with the samples in flowing helium gas at a temperature of ~10 K. Samples of YH_2 and YH_3 doped with Yb, Sm, Eu, and Ce failed to give observable signals. However the cerium samples were particularly sensitive to air oxidation and formed some oxide prior to arc melting so the hydride samples may not have contained significant amounts of Ce.

Results and Discussion

The EPR spectra summarized in Table I are characteristic of the trivalent ions of Er, Dy, and Gd, thus confirming the +3 oxidation state for the metal ions with three electrons presumably donated to the conduction band in the dihydrides. Sm^{3+}, with a Γ_8 ground state in a cubic hydridic crystal field,[9] should have an anisotropic EPR transition so that failure to observe spectra for samarium is consistent with the +3 state. Europium might be expected to remain as Eu^{2+} with an easily observable isotropic $^8S_{7/2}$ ground state since pure EuH_2 cannot be converted to a higher hydride,[1] so failure to observe spectra for samples doped with europium is consistent with Eu^{3+} in YH_x. Ytterbium, which could be expected to exhibit an isotropic Γ_7 ground state if present as Yb^{3+}, apparently remains in the diamagnetic +2 state as it does in pure orthorhombic YbH_2 since spectra are not observed for Yb in this cubic host. Preliminary studies of pure YbH_2, however, did give EPR transitions at $g = 4.7$ and 3.9 perhaps indicating some Yb^{3+} in this lower symmetry environment as has been suggested[1] to explain the slight room-temperature paramagnetism of YbH_2.

In the cubic environment of YH_2, Er^{3+}, and Dy^{3+} both exhibit isotropic *g* values characteristic of a Γ_7 state consistent with the hydridic point charge model and not with the protonic point charge model for the crystal field.[7-10] The *g* value for Er of 6.60 ± 0.05 in YH_2 is lowered only slightly from the value of 6.77 predicted for a Γ_7 ground state and the value 6.778 ± 0.003 measured by Venturini[14] for Er^{3+} in $YH_{1.99}$ at 2 K. The difference in the measured *g* values is due to the measurements being done at different temperatures. The observed *g* value of 6.9 for Dy in YH_2 is somewhat further lowered from the predicted value of 7.56 for a Γ_7 ground state, presumably due to the temperature dependence of the conduction electron coupling.[20,21] As the symmetry of the crystal field is reduced upon going from YH_2 to YH_3, the powder spectra of Er^{3+} and Dy^{3+} become considerably more complex. The *g* values for Er^{3+}:YH_3 reported in Table I agree with the values assigned to Er in a biaxial site in $YH_{2.94}$ by Venturini.[13] No specific assignments were made for the Dy:YH_3 spectrum.

Gd^{3+} gives a single isotropic line at $g = 1.996$ in YH_2 and $g = 1.96$ in $LaH_{2.0}$ as expected for an S-state ion, although the zero-field splitting expected even in a cubic environment[12] is absent. Such collapse of a zero-field multiplet into a single line is characteristic of exchange narrowing through coupling via conduction electrons as is found for Gd in gold[20] and for Gd in d-band intermetallic compounds.[21] The broadening of the Gd^{3+} resonance line in LaH_x as *x* increases from 2.0 to 2.6 could reflect either the decrease in conductivity or the decrease in site symmetry, or both, as hydrogen occupies additional octahedral sites. The complex spectra obtained for Gd^{3+} in YH_3 show that exchange narrowing by coupling through conduction band electrons is no longer effective as the hydride loses its metallic character.

The absence of EPR signals for Er and Dy in LaH_{2-3} could be due to a number of factors. First of all the experiments were performed at ~10 K where Venturini has shown that cubic lines could be considerably broadened.[13] Second, the concentrations of Er and Dy were considerably higher than in the YH_{2-3} samples which also could cause line broadening.

This work and Venturini's work show that considerable information may be obtained from EPR experiments on hydridic materials and point the way for future experiments.

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Registry No. Er^{3+}, 18472-30-5; Dy^{3+}, 22541-21-5; Gd^{3+}, 22541-19-1; YH_2, 13598-35-1; YH_3, 13598-57-7; LaH_2, 13823-36-4; LaH_3, 13864-01-2.

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HSAB Theory Applied to Rearrangements in the Mass Spectra of Fluorinated Metal β-Diketonate Complexes

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In a recent discussion of the application of hard/soft acid/base (HSAB) theory to rearrangements in the mass spectra of organometallic compounds,[1] an important class of comparable data appears to have been overlooked. In addition to rearrangements of fluorine from ligands such as C_6F_5 to a variety of central atoms, there exists a body of data for a similar rearrangement from a variety of fluorinated β-diketonate ligands to several metals.[2-4] That these rearrangements occur as unimolecular gas-phase ion reactions is well established by the observation of metastable transitions corresponding to these reactions.[4] Whether HSAB correctly predicts the importance of the fluorine migration in these systems is an important test of the hypothesis of Miller, Jones, and Deacon (MJD). We would expect, pursuing the reasoning of MJD, to find the relative importance of M–F produced to be dependent on the acidity of the metal site for a given fluorinated ligand. Further, if more electron-rich ligands are used we might reasonably expect a softening of the acidity at the metal accompanied by a corresponding change in reactivity.

The complexes of the anions of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) with Co(II), Fe(III), Fe(II), Cr(III), Al(III), Zn(II), Ni(II), Mn(II), and Cu(I) have been examined in a mass spectrometer. Many exhibit peaks corresponding to rearrangement of a fluorine to the metal, and several demonstrate the loss of neutral metal fluorides via metastable transitions. It is important to note that Co(II), Fe(II), and Cu(I) result from intramolecular reduction of complexes of metals of one unit higher oxidation. This process was first noted by Lacey and Shannon[6] and has been verified by a number of groups.[2,7]

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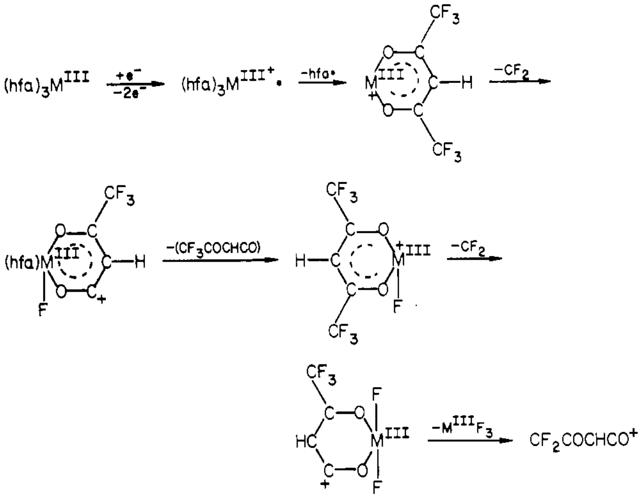
Scheme I. Generalized Mechanism for Fluorine Rearrangement to Metal and Loss of Neutral Metal Fluorides for $(hfa)_3M^{III\,a}$



[a] Each step is verified by a metastable transition in the chromium complex.

Table I. Fluorine Migration to Metal for Several $M(hfa)_n$ Complexes

metal	neutral fragment $MF_n^{0\,a}$	precursor ion $MF_x(L\text{-}CF_3)^{+\,b}$
Mn(II)	*c*	*c*
Al(III)	*e*	*c*
Cr(III)	*c*	*c*
Fe(III)	*c*	*c*
Fe(II)	*c*	*c*
Co(II)	*c*	*c*
Ni(II)	*c*	*c*
Zn(II)	*d*	*c*
Cu(I)	*d*	*d*

[a] $n = 2, 3$. [b] $x = 1, 2$. [c] Reaction indicated by metastable transition. [d] Product not observed. [e] AlF_2L is eliminated as a neutral for this complex.

With the notable exception of copper(I) rearrangement of fluorine to the metal to form either M–F containing ions or neutrals occurs (Scheme I). Clearly HSAB theory is not a sufficiently refined concept to account for subtle differences in these rearrangement reactions. For example, elimination of neutral AlF_2L instead of AlF_3 parallel to CrF_3 and FeF_3 is not explained. Nor is the case for zinc, where a neutral metal fluoride does not appear to be produced even though evidence that migration of fluorine to the metal exists. In spite of these reservations, we find no conflict between the hypothesis of MJB and our data. The large number of compounds readily prepared or available for the metal β-diketonates, in fact, suggests this class of compounds as an appropriate vehicle for extending the exploration of this concept.

In the gas phase, the acidity of the metal is dependent only on its ligands as no solvent is present. It appears consistent to assume that among the fluorinated or partially fluorinated β-diketonates the hardest acid case would be the hfa complexes. Replacing a CF_3 group with more electron-rich species may be expected to soften the acidity of the metal with the expected consequence that fluorine rearrangement to the metal is less prevalent than for hfa complexes.

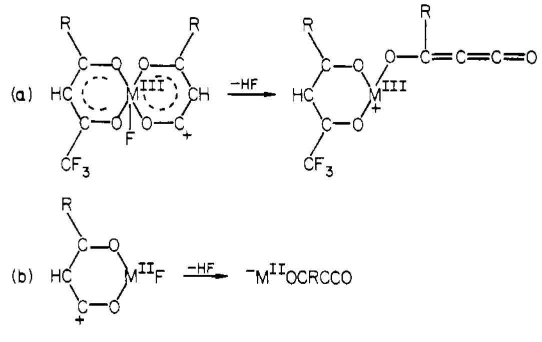
Relevant data for complexes of $[CF_3COCHCOR]_3M^{III}$ where R is the trifluoromethyl, methyl, ethyl, isopropyl, *tert*-butyl, phenyl, and thienyl group, respectively, are given in Table II.

Table II. Fluorine Rearrangement Ions for $[CF_3COCHCOR]_3M^{III\,a}$

ion/R	CF_3	CH_3	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	C_6H_5	C_4H_3S
$Fe^{III}F_2(L\text{-}CF_3)^+$	5	1.5	0.3	0	0	1.5	2
$Fe^{II}F(L\text{-}CF_3)^+$	80	46	33	30	29	27	25
$Cr^{III}F_2(L\text{-}CF_3)^+$	20	12	7	4	0	9	*b*
$Cr^{II}F(L\text{-}CF_3)^+$	21	20	16	17	14	13	0

[a] Intensity relative to $ML_2^+ = 100$. [b] Data not taken.

Scheme II. Loss of HF for (a) $M^{III}L_3$ and (b) $M^{II}L_2$



The most obvious effect of replacing CF_3 by an alkyl or phenyl group is the removal of the elimination of metal fluorides as a reaction. The precursor ions to these eliminations for the hfa complexes are still observed for the other complexes, however. While it is dangerous to draw conclusions based on relative intensities of ions from different molecules, there is a striking dependence of the relative intensity of these ions on the nature of the substituent. That dependence parallels ones expectations in that the F rearrangement ion becomes less important as the softness of the metal environment increases.

A number of the β-diketonate complexes mentioned above also give rise to a reaction in which HF is lost. In every example we discuss, this loss is verified by a metastable peak. Among the hfa complexes only chromium(III) loses HF (Scheme II).

When one of the CF_3 substituents is replaced by methyl or phenyl, iron and aluminum complexes demonstrate HF loss as well, and the relative intensities for reactions 1 and 2 increase from 1.3 and 4 to 15 and 11, respectively.

$$Cr^{III}FL(L\text{-}CF_3)^+ \xrightarrow{-HF} CrL(L\text{-}CHF_3)^+ \qquad (1)$$

$$Cr^{III}F(L\text{-}CF_3)^+ \xrightarrow{-HF} Cr(L\text{-}CHF_3)^+ \qquad (2)$$

For ligands where other hydrogens are present, deuterium labeling has been used to demonstrate that HF loss involves only the γ-hydrogen of the ligand.

If one considers these reactions as a probe in the sense of an internal competition between the metal acid and the proton, then the conclusion is that softening the metal environment weakens its ability to compete with H for the fluorine.

It is apparent from the data presented that the attempt of Miller, Jones, and Deacon to examine mass spectral data for metal complexes in HSAB terms[1] is not misleading when applied to an entirely different class of compounds. Further exploration of this idea seems justified.

Registry No. $Mn(hfa)_2$, 19648-86-3; $Al(hfa)_3$, 15306-18-0; $Cr(hfa)_3$, 14592-80-4; $Fe(hfa)_3$, 17786-67-3; $Fe(hfa)_2$, 28736-68-7; $Co(hfa)_2$, 19648-83-0; $Ni(hfa)_2$, 14949-69-0; $Zn(hfa)_2$, 14949-70-3; $[CF_3COCHCOCH_3]_3Fe$, 14526-22-8; $[CF_3COCHCOC_2H_5]_3Fe$, 77662-10-3; $[CF_3COCHCO\text{-}i\text{-}C_3H_7]_3Fe$, 77662-11-4; $[CF_3COCHCO\text{-}t\text{-}C_4H_9]_3Fe$, 21703-71-9; $[CF_3COCHCOC_4H_3S]_3Fe$, 14319-78-9; $[CF_3COCHCOCH_3]_3Cr$, 14592-89-3; $[CF_3COCHCOC_2H_5]_3Cr$, 77662-12-5; $[CF_3COCHCO\text{-}i\text{-}C_3H_7]_3Cr$, 71869-69-7; $[CF_3COCHCO\text{-}t\text{-}C_4H_9]_3Cr$, 21703-69-5; $[CF_3COCHCOC_4H_3S]_3Cr$, 15488-08-1; $[CF_3COCHCOC_6H_5]_3Fe$, 14524-54-0; $[CF_3COCHCOC_6H_5]_3Cr$, 28096-65-3.