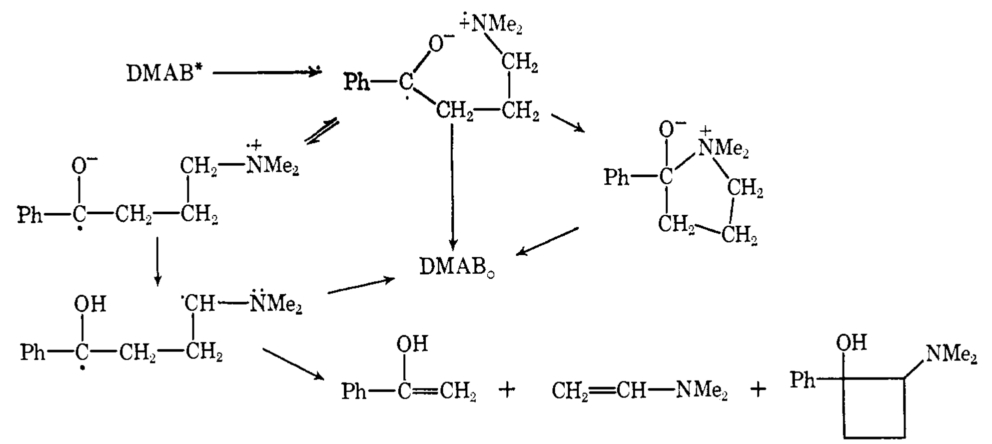
Scheme I



processes[16] is especially marked for γ-DMAB. In benzene, the quantum yield of acetophenone formation is only 8% that from valerophenone, while the triplet decay rate is 60 times faster. *There is no such correspondingly low quantum yield for bimolecular photoreduction of ketones by tertiary amines.*[1b,c] Moreover, both α-dimethylamino-[17a] and α-dibenzylaminoacetophenone[17b] undergo type II photoelimination in respectable quantum yields (~0.16). We have already presented considerable evidence that quantum yields of type II processes are low in hydrocarbon solvents because of the disproportionation of biradical intermediates,[16] which reaction is prevented by polar solvents.[18] Acetonitrile does double Φ_{II} for γ-DMAB, and we shall assume that this increase accounts for all the biradicals. Consequently, 95% of the γ-DMAB triplets in benzene or acetonitrile and 75% in methanol probably do not yield a biradical. Revertible[19] electron transfer has been suggested by Cohen as the cause of the moderate quantum efficiencies in amine–ketone photoreactions.[1,2] However, something further must prevent the supposed γ-DMAB zwitterionic intermediate from proceeding on to biradical. One possibility is that in nonpolar and aprotic solvents, the positive and negative ends of the zwitterion do not separate sufficiently for a γ proton to approach the negative oxygen. It is also possible that the zwitterion cyclizes, as shown in Scheme I.

(5) Transannular interactions have been reported for cyclic amino ketones.[20] There is no evidence in the uv, ir, or nmr spectra of γ-DMAB for ground-state interactions between the amino and carbonyl functions. The phosphorescence spectrum[21] of γ-DMAB looks very much like that of valerophenone, with the important exception that the emission from γ-DMAB is much longer lived. This phenomenon will be reported separately and is mentioned here simply to emphasize that a significant interaction between the amino group and the *excited* carbonyl can be detected spectroscopically.

(6) Tetraethylammonium bromide does not quench valerophenone. Protonation of the amino group of γ-DMAB increases its triplet lifetime substantially. The quantum yield of γ-DMAB–HCl disappearance is eight times greater than that of acetophenone formation, so that photoreduction by solvent must be the main reaction. We estimate that the γ hydrogens in γ-DMAB–HCl are $<{}^1/_{100}$ as reactive as those on valerophenone and $<{}^1/_{4000}$ as reactive as those on γ-DMAB.

In summary, the data in Table II and the very low type II quantum yield of γ-DMAB are inconsistent with simple hydrogen atom abstraction being the primary process between amines and ketone triplets. However, the solvent effects on rates are seemingly inconsistent with an actual electron-transfer process. Consequently, we conclude that the formation of some sort of charge-transfer complex between tertiary amines and ketones must occur. This complex can then proceed on to actual radical ion pairs or transfer hydrogen to the carbonyl oxygen directly. Since the CT process merely creates a large dipole and not necessarily free charge, solvent effects can be expected to differ from those observed in electron-transfer processes. Koizumi has recognized this possibility in his fluorescence quenching studies.[13] In particular, the reorganized solvation of the CT complex may not be sufficient to offset the decreased availability of a hydrogen-bonded amine lone pair.[22]

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(16) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **90**, 5896 (1968).

(17) (a) P. J. Wagner, unpublished work; (b) A. Padwa, W. A. Eisenhardt, R. Gruber, and D. Pashayan, *J. Am. Chem. Soc.*, **91**, 1857 (1969).

(18) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(19) This term is preferable to "reversible" since the latter, taken strictly, would imply that excited ketone is re-formed. Moreover, one connotation of "revert" is "return to an ancestral form."

(20) N. J. Leonard, D. F. Morrow, and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 5476 (1957), and preceding papers.

(21) We thank David Graber and Professor Alfred Haug of the Michigan State University AEC Plant Radiation Laboratory for the emission spectra.

(22) This work is being supported by a grant from the National Science Foundation.

(23) Alfred P. Sloan Fellow, 1968–1970.

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Loss of Neutral Metal Fluorides in the Mass Spectra of Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)metal Complexes

Sir:

In several recent mass spectral studies of the metal chelates of acetylacetone and its derivatives, a large body of indirect evidence has been accumulated to

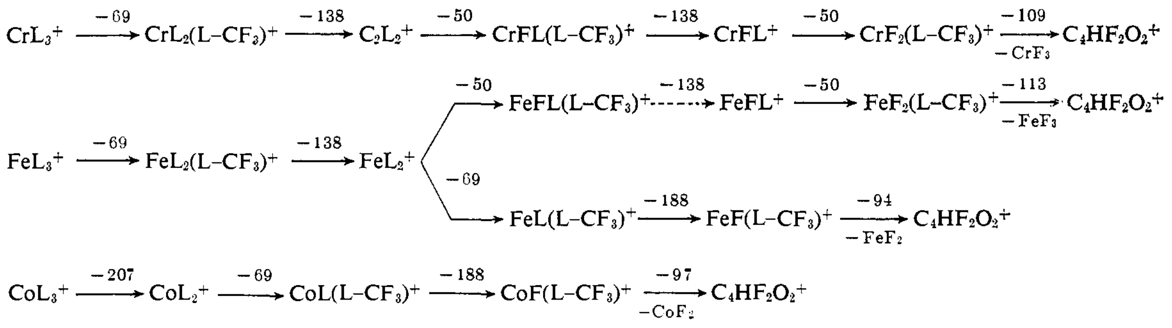

Figure 1. Flow diagram for the decomposition of metal hexafluoroacetylacetonates (ML_3) leading to the elimination of neutral meta fluorides.

substantiate the hypothesis that, for these compounds, elimination of an odd-electron fragment from an even-electron ion is accompanied by a change in the oxidation state of the chelated metals.[1-5] We wish to present direct evidence that such a reduction is actually occurring.

Table I. Metastable Transitions Leading to the Elimination of Neutral Metal Fluorides in Metal Hexafluoroacetylacetonates (ML_3)

	Metastable peak		
Transition	Cr	Fe	Co
$ML_3^+ \rightarrow ML_2(L\text{-}CF_3)^+$	542.1	546.0	...
$ML_2(L\text{-}CF_3)^+ \rightarrow ML_2^+$	359.5	363.3	...
$ML_3^+ \rightarrow ML_2^+$	322.7	326.2	329.9
$ML_2^+ \rightarrow ML(L\text{-}CF_3)^+$	...	342.1	345.1
$ML_2^+ \rightarrow MFL(L\text{-}CF_3)^+$	372.0	375.3	...
$ML(L\text{-}CF_3)^+ \rightarrow MF(L\text{-}CF_3)^+$	...	113.1	115.5
$MFL^+ \rightarrow MF_2(L\text{-}CF_3)^+$	187.0	190.9	...
$MF(L\text{-}CF_3)^+ \rightarrow C_4HF_2O_2^+$	...	66.5	65.6
$MF_2(L\text{-}CF_3)^+ \rightarrow C_4HF_2O_2^+$	62.1	61.0	...

Major fragments in the mass spectra of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) (L) complexes of Cr(III), Fe(III), and Co(III) are incorporated in the flow diagram of Figure 1. Each process represented by a solid line in the flow diagram is confirmed by the presence of a metastable peak (Table I). Such peaks have long been accepted as direct evidence for a given decomposition.[6] There is uncertainty about the existence of metastable peaks for the explusion of neutral fragment 138 from $MFL(L\text{-}CF_3)^+$ in both Cr and Fe complexes. The region where such a peak would be anticipated is masked by the strong metastable associated with the rearrangement $MFL^+ \rightarrow MF_2(L\text{-}CF_3)^+$. However, the loss of 138 is observed from $ML_2(L\text{-}CF_3)^+$ to give ML_2^+. This is analogous to the production of MFL^+ from $MFL(L\text{-}CF_3)^+$, and we feel reasonably certain that this reaction occurs.

Loss of *m/e* 50 (CF_2) with rearrangement of the remaining fluorine to the metal has been previously reported by Reichert, Westmore and Gesser for tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum(III) and tris(1,1,1-trifluoro-2,4,-pentanedionato)-aluminum(IIII).[3]

m/e 69 lost from FeL_2^+ is the radical fragment CF_3. According to the hypothesis of MacDonald and Shannon, reduction of Fe(III) to Fe(II) accompanies such a loss.[2] The subsequent loss of 188 amu (even electron fragment) and 94 amu indicates that Fe(II) has indeed been formed. The mass lost, 94 amu, in the last step corresponds to the stoichiometry of FeF_2. This is to be contrasted to the alternate path for decomposition of FeL_2^+ by loss of even-electron fragments only. In this case the final step is the loss of a fragment of 113 amu, FeF_3. Here the metal has retained its original +3 oxidation number. There can be little doubt that the metastable transitions which we assign to the loss of neutral metal fluorides derive from the decomposition of a metal-containing ion. None of the metastable peaks cited in Table I is found in the mass spectrum of pure hexafluoroacetylacetone.[5] Further, each metastable peak appears at a distinctly different *m/e* ratio for each metal.

Parallels for the two reaction sequences discussed for FeL_3 can be seen with CrL_3, which eliminates CrF_3, and CoL_3, which eliminates CoF_2. The correlation between the relative stability of the (III)/(II) oxidation states for the metals involved and the stoichiometry of the eliminated neutral metal fluoride cannot be denied. One is thus led to the conclusion that, for the difluorides to be eliminated during a reaction sequence traceable directly to a M(III) precursor, a reduction of the metal must have occurred. In light of the large body of data which illustrates the probability of an even-electron ion eliminating an even-electron fragment,[7] one

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[1] J. S. Shannon and J. M. Swan, *Chem. Commun.*, 3, 33 (1965).

[2] C. G. MacDonald and J. S. Shannon, *Australian J. Chem.*, **19**, 1545 (1966).

[3] C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 5, 782 (1967).

[4] M. J. Lacy, C. G. MacDonald, and J. S. Shannon, *Org. Mass Spectry.*, **1**, 114 (1968).

[5] A. L. Clobes, M. L. Morris, and R. D. Koob, in preparation.

[6] R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1965, p 124.

[7] F. W. McLafferty, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 309.

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.

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

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

(10) R. S. Juvet and R. P. Durbin, *J. Gas Chromatog.*, **1** (12), 14 (1963).

(11) H. Veening, W. E. Bachman, and D. M. Wilkinson, *ibid.*, **5** (5), 248 (1967).

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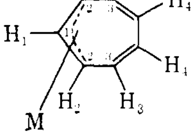
Variable-Temperature Proton Resonance Spectra of *Trihapto*cycloheptatrienylmetal Complexes

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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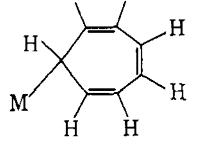

II

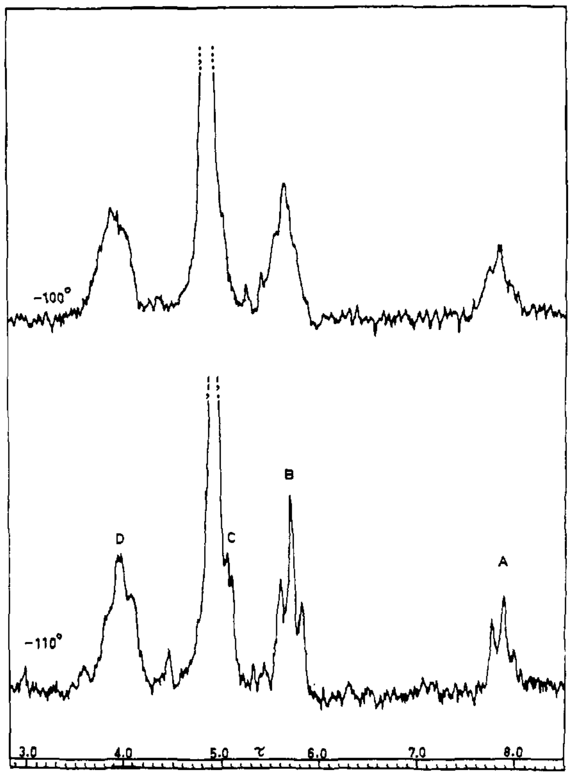

Figure 1. Proton resonance spectra of $h^5-C_5H_5Mo(CO)_2-h^3-C_7H_7$ in 1:2 $CFCl_3-CS_2$ (∼10 mg/0.5 ml) at −100 and −110°.

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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(1) R. B. King and M. B. Bisnette, *Tetrahedron Letters*, 1137 (1963).

(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).

(5) R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 (1967).

(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).

(8) W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).