

free-radical derivative of a carcinogen, benzo[*a*]pyrene, will be reported elsewhere.

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A Stopped-Flow Pulse Fourier Transform Nuclear Magnetic Resonance Investigation of the Rates of Chlorination of Metal Acetylacetonates by *N*-Chlorosuccinimide

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Abstract: The rates of chlorination by *N*-chlorosuccinimide at the C3 position of pentane-2,4-dionate ion (acacH⁻) chelated to Co^{III}, Rh^{III}, Ir^{III}, Al^{III}, and Ga^{III} (M^{III}), in [M^{III}(acacH)₃] and in [Be(acacH)₂], have been measured in a range of solvents at 297 K by stopped-flow pulse FT ¹H NMR. The solvent dependence of the rates and the absence of free radicals in most cases, and of hydrogen isotope effects in the reaction of [Co^{III}(acacD)₃], support an S_E2 mechanism. However, CIDNP-enhanced resonances from intermediates indicate a minor free-radical pathway for the chlorination of the Co^{III} complex in chloroform. The S_E2 reaction rates are not strongly dependent upon which trivalent metal ion is chelated, although the rate for the Be^{II} complex is substantially less than for most of the trivalent metal complexes. The rates can all be rationalized in terms of ligand binding energies and solvent accessibility of the complexes. Substitution by Cl and NO₂ groups (X) at the C3 position of one of the other chelate rings in [M(acacX)₂(acacH)] or [M(acacX)(acacH)₂] slows the chlorination rates of the remaining unsubstituted ligands by factors of between 2 and 12, in a manner analogous to substituent effects in electrophilic aromatic substitution. The presence of a methyl group at the C3 position, however, leads to chlorination at the 3-methylpentane-2,4-dionate ring rather than at the unmethylated pentane-2,4-dionate rings, followed by other side reactions. The corresponding bromination rates, using *N*-bromosuccinimide, are at least 10⁶ times as fast as the rates of chlorination, and are too fast to measure by stopped-flow FT NMR even for the least reactive complex investigated, [Rh(acacCl)₂(acacH)].

The mechanisms of the reactions of the coordinated pentane-2,4-dionate ligands in [M(acacH)₃] (M = trivalent metal ion; [acacX]⁻ = CH₃COCXC(O⁻)CH₃) have not been extensively studied, although the pseudoaromatic character of

the six-membered chelate rings is well documented.¹ Replacement of the methine protons by a wide range of substituents (X) to give [M(acacX)₃] can be achieved usually by the use of electrophilic reagents such as *N*-halogenosuccinimide

Table I. Rates of Chlorination of (Pentane-2,4-dionato)metal Complexes by *N*-Chlorosuccinimide in CDCl₃ at 297 K

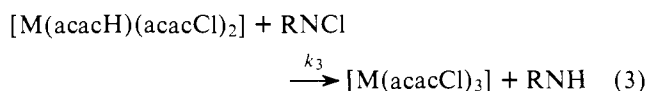
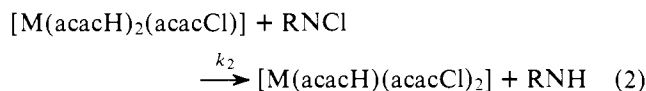
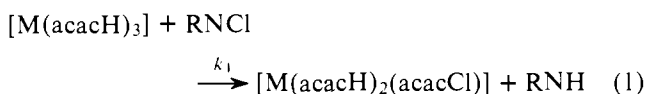
Complex	[Complex], mol dm ⁻³	<i>k</i> _{obsd} , s ⁻¹ ^a	(<i>k</i> _{obsd} /[complex] = <i>k</i> ₁), dm ³ mol ⁻¹ s ⁻¹
[Co ^{III} (acacH) ₃]	0.16	3.7 (±0.1) × 10 ⁻²	0.23 ± 0.01
[Co ^{III} (acacH) ₃]	0.12	2.5 (±0.2) × 10 ⁻²	0.21 ± 0.02
[Co ^{III} (acacH) ₃]	0.10	2.2 (±0.1) × 10 ⁻²	0.22 ± 0.01
[Co ^{III} (acacH) ₃]	0.08	1.8 (±0.1) × 10 ⁻²	0.22 ± 0.01
[Co ^{III} (acacH) ₃]	0.05	1.2 (±0.1) × 10 ⁻²	0.24 ± 0.02
[Co ^{III} (acacH) ₃] + 10% [Cr ^{III} (acacCl) ₃] ^d	0.10	2.0 (±0.1) × 10 ⁻²	0.20 ± 0.01
[Co ^{III} (acacD) ₃]	0.10	2.1 (±0.1) × 10 ⁻²	0.21 ± 0.01
[Rh ^{III} (acacH) ₃]	0.05	3.4 (±0.2) × 10 ⁻³	0.068 ± 0.004
[Ir ^{III} (acacH) ₃]	0.02		0.033 ± 0.001 ^b
[Al ^{III} (acacH) ₃]	0.05	1.1 (±0.1) × 10 ⁻²	0.22 ± 0.02
[Ga ^{III} (acacH) ₃]	0.05	1.0 (±0.1) × 10 ⁻²	0.20 ± 0.02
[Be ^{II} (acacH) ₂]	0.05	<10 ⁻⁴ ^c	<0.002 ^c

^a Pseudo-first-order rate constants. ^b Reaction carried out under second-order conditions, and *k*₁ is obtained from a straight-line plot of 1/(peak height) vs. time. ^c Secondary reaction involving ligand loss precluded accurate measurement. ^d [Cr(acacCl)₃] was added as a relaxing agent to check that saturation of observed resonances was not occurring.

(halogenation)² or metal nitrates in acetic anhydride (nitration).³ Friedel-Crafts reactions are also possible which give acyl derivatives.⁴

In this study the kinetics and mechanisms of the chlorination reactions have been investigated using the relatively new technique of stopped-flow pulse Fourier-transform ¹H NMR (SFPFTNMR).⁵ This technique is particularly suitable for reactions of this type since it gives a much more detailed picture of the reaction mechanisms than is possible by UV-visible spectrophotometry, by permitting the study and comparison of a substantial range of complexes. Indeed most of the reactions studied here do not give rise to measurable UV-visible changes. Substitution at the periphery of a metal complex does not usually bring about a marked change in its UV-visible spectrum since the donor atoms have not themselves changed, whereas ¹H NMR is much more indicative of the structural changes involved and can also readily detect minor side reactions as the present results show. SFPFTNMR can be used to obtain complete ¹H NMR spectra ca. 0.2 s after mixing two solutions, and at a repetition rate of one spectrum every 0.6 s if necessary.⁶ Since the half-lives of the reactions studied here are in the range 5–10³ s, this method is ideal for the present study. For the slower reactions the signal/noise ratio was further improved by signal averaging.

The rates of the monochlorination of the Co^{III}, Rh^{III}, Ir^{III}, Al^{III}, Ga^{III}, and Be^{II} complexes with *N*-chlorosuccinimide are reported in CDCl₃ at 297 K using an excess of metal complex (reaction 1, RNCl = *N*-chlorosuccinimide, RNH = succinimide).



Reactions 2 and 3 were investigated for Co^{III} and Rh^{III} after separation of the mono- and dichloro complexes so that their subsequent chlorination reactions could be independently studied. Reaction 1 (M = Co^{III}, Rh^{III}, Al^{III}, and Ga^{III}) was also studied in CD₃OD and in C₆D₆ solutions, and the reaction of [Co(acacD)₃] with *N*-chlorosuccinimide was investigated in CDCl₃ and CD₃OD for comparison with the rate of reaction with [Co(acacH)₃]. Finally, the relative electron-withdrawing abilities of NO₂ and Cl groups was established by comparing the rates of chlorination of [Co^{III}(acacH)₂(acacNO₂)], [M(acacH)₂(acacCl)], and [M(acacH)(acacCl)₂] (M = Co^{III}, Rh^{III}). Preliminary results for the chlorination of [Co(acacH)₂(acacMe)] and [M(acacMe)₃] (M = Co^{III}, Rh^{III}; acacMe⁻ = 3-methylpentane-2,4-dionate ion) are also reported.

Results

Main Reaction. Chlorination of [Co(acacH)₃] by *N*-chlorosuccinimide is first order in each reactant and second order overall as shown by linear rate plots, and the variation of the pseudo-first-order rate constants with the complex concentration (Table I). Only a narrow range of complex concentrations (0.05–0.16 mol dm⁻³) could be studied, the lower limit being determined by the relatively low sensitivity of the method used, and the upper limit by the complex solubilities.

Values of the second-order rate constants, *k*, are 0.22 ± 0.02 and 2.05 ± 0.10 dm³ mol⁻¹ s⁻¹ for the chlorination of [Co(acacH)₃] in CDCl₃ and CD₃OD, respectively, and for [Co(acacD)₃] the corresponding values are the same within experimental error (0.21 ± 0.02 and 2.20 ± 0.15 dm³ mol⁻¹ s⁻¹, respectively). Proton loss is, therefore, not rate determining, and an S_E2 mechanism is favored for all of the reactions studied. The solvent variation shown in Table II supports an S_E2 mechanism. Traces of a minor free-radical pathway were only detected for the reactions of the Co^{III} complexes in CDCl₃, as outlined in the next section.

The effects on *k* of replacing a nonreacting acacH⁻ by acacX⁻ (X = Cl, NO₂) are listed in Table III; all of these reactions were carried out in CDCl₃. The last column in Table III gives the rate constant per mole of available ligand rather than per mole of complex, to assist direct comparison of the substituent effects. It will be seen that each distant substitution of acacCl for acacH reduces the rate of chlorination of a remaining acacH⁻ ring by about a factor of 2.5 for Co^{III} and ca. 4 for Rh^{III}. Substitution of acacNO₂ for acacH reduces the rate of chlorination by a factor of ca. 5 for Co^{III}. Corresponding experiments could not be carried out with Al^{III} and Ga^{III} because of ligand scrambling. However, there are qualitative indications from reactions run under second-order conditions that the Cl substituent effects with Al^{III} are similar to those for Co^{III}.

All our attempts to follow the corresponding bromination by *N*-bromosuccinimide failed because the reaction is too fast. For example, the bromination of 0.0125 mol dm⁻³ [Rh^{III}(acacCl)₂(acacH)] (the least reactive complex studied) in CDCl₃ is complete within 0.2 s. Now for the corresponding chlorination at a concentration of 0.05 mol dm⁻³, *k*_{obsd} = 7.6 × 10⁻⁵ s⁻¹. Therefore the bromination rate is at least a factor of 10⁶ faster. However, no evidence of free-radical formation was detected.

Table II. Solvent Dependence of the Chlorination Rates

Solvent	$k_1, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$					
	Al ^{III}	Ga ^{III}	Co ^{III}	Rh ^{III}	Ir ^{III}	Be ^{II}
CD ₃ OD ^a	13.5 ± 0.5	78.0 ± 1.0	2.0 ± 0.1	0.71 ± 0.01		0.90 ± 0.01
CDCl ₃	0.22 ± 0.02	0.20 ± 0.02	0.22 ± 0.01	(6.8 ± 0.4) × 10 ⁻²	(3.3 ± 0.1) × 10 ⁻²	<2 × 10 ⁻³
C ₆ D ₆	(6.3 ± 0.1) × 10 ⁻³	(1.6 ± 0.1) × 10 ⁻²	(6.2 ± 0.2) × 10 ⁻²	(9.0 ± 0.1) × 10 ⁻³		

^a For comparison, the chlorination of Na(acacH) in CD₃OD was too fast to measure ($k_1 \gg 100 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$).

Table III. Substituent Effects on the Rate of Chlorination of Some 3-Substituted Tris(pentane-2,4-dionato)metal Complexes in CDCl₃ at 297 K

Complex	[Complex], mol dm ⁻³	$k_{\text{obsd}}, \text{s}^{-1}$ ^a	$(k_{\text{obsd}}/[\text{complex}] = k), \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ^b	$k', \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ^c
Co ^{III} (acacH) ₃	0.1	(2.2 ± 0.1) × 10 ⁻²	0.22 ± 0.01	0.07 ± 0.01
Co ^{III} (acacH) ₂ (acacCl)	0.1	(5.3 ± 0.4) × 10 ⁻³	0.053 ± 0.004	0.026 ± 0.004
Co ^{III} (acacH)(acacCl) ₂	0.1	(1.2 ± 0.1) × 10 ⁻³	0.012 ± 0.001	0.012 ± 0.001
Rh ^{III} (acacH) ₃	0.05	(3.4 ± 0.2) × 10 ⁻³	0.068 ± 0.004	0.022 ± 0.004
Rh ^{III} (acacH) ₂ (acacCl)	0.05	(4.1 ± 0.1) × 10 ⁻⁴	0.0082 ± 0.0003	0.0041 ± 0.0003
Rh ^{III} (acacH)(acacCl) ₂	0.05	(7.6 ± 0.5) × 10 ⁻⁵	0.0015 ± 0.0001	0.0015 ± 0.0001
Co ^{III} (acacH) ₂ (acacNO ₂)	0.1	(2.7 ± 0.5) × 10 ⁻³	0.027 ± 0.005	0.013 ± 0.005

^a Pseudo-first-order rate constants, with [*N*-chlorosuccinimide] = 0.1 [complex]. ^b Second-order rate constants. ^c Second-order rate constant per mole of available ligand.

Secondary Reactions. When (and only when) [Co^{III}(acacH)₃] or [Co^{III}(acacH)₂(acacCl)] are chlorinated in CDCl₃, various resonances are observed to grow and then decay again during the course of the reaction, as we have reported previously for [Co(acacH)₃].⁷ These resonances are at δ 6.01, 5.71, 5.31, and 2.33 ppm. The absence of the first three resonances in the corresponding chlorinations of [Co^{III}(acacD)₃] shows that they must arise from the methine protons. Additional weak resonances were observed at δ 6.75 and 5.79 ppm (in emission) and at δ 5.14 and 4.73 ppm (in absorption) when the solvent is changed from 99.9% CDCl₃ to 90% CDCl₃/10% CHCl₃. The appearance of these resonances shows a small but definite induction time (ca. 2 s for the first chlorination stage, and 17 s for the second chlorination stage) which further confirms their free-radical derivation, and the detection of peaks in emission (Figure 1) strongly suggest that the resonances are enhanced by CIDNP. However, the free radicals were not present in sufficient concentration to be detectable by electron spin resonance.

A different secondary reaction was observed for the Al^{III}, Ga^{III}, and Be^{II} complexes when the mole ratio of *N*-chlorosuccinimide to complex exceeded 1:1. A new resonance appeared at δ 2.46 in the later stages of these reactions which we assign on the basis of this shift to uncoordinated 3,3-dichloropentane-2,4-dione. It would appear, therefore, that for the more labile metal complexes chlorination can lead to ligand loss.

Reactions of [Co^{III}(acacMe)₃] and [Rh^{III}(acacMe)₃]. An investigation of the chlorination of [Co^{III}(acacH)₂(acacMe)] indicated that substantial reaction was occurring at the 3 position of the methylated ligand and not at the acacH⁻ ligands. Therefore, we prepared [Co^{III}(acacMe)₃] and studied its chlorination. The reaction in CDCl₃ is complex with many CIDNP enhanced resonances from intermediate species (Figure 2). Furthermore, the stoichiometry indicates that the solvent is also acting as a chlorinating agent; all the coordinated 3-methylpentane-2,4-dionate resonances disappear upon reaction of a 4:1 mixture of *N*-chlorosuccinimide and complex, but 66% unreacted *N*-chlorosuccinimide remains. However, the reaction proceeds initially as with [Co^{III}(acacH)₃] when the stoichiometry is 1:1, k_1 being ca. 0.70 dm³ mol⁻¹ s⁻¹ (7 × 10⁻² dm³ mol⁻¹ s⁻¹ for the reaction in C₆D₆) (cf. 0.22 and 6.2 × 10⁻² dm³ mol⁻¹ s⁻¹ for [Co^{III}(acacH)₃] in these solvents).

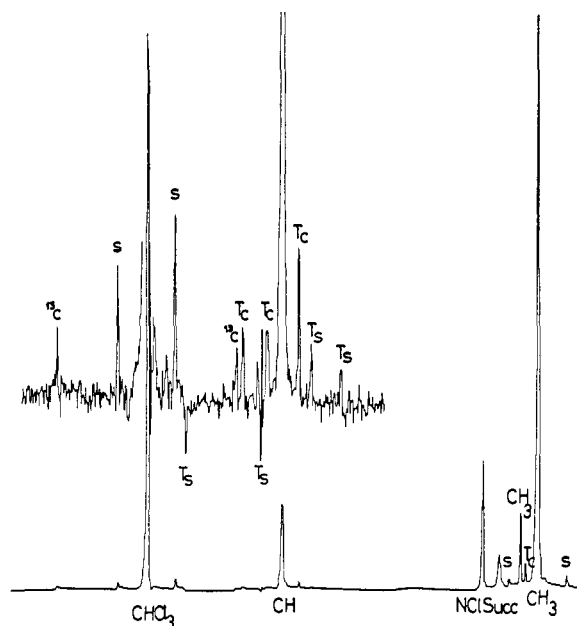


Figure 1. ¹H NMR spectrum of Co^{III}(acacH)₃ + *N*-chlorosuccinimide in 10% CHCl₃-90% CDCl₃, 9 s after mixing at 297 K. Solvent-derived transients, T_s; Complex-derived transients, T_c; Spinning side bands, s.

The subsequent reactions are complex, always resulting in the loss of the ligand (3-methyl-3-chloropentane-2,4-dione) and the precipitation of polymeric paramagnetic cobalt(II) species from the reaction mixture.

However, the reactions of [Rh^{III}(acacMe)₃] with *N*-chlorosuccinimide give no indication of ligand loss, and there is evidence for the attack of succinimide anion at the carbonyl of the coordinated 3-methyl-3-chloropentane-2,4-dione ligand. These reactions are presently undergoing further investigation.

Discussion

Main Reaction. The solvent dependence of the second-order rate constants (k_1), the normal absence of CIDNP, the absence of a hydrogen isotope effect, and the simple reaction kinetics all support an S_E2 mechanism, involving a transition state of

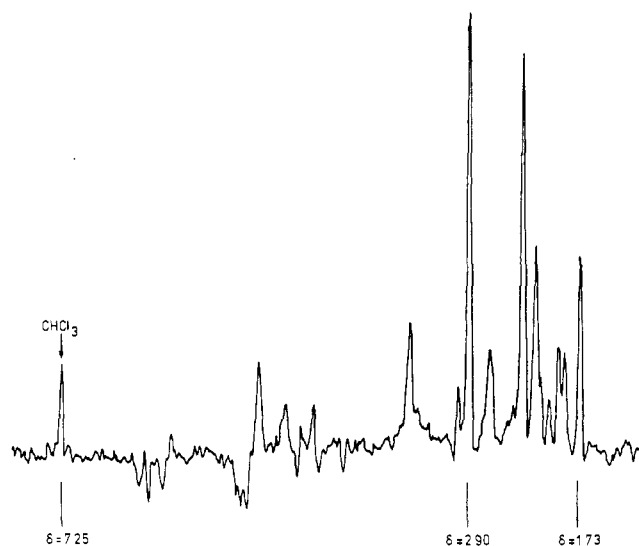
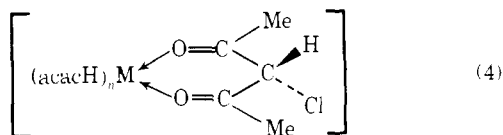


Figure 2. ^1H NMR spectrum 6 s after mixing $[\text{Co}^{\text{III}}(\text{acacMe})_3]$ with *N*-chlorosuccinimide at 297 K in CDCl_3 .

type 4 which probably forms a transient ion pair with the succinimide anion.



A structure analogous to (4) has recently been reported;⁸ in *trans*-diaquobis(2,4-pentanedione)nickel(II) perchlorate, refinement and location of the hydrogen atoms has established that 2,4-pentanedione is capable of coordination in a diketone form.

The comparative insensitivity of the k_1 values to changes in the trivalent metal ion is somewhat surprising, but can be correlated with the relatively small differences in the metal-oxygen bond distances. Some properties of these complexes derived from x-ray crystallography are listed in Table IV, along with selected data derived from Table II. In general, k_1 is increased somewhat by an increase in metal-oxygen bond distance $r_{\text{M-O}}$. This has a simple interpretation; in the transition state 4 the ligand to metal bond is weakened by the loss of negative ligand charge. Thus the transition state is less accessible when the ligand is tightly bound, and particularly with Be^{II} , which evidently prefers to bind two ligands very tightly instead of three less tightly. This is confirmed by the very rapid chlorination of the free enolate anion. In the case of Co^{III} , Rh^{III} , and Ir^{III} the ligand binding energy is affected not only by $r_{\text{M-O}}$ but also by crystal field effects, which are larger for Rh^{III} and Ir^{III} . It should be noted that although values of k_1 for Co^{III} and Al^{III} are similar, the values are not strictly comparable for these two metals because of the influence of the t_{2g}^6 electrons in Co^{III} .

The differences in solvent effect are more substantial, although only that for the Be^{II} complex compares with known effects in $\text{S}_{\text{E}2}$ reactions of aromatic compounds, which are of the order of 10^6 . The metal-ion dependence of the solvent effects implicates the complex rather than the *N*-chlorosuccinimide as being the affected species. Polar solvation at the relatively less accessible carbonyl groups would certainly increase k_1 , and would explain why $k(\text{CD}_3\text{OD})/k(\text{C}_6\text{D}_6)$ increases in general with increasing molecular size (Table IV), but is less for Co^{III} and Rh^{III} because of the more compact structure (greater bite angle) and the steric repulsion of the filled t_{2g} orbitals. $k(\text{CD}_3\text{OD})/k(\text{C}_6\text{D}_6)$ is also greater for Be^{II} because of its more accessible structure.

Table IV. Some Properties of Metal Acetylacetonates

Complex	$r_{\text{M-O}}$, pm ^a	$\angle\text{OMO}$ ("bite" angle), deg	$k(\text{C}_6\text{D}_6)$, dm ³ mol ⁻¹ b	$k(\text{CD}_3\text{OD})/k(\text{C}_6\text{D}_6)$ ^c
$\text{Co}^{\text{III}}(\text{acacH})_3$	190	97	0.062	36
$\text{Al}^{\text{III}}(\text{acacH})_3$	189	91	0.0063	2100
$\text{Ga}^{\text{III}}(\text{acacH})_3$	195	92	0.016	4900
$\text{Rh}^{\text{III}}(\text{acacH})_3$	199	95	0.0093	76
$\text{Be}^{\text{II}}(\text{acacH})_2$	170	105		d

^a Metal-oxygen bond distances. ^b Second-order rate constants for chlorination in deuteriobenzene. ^c Relative rates of chlorination in CD_3OD and C_6D_6 . ^d $k(\text{CD}_3\text{OD})/k(\text{CDCl}_3) > 450$ compared with 370 for Ga^{III} .

The solvation effects are substantiated by the recent work of Vigeo and Watkins,⁹ who have shown that in the case of tris(2,4-pentanedione)chromium(III) specific solvation in the second coordination sphere does take place. They conclude that in the case of methanol there is preferential hydrogen bonding of the methanol OH to the oxygens of the chelated 2,4-pentanedione, whereas the interaction with benzene is less specific.

Kuroda et al. have recently reported a rate constant of 1.68 mol⁻¹ dm³ s⁻¹ at 308 K for the reaction of *N*-chlorosuccinimide with the $[\text{Co}^{\text{III}}(\text{en})_2(\text{acacH})]^{2+}$ ion in water (en = 1,2-diaminoethane).¹⁰ This rate is comparable to our observed rate for $[\text{Co}^{\text{III}}(\text{acacH})_3]$ in methanol. It would appear that the expected reduction in k_1 due to the formal 2+ charge on the metal is offset by the effect of the very polar solvent in this case.

Substituent Effects. The reductions in the rates of chlorination caused by Cl and NO_2 substitution at another ligand are attributable to ordinary inductive effects, and further support the $\text{S}_{\text{E}2}$ mechanism. That they are slightly greater for Rh^{III} than for Co^{III} shows that the inductive effect is primarily through bond rather than through space, because the interligand distances are all greater for the Rh^{III} complexes. The qualitative similarity of Al^{III} to Co^{III} implicates σ rather than π bonds as the charge transmitters. All this is consistent with simple electrostatics, which predicts that if one ligand is made to bind less strongly, then the others will bind correspondingly more strongly, and will thus (using our previous reasoning) be less reactive. The observed dependence of reaction rate upon the extent of substitution would appear to vitiate earlier measurements based on "overall chlorination rate".¹¹

The increased reactivity of $[\text{Co}^{\text{III}}(\text{acacMe})_3]$ over $[\text{Co}^{\text{III}}(\text{acacH})_3]$ could have a second cause, however, namely, the relief of steric strain between the three methyl groups upon formation of a tetrahedral intermediate. This second cause may also contribute to the surprising reactivity of the chlorinated ligand in the Al^{III} , Ga^{III} , and Be^{II} complexes shown in the secondary reaction which leads to ligand loss. That this secondary reaction does not occur with the Co^{III} , Rh^{III} , and Ir^{III} complexes is no doubt due to their greatly reduced lability.

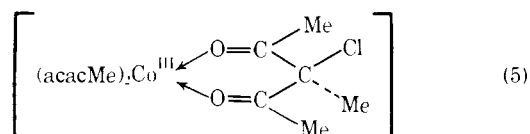
Side Reaction. CIDNP is capable of producing very large intensity enhancements, and it therefore seems likely that the transient species observed with the Co^{III} complexes in chloroform represent a very minor pathway. This is borne out by the totally normal kinetics of the main reaction, and indicates the power of the SFPFTNMR method to detect minor free-radical pathways. The increase in free-radical production when the deprotonation step is blocked implicates the transient species 5 as a radical initiator. Its unique reactivity in this respect may well be related to the presence of an accessible divalent metal oxidation state; an oxidative fission of chloroform involving a $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$ change could generate several Cl radicals which would eventually reoxidize 5 or 4 to its original

Table V. Chemical Shifts of Complexes Studied (δ relative to CHCl_3 at δ 7.25)

M	A. $[\text{M}(\text{acacH})_3]$						
	Unchlorinated		Monochlorinated		Dichlorinated		Trichlorinated
	CH	CH ₃	CH	CH ₃	CH	CH ₃	CH ₃
Al ^{III}	5.49	1.99	5.47	2.245 1.99	5.51	2.250 1.99	
Ga ^{III}	5.41	1.99	5.43	2.26 1.99			
Be ^{II a}	5.60	2.06	5.61	2.30 2.06		2.32	
Co ^{III}	5.509	2.16	5.52	2.38 2.19 2.16	5.54	2.42 2.39 2.18	2.46
Rh ^{III}	5.47	2.14	5.49	2.41 2.16 2.15	5.50	2.41 2.40 2.16	2.42
Ir ^{III}	5.46	1.99	5.47	2.23 2.01 1.99	5.48	2.25 2.24 2.02	2.26

B. Other Complexes and Ligands			
Complex	CH	1,5-Methyls	3-Methyl
$[\text{Co}^{\text{III}}(\text{acacH})_2(\text{acacNO}_2)]$	5.57	2.44 2.26 2.18	
$[\text{Rh}^{\text{III}}(\text{acacCl})_2(\text{acacBr})]$		2.51 ^c 2.42 ^d	
$\text{K}^+[\text{Co}^{\text{III}}(\text{acacH})_2(\text{CO}_3)]^-$ ^b	5.88	2.29 2.22	
$[\text{Co}^{\text{III}}(\text{acacH})_2(\text{acacCH}_3)]$	5.49	2.25 2.16 2.14	1.92
$[\text{Co}^{\text{III}}(\text{acacCH}_3)_3]$		2.21	1.90
$[\text{Rh}^{\text{III}}(\text{acacCH}_3)_3]$		2.19	1.94
3-Methyl-acac(enol) ^e		2.05	1.76
3-Methyl-acac(keto)	3.60	2.12	1.24
3-Chloro 3-methylpentane-2,4-dione		2.26	1.66
3,3 Dichloropentane-2,4-dione		2.46	

^a $[\text{Be}(\text{acacH})_2]$. ^b Reference DSS in D_2O . ^c Methyls of brominated pentane-2,4-dionate ring. ^d Methyls of chlorinated pentane-2,4-dionate rings (unresolved). ^e OH resonance at δ 7.52.



form. This would explain the three transient complex-derived CH resonances previously observed⁷ for the chlorination of $[\text{Co}^{\text{III}}(\text{acacH})_3]$, the increase in free-radical production in the reaction of $[\text{Co}^{\text{III}}(\text{acacMe})_3]$ and *N*-chlorosuccinimide, and the total absence of any CIDNP species in the reaction of $[\text{Rh}^{\text{III}}(\text{acacMe})_3]$ in chloroform.

Experimental Section

Materials. Deuterated solvents were obtained from Merck Sharp and Dohme, Ltd. *N*-Chlorosuccinimide was recrystallized from chloroform before use. Most of the tris(pentane-2,4-dionato) complexes were prepared by published methods¹²⁻¹⁴ using redistilled acetylacetonate and highest purity metal salts available. The complexes were shown to be pure by ¹H NMR and by mass spectrometry. They were stored in the dark in a refrigerator. The observed chemical shifts are reported in Table V. The Co^{III} complexes were recrystallized repeatedly from 40:60 toluene-petroleum ether to remove traces of Co^{II} .

Mixed complexes of the type $[\text{M}(\text{acacX})_n(\text{acacH})_{3-n}]$ ($n = 1$ or 2) were prepared in one of two ways. When $\text{X} = \text{Cl}$ or NO_2 and $\text{M} = \text{Co}^{\text{III}}$ or Rh^{III} , mixtures of products obtained by reactions with approximately 1 or 2 equiv of *N*-chlorosuccinimide, or copper nitrate in acetic anhydride, were separated by preparative thin layer chromatography on neutral aluminum oxide with toluene as solvent. The

R_f values are in the order $[\text{M}(\text{acacX})_3] > [\text{M}(\text{acacH})\text{acacX}]_2 > [\text{M}(\text{acacH})_2(\text{acacX})] > [\text{M}(\text{acacH})_3]$.

$[\text{Co}^{\text{III}}(\text{acacMe})(\text{acacH})_2]$ was prepared via the $[\text{Co}^{\text{III}}(\text{CO}_3)_3]^{3-}$ ion as follows: to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (5.95 g) in water (12.5 mL) was added hydrogen peroxide (4 mL). This solution was then added to an ice-cold slurry of KHCO_3 (16.26 g) in water (20 mL) with stirring. To the resulting green solution of $[\text{Co}^{\text{III}}(\text{CO}_3)_3]^{3-}$ was added acetylacetonate (5 mL) and the mixture was heated with stirring at 60 °C for 1 h. The solution was chloroform extracted to remove any tris(pentane-2,4-dionato)cobalt(III), and the aqueous layer then passed down a column of Dowex-1 anion exchange resin (1 × 8-50) in the chloride form. Elution with water gave a green solution of the $[\text{Co}(\text{acacH})_2(\text{CO}_3)]^-$ ion, leaving a green band (presumably the $[\text{Co}(\text{acacH})(\text{CO}_3)_2]^{2-}$ ion) on the resin.

The solution of $[\text{Co}(\text{acacH})_2(\text{CO}_3)]^-$ ion was concentrated to 20-30 mL by rotary evaporation and 5 mL of 3-methylpentane-2,4-dione(acacMe) was added to give green insoluble $[\text{Co}^{\text{III}}(\text{acacH})_2(\text{acacMe})]$. This was collected by filtration after 10 min. Anal. ($\text{C}_{16}\text{H}_{23}\text{O}_6\text{Co}$) C, H. $[\text{M}(\text{acacMe})_3]$ ($\text{M} = \text{Co}^{\text{III}}$, Rh^{III}) were prepared by standard methods^{13,14} substituting 3-methylpentane-2,4-dione for acetylacetonate. Anal. ($\text{C}_{18}\text{H}_{27}\text{O}_6\text{Rh}$) C, H.

3,3-Dideuteriopentane-2,4-dione was prepared by stirring pentane-2,4-dione (6 mL) with D_2O (30 mL) overnight, then extracting the aqueous solution with CH_2Cl_2 , repeating the deuteration with a further 30 mL of D_2O , and extracting and fractionally distilling off the 3,3-dideuteriopentane-2,4-dione. This was shown to be 99% deuterated at the methine position by ¹H NMR.

$[\text{Co}^{\text{III}}(\text{acacD})_3]$ was prepared by the published method for $[\text{Co}^{\text{III}}(\text{acacH})_3]$ substituting acacD for acacH and D_2O_2 for H_2O_2 . (D_2O_2 was prepared from Na_2O_2 and $\text{DCl}/\text{D}_2\text{O}$). The recrystallized $[\text{Co}^{\text{III}}(\text{acacD})_3]$ was shown to be 99% deuterated by ¹H NMR. The

use of H_2O_2 instead of D_2O_2 in this preparation gave a product which was only ca. 60% deuterated.

3-Methylpentane-2,4-dione was prepared by the action of 1 mol of methyl iodide and 1 mol of sodium pentane-2,4-dionato ion in ethanol.¹⁵ The pure ligand was fractionally distilled at 435 ± 1 K (1 atm) and was shown to be pure by ^1H and ^{13}C NMR [^1H NMR shifts in Table V; ^{13}C shifts relative to Me_4Si at δ 12.54, 28.86, 61.36, and 205.13 (keto form), and at 21.32, 23.27, 105.03, and 190.63 ppm (enol form)].

Kinetics. Reactions were studied at 297 ± 1 K in deuterated solvents, using the stopped-flow attachment for a Bruker WH90 pulse Fourier-transform NMR spectrometer described previously.⁵ Complete ^1H NMR spectra were recorded as free induction decays every few seconds after mixing, and after Fourier transformation the decaying *N*-chlorosuccinimide ^1H resonance at δ 2.90 ppm was used to obtain the rate constants. Most reactions were studied under pseudo-first-order conditions with at least a 10:1 ratio of metal complex to *N*-chlorosuccinimide. The pseudo-first-order rate constants were obtained by least-squares analysis from the slopes of plots of \ln (peak height or peak integral) vs. time. Because of solubility problems a few reactions were studied under second-order conditions with $[\text{complex}] = [N\text{-chlorosuccinimide}]$; second-order rate constants were then obtained from the slopes of plots of $(\text{peak height})^{-1}$ vs. time. Reaction rates were also checked by following the appearance of the methyl resonance of the chlorinated pentane-2,4-dionato ring to low field of the unchlorinated rings, and good agreement with the value obtained from the decaying *N*-chlorosuccinimide resonance was observed.

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An Analysis of the Effects of Alkyl Substituents on the Ionization Potentials of *n*-Alkenes

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Abstract: We report the two highest vertical ionization potentials, as measured by photoelectron spectroscopy, for a large number of straight-chain olefins, and compare these experimental data to the results of molecular orbital calculations by the Fenske-Hall method. It is found that the *cis* and *trans* isomers of a given compound have essentially identical π ionization energies, but some differences are noted for the first σ ones. When these molecules are considered as alkyl-substituted derivatives of ethylene, of the general form $\text{R}_1\text{CH}=\text{CHR}_2$, it is seen that there is a nonlinear decrease in both experimental ionization potentials with alkyl chain length, tending to an asymptotic limit for long substituents. However, the combined effect of two alkyl substituents is not equal to the sum of the effect of each, and the interactions between these two substituents must also be considered. The Fenske-Hall method gives satisfactory correlation with the photoelectron spectral data and their trends and is shown to be useful for interpreting and understanding them.

Introduction

The usefulness of photoelectron spectroscopy (PES) as a method of measuring some of the vertical ionization potentials (IPs) of a compound has been established by its successful application to many systems.¹ One can also derive empirical rules relating IPs, or their changes over a series of related molecules, to differences in functional groups or geometric conformations.² In this work we investigate the IPs of a set of *n*-alkenes and try to determine the effects on them of alkene chain length, position of the double bond, and *cis-trans* isomerism. This field of the substituent effects on the IPs of hydrocarbons and their derivatives has been previously investigated by such other workers as Demeo and El-Sayed,³ Kinsinger,⁴ Masplet et al.,⁵ and Carlier et al.^{6,7} However, this previous research was incomplete, and we hope to systematize and explain the data for the *n*-alkenes. We are especially in-

terested in looking at trends in these data and in making comparisons throughout the set of compounds and also in meaningful subsets.

In addition, these experiments are supplemented by molecular orbital (MO) calculations on these molecules, to provide a theoretical means for understanding the IPs and their changes. The Fenske-Hall method was chosen for this because it was developed to simulate the results and trends observed from rigorous *ab initio* calculations, but with much less computer time and cost.^{8,9} The Fenske-Hall eigenvalues are correlated with the experimental IPs by the application of Koopmans' theorem.¹⁰ Since this theorem assumes that the nuclei remain fixed upon ionization of the molecule, and that the remaining electrons do not reorganize, we report vertical PES ionization energies rather than adiabatic ones. It has previously been demonstrated that this procedure can be used