

REACTIVITY OF CHROMIUM(III) AND COBALT(III) ACETYLACETONATO COMPLEXES

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Abstract—A comparative study of the ligand reactivity at the 3-position in trisacetylacetonates of Cr(III) and Co(III), by means of nitration and Vilsmeier-Haack reactions, was attempted. The sequence $\text{Co} > \text{Cr}$ in both reactions was found. Hückel calculations of reactivity indices were performed and theoretical reactivity results agreed with experiment.

INTRODUCTION

TRANSITION metal acetylacetonates may undergo various substitutions reactions at the 3-position in the same way that aromatic compounds do [1–8], and there is experimental evidence that in Cr(III), Co(III) and Rh(III) complexes they occur while maintaining the integrity of the chelated rings [5, 9]. It has been demonstrated, besides, that there exist intramolecular interannular effects transmitted through the central atom, said transmission being most likely due to delocalization. This was done, for example, by Collman [3] with studies of the NMR spectra and reactivity of mono and disubstituted transition metal acetylacetonates at the 3-position with electron acceptor groups.

The ligand reactivity may be modified by chelation for both steric and electronic effects. Taking into account the available data regarding structure [10], it appears reasonable to assume, when comparatively studying the reactivity of complexes that are very similar in structure, that the steric effects are nearly constant. The electronic effects might be conditioned by the nature and the degree of participation of the central atom in the conjugated system.

Among the reports on metallic acetylacetonates, only a few appear to have focused on the differences in reactivity of complexes with different central atom. Collman [3] has established the sequences of reactivity: $\text{Co} \sim \text{Cr} > \text{Rh}$ and $\text{Cr} > \text{Co} > \text{Rh}$, for halogenation with N-halosuccinimides and Friedel-Crafts acetylation, respectively. However, in the case of Cr(III) and Co(III) complexes, the sequence reported for acetylation is based upon the yield of trisubstituted derivative only.

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The present work attempts to detect the existence of differences in reactivity of Cr(III), Fe(III) and Co(III) acetylacetonates in nitration [6, 8] and in a modified Vilsmeier-Haack reaction [6, 11, 12], under identical experimental conditions for each case. Furthermore, a theoretical analysis of reactivity by LCAO-MO approximation was attempted, by employing the reactivity indices usually applied to aromatic systems. These particular substitution reactions were chosen because, in the case of nitration, the reaction products are relatively stable and they afford mono, di and trisubstituted derivatives, while in the case of Vilsmeier-Haack formylation, although it does not afford trisubstituted derivatives, the reaction is slow enough to allow a study of the corresponding yields at different reaction times. The results of the experiments carried out with Fe(III) complex were uncertain, probably because the chelate is destroyed under the employed experimental conditions. Consequently, only theoretical results concerning this complex are included.

EXPERIMENTAL

Nitration of tris(acetylacetonato) chromium(III) and tris(acetylacetonato) cobalt(III)

A series of nitration reactions were carried out according to the technique described by Collman *et al.* [6] with some modifications for obtaining homogeneous phase. The nitrating solution was prepared as follows: Copper(II) nitrate trihydrate (0.091 mole) was suspended in acetic anhydride (3.177 mole) and the slurry was stirred in a stoppered flask for 6 hr at room temperature and then filtered. Cu(II) concentration was determined in the filtrate (nitrating solution) by iodimetry and Nitrogen content was determined through reduction to NH_3 by means of Devarda alloy and further acidimetry. The results were: Cu(II) = 0.0065 mole/l. and Nitrogen = 0.611 mole/l., presumably as acetyl nitrate [8, 13, 14].

Tris(acetylacetonato)Cr(III) 0.0308M (20 ml) and tris(acetylacetonato)Co(III) 0.0293M (20 ml) in acetic anhydride were treated separately, and stirring, with nitrating solution (70 ml) at 7°C. Aliquots of 9 ml were taken at various reaction times and were immediately treated with 2% sodium acetate in water (150 ml) to arrest the reaction and render the nitrated products insoluble. These were further collected by filtration, dried and dissolved in benzene. The amount of chelated metal was determined in each one of the resulting solutions, with the purpose of assessing the proper recovery of the substituted products after their chromatographic separation. The relative amounts of various nitrated derivatives in the solutions was checked. The separation was carried out by thin layer chromatography on silica gel H/starch 10:1 plates, using a special solvent mixture, i.e. benzene/cyclohexane/methanol/formic acid, 30:12:2:1.7, as an eluent. The chromatograms revealed four components or bands, *a*, *b*, *c*, and *d* in order of elution, which did not split with longer elution times and were found to be homogeneous in previous characterization (Table 1). They were carefully scraped from the plates and were brought into solution first with ethanol and then with benzene. The solutions were filtered and the products recovered by evaporation of the solvents. The concentrations of each one of the nitrated derivatives at the various reaction times were determined spectrophotometrically at 559 m μ for the Cr(III) compounds and at 596 m μ for the Co(III) compounds.

Under the above conditions, it was possible to evaluate the yields of the di and trinitrated derivatives only. In order to attempt a study of the first steps of the reactions, another series of determinations was conducted under less severe conditions: The nitrating solution was obtained from 0.091 mole of Copper salt and 5.294 mole of acetic anhydride. Chromium(III) complex 0.0292M (80 ml) and cobalt(III) complex 0.0283M (80 ml) in acetic anhydride were treated separately with the above nitrating solution (80 ml) at 0°C. The unreacted complex, which does not precipitate on treating the

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Table 1. Nitration-characterization of chromatographic bands by analysis (figures are given in %)

Band		C	H	N	Metal
<i>a</i> = Tris(3-nitroAA)Cr(III)	Calc.	37.20	3.75	8.68	10.73
	Found	37.70	3.70	8.10	10.40
<i>b</i> = Bis(3-nitroAA)mono(AA)Cr(III)	Calc.	41.01	4.36	6.38	11.83
	Found	41.10	4.50	6.70	11.60
<i>c</i> = Mono(3-nitroAA)bis(AA)Cr(III)	Calc.	45.52	5.60	3.55	13.18
	Found	46.90	5.40	3.10	12.90
<i>d</i> = Unreacted tris(AA)Cr(III)					
<i>a</i> = Tris(3-nitroAA)Co(III)	Calc.	36.67	3.69	8.68	11.99
	Found	36.30	3.70	8.30	11.50
<i>b</i> = Bis(3-nitroAA)mono(AA)Co(III)	Calc.	40.37	4.29	6.28	13.20
	Found	40.10	4.40	5.90	13.10
<i>c</i> = Mono(3-nitroAA)bis(AA)Co(III)	Calc.	44.90	5.02	3.49	14.69
	Found	46.00	5.20	3.10	14.40
<i>d</i> = Unreacted tris(AA)Co(III)					

AA = Acetylacetonate.

aliquots with aqueous sodium acetate, was recovered at each reaction time by extraction with benzene. Its amount was determined in the same way as with nitrated derivatives. The reaction path was studied in this case only on the basis of the mononitro derivative yield and the amount of unreacted metal chelate.

Formylation of tris(acetylacetonato)chromium(III) and tris(acetylacetonato)cobalt(III)

Formylation was carried out according to the procedure described by Collman *et al.* [6]. A series of determinations was performed separately for each chelate as follows: To a 0.1M solution of the chelate in dry dimethylformamide (19 ml) was added dropwise, with stirring, 1 ml (0.011 mole) of phosphorus oxychloride. The solution was maintained at 18°C during a predetermined time, after which a saturated aqueous solution of sodium carbonate (500 ml) was added and the slurry was stirred for 3 hr. The formylated derivatives were filtered, washed with small portions of water and recrystallized from benzene/petroleum ether 60°–80°. The separation was carried out by thin layer chromatography on silica gel H/starch 10:1 plates, using chloroform as an eluent. Three bands were obtained: A, B and C, in order of elution. According to the preceding characterization (Table 2) each band was found to be homogeneous and the faster moving of the three (A) was found to be unreacted metal chelate. The other two were identified by elementary analysis (Table 2) and by comparison of their

Table 2. Formylation-Characterization of chromatographic bands by analysis (figures are given in %)

Band		C	H	Metal
<i>A</i> = Unreacted tris(AA)Cr(III)				
<i>B</i> = Mono(3-formylAA)bis(AA)Cr(III)	Calc.	50.93	5.57	13.78
	Found	50.90	5.70	13.80
<i>C</i> = Unidentified				
<i>A</i> = Unreacted tris(AA)Co(III)				
<i>B</i> = Mono(3-formylAA)bis(AA)Co(III)	Calc.	50.01	5.51	15.34
	Found	50.20	5.40	15.50
<i>C</i> = Bis(3-formylAA)mono(AA)Co(III)	Calc.	49.51	5.14	14.29
	Found	49.30	5.10	14.30

AA = Acetylacetonato.

i.r. spectra with an authentic sample. In the case of the Cr(III) complex, the band C, corresponding probably to the diformylated derivative, could not be identified because of an obvious alteration of the product while drying. The amounts of each product at the various reaction times were determined spectrophotometrically. The same procedure was applied to the products that remained in aqueous solution when the reaction was arrested, once they were extracted with benzene.

Experimental results were considered valid whenever they reflected a defined kinetic behavior and whenever the recovery of the products was considered acceptable within the limits of our experimental method. The overall error in recovering was measured as the percentage of deviation of the sum of the recovered products with respect to the initial concentration of the complex in the reaction media. A recovery of more than 85 per cent was considered acceptable. The average error in the yields of di and trisubstituted nitrated derivatives (first series of experiments in nitration) was 3 per cent for the Cr(III) complex and 11.4 per cent for the Co(III) complex. These figures include a 3 per cent and a 4 per cent error, respectively, associated exclusively with the chromatographic separation step. The greater error in the evaluation of the Cobalt compounds might be due to a slight decomposition of the trinitroderivative, which may be visually detected when the product is left on the chromatogram for more than 12 hr. This would justify the greater deviation of the experimental data from the theoretical curve in Fig. 1 at the times: 8, 15 and 30 min.

In studying the variation of the yields of mononitroderivative (second series of experiments in nitration), the validity of the experimental results was based only on the coincidence found with a definite kinetical model, since only recuperation of the monosubstituted derivative was attempted. In same way, in formylation this criterion lead to the disregarding of the results corresponding to the unreacted complex and the disubstituted derivative. In this case, only the results of monosubstituted compounds were considered acceptable.

The analysis of C, H and N was made in the Organic Microanalysis Laboratory in our School.

RESULTS AND DISCUSSION

The yields of the substituted products (molarities in the reaction media) were plotted vs. the corresponding reaction times (Figs. 1-3).

Taking into account both the behavior of the complexes as moderately reactive aromatic substrates as well as the predetermined reaction conditions of using an excess of substituting agent, an attempt was made to describe the experimental

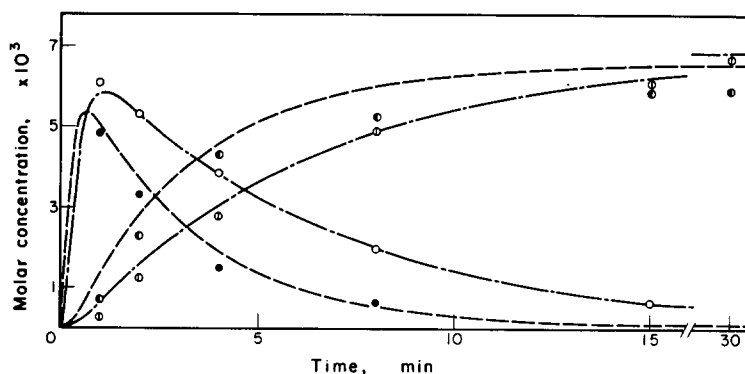


Fig. 1. Nitration: Yields of di and trisubstituted derivatives vs. time at 7°C, when using an excess of nitrating agent ($\sim 0.47M$). Complex concentration: $Cr(AA)_3 = 6.84 \times 10^{-3} M$; $Co(AA)_3 = 6.51 \times 10^{-3} M$. Experimental \circ —dinitrated Cr(III) complex; \oplus trinitrated Cr(III) complex; \bullet —dinitrated Co(III) complex; \bullet trinitrated Co(III) complex. Theoretical $-\cdot-\cdot-$ Cr(III) compounds; $k_1 = 1.1 \times 10^{-1}$, $k_2 = 5.7 \times 10^{-2}$ and $k_3 = 2.7 \times 10^{-3}$; $----$ Co(II) compounds; $k_1 = 1.8 \times 10^{-1}$, $k_2 = 8.4 \times 10^{-2}$ and $k_3 = 5.4 \times 10^{-3}$ (k values are given in sec^{-1}).

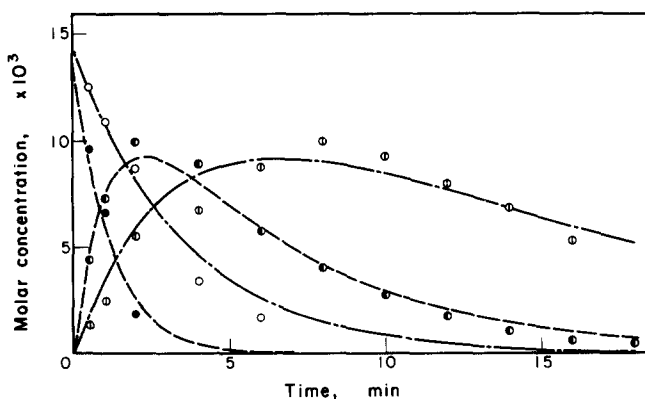


Fig. 2. Nitration: Yields of monosubstituted derivatives vs. time at 0°C, when using an excess of nitrating agent ($\sim 0.18M$). Complex concentration. $Cr(AA)_3 = 1.46 \times 10^{-2}M$; $Co(AA)_3 = 1.41 \times 10^{-2}M$. Experimental \circ —unreacted Cr(III) complex; \odot —mononitrated Cr(III) complex; \bullet —unreacted Co(III) complex; $\bullet\odot$ —mononitrated Co(III) complex. Theoretical - - - - - Cr(III) compounds; $k_1 = 4.7 \times 10^{-3}$ and $k_2 = 1.2 \times 10^{-3}$; - - - - - Co(III) compounds; $k_1 = 1.4 \times 10^{-2}$ and $k_2 = 3.0 \times 10^{-3}$ (k values are given in sec^{-1}).

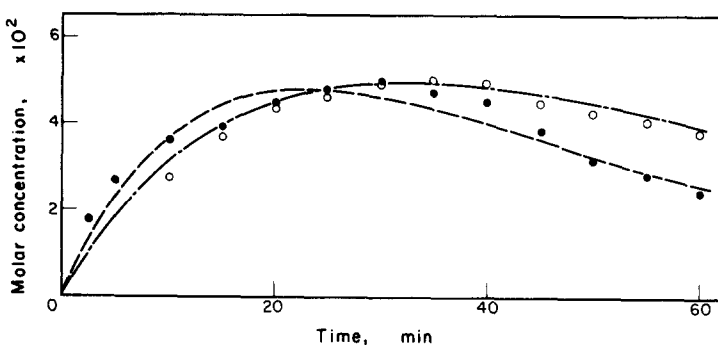


Fig. 3. Formylation: Yields of monosubstituted derivatives vs. time at 18°C, when using an excess of formylating agent ($\sim 0.55M$). Complex concentration $Cr(AA)_3 = 9.5 \times 10^{-2}M$; $Co(AA)_3 = 9.5 \times 10^{-2}M$. Experimental \circ —monoformylated Cr(III) complex; \bullet —monoformylated Co(III) complex. Theoretical - - - - - Cr(III) compound; $k_1 = 7.5 \times 10^{-4}$ and $k_2 = 3.4 \times 10^{-4}$; - - - - - Co(III) compound; $k_1 = 1.0 \times 10^{-3}$ and $k_2 = 5.0 \times 10^{-4}$ (k values are given in sec^{-1}).

results according to the kinetics of consecutive pseudo-first order reactions. The theoretical plot concentration vs. time as well as the sets of rate constants for each experiment are shown in Figs. 1–3.

The lower k values for mononitration experiments (Fig. 2) in comparison with the ones for di and trinitration (Fig. 1) were to be expected since the temperature was lower. Furthermore, on the assumption that the actual order of reaction with respect to the active species is greater than zero, a reduction of k should also be expected from the decrease of nitrating agent concentration.

Assuming that the obtained rate constants reflect the reactivity of the chelated species involved in each consecutive reaction series, the deactivating interannular

effects arising from the substituent groups are illustrated by comparing the constants for a single complex. Thus, for the first series of determinations in nitration (Fig. 1), the average rate constant quotients are: $k_1:k_2:k_3 = 41:21:1$, for the Cr(III) complex and $k_1:k_2:k_3 = 33:16:1$, for the Co(III) complex. For the second series of determinations in nitration (Fig. 2), the rate constant quotients are: $k_1:k_2 = 3.9$, for the Cr(III) complex and $k_1:k_2 = 4.7$ for the Co(III) complex. Finally, in the Vilsmeier-Haack reaction (Fig. 3) the rate constant quotients are: $k_1:k_2 = 2.2$ and $k_1:k_2 = 2.0$ for Cr(III) and Co(III) complexes, respectively.

According to the probable nature of the substituent group in the Vilsmeier-Haack reaction [12, 17], much greater rate constant quotients might be expected. The closeness for k_1 and k_2 values might be due to the coplanarity hindrance of the π -systems of the attached substituent group and the chelated ring, because of shielding caused by methyl groups of the substituted ligand, which might prevent the positive charge delocalization towards the π -system of the metal complex.

It should be observed that under the same experimental conditions the rate constant quotients are of the same order for both complexes.

Although the differences between the reaction rate values obtained are not remarkable, they suggest in all the cases that the Co(III) complex exhibits a greater reactivity, which is not in agreement with the sequence established by Collman for Friedel-Crafts acetylation [3]. In the determinations of yields of the di and trinitrated derivatives (Fig. 1), under the experimental conditions employed, the rate constant quotients for a given step were: $k_1(\text{Co}):k_1(\text{Cr}) = 1.64$, $k_2(\text{Co}):k_2(\text{Cr}) = 1.47$ and $k_3(\text{Co}):k_3(\text{Cr}) = 2.00$. When studying the formation of mononitrated derivative (Fig. 2), the quotients were: $k_1(\text{Co}):k_1(\text{Cr}) = 2.98$ and $k_2(\text{Co}):k_2(\text{Cr}) = 2.50$. Finally, for the formylation reaction it was found that: $k_1(\text{Co}):k_1(\text{Cr}) = 1.33$ and $k_2(\text{Cr}) = 1.47$. It can be observed that the transmission of the deactivating effects is relatively independent upon the nature of the metal and that the reactivity sequence of the original compounds is maintained in the substituted compounds.

The greatest uncertainty in the k values is the one corresponding to k_1 and k_2 for the first series of experiments in nitration (Fig. 1). This is because they were obtained taking into account just data of variation of yield of di and trisubstituted derivatives and there are more than a pair of values able to reproduce an average result close to the experimental data.

Taking into account the actual relative amounts of Cu(II) and nitrogen, it seems that, since the preparation of the nitrating solution greatly resembles the ones currently employed for aroyl nitrates [13], the nitrating solution consists of an acetyl nitrate solution in acetic anhydride, comprising acetic acid from the hydrolysis of the solvent produced by the water of hydration of the copper salt. This, in conjunction with recent studies of nitration by acyl nitrates [14], permit it to be assumed that the active species of the nitration referred to herein is the protonated acetyl nitrate, which might act by transferring a nitronium ion to the substrate.

In the case of the Vilsmeier-Haack reaction, the active species is probably the addition compound:

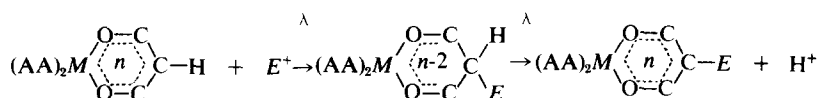


[12, 15, 16, 18], although the above one is not the only structure proposed for the substituting reagent [17, 19]. The substitution products are, probably, cationic dimethylaminomethylene derivatives of the metal complexes. The addition of an aqueous solution of sodium carbonate, together with arresting the reaction by hydrolysis of the reagent, causes, as well, the hydrolysis of the ionic derivative rendering the formylated compound.

In order to investigate from a theoretical point of view the electronic effects induced by the central atom in the 3-position of the ligand, LCAO-MO calculations of electron densities (q_r) and localization energies for electrophilic substitution (L_r^+) were performed. The choice of these particular reactivity indices was based on the nature of the substitution reagents, which involves positively charged active species in both reactions. The trisacetylacetonato complexes of chromium(III), Iron(III) and Co(III) were studied, as well as an ideal "non-metal-oxygen π -bonding" species, which is represented by $m(\text{AA})_3$.

The intermediate model was built assuming that in the critical stage of the substitution process (transition stage) the metal-oxygen σ -system remains structurally unchanged [5, 9] and that the electronic configuration and spin multiplicity of the metal are maintained throughout the reaction pathway.

The electrophilic substitution mechanism within the Wheland's approximation can be illustrated by means of the following scheme:



where n is the number of electrons in the π -system of the metal complex.

The calculated reactivity indices are listed in Table 3, where the localization energies are expressed in β_{CC} , according to the α_{C} and β_{CC} values included in Table 4 (Appendix).

According to the localization energy values, the sequence of reactivity is: $\text{Co}(\text{AA})_3 > m(\text{AA})_3 > \text{Cr}(\text{AA})_3 > \text{Fe}(\text{AA})_3$. The electron densities tend to confirm this prediction: $\text{Co}(\text{AA})_3 > m(\text{AA})_3 > \text{Fe}(\text{AA})_3 \sim \text{Cr}(\text{AA})_3$. In the cases of Cr(III) and Co(III) complexes the theoretical prediction is in agreement with the experimental results; however, the difference between localization energies turns out to be too large, since it leads to a theoretical rate constant quotient, $k_1(\text{Co}) : k_1(\text{Cr})$, of a higher order than that observed experimentally.

Table 3. Reactivity indices

	$\text{Cr}(\text{AA})_3$	$\text{Fe}(\text{AA})_3$	$\text{Co}(\text{AA})_3$	$m(\text{AA})_3$
q_{C3}	1.073	1.075	1.164	1.156
L_{C3}^+	2.259	2.266	2.140	2.206

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Table 4. π -Symmetry orbitals of trisacetylacetonato complexes

A_1	$\frac{1}{\sqrt{3}}(d_{xy} + d_{xz} + d_{yz})$	A_2	$\frac{1}{\sqrt{6}}(\phi_{a1} + \phi_{a2} + \phi_{a3} + \phi_{e1} + \phi_{e2} + \phi_{e3})$
	$\frac{1}{\sqrt{6}}(\phi_{a1} + \phi_{a2} + \phi_{a3} - \phi_{e1} - \phi_{e2} - \phi_{e3})$		$\frac{1}{\sqrt{6}}(\phi_{b1} + \phi_{b2} + \phi_{b3} + \phi_{d1} + \phi_{d2} + \phi_{d3})$
	$\frac{1}{\sqrt{6}}(\phi_{b1} + \phi_{b2} + \phi_{b3} - \phi_{d1} - \phi_{d2} - \phi_{d3})$		$\frac{1}{\sqrt{3}}(\phi_{c1} + \phi_{c2} + \phi_{c3})$
E'	$\frac{1}{\sqrt{6}}(2d_{xy} - d_{xz} - d_{yz})$	E''	$\frac{1}{\sqrt{2}}(d_{xz} - d_{yz})$
	$\frac{1}{2\sqrt{3}}(2\phi_{a1} - 2\phi_{e2} - \phi_{a2} - \phi_{a3} + \phi_{e1} + \phi_{e3})$		$\frac{1}{2}(\phi_{a2} - \phi_{a3} + \phi_{e1} - \phi_{e3})$
	$\frac{1}{2}(\phi_{a2} - \phi_{a3} - \phi_{e1} + \phi_{e3})$		$\frac{1}{2\sqrt{3}}(2\phi_{a1} + 2\phi_{e2} - \phi_{a2} - \phi_{a3} - \phi_{e1} - \phi_{e3})$
	$\frac{1}{2\sqrt{3}}(2\phi_{b1} - 2\phi_{d2} - \phi_{b2} - \phi_{b3} + \phi_{d1} + \phi_{d3})$		$\frac{1}{2}(\phi_{b2} - \phi_{b3} + \phi_{d1} - \phi_{d3})$
	$\frac{1}{2}(\phi_{b2} - \phi_{b3} - \phi_{d1} + \phi_{d3})$		$\frac{1}{2\sqrt{3}}(2\phi_{b1} + 2\phi_{d2} - \phi_{b2} - \phi_{b3} - \phi_{d1} - \phi_{d3})$
	$\frac{1}{\sqrt{2}}(\phi_{c1} - \phi_{c2})$		$\frac{1}{\sqrt{6}}(2\phi_{c3} - \phi_{c1} - \phi_{c2})$

On the other hand, by comparing the reactivity indices of metal complexes with those of the ideal species, it appears that the effect of the π -type interaction between the metal $3d_\epsilon$ orbitals and the delocalized system of the ligands depends upon the metal electronic distribution. Thus, in the complex with $d_\epsilon^6 d_\gamma^0$ distribution (Co) the presence of metal-oxygen π -bonding induces an increase of electron density and a decrease of the potential barrier for electrophilic substitution in the 3-position of the ligand's ring, a completely opposite effect being observed in the metal complex with $d_\epsilon^3 d_\gamma^g$ distribution ($g = 0, 1$ or 2). The changes in electron density may be attributed to the presence of a considerable contribution of the 3-carbon $2p$ AO in the highest occupied MO's, which belong to the representation E and correspond to $3d_\epsilon$ levels of the central atom. The changes in potential barrier could be attributed to the fact that the energy levels with greater ligand contribution, belonging to the representation B of the Wheland's intermediate, are raised toward higher energies with respect to the original levels of the metal complex (representations A_2 and E''), while the level with greater metal contribution of the same representation (B) is more stable than the $d_\epsilon(E'')$ level of the original molecule.

APPENDIX

LCAO-MO Calculations

Electron densities and localization energies were calculated by Hückel's approximation. The secular determinants were factored by the usual group theoretic techniques, since, according to the available information concerning structure [10], the complexes studied belong to the point group D_3 . The proposed intermediates were treated under C_2 symmetry. The π -symmetry orbitals of both molecular species are listed in tables 4 and 5, were the AO's basis for MO expansions are labeled according to the designation established in Fig. 4.

Table 5. π -Symmetry orbitals of Wheland's intermediates

A	d_{xy}	B	$\frac{1}{\sqrt{2}}(d_{xz} - d_{yz})$
	$\frac{1}{\sqrt{2}}(d_{xz} + d_{yz})$		$\frac{1}{\sqrt{2}}(\phi_{a3} + \phi_{e3})$
	$\frac{1}{\sqrt{2}}(\phi_{a3} - \phi_{e3})$		$\frac{1}{\sqrt{2}}(\phi_{a1} + \phi_{e2})$
	$\frac{1}{\sqrt{2}}(\phi_{a1} - \phi_{e2})$		$\frac{1}{\sqrt{2}}(\phi_{a2} + \phi_{e1})$
	$\frac{1}{\sqrt{2}}(\phi_{a2} - \phi_{e1})$		$\frac{1}{\sqrt{2}}(\phi_{b3} + \phi_{d3})$
	$\frac{1}{\sqrt{2}}(\phi_{b3} - \phi_{d3})$		$\frac{1}{\sqrt{2}}(\phi_{b1} + \phi_{d2})$
	$\frac{1}{\sqrt{2}}(\phi_{b1} - \phi_{d2})$		$\frac{1}{\sqrt{2}}(\phi_{b2} + \phi_{d1})$
	$\frac{1}{\sqrt{2}}(\phi_{b2} - \phi_{d1})$		$\frac{1}{\sqrt{2}}(\phi_{c1} + \phi_{e2})$
	$\frac{1}{\sqrt{2}}(\phi_{c1} - \phi_{e2})$		

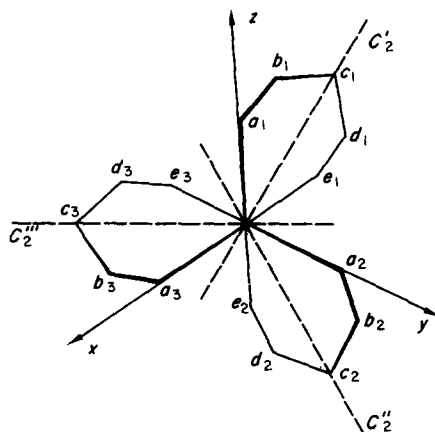


Fig. 4. Geometry and labeling of trisacetylacetonato complexes.

The $2p$ Coulomb integrals associated with the ligand atoms were assumed to be constant parameters and were approximated as $2p$ orbital ionization energies [20]. The exchange integrals involving the ligand atoms were determined by means of the Wolfsberg-Helmholz formula [21]: $\beta_{rs} = F(\alpha_r + \alpha_s)S_{rs}$. The necessary overlap integrals, S_{rs} , were calculated by means of SCF radial functions [22, 23] and by employing the experimental bond lengths [10]. The values obtained were: $S_{CC}(1.39\text{\AA}) = 0.3434$ and $S_{CO}(1.274\text{\AA}) = 0.2782$. The constant F was determined by plotting the variation of the theoretical value of the $\pi_3(B) \rightarrow \pi_4(A)$ free-ligand

20. C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* p. 122. Benjamin, New York (1965).
21. M. Wolfsberg and L. Helmholz, *J. chem. Phys.* **20**, 837 (1952).
22. R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. chem. Phys.* **17**, 1257 (1949).
23. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.* **1**, 120 (1962).

transition vs. F and interpolating the experimental spectral value [24] in the curve obtained. It was thus found that $F = 0.86$ reproduces approximately the experimental transition. The Coulomb and the exchange integrals of the ligand are listed in Table 6.

Table 6. Energy parameters and electronic transitions (figures are given in kK)

		Cr(AA) ₃	Fe(AA) ₃	Co(AA) ₃	m(AA) ₃
$\alpha m(3d)$		-106.04	-106.79	-110.69	
$\alpha o(2p)$		-128.00	-128.00	-128.00	-128.00
$\alpha c(2p)$		-86.00	-86.00	-86.00	-86.00
$\beta co(\pi)$		-25.60	-25.60	-25.60	-25.60
$\beta cc(\pi)$		-25.40	-25.40	-25.40	-25.40
$\beta mo(\pi)$		-8.08	-12.90	-13.73	
$\pi_3(E) \rightarrow \pi_4(A_1)$	Obs.*	39.30	42.50	43.90	
	Calc.	39.29	42.52	43.90	34.85
$d_e(A_1) \rightarrow \pi_4(E)$	Obs.*	30.20	28.50	31.00	
	Calc.	30.20	28.50	31.00	

*Values from Ref. [26].

The determination of the $3d_e$ Coulomb terms for the central atoms and the metal-oxygen exchange integrals was based upon the assignment of the experimental electronic spectra of trisacetylacetonato complexes of transition metal ions established by Barnum [25, 26]. The method consists of obtaining by iteration the parameter values that most accurately reproduce the experimental absorption bands assigned by Barnum to the transitions $d_e(A_1) \rightarrow \pi_4(E)$ and $\pi_3(E) \rightarrow \pi_4(A_1)$, which are theoretically sensitive enough to the variations of the $3d_e$ Coulomb integrals and metal-oxygen exchange terms, respectively. The final values of energy parameters are included in Table 6, together with the experimental as well as the calculated reference transitions.

The remaining theoretical transitions were also in agreement with the experimental data [26]; however, the prediction of absorption bands superpositions turned out to be different than the one described in Ref. [26].

The energy calculations of the Wheland's intermediate π -system were performed also with the parameters listed in Table 6.

The secular matrices were diagonalized using FORTRAN on the IBM 360/40 computer of "centro de Computación de la Universidad de Chile".

24. R. L. Belford, A. E. Martell and M. Calvin, *J. inorg. nucl. Chem.* **2**, 11 (1956).

25. D. W. Barnum, *J. inorg. nucl. Chem.* **21**, 221 (1961).

26. D. W. Barnum, *J. inorg. nucl. Chem.* **22**, 183 (1961).