Electron Spin Resonance Studies of the Reduction of Transition Metal Complexes with Grignard Reagents. 1. Dianion Radicals of β-Diketonates

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Abstract: Well-resolved electron spin resonance spectra of a series of stable dianion radicals (DAR) derived from β-diketones are observed in solution when a variety of metal keto enolates are reduced with Grignard reagents. Unambiguous assignments of the spectra are achieved by specific deuterium labeling of carbon 2 in acetylacetonate and dibenzoylmethide. The structure of acetylacetonate DAR is related to a chelate model based on INDO molecular orbital calculations by fitting the observed proton hyperfine splittings. Selective line broadening observed in the ESR spectrum of dibenzoylmethide DAR may be related to hindered rotation about the phenyl carbon in the planar conformation, which also pertains to benzoylacetonide DAR. The optical and ESR spectra of anion radicals generated from the reduction of tris(dibenzoylmethido)iron(III) with Grignard reagent are compared with those obtained by reduction with the sodium mirror technique. The absence of the triplet spectrum (shown previously for DAR dimers) in frozen solutions resulting from the Grignard reduction is attributed to the binding of the DAR as a magnesium chelate. The presence of reduced iron in the form of paramagnetic iron(I) species is discussed.

Introduction

Transition metal complexes are widely employed in a variety of catalyzed organic reactions.[1] In a number of these processes, the complex undergoes prior reduction to a metastable subvalent species, which is the effective catalyst. For example, the efficient cross coupling reaction of aryl and alkenyl halides with Grignard reagents is induced by a number of iron(III) complexes.[2] The actual catalyst in this system is a reduced iron

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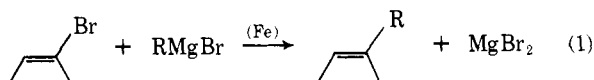
species formed by the rapid reaction of the iron(III) complex and Grignard reagent.

Grignard reagents are indeed efficient and potent reducing agents for many transition metal complexes.[3] The products of these highly reducing solutions are metastable and quite reactive, which generally precludes their isolation. Therefore, it is important to develop techniques that allow the direct examination of metastable intermediates in solution. In this paper we report the use of electron spin resonance (ESR) spectroscopy to probe for paramagnetic intermediates formed in the reduction of various iron(III) complexes with Grignard reagents. Attention is focused on keto enolate ligands derived from β-diketones, since we have found the Grignard reagent to be uniquely suited to generate a new series of dianion radicals of exceptional stability. The latter is especially noteworthy, since earlier conclusions[4] regarding the ESR spectra of dianion radicals of keto enolates have been seriously questioned.[5]

Results

Reduction of Tris(acetylacetonato)iron(III) by Grignard Reagent in THF Solution. A solution (0.2 ml of 1 M) of ethylmagnesium bromide in tetrahydrofuran (THF) was added to 2 ml of 10^{-3} M Fe(acac)$_3$ in THF under an argon atmosphere. The red solution immediately turned dark red-brown, but remained clear and homogeneous, no precipitate being formed even on prolonged standing.

The ESR spectrum of the solution shown in Figure 1 consists of a broad and structureless band centered at $\langle g \rangle$ = 2.08 with a peak-to-peak linewidth (H_{pp}) of approximately 230 G. It is assigned to a low-spin d^7 iron(I) species (vide infra). Superimposed on this broad resonance is another spectrum at $\langle g \rangle$ = 2.0032 showing hyperfine structure. The details of the sec-

ond spectrum are presented in Figure 2, the resolved features clearly consisting of a septet (13 G) of doublets (2.79 G) assigned to the dianion radical (DAR) of acetylacetonate. The doublet splitting is attributed to the proton at carbon 2, since it disappears on deuteration of acetylacetonate. Use of deuterated ethylmagnesium bromide (CD$_3$CH$_2$MgBr),[2c] as expected, led to the same spectrum shown in Figure 2. It is reasonable to expect the DAR of acetylacetonate to exist under these conditions as a metal complex I (vide infra).

I
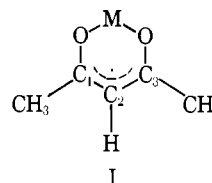
The broad as well as the resolved ESR spectrum in Figure 1 appeared immediately after mixing the ethyl Grignard and iron(III) solution (taking into account the time (~2 min) required to tune the spectrometer). The same reduction carried out with methylmagnesium bromide proceeded more slowly, as visually evident by the intermediate formation of a gray-green color. Furthermore, the appearance of the spectrum of the DAR was delayed by approximately 10 min, although the broad spectrum centered at $\langle g \rangle$ = 2.08 could be observed immediately upon mixing.

If a small amount of oxygen (0.5 ml) was added to the sample tube, the ESR spectrum of the DAR was quenched immediately. Increasingly larger amounts of oxygen were required before the intensity of the broad singlet was diminished and eventually removed entirely, whereupon the color of the solution faded to yellow. The solution remained homogeneous and no precipitate was observed.

Attempts to reduce a solution of tris(acetylacetonato)-iron(III) dissolved in THF (10^{-3} M) by the sodium mirror method[6] produced no ESR spectrum of the DAR. However, the broad singlet centered at $\langle g \rangle$ = 2.08 could be observed after prolonged contact of the solution with the sodium mirror.

Reduction of Metal Acetylacetonate Complexes with Grignard Reagents. In order to investigate the generality of the reduction with Grignard reagent, we also examined the acetylacetonato complexes of a series of other metals. Emphasis was placed primarily on the ESR observation of the
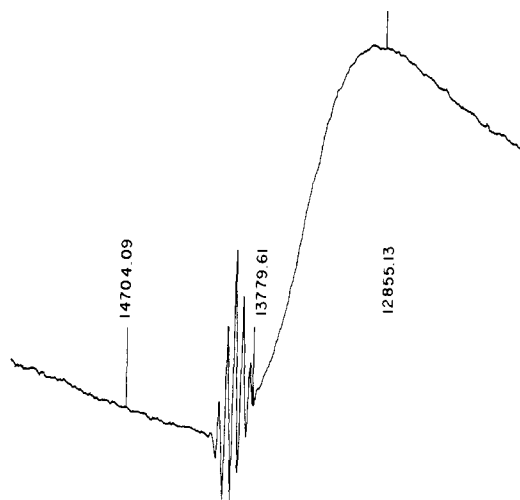
Figure 1. ESR spectrum obtained from the reduction of tris(acetylacetonato)iron(III) with ethylmagnesium bromide in THF solution.
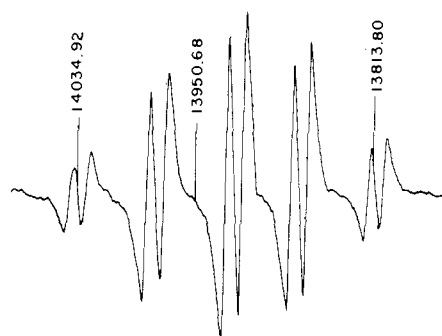

Figure 2. High resolution of the portion of the spectrum in Figure 1 at $\langle g \rangle$ = 2.00. NMR field markers are in kilohertz.

DAR of acetylacetonate. Thus, reduction of bis(acetylacetonato)cobalt(II) with ethylmagnesium bromide afforded an intense ESR spectrum of the DAR of acetylacetonate similar to the one illustrated in Figure 2. Reduction of the monodeuterated analogue, $Co(CH_3COCDCOCH_3)_2$, afforded the spectrum in Figure 3, in which the inset shows the partially resolved deuterium triplets (a_D = 0.43 G) of the m_I = 1 line due to splitting by six equivalent methyl protons.

The spectral parameters of the DAR's derived from other metal acetylacetonates were all quite similar, showing only minor variations of the isotropic g factors and proton hyperfine splitting (hfs in Table I). In none of the complexes did we observe hyperfine splitting from the metal. These observations suggest that the DAR of acetylacetonate is free of the transition metal, but probably associated with the ubiquitous magnesium (vide infra). The latter is supported by our inability to observe the DAR spectrum when either a sodium mirror or methyllithium is employed as a reductant.

The elapsed time before the appearance of the ESR spectrum of acetylacetonate DAR varied considerably with the metal complex and the Grignard reagent, as indicated by the last column of Table I. The delay in some cases lasted as long as 15 min, despite the rapid color changes attendant upon the addition of th Grignard reagent. Transition metal derivatives generally afforded the best ESR spectra of acetylacetonate DAR. The main group metals, with the exception of beryllium, which afforded a well-resolved spectrum but of medium quality, were generally ineffective.

The difference between methyl and ethyl Grignard reagents as reducing agents is clearly delineated in the behavior of manganese(III) and copper(II) acetylacetonates. Thus,
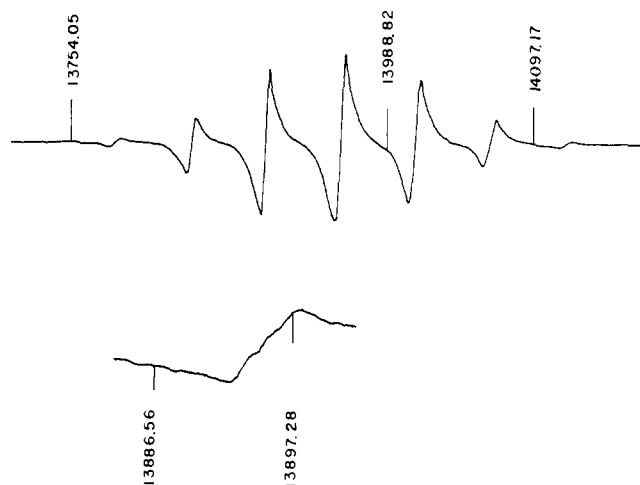

Figure 3. ESR spectrum from the reduction of bis(acetylacetonato-d_1)cobalt(II) with ethylmagnesium bromide in THF solution. Inset below is a high resolution portion (m_I = 1 line) of the spectrum above after dilution showing the partially resolved deuterium splittings.

treatment of either complex with methylmagnesium bromide produced no ESR signal of the DAR, although reduction of the metals does occur, as seen by the changes in the colors of the solutions from brown to yellow for manganese and blue to colorless for copper. In the latter case, the characteristic ESR spectrum of copper(II) (a_{Cu} = 68.68 G, $\langle g \rangle$ = 2.13) also disappears. On the other hand, the use of ethylmagnesium bromide under the same conditions resulted in solutions showing intense ESR spectra of the DAR of acetylacetonate. The formation and decomposition of a metastable intermediate, probably a subvalent metal keto enolate, is consistent with all of these observations.

Dianion Radicals of β-Keto Enolates. After establishing the identity of the DAR of acetylacetonate, we turned our attention to using this method to generate analogous species from other β-diketones.

Dibenzoylmethide DAR. On treatment of bis(dibenzoylmethido)cobalt(II), $Co(dbm)_2$, with ethylmagnesium bromide, the solution turned from orange to green and an unresolved singlet centered around $\langle g \rangle$ = 2.00 was observed in the ESR spectrum. Upon standing, the solution turned blue then wine-red and fine structure emerged coincidentally from the ESR spectrum. After 24 h the resolved spectrum shown in Figure 4 was obtained. Similarly, reduction of tris(dibenzoylmethido)iron(III) with either methyl- or ethylmagnesium bromide afforded solutions showing the same ESR spectrum as that given in Figure 4.

The complex hyperfine splittings in the spectrum in Figure 4 were difficult to assign accurately. We resorted, therefore, to a simpler spectrum shown in Figure 5 resulting from the reduction of the deuterated analogue, $Co(PhCOCDCOPh)_2$. The computer simulated spectrum in Figure 5 using the hyperfine splittings in Table II is in excellent accord with the experimental spectrum. Furthermore, the computer simulated spectrum of the completely protiated DAR of dibenzoylmethide shown in Figure 4 could be generated from the same data (compare Table II). Indeed, except for minor unresolved features and line intensities (vide infra), the simulated spectrum is a reasonable representation of the experimental one.

Closer comparison of the well-resolved experimental and simulated spectra in Figure 5 shows that the intensity ratios of the lines differ from the theoretical ones. Especially noticeable is the diminished intensities of each line of the central multiplet. The effect is pronounced in spectra obtained in the early phases of the reduction, but these gradually approach the

Table I. Reduction of Metal Acetylacetonates in Tetrahydrofuran Solutions[a]

| M(acac)$_n$ | Method of redn | Color change | | ⟨g⟩ | a CH$_3$,[b] G | a H,[c] G | Time delay[d] |
		Before	After				
Fe(acac)$_3$	CH$_3$MgBr	Red	Gray-green	2.0033	13.00	2.79	Yes
	CH$_3$CH$_2$MgBr		Brown-red	2.0033	13.25	2.79	No
	Na		Brown	e			
Fe(acac)Cl$_2$	CH$_3$MgBr	Red	Brown-red	2.0033	13.25	2.79	Yes
Cr(acac)$_3$	CH$_3$MgBr	Purple	Red-brown	2.0032	13.36	2.76	Yes
Mn(acac)$_3$	CH$_3$MgBr	Brown	Yellow	e			
	CH$_3$CH$_2$MgBr		Amber	2.0032	13.07	2.78	No
Co(acac)$_3$	CH$_3$MgBr	Green	Red-brown	2.0033	13.00	2.77	Yes
Co(acac)$_2$	CH$_3$MgBr	Pink	Red-brown	2.0033	13.02	2.79	No
	CH$_3$CH$_2$MgBr		Red-brown	2.0033	13.15	2.79	No
	CH$_3$Li		Blue	e			
Co(acac-d_1)$_2$	CH$_3$CH$_2$MgBr	Pink	Red-brown	2.0033	13.20	0.43[f]	No
Ni(acac)$_2$	CH$_3$MgBr	Green	Brown	2.0033	13.19	2.74	No
Cu(acac)$_2$	CH$_3$MgBr	Blue	Colorless	e			
	CH$_3$CH$_2$MgBr		Purple	2.0034	13.07	2.77	No
Be(acac)$_2$	CH$_3$CH$_2$MgBr	Colorless	Yellow-green	2.0037	13.15	2.83	No
	Na	g	e				
Na(acac)	CH$_3$MgBr	Colorless	Colorless	e			
Mg(acac)$_2$	Na	Colorless	Colorless	e, h			

[a]Containing $\sim 10^{-3}$ M M(acac)$_n$ at room temperature. [b]Septet splitting. [c]Doublet splitting. [d]No time delay indicates DAR appears immediately ($\sim$2 min). [e]No DAR of acac. [f]Deuterium 1:1:1 triplet. [g]White layer attached to Na mirror. [h]Metallic particles (presumably magnesium) observed.
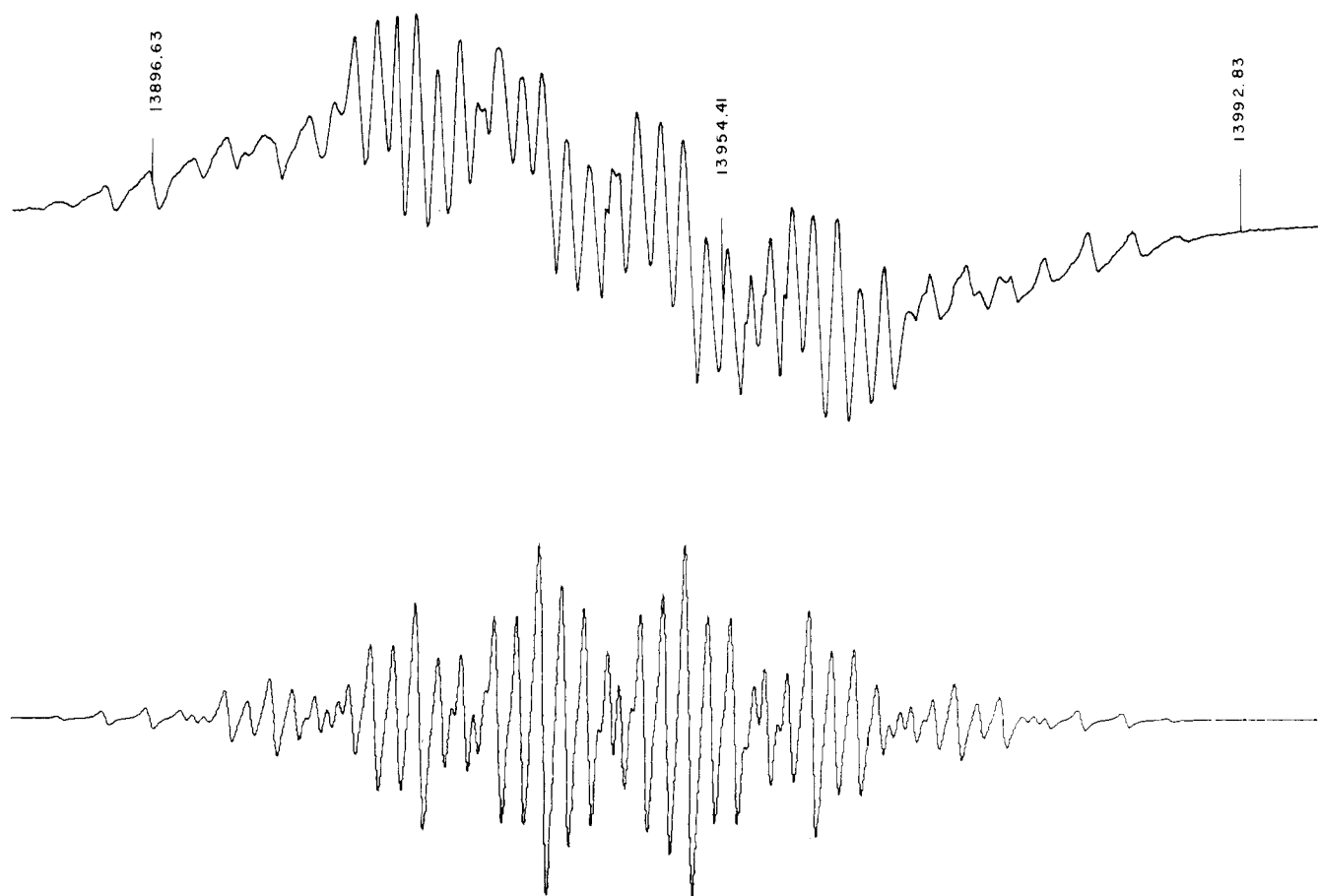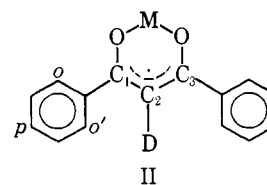

Figure 4. Upper: ESR spectrum obtained from the reduction of bis(dibenzoylmethido)cobalt(II) with ethylmagnesium bromide in THF solution. Proton NMR field markers are in kilohertz. Lower: Computer simulated spectrum using the hyperfine splittings in Table II. See remarks in the text regarding the line intensities.

more normal spectrum as the solution is allowed to stand. In the ESR spectrum of the DAR of dibenzoylmethide-d_1, the seven groups of multiplets correspond roughly to splitting by six ortho and para aromatic protons with similar hyperfine coupling constants (see Table II). If the stable conformation of the dianion radical of dbm-d_1 is one in which a phenyl ring is coplanar with the three-carbon skeleton, the ortho protons would be magnetically inequivalent.

II

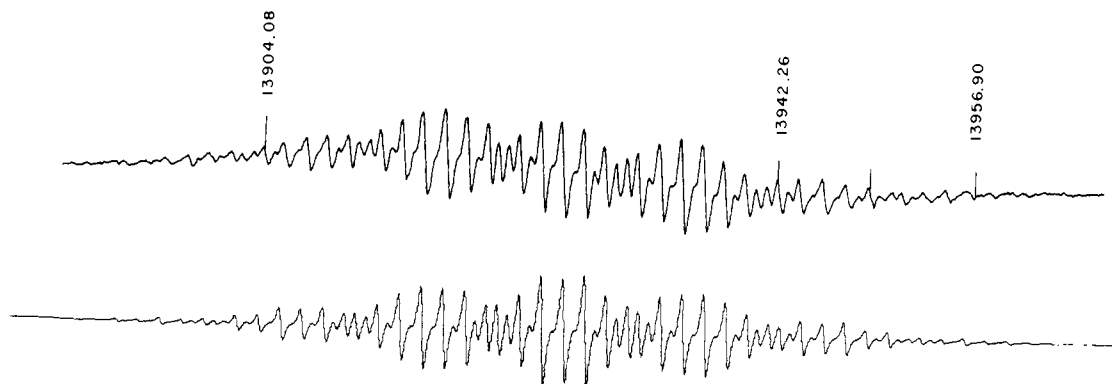The abnormal distribution of line intensities can be ex-

Figure 5. Upper: ESR spectrum obtained from the reduction of bis(dibenzoylmethido-d_1)cobalt(II) with ethylmagnesium bromide in THF solution. Lower: Computer simulated spectrum using the hyperfine splittings in Table II.

Table II. Proton Hyperfine Coupling Constants for the DAR of Dibenzoylmethide

	Hyperfine coupling constant, G	
Position[a]	PhCOCHCOPh	PhCOCDCOPh
2	2.51[b]	0.38$_6$
o,o	2.12	2.12
o',o'	2.12	2.12
m,m	0.77	0.77
p,p	2.51	2.51

[a] See II for designation of position. [b] Obtained from the value of a_D in PhCOCDCOPh after multiplication by the theoretical factor of 6.514.

plained either by the presence of anisotropic g and hyperfine tensors or a dynamic process involving the out-of-phase modulation of the hfs of slightly inequivalent ortho and ortho' protons due to restricted rotation about the phenyl–carbon bonds. The diminished intensity of the central group of lines is quite pronounced in spectra taken in the early stages of reduction (see Experimental Section for further elaboration). The origin of this interesting phenomenon must await a line shape analysis presently in progress.

Dipivaloylmethide DAR. The reduction of tris(dipivaloylmethido)iron(III) with ethylmagnesium bromide readily afforded a solution showing an intense ESR spectrum. However, no ESR spectrum was obtained when methylmagnesium bromide was employed under the same conditions. The magnitude of the doublet splitting (a_H = 2.79 G) as well as the g factor of 2.0033, which are similar to those of the DAR of other keto enolates, lend support for the assignment of the spectrum in Figure 6 to the DAR of dipivaloylmethide III.

III
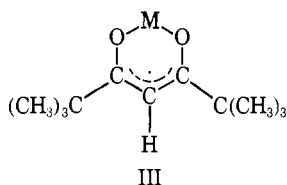
Several sets of satellite lines are also observed in the spectrum. The outer set of satellites appear as doublets (a = 21.47 G) due to ^{13}C splitting, with intensities of about 2% of the parent lines. We tentatively assign this ^{13}C splitting to C(1), although the theoretical line intensity should be 1.1%. In allyl radical, INDO calculations predict a coupling constant of 28 G for C_α.[7] Furthermore, experimental values of 21–26 G have been recently reported for 1,1,3-tri-*tert*-butylallyl radical.[8] If the inner set of satellites in Figure 6 also represent ^{13}C splittings, it is partially obscured by the parent lines. With this interpretation in mind, interpolation affords a doublet splitting
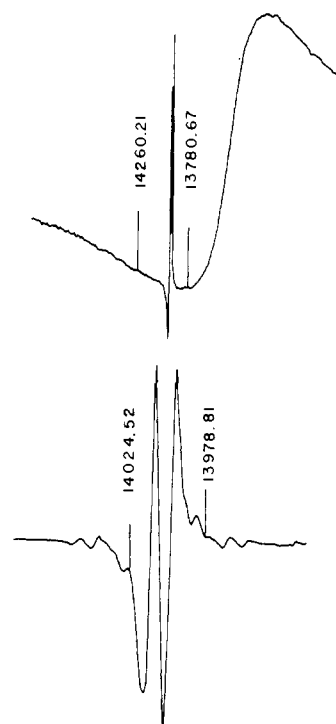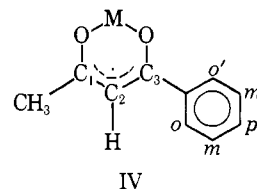

Figure 6. Upper: ESR spectrum obtained from the reduction of tris(dipivaloylmethido)iron(III) with ethylmagnesium bromide in THF. Lower: High resolution portion of the spectrum above centered at ⟨g⟩ = 2.00 showing resolved carbon-13 splittings.

of about 6.5 G, and the greater intensity of the line favors an assignment to C_{CH_3} (theoretical intensity = 3.2%).

Benzoylacetonate DAR. Reduction of a 10^{-3} M THF solution of tris(benzoylacetonate)iron(III) with ethylmagnesium bromide afforded a brown solution showing the ESR spectrum (⟨g⟩ = 2.0033) in Figure 7. The hyperfine coupling constants listed in Table III for benzoylacetonate DAR IV were used in the simulated spectrum. In the computer simulated spectrum, it was necessary to include two coupling constants for the ortho and ortho' protons, which suggests that the phenyl ring lies in the plane formed by the carbon framework. A similar situation

IV

has been described for the acetophenone ketyl radical anion, in which the coupling constants of the ortho protons are in-

Figure 7. Upper: ESR spectrum obtained from the reduction of tris(benzoylacetonato)iron(III) with ethylmagnesium bromide in THF. Lower: Computer simulated spectrum using the hyperfine splittings in Table III.

Table III. Isotropic Proton Hyperfine Coupling Constants of the Dianion Radical of Benzoylacetonate

Position	Hyperfine coupling constant, G
2	2.42
CH_3	7.74
o,o'	3.06, 3.45
m,m'	1.10, 1.10
p	4.13

Table IV. Triplet Spectrum of Dibenzoylmethide DAR Generated by Several Methods in Rigid THF

Method[a]	T, °C	Radical $\langle g \rangle$	Biradical[b] D, G A	B	A/B
dbmH + Na	−180	2.003_2	77	90	1
Fe(dbm)₃ + Na	−161	2.003_0	76	89	4
Fe(dbm)₃ + EtMgBr	−180	2.003_4	None	None	

[a] dbm = dibenzoylmethide. [b] Compare ref 10.

equivalent, the hfs being CH_3, 6.9; o, 4.25; o', 3.7; m, 1.07; m', 0.88; p, 6.60 G.[9]

Reduction of Fluorinated β-Keto Enolate Complexes. The reduction of tris(hexafluoroacetylacetonato)iron(III) with either methyl, ethyl or *tert*-butylmagnesium bromide produced solutions showing broad ESR resonances at $\langle g \rangle$ = 2.08. The spectrum of the DAR of hexafluoroacetylacetonate was not observed. Similarly, the spectrum of the DAR of trifluoroacetylacetonate was not observed in a solution resulting from the reduction of bis(1,1,1-trifluoroacetylacetonato)cobalt(II). Only a broad unresolved resonance centered at $\langle g \rangle$ = 2.17 with H_{pp} = 300 G was obtained. The relatively narrow line width together with the absence of a metallic precipitate suggest that the signal was not due to the ferromagnetic resonance of cobalt metal. We speculate that the signal is due to a cobalt(0) species consistent with the large g factor due to unpaired electron density centered on the metal.

Triplet Spectra of Dianion Radicals. The ESR spectrum of a frozen solution of sodium dibenzoylmethide DAR obtained by the reduction of dbm with a sodium mirror shows absorption peaks at half field (Δm = 2 transitions) due to biradical species.[10] The spectrum at full field consisted of a strong signal at $\langle g \rangle$ = 2.0 together with two sets of signals attributed to triplet species with dipolar (zero field) interaction parameters D of about 80 and 90 G (Table IV). The same triplet spectrum was previously assigned to two dimers of dibenzoylmethide DAR, designated as A and B, respectively, by van Willigen and Weissman.[10] Our comparison of the experimental spectrum with the calculated line shapes suggests the presence of roughly equal amounts of A and B.

The triplet spectrum obtained from the reduction of tris-(dibenzoylmethido)iron(III) with sodium mirror showed the presence of A and B, although in different relative amounts. Only the doublet spectrum was observed when either Fe(dbm)₃ or Co(dbm)₂ was reduced with ethylmagnesium bromide.

ESR Studies of Iron(I) Species. Various iron(III) complexes listed in Table V were reduced with Grignard reagents by the same procedure used for tris(acetylacetonato)iron(III). Structureless ESR signals centered around $\langle g \rangle$ = 2.08 were obtained consistently, and the line widths (H_{pp}) were all less than 230 G except for that derived from iron(III) chloride. The mixtures were initially homogeneous, but precipitation was observed occasionally if the solutions were allowed to stand. No precipitation was observed even for days after tris(dibenzoylmethido)iron(III), Fe(dbm)₃, was reduced.

Reduction of iron(III) chloride using the sodium mirror method produced no ESR signal, and black layers, presumably

Table V. Reduction of Iron(III) Complexes[a]

Iron(III) complex	Method of redn	⟨g⟩	H_{pp}, G
Fe(CH₃COCHCOCH₃)₃	CH₃MgBr	2.08	180
	CH₃CH₂MgBr	2.08	220
	Na	2.08	250
Fe(CH₃COCHCOCH₃)Cl₂	CH₃CH₂MgBr	2.07	250
Fe(PhCOCHCOPh)₃	CH₃CH₂MgBr	2.08	250
	Na	2.11	430
Fe(ᵗBuCOCHCOᵗBu)₃	CH₃CH₂MgBr	2.08	200
	CH₃MgBr	2.07	160
Fe(PhCOCHCOCH₃)₃	CH₃CH₂MgBr	2.09	170
Fe(CF₃COCHCOCF₃)₃	CH₃CH₂MgBr	2.08	190
Fe[O₂CC(CH₃)₃]₃	CH₃MgBr	2.07	220
FeCl₃	CH₃MgBr	2.07	400
	Na	b	b

[a] In THF solution containing approximately 10^{-3} M iron(III) at room temperature. [b] Metallic (iron) particles attached to sodium mirror.

of metallic iron particles, were found to be attached to the sodium mirror. On the other hand, the reduction of Fe(dbm)₃ wth a sodium mirror led initially to a pink diamagnetic solution which had the same optical absorption spectrum as that of bis(dibenzoylmethido)iron(II) reported earlier.[2b] Further contact of the solution with the sodium mirror led to a green solution showing an ESR spectrum consisting of a broad signal centered at ⟨g⟩ = 2.11 and a rather narrow unresolved singlet at 2.0032. The solution finally turned blue and the amplitudes of both resonances diminished markedly. Under these conditions Fe(dbm)₃ was apparently reduced to Fe(II) and then to Fe(I) and finally Fe(0) species.

Discusssion

ESR Spectra of Dianion Radicals from β-Keto Enolates. Dianion radicals of β-keto enolates can be effectively generated for ESR study by the reduction of transition metal complexes (especially those of iron and cobalt) with Grignard reagents. The technique is applicable where other well-known reductive methods such as the use of a sodium mirror and cathodic electrolysis have failed or led to ambiguous results. Thus, well-resolved ESR spectra of the previously unreported dianion radicals of acetylacetonate, dibenzoylmethide, pivaloylmethide, and benzoylacetonide can be obtained under relatively simple experimental conditions.

R,R′ = CH₃,(CH₃)₃C,C₆H₅
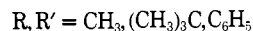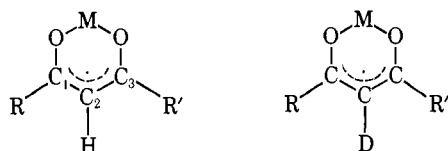
In the ESR spectra of keto enolate DAR's, the small doublet splittings due to the unique proton all lie in the range of 2.4–2.8 G, consistent with a node in the highest occupied molecular orbital at carbon 2. The relatively high acidity of this proton in the free ligand allows it to be exchanged with deuterium under more or less neutral conditions. This ready and specific incorporation of deuterium into the ligand enabled the ESR spectra of the DAR's of β-keto enolates to be assigned unambiguously. Furthermore, monodeuteration of dibenzoylmethide led to considerable simplification and analysis of the complex ESR spectrum of the DAR.

The spin densities at various positions in the DAR's can be computed from the values of the proton hyperfine coupling constants using the McConnell equation ($a_i = Q_\alpha\rho_i$). These values for dibenzoylmethide are compared in Table VI with those previously calculated by the HMO and McLachlan methods.[4]

Table VI. Hyperfine Coupling Constants and Spin Densities for Dibenzoylmethide DAR

| Position[a]	Coupling constant, G	ρ or S[d]	McLachlan[b]	HMO[c]
2	2.51	0.093	−0.056	0
o	2.12	0.078	0.064	0.052
m	0.77	0.028	−0.018	0.009
p	2.51	0.093	0.116	0.085

[a] For assignment see II. [b] Total spin density (S_i), see ref 4. [c] Odd electron density (ρ_i), see ref 4. [d] Absolute value calculated from Q_α = 27 G.

Table VII. Proton Hyperfine Coupling Constants of Acetylacetonate DAR and Substituted Allyl Radicals

X	Y	W	Z	CH₃	H₂	H₁	⟨g⟩	Ref
O	O	CH₃	CH₃	13.00	2.79		2.0032	b
H	H	H	H		4.06	13.92 14.83	2.00254	11
H	H	CH₃	H	16.43	3.85	13.83 14.78	2.00263	12
H	CH₃	H	H	14.01	3.83	14.17 14.94 13.52		13
OH	H	H	H		3.66	13.15 14.23	2.00296	14a
H	H	OH	H		3.16	13.86 13.33	2.00287	15a

[a] These assignments may be interchanged. [b] This work.

In a formal sense, the DAR of acetylacetonate can be considered as a 1,3-dioxy analogue of 1,3-dimethylallyl radical.
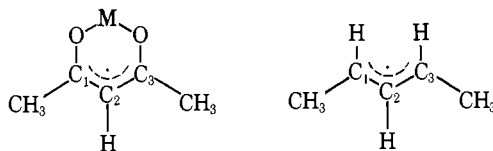
Indeed, the proton hyperfine coupling constants of acetylacetonate DAR are similar to those of a variety of isostructural allylic radicals listed in Table VII.[11-14] The trend for the hfs of hydrogen 2 to decrease and the g factor to increase as oxygen is substituted for hydrogen in allyl radical follows from the greater electronegativity and larger spin orbit coupling constant ($\xi = 151$ cm⁻¹) for oxygen.

Using values of $Q_\alpha = -27$ G for the methine proton and Q_β = 24 G for the methyl protons, we compute that roughly 85% of the unpaired spin density resides on the three allylic carbons of acetylacetonate DAR.

Molecular orbital calculations (see Experimental Section) using the INDO approximation also afford interesting insight into the structure of acetylacetonate DAR. Thus, the hyperfine splittings calculated for the dianion radical itself of acetylacetonate shown below are significantly larger than the experi-

CH₃⎯C...C⎯CH₃ (15.63 G)

(4.97 H)
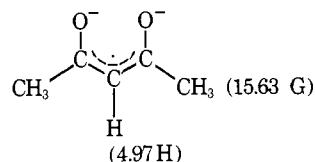
mental values. Moreover, the π spin density on the allyl framework is only 0.32, whereas it is more than 0.5 on the pair of oxygens. On the other hand, neutralization of both negative charges by chelation to a metal ion has the significant effect of lowering the value of the methyl hyperfine splitting to a value remarkably close to the experimental one of 13 G. (In

(5.92 G)
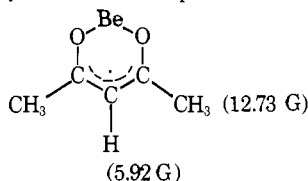
the INDO calculations, beryllium was employed as a first row replacement for magnesium, with which it should be chemically similar.) The fit of the calculated value of the hfs of hydrogen 2 to the experimental splitting of 2.8 G is not quite as good. Interestingly, roughly 60% of the spin density in the chelate is localized in the allylic carbon framework and about 36% on the oxygens. The spin density on the metal in this model is 0.0061, and judging from the small value of its nuclear hyperfine coupling term ($a(^9Be) = 128$ G, compare $a(^{25}Mg) = 119$ G), the splitting would be unresolved. The measurements of the ^{13}C and ^{17}O splittings in an enriched sample (^{17}O, $I = \frac{5}{2}$, 0.004% natural abundance) would doubtlessly help to refine the structure of acetylacetonate DAR.

Structures of Keto Enolate Dianion Radicals from Metal Complexes. Keto enolates exist in solution as metal chelates,[15] and it would certainly be expected that the corresponding *doubly* charged anion radicals also exist in a similar form. We judge from the extant literature that the stability of the DAR's of keto enolates differ, according to the method of generation. These studies have shown that the disappearance of keto enolate anion radicals can occur by apparently first-order as well as second-order processes. Thus, ammonium dibenzoylmethide is reductively cleaved electrochemically to anion radicals of acetophenone and 1-phenyl-1,2-propanedione depending on the solvent (dimethyl sulfoxide or dimethylformamide).[5]

$$PhCOCHCOPh^- \xrightarrow{e} PhCOCH_2^{\cdot-} \xrightarrow[DMF]{} PhCOCOCH_3^{\cdot-} \quad (2)$$

Furthermore, ESR studies following the electrochemical reduction of the cobalt(II) and nickel(II) complexes of acetylacetonate only led to broad unresolved signals due to the formation of ferromagnetic precipitates of cobalt and nickel, respectively.[16] Coupling of β-diketones can also occur during electrochemical reduction, and the observation of the anion radical of benzil during electroreduction of dibenzoylmethane has been attributed to retroaldol cleavage subsequent to the reductive dimerization.[17]

The results of the reduction of sodium β-keto enolates with sodium mirrors are also inconclusive. With the possible exception of 3-phenylacetylacetonate, reduction by this method has afforded ambiguous results.[4] Thus, sodium dibenzoylmethide on reduction with a sodium mirror produced a poorly resolved spectrum having the gneral features of the spectrum obtained electrochemically. The latter has been subsequently shown to be due to 1-phenyl-1,3-propanedione anion radical.[5,18] Sodium acetylacetonate could not be reduced.

We tentatively postulate that the stability of the DAR of keto enolates produced by reduction with Grignard reagent is due to chelation with magnesium. The formation of a stable metal chelate would not only stabilize the ion radical relative to fragmentation (eq 2) but also to dimerization (eq 3). The
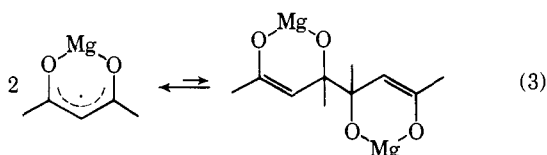
enhanced stability of the magnesium chelate is also consistent with our failure to observe the DAR spectra when iron(III) and cobalt(II) complexes were reduced with only a sodium mirror or methyllithium.

The elegant studies of Dessy and co-workers generally demonstrated that the spin density in metal complexes of anion radicals can be largely localized on the ligand and the charge density on the metal.[19] Thus, the ESR parameters of the bipyridine, phenanthroline, and olefinic ligands in a series of chromium, molybdenum, tungsten, and iron anion radicals are quite similar to those of the uncomplexed species.[20] No hyperfine splitting from the metal was observed. These results are in general accord with our ESR studies of keto enolate DAR's, which indicate high localization of unpaired spin density in an orbital predominantly ligand in character. Thus, the observation of only a single ESR spectrum from all the complexes in Table I (none showing hyperfine splitting to the metal and all having the same isotropic g factors) could indicate either the existence of species with only small interactions with the metal or the conversion of the DAR to a common magnesium chelate.[21] We feel that the latter is more likely, since even nontransition metal complexes of acetylacetonate, such as that of beryllium, also react with Grignard reagent to afford solutions from which the ESR spectrum of the DAR can be obtained. It is interesting to note that the ESR spectrum of acetylacetonate DAR derived from the beryllium complex shows no resolved metal splitting[22] (^9Be with $I = \frac{3}{2}$, 100% natural abundance).

The metal counterion also plays an important role in the monomer–dimer equilibria of DAR in solutions.[23] Indeed, the earlier failure to obtain well-resolved ESR spectra may be associated with the presence of such equilibria which are dependent on the metal.

$$2DAR \rightleftharpoons (DAR)_2$$

For example, the reduction of sodium dibenzoylmethide by sodium mirror in THF has been carried out stepwise to form first the paramagnetic green dianion radical, which showed two distinct absorption bands at λ_{max} 855 and 400, 350 nm.[10] The ESR spectrum of the dianion radical formed in solution under these conditions is broadened and incompletely resolved. We find essentially the same results when tris(dibenzoylmethido)iron(III) is treated with sodium mirror under the same conditions. In both cases, relatively sharp triplet spectra can be obtained in a rigid matrix at -160 °C, showing the presence of two dimers of the DAR (compae Table IV). van Willigen and Weissman[10] assigned the two widely separated bands at 855 and 400 nm in the optical spectrum to dimeric and the monomeric DAR, respectively. The assignment is consistent with the observation of the doublet ESR spectrum in solution for the monomer DAR and the triplet spectrum in the rigid matrix for the dimer.

In contrast, optical and ESR studies of the solution resulting from the reduction of tris(dibenzoylmethido)iron(III) and with Grignard reagent show distinct differences as well as certain similarities from that obtained from sodium mirror reduction. Thus, the absorption spectrum obtained from a solution of Fe(dbm)$_3$ and isopropylmagnesium bromide exhibits a broad band at λ_{max} 708 nm and a doublet band at short wavelengths (λ_{max} 378, 393 nm), shown in Figure 8. The two bands in spectrum b are not associated with the same species, since their behavior differs when various Grignard reagents are employed. Thus, the band shapes and absorption maxima of the high energy band vary with the use of methyl-, isopropyl-, cyclohexyl-, and phenylmagnesium bromides, whereas the band at 700 nm remains unchanged (Table VIII). The latter is similar to the visible spectrum of the blue diamagnetic trianion of dibenzoylmethide (λ_{max} 700 (MTHF),[10] 695 nm (THF)[4]). As seen in Figure 8, no absorption is observed at lower energies
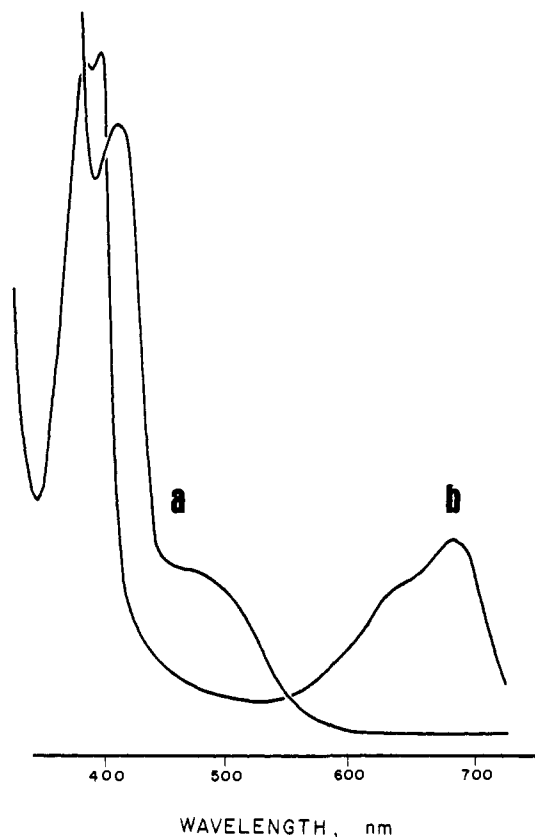
WAVELENGTH, nm

Figure 8. (a) Visible absorption spectrum of 1×10^{-3} M Fe(dbm)$_3$ in 0.7 ml of THF. (b) After addition of 0.2 M isopropylmagnesium bromide in 1.0 ml of THF to (a).

Table VIII. Absorption Spectra of Reduced Iron Species from Fe(dbm)$_3$ and Grignard reagent[a]

| Grignard reagent	Absorption spectrum, nm	
	Band I	Band II
CH$_3$MgBr	360	703, 660 (sh)
(CH$_3$)$_2$CHMgBr	378	708, 660 (sh)
	393	
c-C$_6$H$_{11}$MgBr	379	709, 660 (sh)
	394	
C$_6$H$_5$MgBr	386	706, 660 (sh)

[a] In THF solution. [b] Based on total conversion of Fe(dbm)$_3$.

characteristic for the DAR dimers (λ_{max} 855 nm[10]). The absence of the dimer band in the optical spectrum is in accord with the absence of a triplet ESR spectrum when this solution is frozen to less than -160 °C. The high energy absorption showing a doublet band at 378 and 393 nm in Figure 8 is similar to that from monomeric sodium dibenzoylmethide DAR (λ_{max} 400 nm (unresolved)) observed previously.[10] We conclude from these comparisons that ground state triplets corresponding to dimers of dibenzoylmethide DAR are unimportant when Fe(dbm)$_3$ is reduced by Grignard reagent. Essentially the same results are obtained if Co(dbm)$_2$ is treated under similar conditions. The chelation of the dianion radical with magnesium instead of sodium could account for the differences in the optical and ESR spectra of dibenzoylmethide DAR generated from Fe(dbm)$_3$ by reduction with Grignard reagent or sodium mirror, respectively.
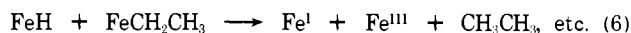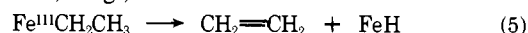
Reduction of Iron(III) Keto Enolates with Grignard Reagent. Various iron(III) complexes can be readily reduced by Grignard reagents. Thus, iron(III) chloride and isopropylmagnesium bromide in the presence of olefins afford reduced iron-olefin complexes. Alkyliron intermediates which de-

compose thermally or photochemically to coordinatively unsaturated iron species via β-hydrogen elimination has been suggested.[2c,24] Grignard reagents are also capable of effecting reduction of metal complexes by electron transfer processes.[25]

Product studies show that reduction of tris(dibenzoylmethido)iron(III) in THF is accompanied by the oxidation of ethylmagnesium bromide to a mixture of ethane and ethylene. The half-reaction for the oxidation of ethylmagnesium bromide

$$CH_3CH_2MgBr$$
$$\longrightarrow CH_3CH_3 + CH_2{=}CH_2 + 2MgBr^+ + 2e \quad (4)$$
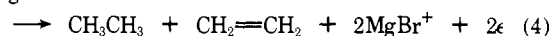
is not consistent with an electron transfer process, since the bimolecular reactions of ethyl radicals so formed should afford approximately six times more butane (by dimerization) than ethane and ethylene (by disproportionation; i.e., $k_{comb}/k_{disp} \simeq 6$ for CH$_3$ĊH$_2$[26]). The singular absence of butane suggests that the reduction of iron(III) proceeds by β elimination of an alkyl derivative,[27] e.g.,

$$Fe^{III}CH_2CH_3 \longrightarrow CH_2{=}CH_2 + FeH \quad (5)$$

$$FeH + FeCH_2CH_3 \longrightarrow Fe^I + Fe^{III} + CH_3CH_3, \text{ etc. } (6)$$

Examination of the reduced iron solution by ESR shows a signal centered at $\langle g \rangle = 2.08$. Bagguley has reported the ferromagnetic resonance centered at $\langle g \rangle = 2.06 \pm 0.02$ from a colloidal suspension of pure metallic iron particles.[28] However, the line widths (700 G) were significantly larger than those listed in Table V. Moreover, the symmetric Lorentzian line shapes we have observed are not in accord with the asymmetric line shapes characteristically obtained for such ferromagnetic resonance. The isotropic g factor of 2.08 for iron(I) species is consistent with those of other paramagnetic iron(I) complexes, such as the red hydridobis(diphenylphosphino)ethaneiron (H Fe(dppe), $\langle g \rangle = 2.085$) reported by Gargano et al.,[29] the various allyl-dicarbonyliron complexes (C$_3$H$_5$Fe(CO)$_2$L, $\langle g \rangle \simeq 2.05$) examined by Muetterties et al.,[30] and the phenyliron macrocycle (C$_6$H$_5$Fe(tetraeneN$_4$), $\langle g \rangle = 2.093$).[30] Low-spin d^7 complexes of Co(II) and Ni(III) are also found with $\langle g \rangle$ in the range of 2.08.[31]

Experimental Section

Materials. Tetrahydrofuran from E. I. DuPont de Nemours Co. was refluxed over calcium hydride and distilled into a storage bottle containing Na–K alloy, then transferred in vacuo as needed. Methyl- and ethylmagnesium bromides, prepared from triply sublimed magnesium in THF, were colorless solutions containing approximately 1 M reagent.[2] Acetylacetone was from Fisher Scientific Co. Dibenzoylmethane was from Eastman Kodak Co. and benzoylacetone from Aldrich Chemical Co.

Iron(III) tris complexes of acetylacetone, dibenzoylmethane, dipivaloylmethane, benzoylacetone, and hexafluoroacetylacetone were prepared earlier[2] and vacuum dried before use. Acetylacetonato complexes of chromium(II), manganese(III), cobalt(II) and (III), nickel(II), and copper(II) were obtained from Shepherd Chemical Co., recrystallized from ethanol, and dried in vacuo at 58 °C before use.

ESR Spectral Measurements. The ESR spectrometer and details of the measurement of the g factors have been described previously.[32] The solutions were prepared in a two-compartment cell attached to the ESR tube. A weighed amount of metal complex was placed in one compartment and the cell attached to a vacuum line through which pure THF was distilled in vacuo. Pure argon was then introduced to bring the apparatus to atmospheric pressure and a solution of Grignard reagent was added via a hypodermic syringe under a flow of argon. The system was sealed and the components then allowed to mix. Optimal concentrations could be obtained by varying the relative amounts of reactants.

The procedure for reductions using a sodium mirror was similar to a previously described method.[6] Preparation of the sodium mirror was accomplished in the following manner. A capillary containing a small piece of sodium metal was sealed in the side arm of an ESR tube. The side arm was constricted in three places between the capillary and the ESR tube. With gentle heating, the sodium metal was sequentially
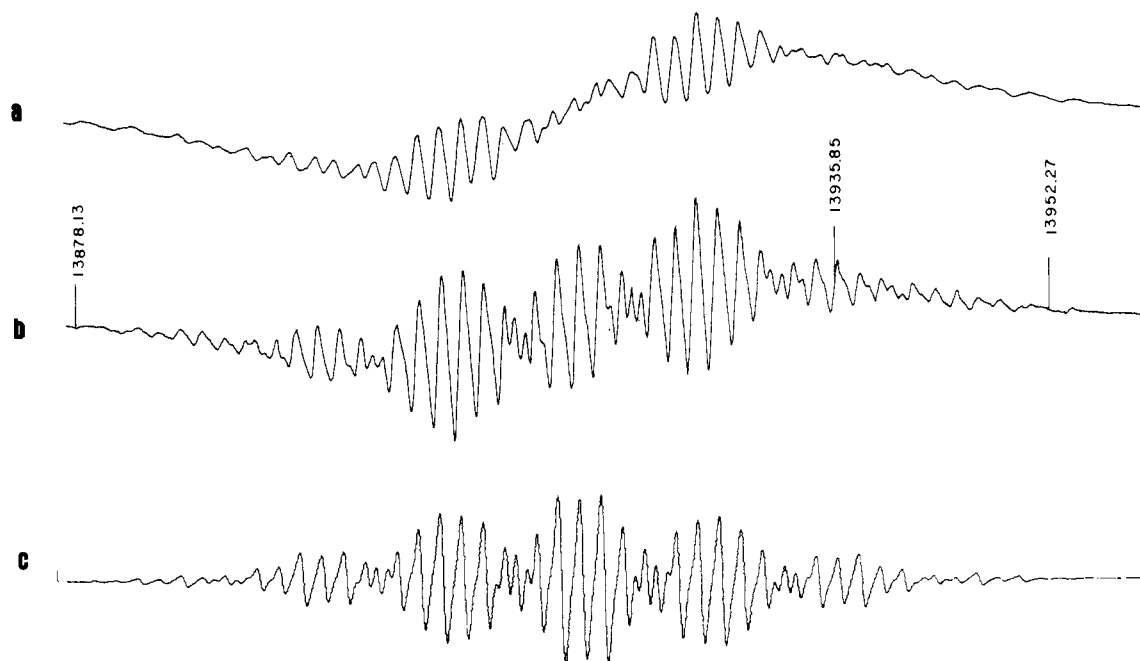
Figure 9. ESR spectra obtained from the reduction of tris(dibenzoylmethido-d_1)iron(III) with ethylmagnesium bromide in THF solution: (a) spectrum after approximately 1 h; (b) spectrum after 24 h; (c) computer simulated spectrum using the hyperfine splittings in Table II. Proton NMR field markers are in kilohertz.

Table IX. Hyperfine Splitting and Spin Densities of Acetylacetonate DAR Calculated by INDO Molecular Orbital Theory
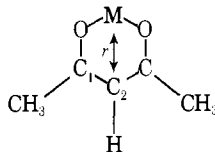
Structure,[a] M	r,[b] Å	Hyperfine splitting, G				Spin density[c]		
		CH_3	H	C_1	C_2	C_1	C_2	O
None[d]		15.6	4.97	−16.5	13.1	0.32	−0.29	0.27
Be	1.82	12.7	5.92	−13.3	16.2	0.44	−0.27	0.18
Be	2.30	0.92	1.67	−1.6	7.5	0.045	−0.003	0.001
Be	2.80	0.65	1.74	−0.59	2.31	−0.003	0.002	−0.007

[a] Using geometry in ref 36. [b] Metal symmetrically placed between oxygen atoms. [c] P_z. [d] Dianion radical.

sublimed in vacuo past each constriction and the tube sealed at the last constriction to isolate a pure sodium mirror. Reduction proceeds upon bringing the solution of the metal complex into contact with the sodium mirror.

Bis(acetylacetonato-d_1)cobalt(II). Acetylacetone (1.8 g) was dissolved in a mixture of 10 g of deuterium oxide (99.9%) and 9 g of tetrahydrofuran. The mixture was refluxed for 5 h and then allowed to stir for 72 h. The solution was then added with vigorous stirring to a solution of cobalt(II) acetate in D_2O. The mass spectrum of bis-(acetylacetonato)cobalt(II) showed principal peaks at m/e (%): 257 (71), 242 (72), 158 (100), and 43 (34), which compares with the deuterio analogue: 259 (69), 258 (4.6), 244 (72), 159 (100), 158 (4.1), and 43 (27). A 97% deuteration of bis(acetylacetonato)cobalt(II) is indicated. Anal. Calcd for $Co(C_5H_6DO_2)_2$: C, 46.34; H(D), 6.24. Found: C, 46.25; H(D), 6.31.

Bis(dibenzoylmethido-d_1)cobalt(II). Dibenzoylmethane (1 g) was dissolved in a mixture of 15 ml of THF and 10 ml of D_2O. The mixture was refluxed for 5 h and stirred at room temperature overnight. Addition of a solution of 0.5 g of cobalt(II) acetate in 5 ml of D_2O with vigorous stirring afforded gold yellow crystals, which were removed by filtration and dried in vacuo. The mass spectrum of the all protio bis(dibenzoylmethido)cobalt(II) has principal peaks in the mass spectrum at m/e (%): 505 (100), 282 (47), 205 (22), 105 (61), and 77 (43), which compares with bis(dibenzoylmethido-d_1)cobalt(II): 507 (100), 505 (< 0.5), 283 (18), 224 (13), 105 (60), and 77 (49). The deuteration of the ligand is 99.5% complete. Anal. Calcd for $Co(C_{15}H_{10}DO_2)_2$: C, 71.01; H(D), 4.76. Found: C, 71.00; H(D), 4.81.

Bis(acetylacetonato)beryllium. A suspension of beryllium hydroxide (1.13 g) in 45 ml of H_2O was treated with 6 N hydrochloric acid dropwise with heating until the solution became clear. The solution was then added to a solution of ammonium acetylacetonate. The latter was prepared from 9 g of acetylacetone in 45 ml of water by adding 6 N ammonium hydroxide until dissolution was complete. The colorless crystals were filtered and dried in vacuo and recrystallized from a mixture of benzene, yielding large, colorless, monoclinic crystals; hexane mp 108–109 °C.[33]

Bis(hexafluoroacetylacetonato)cobalt(II). 1,1,1,5,5,5-Hexafluoropentane-2,4-dione (0.9 g) was dissolved in 5 ml of THF, which was added to a solution of cobalt(II) acetate in 5 ml of water with vigorous stirring. The orange crystals were removed by filtration and dried in air. After crystallization from a mixture of THF and hexane, the crystals were dried in vacuo.

Bis(benzoylacetonato)cobalt(II). Benzoylacetone (0.9 g) in 15 ml THF and cobaltous acetate (0.7 g) dissolved in 10 ml of water were mixed with vigorous stirring. The orange crystals were recrystallized from chloroform to afford pink crystals which were dried in vacuo.[34] Anal. Calcd for $Co(C_{10}H_9O_2)_2$: Co, 15.46; C, 63.0; H, 4.76. Found: C, 62.98; H, 4.68. The mass spectrum showed principal peaks at m/e (%): 381 (100), 366 (41), 220 (50), 105 (52), 77 (34), and 43 (17).

ESR Spectrum of Dibenzoylmethide-d_1 DAR. The ESR spectrum of the DAR of dibenzoylmethide-d_1 undergoes an interesting time-dependent behavior described in the text. The spectrum in Figure 9b consists more or less of seven groups of lines each split further. In Figure 9a the central and penultimate groups of lines are missing. The difference may be attributed either to the existence of two species in

9a and 9b, or a selective broadening of the lines in the spectrum. For the latter, if we assume that the para and the two ortho protons have the same hyperfine splittings, we can treat the system hypothetically as two quartets with $I = \frac{3}{2}$ and $I' = \frac{3}{2}$, each with the intensity ratios of 1:3:3:1 for $m_I = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. Exchange between the two sets of protons is shown by the modulation diagram constructed below according to Freed and Fraenkel[37] in which the selective line broadening is qualitatively accounted for.
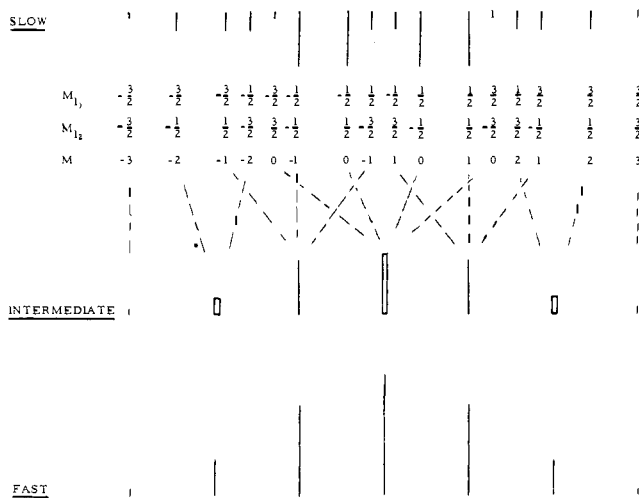
INDO Molecular Orbital Calculations of Acetylacetonate DAR.

The molecular orbital calculations were carried out using the INDO approximation.[35] The geometry and bond lengths of the ligand were taken from a crystallographic structure of tris(acetylacetonato)iron(III) determined by Roof.[36] The values of the hyperfine splittings and π spin densities of acetylacetonate DAR calculated in this manner are listed in Table IX. The ESR parameters are also calculated for the beryllium complex as a function of the location of the metal nucleus. The results show that the hyperfine splittings depend critically on the location of the beryllium in the complex.

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