ is given in Figure 2 and Table I. Although the limiting spectrum has obviously not been reached, the general similarity to the spectrum of **1** is evident.

Assuming the correctness of the π-allylic structure I, the signal at highest field (A) must be assigned to the central π-allylic proton H_1, and peak B must be due to the terminal π-allylic protons H_2. Peaks C and D are almost identical in position and profile to the two low-field absorptions in the limiting spectra of $h^4-C_8H_8Fe(CO)_3$[7] and $h^4-C_8H_8Ru(CO)_3$,[8] and are therefore assigned analogously to the uncoordinated diene protons H_4 and H_3, respectively.[8] Attempts to confirm the assign-

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(2) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

(3) Using the nomenclature suggested by F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968), these complexes may be termed *trihapto*-1,2,3-cycloheptatrienyls.

(4) R. B. King and A. Fronzaglia, *ibid.*, **88**, 709 (1966).

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(6) For a recent review of fluxional organometallic molecules, see F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(7) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Am. Chem. Soc.*, **89**, 6864 (1967).

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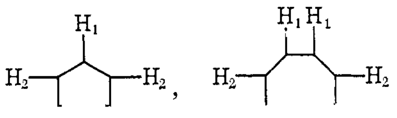
Table I. Proton Resonances in h^3-C_7H_7 and Comparable Compounds[a]

Compound	$\tau(H_1)$	$\tau(H_2)$	$\tau(H_3)$	$\tau(H_4)$	Ref
1	7.90 (t, 1, $J = 6.7$ Hz)	5.73 (t, 2, $J = 6.7$ Hz)	4.0 (t, 2)[b]	5.00 (d)[c]	This work
h^5-$C_5H_5Mo(CO)_2$-h^3-C_3H_5	6.72	7.40	...	...	*d*, 17
h^5-$C_5H_5Mo(CO)_2$-h^3-$CH_2C_6H_5$	...	7.18	...	...	4
2	6.5 (t, 1)[b]	5.05 (t, 2)[b]	~3.5 (br, 2)	~4.2 (br, 2)	This work
h^3-$C_3H_5Co(CO)_3$	5.09	6.34	...	...	*e*
h^4-$C_8H_8Fe(CO)_3$	5.22	5.45	3.55[f]	3.81[f]	7
h^4-$C_4H_6Fe(CO)_3$	4.63	8.27	...	...	*g*

[a] Numbering of protons



and I; br = broad. [b] Ill-resolved. [c] Overlaps singlet due to h^5-C_5H_5 protons, total intensity 7. [d] M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963). [e] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1604 (1961). [f] Reference 7 interchanges the assignment of H_3 and H_4 compared to ref 8; our assignment follows ref 8. [g] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

ments in the case of **1** by double resonance at −110° have not so far been successful.

It is surprising at first sight that the resonance of the central allylic proton H_1 appears 1.5–2.0 ppm to higher field than the resonances of the terminal protons H_2, which is the reverse of the order usually found for π-allyl complexes.[9] The terminal allylic protons H_2 of complex **1** are deshielded by 1.67 ppm compared with those of h^5-$C_5H_5Mo(CO)_2$-h^3-C_3H_5, whereas the central proton H_1 is shifted upfield by ~1.2 ppm (Table I). Likewise, for complex **2**, H_2 is shifted downfield by 1.29 ppm and H_1 upfield by ~1.4 ppm compared with the values for the same protons in h^3-$C_3H_5Co(CO)_3$. A similar effect is evident from comparison of the coordinated olefinic proton resonances of the iron tricarbonyl complexes of cyclooctatetraene and butadiene (Table I), and this must be associated with the presence of the uncomplexed conjugated diene moiety. In the 1,2,7-h^3-benzyl complex h^5-$C_5H_5Mo(CO)_2$-h^3-$CH_2C_6H_5$,[4] in which the coordinated π-allylic group is flanked by an uncomplexed conjugated diene system, the terminal proton H_2 is *not* strongly deshielded compared with the same protons in h^5-$C_5H_5Mo(CO)_2$-h^3-C_3H_5. However, X-ray study of the corresponding 4-methylbenzyl complex[10] has shown that the benzyl group is nearly planar, whereas in h^4-$C_8H_8Fe(CO)_3$ the plane containing the uncoordinated diene makes an angle of 139° with the plane of the coordinated diene;[11] this feature may well be significant in determining the chemical shifts of the coordinated olefinic protons. The nmr spectra of **1** and **2** are therefore consistent with the π-allylic structure I, the seven-membered ring being hinged either at C-3, as previously suggested,[1,2] or at C-2, as in h^4-$C_8H_8Fe(CO)_3$.[11]

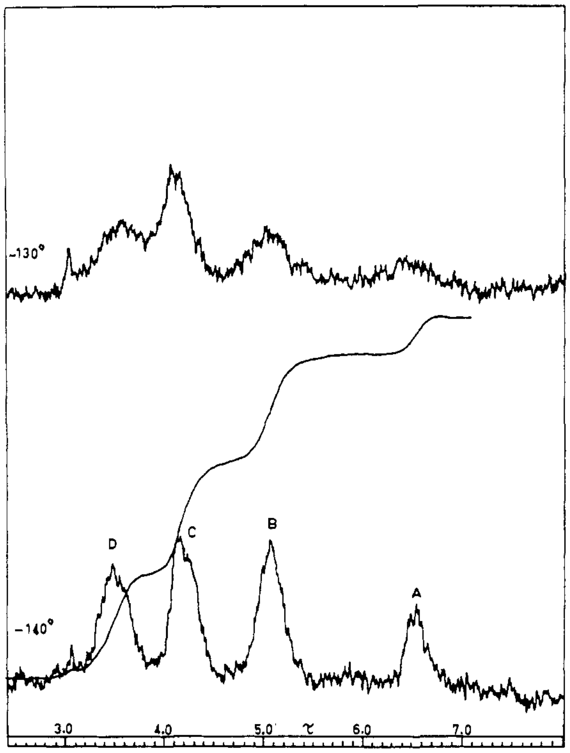


Figure 2. Proton resonance spectra of h^3-$C_7H_7Co(CO)_3$ in CF_2Cl_2 (~10 mg/0.5 ml) at −130 and −140°.

An alternative interpretation of the anomalous chemical shifts observed for **1** and **2** is that the complexes in solution adopt a structure containing a σ-bonded C_7H_7 ring (II),[12] possibly with additional coordination from one of the three double bonds to preserve the 18-electron configuration. Peak A can then be assigned to the proton on the σ-bonded carbon atom, C-1; *cf.* $\tau(H_1)$ in h^5-$C_5H_5Fe(CO)_2$-h^1-C_5H_5 = 6.5.[13] This interpretation receives some support from the similarity of the nmr spectra of **1** and **2** to that of 7-methylcycloheptatriene.[14] However, the example of $C_4H_6Fe(CO)_3$[15] shows the dubious validity of structural

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(9) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 332 (1964).

(10) F. A. Cotton and M. D. La Prade, *J. Am. Chem. Soc.*, **90**, 5418 (1968).

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(12) The possibility that σ-C_7H_7 complexes may show fluxional behavior has been mentioned,[6] and a σ-benzyl complex is a suggested intermediate in the fluxional behavior of h^5-$C_5H_5Mo(CO)_2$-h^3-$CH_2C_6H_5$.[4]

(13) M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

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(15) H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **88**, 2710 (1966).

deductions based solely on upfield chemical shifts of coordinated olefinic protons, and we feel that the similarity to the h^4-$C_8H_8M(CO)_3$ (M = Fe, Ru) complexes provides compelling evidence in favor of the first interpretation. This similarity is further emphasized by the observation that peaks A, B, and D in the nmr spectrum of **2** collapse more rapidly than peak C as the temperature is raised from $-140°$ (Figure 2). Provided the assignments of the two low-field multiplets are correct, this implies that a sequence of 1,2 shifts is responsible for the proton averaging, as found for h^4-$C_8H_8M(CO)_3$ (M = Fe, Ru)[8] and h^5-$C_5H_5Fe(CO)_2$-h^1-C_5H_5.[13]

Finally, we confirm the observation[16] that **1** in solution shows four bands (cm^{-1}) due to C–O stretching modes at 1970 (6), 1961 (10), 1914 (4), and 1899 (8) (each ± 3 cm^{-1}), instead of the expected two, indicating the presence of conformers similar to those postulated for complexes of the type h^5-$C_5H_5Mo(CO)_2$-h^3(allyl).[17,18] However, the conformer ratio may obviously vary with temperature since the low-temperature nmr spectrum indicates the presence of only one species. In agreement with this, we find that the bands at 1970 and 1914 cm^{-1} in the infrared almost disappear at $\sim -60°$. The present results do not enable us to decide which is the most stable conformer of the complex **1**.

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(17) A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

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Absolute Rate Constants for Radical–Molecule Reactions over a Wide Temperature Range: $CH_3 + DBr \rightleftarrows CH_3D + Br$. The Heat of Formation and Entropy of the Methyl Radical

Sir:

The rates of virtually all radical–molecule reactions are measured relative to competitive radical reactions, most commonly radical–radical recombination.[1] We wish to report that we have measured the absolute rate constant for the reaction

$$CH_3 + DBr \longrightarrow CH_3D + Br \qquad (a)$$

The accuracy of rate constants derived from competitive studies are limited by the accuracy to which the rate constant of the competing reaction is known. This constraint has been removed from the results reported here.

Our method gives direct access to the back reaction rate constants in atom-abstraction studies in which a radical and stable molecule are produced.[2] The availability of Arrhenius parameters for forward and back reaction rate constants provides values for the heats of formation and entropies of free radicals. As has already been pointed out,[3] kinetic studies provide the most practical approach to obtaining the thermodynamic functions of free radicals. Our apparatus is a modified version of one already described in detail, VLPP.[4]

We do not presently have the capability of measuring radical concentrations directly, as reported by Lossing and others.[5,6] Chemical stoichiometry is used instead. The decomposition of *t*-butyl peracetate (tBPA) was used at the highest temperature (1000°K) to provide $2CH_3$ + acetone + CO_2. The acetone (Ac) and CO_2 are measured absolutely and thus yield rates of CH_3 production. The decomposition of di-*t*-butyl peroxide (dtBP) to give $2CH_3 + 2Ac$ was then used at all five temperatures (1000 to 608°K). Its higher vapor pressure makes it a more convenient methyl radical source in flow experiments. The results of the tBPA experiments confirmed that Br atoms were not abstracting hydrogen from acetone under our experimental conditions. Results based on acetone and CO_2 were identical.

These methyl radical sources were introduced at flow rates corresponding to 0.5 to 5×10^{16} molecules/sec of methyl radicals into the stirred flow reactor.[4] The source flow rate was held approximately constant during any one set of experiments. Decomposition was nearly 100%, except at 608°K. At this lowest temperature dtBP was approximately 70% decomposed. DBr was added at flow rates ranging from 1 to 150×10^{15} molecules/sec.

In the stirred flow reactor used here, it may be shown that

$$\frac{k_{eac}(Ac)}{k_{emed}(CH_3D)} = 1 + \frac{k_{eme}}{k_a(DBr)} \qquad (1)$$

where k_{eac}, k_{emed}, and k_{eme} are the first-order, apparent rate constants for escape from the Knudsen reaction cell[4] of acetone, CH_3D (MeD), and CH_3 radicals (Me), respectively. They are known accurately from the dimensions of the reaction cell.[7] (Ac), (CH_3D), and (DBr) are the steady-state concentrations of the respective species which are measured directly by our mass spectrometer. It follows from eq 1 that a plot of (Ac)/(CH_3D) against 1/(DBr) should give a straight line which may be used to obtain the desired rate constant k_a.

The reduced results are given in Figure 1. Results below 10% titration are not shown so that the fit to eq 1 could be shown at all temperatures conveniently in one figure. However, those results were included in computing the average rate constant.

C_2H_6 formation is not significant under the conditions of our experiment, but there is an appreciable quantity of CH_3Br formed at very high DBr flow rates and the

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(1) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Reactions," NSRDS-NBS 9, National Bureau of Standards, Washington, D. C., 1967.

(2) First report of this new technique: S. W. Benson, D. M. Golden, and R. Jackson, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, Abstract No. S191.

(3) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinetics*, **1**, 217 (1969).

(4) S. W. Benson and G. N. Spokes, *J. Am. Chem. Soc.*, **89**, 2525 (1967). VLPP represents the technique of very low pressure pyrolysis.

(5) F. P. Lossing and A. W. Thickner, *J. Chem. Phys.*, **20**, 907 (1952), and subsequent papers.

(6) (a) E. Hedaya and D. W. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967); (b) C. L. Angell, D. McLeod, Jr., and E. Hedaya, *ibid.*, **89**, 4214 (1967); (c) E. Hedaya, *et al.*, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract No. ORGN 46.

(7) Note that $k_{eac}/k_{emed} = (17/58)^{1/2}$, the square root of the molecular weight ratio, and $k_{eme} = 1.03T^{1/2}$ for our 30-ml vessel with 2.05-mm diameter exit aperture.[4]