

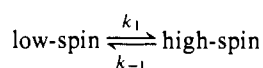
Dynamics of Intersystem Crossing Processes in Solution for Six-Coordinate d^5 , d^6 , and d^7 Spin-Equilibrium Metal Complexes of Iron(III), Iron(II), and Cobalt(II)

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Abstract: Intersystem crossing rates for 14 (low-spin) \rightleftharpoons (high-spin) spin-equilibrium metal complexes of six-coordinate iron(II) ($^1A \rightleftharpoons ^5T$; $\Delta S = 2$), iron(III) ($^2T \rightleftharpoons ^6A$; $\Delta S = 2$), and cobalt(II) ($^2E \rightleftharpoons ^4T$; $\Delta S = 1$) have been investigated in solution by Raman laser temperature-jump kinetics. Measurable first-order rate constants for the forward (k_1) and reverse (k_{-1}) processes range from 4×10^5 to 2×10^7 s⁻¹, with four of the complexes having rate constants too large to measure ($\geq 2 \times 10^7$ s⁻¹) by the technique. The results are interpreted in terms of a model in which the spin multiplicity change is treated as an internal electron-transfer reaction.

A number of first-row transition metal complexes with d^5 , d^6 , and d^7 electronic configurations exhibit magnetic and spectroscopic behavior consistent with a thermal equilibrium between two states of differing spin multiplicity. For complexes in which the coordination number is constant and the donor atom set remains intact this phenomenon has come to be known as a "spin-equilibrium", with the state of lesser multiplicity being the low-spin (ls) state and that of higher multiplicity the high-spin (hs) state. Recent efforts have provided a variety of systems in which the spin equilibrium is present in solution.⁵⁻¹⁰ As a consequence, spin-equilibrium systems can be studied under conditions where perturbing influences from the lattice are minimized, and where the dynamic nature of the spin interconversion process is least likely to be inhibited. In solution it is possible to use rapid perturbation-relaxation kinetics¹¹⁻¹³ to measure directly spin-state lifetimes ($\tau(\text{spin state}) = 1/k$) and intersystem crossing (or spin-interconversion) rate constants.



The fundamental interest in such spin lifetime studies arises from the desire to better understand intersystem crossing phenomena as they pertain to photochemically induced excited states¹⁴ and generally to assess the effect of spin multiplicity changes on electron transfer rates.¹⁵

The transitions between high-spin and low-spin configurations for the group of six-coordinate iron and cobalt complexes studied in this work involve spin multiplicity changes of the type $\Delta S = 2$ [for iron(II) and iron(III)] and $\Delta S = 1$ [for cobalt(II)] so that the inherent differences, if any, between these two types of spin changes can be studied. In developing a consistent view of these transitions as thermally induced internal electron transfer reactions there are a number of fundamental considerations which also need to be evaluated. Included among these is the intrinsic barrier for the transition which arises from the necessity of reorganizing both the inner and the outer coordination spheres about the metal ion prior to the change in the spin state. As in the more conventional redox reactions, such a reorganizational process is expected to accompany these spin transitions because of an increase in the number of electrons in the antibonding e_g^* orbital set in going from the low-spin to the high-spin form. Population of these levels is expected to be accompanied by increases in both the vibrational partition function and the molecular volume

about the high-spin complex relative to that of the low-spin complex. This requires that the nuclear configuration in the activated complex lie somewhere between the equilibrium configurations of the different spin states. These effects will contribute to the activation barrier for the reaction. The molecular contraction-expansion process has been verified in a few cases by variable temperature single-crystal x-ray diffraction studies.^{6,16,17} Some evidence for changes in the vibrational partition function has also been reported. In addition, the rate constants for the spin multiplicity changes may also involve a nonadiabatic factor due to the small interaction energy expected at the crossing point of the potential energy surfaces in these formally spin-forbidden transitions. This will tend to reduce the intersystem crossing rates to an extent greater than predicted by simple thermodynamic considerations.

In this paper we report kinetic data for intersystem crossing in 14 different iron and cobalt spin-equilibrium systems of varying electronic and molecular structure. For the measurements, the stimulated Raman laser temperature-jump technique has been employed which, as reported in earlier publications, is capable of measuring spin relaxation times as short as 30 ns. Some possible correlations between the measured spin lifetimes and the molecular and electronic structure of the complexes are discussed, and the possibility of obtaining activation parameters by the Raman laser temperature-jump method is briefly considered.

Experimental Section

The Raman laser temperature-jump system has been described previously.¹¹ The 1.06- μ radiation from a Q-switched Nd-glass laser (20J/25 ns pulse) is Raman shifted to 1.41 μ (2J/25 ns pulse) in liquid N₂. Water and alcohols absorb at 1.41 μ and these solvents can be directly heated by this technique. Bubble formation in the liquid N₂ is suppressed by saturating the liquid N₂ with helium gas. The temperature jump produces changes in the absorbance of the solution (typically in the region of the intense charge-transfer bands of the low-spin complexes) associated with changes in the temperature-dependent populations of the two spin states. These absorbance changes were monitored using a Xe lamp-monochromator-photomultiplier (RCA 1P28) system. The combined bandwidth of the photomultiplier preamplifier detection system is in excess of 30 MHz. The experimentally observed relaxations were displayed on an oscilloscope and photographed. The first-order relaxation time constant, τ in nanoseconds, was determined from linear log ($I_\infty - I$) vs. time plots, where I is the intensity of the light passing through the solution

Table I. Kinetic Parameters for the (ls) \rightleftharpoons (hs) Intersystem Crossing Processes in Solution as Measured by Laser Raman Temperature-Jump Kinetics

| System | | K_{eq}^a | Experimental conditions Solvent ($T \pm 2^\circ\text{C}$) | τ , ns ^b | k_1 , s ⁻¹ [τ (ls), s] | k_{-1} , s ⁻¹ [τ (hs), s] |
|---------------------------------|---|---|---|--------------------------|--|---|
| (A) R = CH ₃ ; X = H | [Fe(acac ₂ trien)](PF ₆) ^c | 2.26 | Fe(III) (d ⁵ , ² T \rightleftharpoons ⁶ A, $\Delta S = 2$) Acetone (10%)/MeOH (25 °C) | 45 (10) | 1.5×10^7 [6.7 $\times 10^{-8}$] | 6.9×10^6 [1.5 $\times 10^{-7}$] |
| (A) R = Ph; X = H | [Fe(benzac ₂ trien)](PF ₆) | 0.60 | Acetone (10%)/MeOH (20 °C) | ≤ 30 | | |
| (B) X = H | [Fe(Sal ₂ trien)](NO ₃) | 0.34 | H ₂ O (4 °C) | 38 (4) | 6.7×10^6 [1.5 $\times 10^{-7}$] | 2.0×10^7 [5.1 $\times 10^{-8}$] |
| (B) X = H | [Fe(Sal ₂ trien)](NO ₃) | 0.85 | MeOH (4 °C) | 37 (11) | 1.2×10^7 [8.1 $\times 10^{-8}$] | 1.5×10^7 [6.9 $\times 10^{-8}$] |
| (B) X = H | [Fe(Sal ₂ trien)](PF ₆) ^d | 1.03 | MeOH (20 °C) | 35 (8) | 1.5×10^7 [6.7 $\times 10^{-8}$] | 1.4×10^7 [7.1 $\times 10^{-8}$] |
| (B) X = H | [Fe(Sal ₂ trien)](PF ₆) | 0.97 | MeOH (15 °C) | 38 (6) | 1.3×10^7 [7.7 $\times 10^{-8}$] | 1.3×10^7 [7.5 $\times 10^{-8}$] |
| (B) X = H | [Fe(Sal ₂ trien)](PF ₆) ^d | 0.89 | MeOH (4 °C) | 60 (15) | 8.3×10^6 [1.2 $\times 10^{-7}$] | 9.1×10^6 [1.1 $\times 10^{-7}$] |
| (B) X = 5-OCH ₃ | [Fe(5-OCH ₃ Sal ₂ trien)]-(PF ₆) | 3.06 | Acetone (10%)/MeOH (25 °C) | 77 (20) | 1.0×10^7 [1.0 $\times 10^{-7}$] | 3.2×10^6 [3.1 $\times 10^{-7}$] |
| (B) X = 4-OCH ₃ | [Fe(4-OCH ₃ Sal ₂ trien)]-(PF ₆) | 2.98 | Acetone (10%)/MeOH (25 °C) | 44 (20) | 1.7×10^7 [6.0 $\times 10^{-8}$] | 5.6×10^6 [1.8 $\times 10^{-7}$] |
| (B) X = 3-OCH ₃ | [Fe(3-OCH ₃ Sal ₂ trien)]-(PF ₆) | 2.56 | Acetone (10%)/MeOH (25 °C) | 66 (7) | 1.1×10^7 [9.4 $\times 10^{-8}$] | 4.2×10^6 [2.4 $\times 10^{-7}$] |
| (C) X = H | [Fe(Salmeen) ₂](PF ₆) | 1.18 | MeOH (20 °C) | ≤ 30 | | |
| (D) | [Fe(Me ₂ dtc) ₃] | 0.80 | MeOH (20 °C) | ≤ 30 | | |
| | | Fe(II) (d ⁶ , ¹ A \rightleftharpoons ⁵ T, $\Delta S = 2$) | | | | |
| (E) n = 1 | [Fe(6-Mepy)(py) ₂ tren]-(PF ₆) ₂ ^e | 0.05 | MeOH; acetone (10%)/ H ₂ O; (20 °C) | 120 (20) | 4×10^5 [2.5 $\times 10^{-6}$] | 8×10^6 [1.3 $\times 10^{-7}$] |
| (E) n = 2 | [Fe(6-Mepy) ₂ (py)tren]-(PF ₆) ₂ ^e | 0.86 | Acetone (10%)/H ₂ O; acetone (10%)/MeOH (20 °C) | 110 (30) | 4×10^6 [2.5 $\times 10^{-7}$] | 5×10^6 [2 $\times 10^{-7}$] |
| (F) | [Fe(pyImidH) ₃](BPh ₄) ₂ | 1.06 | CH ₃ CN (20%)/MeOH (23 °C) | 48 (8) | 1.1×10^7 [9.1 $\times 10^{-8}$] | 1.0×10^7 [1.0 $\times 10^{-7}$] |
| (F) | [Fe(pyImidH) ₃](BPh ₄) ₂ | 0.59 | CH ₃ CN (20%)/MeOH (-2 °C) | 45 (9) | 8.0×10^6 [1.3 $\times 10^{-7}$] | 1.4×10^7 [5.6 $\times 10^{-8}$] |
| (G) | [iron(hydrotris(1-pyrazolyl)borate) ₂] ^f | 0.47 | MeOH/CH ₂ Cl ₂ (21 °C) | 32 (10) | 1×10^7 [1 $\times 10^{-7}$] | 2×10^7 [5 $\times 10^{-8}$] |
| | | Co(II) (d ⁷ , ² E \rightleftharpoons ⁴ T, $\Delta S = 1$) | | | | |
| (H) R = NH(CH ₃) | [Co(N-R-2,6-pyAld) ₂](PF ₆) ₂ ^g | 0.35 | CH ₃ CN (10%)/MeOH (25 °C) | 83 (23) | 3.2×10^6 [3.1 $\times 10^{-7}$] | 9.1×10^6 [1.1 $\times 10^{-7}$] |
| (I) | [Co(terpy) ₂](PF ₆) ₂ ^f | | MeOH (20 °C) | ≤ 30 | | |

^a Equilibrium constants defined by $K_{eq} = [\text{hs}]/[\text{ls}]$. ^b The error in τ (\pm ns) reflects the range of values obtained from 6-12 different laser experiments on the same sample. ^c Reference 9. ^d Reference 8. ^e Reference 13. ^f Reference 12. ^g Reference 10.

at time t and I_∞ is the limiting value of the intensity at long times. For the small intensity changes measured in these experiments, this is equivalent to plotting the logarithm of the absorbance or concentration changes. Equilibrium constants for the (ls) \rightleftharpoons (hs) processes ($K_{eq} = [\text{hs}]/[\text{ls}]$) were obtained from solution magnetic susceptibility data using the NMR method of Evans.¹⁸ Rate constants, k_1 and k_{-1} , and the lifetimes of the spin states, $\tau(\text{ls}) = (k_1)^{-1}$ and $\tau(\text{hs}) = (k_{-1})^{-1}$, were calculated from the measured values of K_{eq} and τ by solving the equations

$$K_{eq} = k_1/k_{-1} \quad (1)$$

$$\tau^{-1} = k_1 + k_{-1} = [\tau(\text{ls})]^{-1} + [\tau(\text{hs})]^{-1} \quad (2)$$

simultaneously. First-order relaxation times are reported as the average of at least six determinations. Equilibrium constants were found to be solvent and temperature dependent and were determined independently for each set of conditions used.

For these experiments, thermostated cells ($\pm 2^\circ\text{C}$ between -2 and 25°C) with 0.020-0.081-mm path lengths were employed. Solvents were spectroquality grade; water was triply distilled. Synthesis and variable-temperature magnetochemical and electronic spectral data in solution characterizing all the spin-equilibrium compounds studied here have been reported elsewhere: [Fe(II)(hydrotris(1-pyrazolyl)borate)₂];^{5,12} [Fe(II)(6-Mepy)_m(py)_ntren](PF₆)₂;^{6,7,13} [Fe(II)-(pyImidH)₃](BPh₄)₂;^{19a} [Fe(III)(Me₂dtc)₃];^{19b} [Fe(III)(X-Sal₂trien)](Y);⁸ [Fe(III)(acac₂trien)](PF₆);⁹ [Fe(III)(benzac₂trien)]-

(PF₆);⁹ [Fe(III)(Salmeen)₂](PF₆);^{9,19c} [Co(II)(terpy)₂](PF₆)₂;^{19b,20} [Co(II)(N-NH(CH₃)-2,6-pyAld)₂](PF₆)₂.¹⁰

Fundamental limitations on the resolution obtainable in the temperature-jump experiment arise from the finite duration of the heating pulse (~ 25 ns), the magnitude of the enthalpy change (ΔH°) of the spin multiplicity transition, and the differences in the molar absorptivities of the high-spin and low-spin complexes ($\Delta\epsilon$). Although small ΔH° and $\Delta\epsilon$ values decrease the signal to noise ratio, it has been possible to optimize the detection system so that these were not limiting factors and, in practice, only the heating pulse width of ~ 25 ns proved to be a fundamental limitation.

Results

Figure 1 shows schematic representations of all the spin-equilibrium systems studied, along with the abbreviations used to designate the various derivatives. The relaxation times and conditions used are summarized in Table I where they are classified by metal ion and oxidation state. The various experimental conditions were chosen on the basis of the solubility of the complexes and the values of the relaxation times. Mixed solvents enhance the solubility in some cases, while lower temperatures increase the relaxation times which may otherwise be too short to measure at 20-25 °C. Systems for which 30 ns is reported as an upper limit on the lifetime have been deemed unmeasurable.

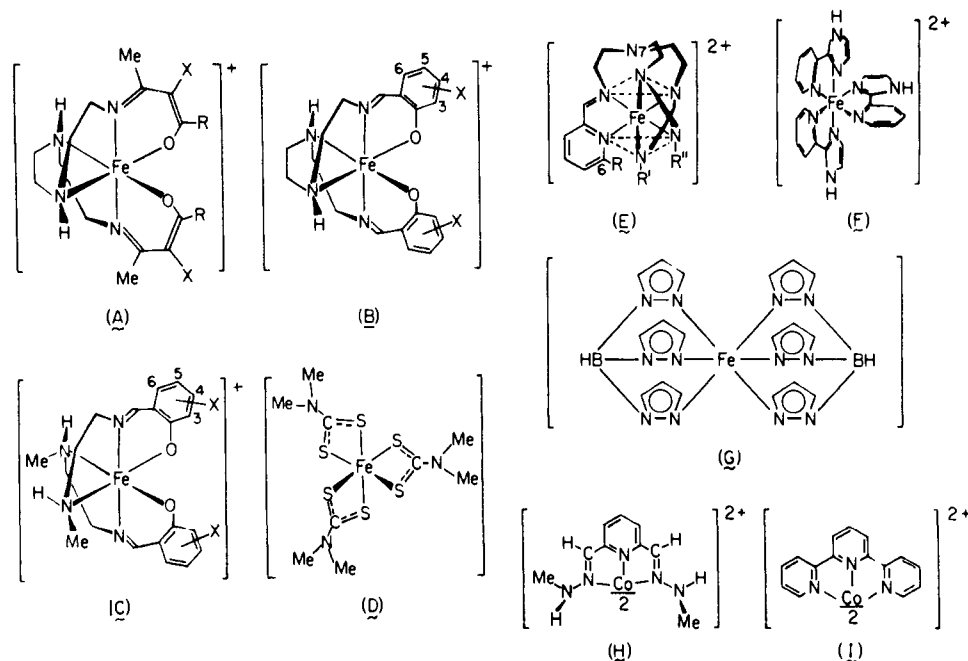


Figure 1. Structures of the iron(III) (d^5), iron(II) (d^6) and cobalt(II) (d^7) spin-equilibrium metal complexes. (A) $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]^+$, $\text{R} = \text{CH}_3$; $\text{X} = \text{H}$. $[\text{Fe}^{\text{III}}(\text{benzac}_2\text{trien})]^+$, $\text{R} = \text{Ph}$; $\text{X} = \text{H}$. (B) $[\text{Fe}^{\text{III}}(\text{X-Sal}_2\text{trien})]^+$, $\text{X} = \text{H}, \text{NO}_2, \text{OCH}_3$. (C) $[\text{Fe}^{\text{III}}(\text{X-Saleen})_2]^+$, $\text{X} = \text{H}, \text{NO}_2, \text{OCH}_3$. (D) $[\text{Fe}^{\text{II}}(\text{Me}_2\text{dtc})_3]$. (E) $[\text{Fe}^{\text{II}}(6\text{-Mepy})_n(\text{py})_m\text{tren}]^{2+}$ ($n = 0, 1, 2, 3$; $m = 3 - n$). (F) $[\text{Fe}^{\text{II}}(\text{pyImidH})_3]^{2+}$. (G) $[\text{Fe}^{\text{II}}(\text{hydrotris}(1\text{-pyrazolyl})\text{borate})_2]$. (H) $[\text{Co}^{\text{II}}(\text{N-NH}(\text{CH}_3)_2\text{-}2,6\text{-pyAld})_2]^{2+}$. (I) $[\text{Co}^{\text{II}}(\text{terpy})_2]^{2+}$.

Before considering the individual results, a few general observations concerning the measurement of spin-state lifetimes by the laser temperature-jump method are in order. The duration of the laser pulse (~ 25 ns) sets a lower limit for measurable optical changes. In order to provide a margin for uncertainties in this figure, relaxation times of less than 30 ns are not considered reliable. When the changes in the absorbance of known spin-equilibrium complexes take place in times ≤ 30 ns there is no assurance that these optical changes are, in fact, due to a spin multiplicity change. An indication that this problem may be of real concern appears in the fact that some spin-invariant complexes (as verified by the variable-temperature magnetic susceptibility studies) do, indeed, show small spectral changes in solution over a large temperature range on a scanning spectrophotometer. In order to investigate this particular problem several of these spin-invariant systems such as E ($n = 0$), which is exclusively low-spin iron(II),¹³ and a derivative of H ($\text{R} = \text{C}(\text{CH}_3)_3$ replacing NHCH_3), which is exclusively high-spin cobalt(II),¹⁰ have been examined at several wavelengths. These complexes showed no sign of a spectral relaxation trace over the relatively small temperature range ($1\text{--}5^\circ\text{C}$) of a single temperature-jump experiment. On the other hand, spin-equilibrium derivatives of E ($n = 1$ and $n = 2$) and compound H did exhibit relaxations on a nanosecond time scale. Thus, the available evidence indicates that the absorbance changes observed in the temperature-jump experiments of the spin-equilibrium systems are due solely to changes in the spin-state populations. For this reason it is likely that the rapid (≤ 30 ns) relaxations, such as those observed for A ($\text{R} = \text{Ph}$; $\text{X} = \text{H}$), C ($\text{X} = \text{H}$), D, and I, are also due to spin interconversions which are simply too rapid to measure with the present laser temperature-jump apparatus. Although unexplored here, it is possible that data analysis techniques based on extensions of the "method of moments" equations²¹ or the simulation technique of Demas and Crosby²² would permit the determination of relaxation times considerably shorter than the 30-ns limitation. In fact, this approach has recently been employed to obtain $\text{fs} \rightleftharpoons \text{ps}$ interconversion rates for the spin-equilibrium protein metmyoglobin hydroxide.²³

Likewise, ultrasonic relaxation techniques²⁴ can, in principle, measure relaxation times down to ~ 5 ns; measurements of this type are presently being made.²⁵

Discussion

Assuming octahedral symmetry for these complexes, the spin-state interconversions studied are of three electronic types: iron(III), d^5 , ${}^2\text{T} \rightleftharpoons {}^6\text{A}$, $\Delta S = 2$; iron(II), d^6 , ${}^1\text{A} \rightleftharpoons {}^5\text{T}$, $\Delta S = 2$; and cobalt(II), d^7 , ${}^2\text{E} \rightleftharpoons {}^4\text{T}$, $\Delta S = 1$. The intersystem crossings in the cobalt(II) complexes are thus "less spin forbidden" than are those in the iron(II) and iron(III) complexes. However, this does not necessarily imply faster intersystem crossing rates for the cobalt(II) systems. Probably a more important electronic factor distinguishing the three systems is the potential for term mixing through spin-orbit coupling. For the iron(II) case, no spin-orbit coupling between the high-spin ${}^5\text{T}$ and low-spin ${}^1\text{A}$ terms can occur. This is true also for the iron(III) high-spin ${}^6\text{A}$ and low-spin ${}^2\text{T}$ terms, but in this case, when conditions for a ${}^2\text{T} \rightleftharpoons {}^6\text{A}$ equilibrium exist, a low-lying ${}^4\text{T}$ state can mix with both the ${}^6\text{A}$ and ${}^2\text{T}$ states separately, thereby providing an indirect mechanism for mixing of the ${}^2\text{T}$ and ${}^6\text{A}$ terms of interest. Involvement of a ${}^4\text{T}$ state in this manner for the tris(dithiocarbamato)iron(III) complexes, such as D, has in fact been suggested as a significant factor in the fast intersystem crossing observed in the solid state ($10^7 < k < 10^{10} \text{ s}^{-1}$) as determined by complementary EPR and Mössbauer studies;²⁶ the tris(monothiocarbamato)iron(III) complexes also appear to behave in the same manner.²⁷ The cobalt(II) compounds differ from the iron(II) and iron(III) complexes in that they possess high-spin ${}^4\text{T}$ and low-spin ${}^2\text{E}$ states which may readily mix through spin-orbit coupling. Thus, on this basis a cobalt(II) complex is expected to undergo more rapid intersystem crossing than an analogous iron(II) or iron(III) complex.

The experimental results in Table I show that the first-order rate constants for intersystem crossing span a fairly wide range with k_1 varying from 4×10^5 to $1.7 \times 10^7 \text{ s}^{-1}$, and k_{-1} from 3.2×10^6 to $2.0 \times 10^7 \text{ s}^{-1}$. The corresponding spin-state lifetime ranges are $\tau(\text{fs})$ 60–2500 ns and $\tau(\text{ps})$ 50–310 ns. There

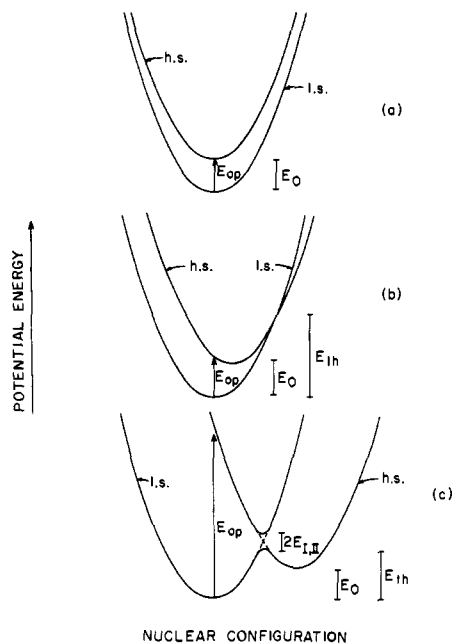


Figure 2. Schematic view of the relative positions of the low-spin and high-spin potential energy surfaces for spin-equilibrium systems in which differing amounts of geometric reorganization accompany the spin-multiplicity change. E_{th} and E_{op} are the thermal and optical energy barriers and E_0 is the zero-point energy difference between the two surfaces.

is, however, no obvious correlation with either metal ion or oxidation state. This result is particularly interesting since on the basis of the above electronic arguments the cobalt(II) complexes are expected to undergo more rapid spin-state interconversion than the iron systems. While this may be the case for $[\text{Co}(\text{terpy})_2]^{2+}$ (I),²⁰ it is not true for the electronically and structurally related $[\text{Co}(N\text{-NH}(\text{CH}_3)\text{-2,6-pyAld})_2]^{2+}$ (H).¹⁰ The intersystem crossing rate for the latter cation is among the slowest listed in Table I. Furthermore, the three iron(II) compounds E, F, and G also provide a dilemma in that, despite their electronic similarity^{5,6,28} as determined by solid state variable-temperature magnetic and Mössbauer studies, their intersystem crossing rates differ greatly (i.e., $k_1 = 4 \times 10^5 \text{ s}^{-1}$ for E ($n = 1$) vs. $k_1 = 1.3 \times 10^7 \text{ s}^{-1}$ for F and $k_1 = 1 \times 10^7 \text{ s}^{-1}$ for G). The observation that both relatively "fast" and "slow" processes can occur within each of the d^5 , d^6 , and d^7 subsets strongly suggests that *nonelectronic* factors can also be significant in determining the intersystem crossing rates.

A spin-state change for a 3d transition metal complex is known to be accompanied by a sizable coordination sphere reorganization in which (metal)-(donor atom) bond distances may change by more than 0.1 Å. For octahedral species, the high-spin form invariably possesses longer (metal)-(donor atom) distances than the low-spin form owing to greater occupancy of the formally antibonding e_g^* orbital set. The degree of occupancy of the nonbonding or slightly bonding t_{2g} set is expected to be of less significance in such structural considerations. For spin-equilibrium cobalt(II) complexes the orbital population fluctuation ($t_{2g}^6 e_g^*(ls) \rightleftharpoons t_{2g}^5 e_g^*2(ls)$) is only half that for the iron(II) ($t_{2g}^6(ls) \rightleftharpoons t_{2g}^4 e_g^*2(ls)$) and iron(III) ($t_{2g}^5(ls) \rightleftharpoons t_{2g}^3 e_g^*2(ls)$) complexes. On this basis cobalt complexes are expected to exhibit somewhat smaller bond distance changes upon spin conversion.

The bond distance changes can be described in terms of the motion of the system on a potential energy surface and the spin-state change can be regarded as a transition from one potential energy surface to another (Figure 2). Thus, each spin state can be represented by a surface with a minimum corresponding to the stable nuclear configuration of the complex

in that spin state. If the surfaces describing the two spin states do not intersect (curve 2a) then it is necessary to treat the spin change as an "ordinary" electronic transition by using, for example, a radiationless transition formalism. On the other hand, if the two potential energy surfaces do intersect and there is splitting into an upper and a lower surface at the intersection (curve 2c), then the spin change can be described in terms of the motion of the system on a single (lower) potential energy surface. Curve 2b illustrates an intermediate situation. The position of the crossing point depends on the relative positions of the minima in the two surfaces. The two spin states shown in 2a have very similar bond distances and angles and thus the minima occur at the same nuclear configuration whereas the spin states described by 2c have relatively different structures and thus the minima in their potential energy surfaces occur at different nuclear configurations.

In terms of absolute rate theory, the rate constant for the spin change in systems in which the potential energy surfaces intersect as in 2c is given by

$$k_e = p \nu_n \exp(-\Delta G^\ddagger/RT) \quad (3a)$$

$$= p \nu_n [\exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)] \quad (3b)$$

where p is the probability of the system remaining on the lower potential energy surface on passing through the intersection region, ν_n is a nuclear frequency factor, and ΔG^\ddagger is the activation energy required to reach the intersection region. The value of p can be estimated from the Landau-Zener formula:

$$p \approx \frac{4\pi^2 E_{I,II}^2}{h\nu |s_I - s_{II}|} \quad (4)$$

In eq 4 ν is the velocity with which the point representing the system moves through the intersection region, s_I and s_{II} are the slopes of the zero-order surfaces at the intersection, and $E_{I,II}$ is the interaction energy. The value of $E_{I,II}$ depends on the multiplicity change for the transition, spin-orbit coupling, orbital overlap, and other factors. For interaction energies on the order of 10 wavenumbers, with $\nu \sim 3 \times 10^4 \text{ cm s}^{-1}$ and $|s_I| = |s_{II}| = 50 \times 10^8 \text{ kcal mol}^{-1} \text{ cm}^{-1}$,²⁹ the value of p is calculated to be $\sim 10^{-3}$. Small interaction energies of this magnitude appear to be reasonable for the spin-forbidden processes under discussion.¹²

The activation energy is the energy required to change the nuclear configuration of the more stable spin state to the configuration appropriate to the intersection region. For harmonic distortions, this energy should be proportional to $(\Delta r_s)^2$, where Δr_s is the difference in the equilibrium bond distances of the two spin states. Estimates of the magnitude of the change in the (metal)-(donor atom) distances in some systems are available. From an assortment of data on a series of iron, cobalt, and ruthenium complexes Stynes and Ibers³⁰ have estimated that the change in bond distance associated with a change in spin state (Δr_s) is $\sim 0.13 \text{ Å}$; the bond distance change associated with a change in oxidation state (+2 vs. +3; Δr_c) is $\sim 0.04 \text{ Å}$. These estimates of Δr appear to be in agreement with the more extensive data collection of Hair and Beattie,³¹ although these authors point out that Δr_c will, in general, depend on the nature of the ligands. A more direct measure of Δr_s is available from the single-crystal data on spin-equilibrium complexes collected in Table II. For the $[\text{Fe}(\text{III})(\text{dte})_3]$ complexes $\Delta r_s \sim 0.11\text{--}0.13 \text{ Å}$ can be estimated from the data in ref 17. A crystal structure for the $[\text{iron}(\text{II})(\text{hydrotris}(1\text{-pyrazolyl})\text{borate})_2]$ (G) is not known; however, the structure of the high-spin cobalt(II) analogue has been determined. From the reported (cobalt)-(nitrogen) distances (2.12 Å) and a typical low-spin (iron)-(nitrogen) distance of 1.95–1.97 Å, Δr_s for the iron(II) complex is estimated to be 0.15–0.17 Å.³² A temperature-dependent difference in the average (iron)-

Table II. Magnetic Moments and Average Metal-Ligand Bond Distances

| | μ_B | $\langle \text{Fe-L} \rangle, \text{ \AA}$ |
|--|------------------|--|
| Iron(III) Complexes | | |
| $[\text{Fe}^{\text{III}}(t\text{-Bu}_2\text{dtc})_3]$ | 5.3 | 2.42 ^a |
| $[\text{Fe}^{\text{III}}(\text{pyrdtc})_3]$ | 5.9 | 2.406 ^a |
| $[\text{Fe}^{\text{III}}(\text{Et}_2\text{dtc})_3]$ | 2.2 | 2.306 ^a |
| Iron(II) Complexes | | |
| $[\text{Fe}^{\text{II}}(6\text{-Mepy})_3\text{tren}]^{2+}$ | 5.0 (300 K) | 2.21 ^b |
| $[\text{Fe}^{\text{II}}(\text{pyrazolylborate})_2]$ | 5.2 ^f | 2.12 ^c |
| $[\text{Fe}^{\text{II}}(6\text{-Mepy})_3\text{tren}]^{2+}$ | 2.0 (205 K) | 2.09 ^b |
| $[\text{Fe}^{\text{II}}(\text{py})_3\text{tren}]^{2+}$ | 0.5 | 1.95 ^d |
| $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ | 0.0 | 1.97 ^e |

^a Reference 17. ^b Reference 6. ^c Taken from the high-spin structure of [cobalt(II)(pyrazolylborate)₂], ref 32. ^d C. Mealli and E. C. Lingafelter, *Chem. Commun.*, 885 (1970). ^e A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, **12**, 1641 (1973). ^f Reference 5.

(nitrogen) distances of 0.12 Å for the $[\text{Fe}^{\text{II}}(6\text{Mepy})_3\text{tren}]^{2+}$ cation ($E, n = 3$) is suggested by the data in Table II. This probably represents a lower limit on Δr_s since intraligand steric interaction plays a significant role in the series of complexes of which this is a member.^{6,7} For the complexes in this series which exhibit a spin-equilibrium in solution ($E, n = 1$ and 2) the lack of symmetry in the substituent pattern provides an added complication. Nevertheless, the range for Δr_s seems to be fairly well established by the available data.

A qualitative estimate of the inner-sphere reorganization energy can be made using the equation³⁰

$$E_r = 6 \left(\frac{k_h + k_l}{2} \right) \left(\frac{\Delta r_s}{2} \right)^2 \quad (5)$$

The limitations of this equation have been discussed.³⁰ For values of Δr_s in the range 0.11–0.17 Å and with typical values for the sum of the high-spin and low-spin force constants ($k_h + k_l$) in the range 1.5×10^5 to 2×10^5 dyn cm⁻¹, the reorganization energy E_r is calculated to be 2.0–6.2 kcal mol⁻¹. This range is consistent with the range of ΔH° values listed in Table III. Inner-sphere reorganization appears, therefore, to provide the dominant enthalpic term in the spin-equilibrium process. On the basis of this evidence alone it is not necessarily safe to conclude that the larger geometric differences always result in slower spin multiplicity changes. Other nonenthalpic factors may also be important. However, over a relatively large range of Δr_s a trend toward decreasing rates with increasing Δr_s ought to be observable. Obviously, extensive structural

information for the other compounds in Figure 1 is desirable and a program to obtain these data has been initiated.³³

From the preceding discussion a consistent model of the spin-equilibrium systems constructed on the basis of an internal electron-transfer reaction (eq 3 and 4 and Figure 2c) appears to be quite reasonable. Taking the frequency (ν_n) as 10^{13} s⁻¹, $p = 10^{-3}$, and $\Delta G_1^\ddagger \sim 5$ kcal mol⁻¹, the rate constant $k_e = k_1$ is estimated to be 2×10^6 s⁻¹. This falls within the range of values observed. A value for $E_{I,II}$ of 10 cm⁻¹ may therefore be considered as "typical" in systems such as these.

Additional quantitative information about these systems can be obtained from this model if it is assumed that the activated complex for the low-spin to high-spin conversion process resembles the high-spin product. Under these conditions eq 6 applies.³⁴

$$\Delta H_1^\ddagger \approx \Delta H^\circ \quad (6a)$$

$$\Delta S_1^\ddagger = \Delta S^\circ - R \ln \left[\frac{(2S+1)_{\text{hs}}}{(2S+1)_{\text{ls}}} \right] \quad (6b)$$

Calculated values of ΔG_1^\ddagger based on eq 6 and $\Delta G_1^\ddagger = \Delta H_1^\ddagger - T\Delta S_1^\ddagger$ are listed in Table III. The negative values for ΔG_1^\ddagger in a few cases probably represent a breakdown in the assumption implicit in eq 6a. It appears that the discrepancies introduced by this assumption could be as large as 1–2 kcal mol⁻¹. Substitution of ΔG_1^\ddagger in eq 3a yields the values of p listed in the last column of Table III. If ΔG_1^\ddagger is assumed to be 1.0 kcal mol⁻¹ larger than the calculated values, p will increase by about a factor of 5. To the extent that $\Delta H_1^\ddagger \geq \Delta H^\circ$, a value of $p \geq 10^{-6}$ represents a lower limit on p . This implies that $E_{I,II} \geq 0.1$ cm⁻¹. Given the uncertainties inherent in these calculations and in the application of eq 6a it appears that for all of these systems $0.1 \leq E_{I,II} \leq 10$ cm⁻¹ and $10^{-6} \leq p \leq 10^{-3}$ can be taken as representative of these parameters.

Of the compounds examined, and relaxation time for $[\text{Fe}(\text{Sal}_2\text{trien})](\text{PF}_6)$ in methanol showed the largest temperature dependence. In spite of the experimental uncertainty in the measurements, which arises mainly from the small accessible temperature range on the present apparatus and a low recorded signal/noise ratio, a qualitative estimation of activation parameters has been attempted from an Eyring plot of the 4, 15, and 20 °C data. From this plot ΔH_1^\ddagger and $R \ln p + \Delta S_1^\ddagger$ have been estimated to be 5.2 kcal mol⁻¹ and -8.2 cal deg⁻¹ mol⁻¹, respectively. This is in good agreement with the above estimates. As anticipated, ΔH_1^\ddagger and ΔH° are not very different and the estimated values suggest that $\Delta H^\ddagger - \Delta H^\circ \approx 1$ kcal mol⁻¹. From eq 6b $\Delta S_1^\ddagger = 11$ cal deg⁻¹ mol⁻¹, and

Table III. Thermodynamic Parameters and Forward Rate Constants, (ls) → (hs)

| | ΔH° , kcal mol ⁻¹ | ΔS° , cal deg ⁻¹ mol ⁻¹ | k_1 , s ⁻¹ | ΔG^\ddagger , ^a kcal mol ⁻¹ | p ^b |
|---------------------------------|--|---|----------------------------|--|---------------------|
| (A) R = CH ₃ ; X = H | 3.1 | 12 | 1.5×10^7 | 0.1 | 2×10^{-6} |
| (A) R = Ph; X = H | 1.3 | 3 | Fast | 1.0 | $>1 \times 10^{-5}$ |
| (B) X = H | 3.8 | 13 | 1.5×10^7 | 0.6 | 4×10^{-6} |
| (B) X = 5-OCH ₃ | 4.3 | 17 | 1.0×10^7 | 0.0 | 1×10^{-6} |
| (B) X = 4-OCH ₃ | 5.3 | 22 | 1.7×10^7 | -0.6 | 6×10^{-7} |
| (B) X = 3-OCH ₃ | 3.5 | 15 | 1.1×10^7 | -0.2 | 8×10^{-7} |
| (C) X = H | 3.8 | 13 | Fast | 0.6 | $>6 \times 10^{-6}$ |
| (D) | 2.0 | 4 | Fast | 1.4 | $>2 \times 10^{-5}$ |
| (E) $n = 1$ | 4.6 | 10 | 4×10^5 | 2.2 | 2×10^{-6} |
| (E) $n = 2$ | 2.8 | 8 | 4×10^6 | 0.9 | 2×10^{-6} |
| (F) | 3.9 | 14 | 1.1×10^7 | 0.8 | 5×10^{-6} |
| (G) | 3.8 | 11 | 1×10^7 | 1.1 | 6×10^{-6} |
| (H) | 3.3 | 9 | 3.2×10^6 | 1.3 | 3×10^{-6} |
| (I) | | | Fast | | |

^a Estimates based on eq 6. Negative values probably result from a breakdown of the assumptions inherent in eq 5a and may imply that ΔH^\ddagger is 1–2 kcal mol⁻¹ larger than ΔH° . ^b Estimates based on the tabulated values of ΔG^\ddagger using eq 3. These values increase by a factor of 5 if $\Delta H^\ddagger - \Delta H^\circ = 1$ kcal mol⁻¹. A value of $k_1 = 2 \times 10^7$ s⁻¹ was assumed in the calculation of p in the cases where only a lower limit is reported.

p is then calculated from either eq 3b or the intercept of the Eyring plot to be $\sim 5 \times 10^{-5}$.

Other interactions, not considered in detail here, may cause deviations from eq 6a and also affect the rates of the spin multiplicity changes in other ways. *Intraligand* steric repulsions between methyl groups and adjacent pyridine rings are known to be of importance in producing the spin-equilibrium phenomenon within the $[\text{Fe}(6\text{-Mepy})_m(\text{py})_n\text{tren}](\text{PF}_6)_2$ series (E).^{6,7} By contrast, crystal structures for several $[\text{Fe}(\text{R}_2\text{dtc})_3]$ complexes (like D)¹⁷ and the Co(II) analogue of [iron(hydrotris(1-pyrazolyl)borate)₂] (G)³² indicate that *intramolecular* steric interactions between ligands are not of much significance in determining their characteristic spin state behavior. Thus, the comparatively long spin-state lifetimes in E as compared, for example, to D, F, and G may reflect the methyl group-pyridine ring nonbonding steric interactions within the hexadentate ligand if such interactions restrict the required coordination sphere reorganization.¹³ Furthermore, if these interactions result in unusually long Fe-N bond distances in the high-spin form (as they apparently do for the $n = 3$ derivative of E with Fe-N_{py} = 2.28 Å), the required geometry change for $h_s \rightarrow l_s$ conversion could also be unusually large, leading to slow $h_s \rightarrow l_s$ conversion rates. Similar arguments may also apply to the Co(II) complexes. Space-filling molecular models indicate that the only other complex in Figure 1 in which steric considerations play a significant role in the spin-equilibrium properties and intersystem crossing kinetics ($\tau = 83$ ns) is the $[\text{Co}(\text{N-R-2,6-pyAld})_2]^{2+}$ species (H, R = NHCH₃). From models, significant *intramolecular* interactions in these bis chelates are predicted to occur between the R groups of one pyridinaldimine ligand and the pyridine π network of the second ligand.¹⁰ An x-ray structure for the structurally and electronically related $[\text{Co}(\text{terpy})_2]^{2+}$ cation (I)³⁵ shows no such steric problem in accommodating the two terpyridyl ligands and a much shorter spin relaxation time ($\tau \leq 30$ ns) is observed.

In the absence of predominating steric effects, mechanical restrictions to fluctuations in the coordination sphere could also depend on other structural considerations. Investigation of these factors is best undertaken for systems which are electronically similar but free of steric interactions which could mask a more subtle effect. For this reason the $[\text{Fe}(\text{X-Salmeen})_2]^+$ series of complexes (C) was synthesized and the $^2\text{T} \rightleftharpoons ^6\text{A}$ processes were characterized and studied in the solution state. As seen in Figure 1, the parent $[\text{Fe}(\text{Salmeen})_2]^+$ (C) and $[\text{Fe}(\text{Sal}_2\text{trien})]^+$ (B) complexes are structurally similar, having the same donor atom set, but the former lacks the ethylenediamine chelate ring of the latter. In solution the variable temperature magnetic and electronic spectral properties for the two $^2\text{T} \rightleftharpoons ^6\text{A}$ spin equilibria are essentially indistinguishable,¹⁹ and yet the intersystem crossing kinetics are measurable only in the $[\text{Fe}(\text{Sal}_2\text{trien})]^+$ case. Since the two complexes appear identical electronically, and differ only in their bis(tridentate) vs. hexadentate ligand structures, it is tempting to rationalize the intersystem crossing disparity in terms of this structural feature. The more flexible tridentate ligand system could conceivably permit greater mechanical latitude, and therefore present less structural constraint to the coordination sphere reorganization process.

Within the $[\text{Fe}(\text{X-Sal}_2\text{trien})](\text{Y})$ series (B), spin lifetime measurements were made as a function of the X-group substituent, counterion Y, solvent, and temperature. The major substituent difference appeared in the measured relaxation time, τ . Owing to variations in solution magnetic behavior, and thus in K_{eq} , the calculated lifetimes are not significantly altered upon changing X = H for X = OCH₃, with $\tau(l_s)$ ranging only from 6.7×10^{-8} to 1.0×10^{-7} s for this substitution. Changing Y = PF₆⁻ to Y = NO₃⁻ for $[\text{Fe}(\text{Sal}_2\text{trien})](\text{Y})$ also produces little, if any, difference in the measured relaxation times as seen

from their 4 °C methanol data in Table I. Similarly, comparison of the 4 °C data for the nitrate salt in methanol and water shows no significant solvent effect. The lack of a solvent effect has also been reported for derivatives of E in methanol, water, and various water-acetone and methanol-acetone mixtures.¹³ There is perhaps some evidence for a contribution from a concentration-dependent relaxation pathway. The lifetimes reported in Table I for $[\text{Fe}(\text{Sal}_2\text{trien})]^+$ ($\tau = 30\text{--}40$ ns) were obtained at $2\text{--}5 \times 10^{-4}$ M complex concentration.⁹ Measurements performed at higher complex concentrations ($4\text{--}5 \times 10^{-3}$ M) gave $\tau = 10\text{--}20$ ns (using a method of moments analysis based on the technique of Demas and Crosby²²). The concentration dependence, although small, probably lies outside the experimental error of the measurements and suggests that ion association or some type of (long-range)³⁶ interaction might become important at high concentrations in certain systems. On the other hand, the lifetimes of the spin states of the [iron(II)(pyrazolylborate)₂] complex¹² were found to be independent of complex concentration in the range $1\text{--}6 \times 10^{-3}$ M.

The results on all of the systems studied are consistent with the proposed model in which the spin multiplicity change is treated as an intramolecular electron transfer reaction dominated by inner-sphere effects. No obvious discrepancies which might have been expected on the basis of either orbital occupation or spin-orbit coupling differences among the metal ions studied have been observed. While these effects may simply be too subtle to be observed with the available data, it is interesting to note that the calculated values of p listed in Table III cover a range of less than two orders of magnitude. Deviations from eq 6a may expand this range slightly. Considerable enhancement of the rate constants can be anticipated as p approaches 1; however, this will require interaction energies on the order of several hundred wavenumbers. The spin-forbidden nature of the spin multiplicity changes appears to be consistent with the present estimates of the transition probabilities and no significant increases in the interaction energies are suggested by any of the results presented here.

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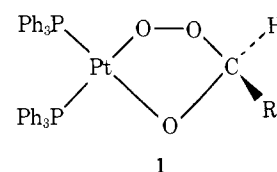
A Kinetic and Mechanistic Study of the Formation of Iridium(III) Ozonide Complexes by the Insertion of Hexafluoroacetone into Complexes IrX(CO)L₂O₂ (X = Halogen, L = Substituted Phosphine or Arsine)

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Abstract: Synthetic and kinetic studies on the formation of iridium(III)ozonide complexes from the addition reaction of compounds IrX(CO)L₂O₂ with hexafluoroacetone are reported. Complexes IrX[O₃C(CF₃)₂](CO)L₂ (L = PPh₃; X = Cl, Br, I; L = AsPh₃, PMePh₂, P(*p*-tolyl)₃, P(*p*-anisyl)₃; X = Cl) have been characterized. The reaction follows the rate law rate = $k[\text{IrX}(\text{CO})\text{L}_2\text{O}_2][\text{CF}_3\text{COCF}_3]$. For L = PPh₃, the rate of reaction follows the sequence for X of Cl > Br > I. For the compound with X = Cl, the relative rates for changing L are AsPh₃ ~ PMePh₂ > PPh₃. First-order rate constants with L = PPh₃ and X = Cl, Br, I are reported using benzene, acetonitrile, and 3-pentanone solvent systems. For the case of the compound IrCl(CO)(PPh₃)₂O₂ the rate is not diminished by the presence of added chloride ion or triphenylphosphine. The results are interpreted on the basis of a mechanism involving direct electrophilic attack of the hexafluoroacetone on the coordinated oxygen molecule to give the iridium(III) ozonide product via an ionic transition state.

Recently we have found that the hexametallal cluster compound Rh₆(CO)₁₆ can be used as a homogeneous catalyst for the oxidation of carbon monoxide to carbon dioxide and also of ketones to carboxylic acids.¹ Subsequently we have found that this catalytic oxidation of ketones can also be effected with the complexes Pt(PPh₃)₂O₂ and IrCl(CO)-(PPh₃)₂.² It was concluded in this study that the catalytic oxidation is a free-radical autoxidation process. In this metal-catalyzed reaction carbon-carbon bond cleavage occurs and a mixture of acids can be formed. While this study was in progress, other workers reported the surprising result that these platinum and iridium complexes were homogeneous catalysts for the oxidation of aldehydes to carboxylic acids by a non-free-radical mechanism.³ These authors made the tentative suggestion that the intermediate in this oxidation reaction was a metalloozonide type complex **1**, previously obtained by treating the compound Pt(PPh₃)₂O₂ with aldehydes. Similar type complexes have also been obtained from treating this platinum oxygen compound with a range of ketones^{4,5,6} and



diketones.⁷ A mechanism for this reaction has been proposed involving initial coordination of the aldehyde or ketone to the coordinately unsaturated complex Pt(PPh₃)₂O₂, followed by insertion into the metal-oxygen bond to form the platinum-ozonide product. Such a proposal is interesting in view of our observation of a similar catalytic reactivity of both IrCl(CO)-(PPh₃)₂O₂ and Pt(PPh₃)₂O₂, since such a pathway is not feasible for the coordinately saturated iridium complex. It is therefore of interest to us to investigate whether the complex IrCl(CO)(PPh₃)₂O₂ will react with aldehydes or ketones to form an iridium(III)-ozonide insertion product of the type obtained with the platinum complex. We have found that such