earlier—ethane (~600%) is obtained. The nature of the ethylene hydrogenation catalyst found in this reaction remains to be determined, but, under similar conditions, $C_2H_4Fe(CO)_4$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ are separately found to be ineffective catalysts for this hydrogenation.

Acknowledgment. This work was supported by the National Science Foundation and the Robert A. Welch Foundation (Grants No. F-067 and F-233). We are also indebted to the National Science Foundation for the purchase of the Syntex $P2_1$ diffractometer (Grant No. GP-37028).

Supplementary Material Available: Table of fractional coordinates and anisotropic thermal parameters (1 page) for both crystallographic data sets. Ordering information is given on any current masthead page.

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(12) That is, each bridging position is occupied, statistically, $^2/_3$ by CO and $^1/_3$ by CH_2. Since the two presumably slightly different C positions would be indistinguishable by this experiment, the crystallographic description is thus one with a full-weight C (i.e., $^2/_3 + {}^1/_3$), a $^2/_3$-weight O ($^1/_3 + {}^1/_3$) and two $^1/_3$-weight H atoms at each bridging position.
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Ground-State Quenching of the ^2E Excited State of $Cr(bpy)_3{}^{3+}$ and $Cr(phen)_3{}^{3+}$ [1]

Sir:

The lowest metal-centered excited state (^2E) of polypyridyl complexes of Cr(III) [$Cr(NN)_3{}^{3+}$] has been shown to be a powerful oxidizing agent capable of engaging in excited-state electron-transfer reactions[2] and photoelectrochemical action.[3] Knowledge of the lifetime (τ) of ^2E is necessary in order to evaluate the photophysics of the state, calculate rate constants (k_q) from Stern-Volmer luminescence quenching, and engineer potential solar energy conversion schemes. Because of the thermal and photochemical stability of $Cr(NN)_3{}^{3+}$ in acidic aqueous solution,[2,4] 1 M HCl has been the medium of choice for many lifetime measurements. Examination of data from many laboratories[5-10] reveals variations in the values of τ and k_q for ostensibly identical systems and experimental conditions. We note, however, that the concentrations of the ground-state complexes are often not specified and can vary over many orders of magnitude depending upon the experimental technique or the application. In this communication we report the dependence of τ of (^2E)$Cr(phen)_3{}^{3+}$ (phen = 1,10-phenanthroline) and (^2E)$Cr(bpy)_3{}^{3+}$ (bpy = 2,2′-bipyridine) upon the concentration of the ground-state substrates.

Table I. Lifetime of (^2E)$Cr(phen)_3{}^{3+}$ in Deaerated Aqueous 1 M HCl Solutions at 22 °C

[$Cr(phen)_3{}^{3+}$], M	τ, ms[a]	[$Cr(phen)_3{}^{3+}$], M	τ, ms[a]
9.2×10^{-6}	0.36	2.7×10^{-4}	0.23
1.2×10^{-5}	0.34	5.6×10^{-4}	0.22
2.3×10^{-5}	0.37	6.7×10^{-4}	0.15
2.7×10^{-5}	0.33	1.2×10^{-3}	0.13
4.4×10^{-5}	0.36	2.0×10^{-3}	0.12
6.9×10^{-5}	0.29	5.0×10^{-3}	0.067
8.1×10^{-5}	0.30	7.5×10^{-3}	0.050
1.6×10^{-4}	0.31	1.0×10^{-2}	0.037
2.3×10^{-4}	0.22		

[a] Each value represents the average of three–ten individual runs.

Table II. Lifetime of (^2E)$Cr(bpy)_3{}^{3+}$ in Deaerated Aqueous 5 M HCl Solutions at 22 °C

[$Cr(bpy)_3{}^{3+}$], M	τ, ms[a]	[$Cr(bpy)_3{}^{3+}$], M	τ, ms[a]
1.2×10^{-5}	0.11	9.4×10^{-4}	0.084
2.8×10^{-5}	0.10	1.0×10^{-3}	0.078
4.6×10^{-5}	0.11	1.2×10^{-3}	0.081
4.7×10^{-5}	0.12	1.5×10^{-3}	0.082
5.7×10^{-5}	0.11	1.8×10^{-3}	0.077
9.4×10^{-5}	0.11	3.6×10^{-3}	0.060
1.0×10^{-4}	0.11	4.8×10^{-3}	0.073
2.0×10^{-4}	0.096	6.0×10^{-3}	0.047
2.8×10^{-4}	0.093	1.0×10^{-2}	0.041
4.7×10^{-4}	0.085	1.1×10^{-2}	0.044
6.0×10^{-4}	0.087	1.2×10^{-2}	0.042
9.0×10^{-4}	0.086		

[a] Each value represents the average of three–ten individual runs.

The complexes as $ClO_4{}^-$ salts were available from our previous studies.[2] Solutions were prepared from reagent grade (Fisher) HCl (10^{-5} % Fe and heavy metals) and water that had been distilled from $KMnO_4$ and/or purified by passage through a Millipore train; solutions were deaerated by bubbling with prepurified N_2 or Ar for 30 min. Values of τ were determined at 22 ± 1 °C by the monitoring of the first-order decay of the emission from ^2E at 727 nm excited by pulsed laser illumination. The apparatus in Montreal consisted of a 1-kW N_2 laser providing 4-ns pulses at 337 nm as previously described by Demas and Flynn.[11] The apparatus in Boston utilized a frequency-doubled ruby laser providing 30-ns pulses at 347 nm. The values of τ ($= 1/k_{obsd}$) within a single experimental set were reproducible with <10% variation; the standard deviation of values from replicate experiments were of the order of 10–15%.

The data for $Cr(phen)_3{}^{3+}$ in 1 M HCl given in Table I show that τ decreases by an order of magnitude as [$Cr(phen)_3{}^{3+}$] is increased from 1×10^{-5} to 1×10^{-2} M. The data produce a linear plot of k_{obsd} vs. [$Cr(phen)_3{}^{3+}$] (Figure 1) with a slope of 2.3×10^6 M^{-1} s^{-1} and an intercept of 3.0×10^3 s^{-1}. By comparison, the average of ten individual experiments yields τ = 0.25 (±0.03) ms over the substrate concentration range 1.2×10^{-5} to 1.2×10^{-3} M in the absence of HCl; solubility restrictions prevent the extension of the range in neat H_2O. The quenching phenomenon is the same in either 1 M HCl or 1 M NaCl. In contrast, τ values for (^2E)$Cr(bpy)_3{}^{3+}$ in 1 M HCl and neat H_2O are virtually indistinguishable: τ = 0.073 (±0.008) ms in 1 M HCl and 0.068 (±0.008) ms in H_2O over the substrate concentration range 1.4×10^{-5} to 2.5×10^{-3} M. In order to observe the ground-state quenching phenomenon for $Cr(bpy)_3{}^{3+}$, 5 M HCl was used; the data (Table II) result in a linear quenching plot (Figure 2) with a slope of 1.3×10^6 M^{-1} s^{-1} and an intercept of 1.0×10^4 s^{-1}.

The use of different samples of the recrystallized complexes, analytical reagent grade acid, and purified water had no effect on the results. In order to exclude free ligand within the sub-

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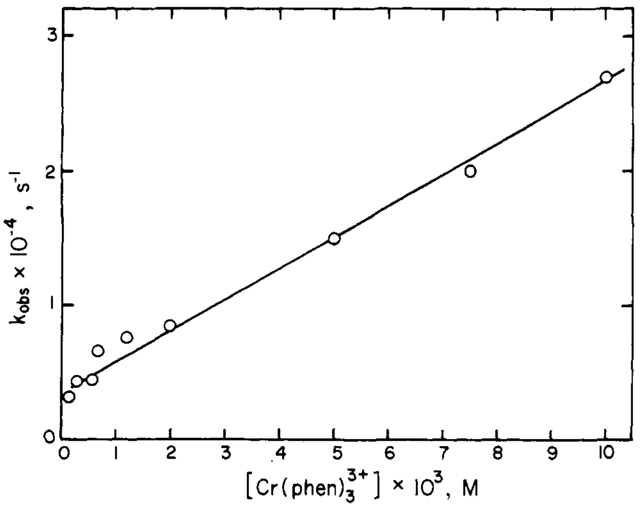


Figure 1. Quenching plot of the data for $(^2E)Cr(phen)_3{}^{3+}$ in deaerated aqueous 1 M HCl solutions at 22 ± 1 °C; points at [substrate] $<2 \times 10^{-4}$ M cannot be shown owing to the scale used. Correlation coefficient of least-squares plot of all the points = 0.995.

strate samples as the cause of the quenching phenomenon, despite the excellent elemental analyses of the complexes,[2] we have demonstrated that the presence of up to 1×10^{-3} M phen (or 5×10^{-3} M bpy) in 5×10^{-5} M $Cr(phen)_3{}^{3+}$ [or $Cr(bpy)_3{}^{3+}$] in the appropriate HCl medium does not quench the luminescence from ^2E.

The quenching phenomenon is described by the equation $k_{obsd} = k_0 + k_g\,[Cr(III)]$ where k_0 is the first-order rate constant for the decay of ^2E at infinite substrate dilution and k_g is the second-order rate constant for the quenching of ^2E by ground-state species. Inasmuch as concentration quenching is not seen in the absence of Cl^-, it is clear that the ground-state quenching reaction is mediated by the anion. Nevertheless, the presence of Cl^- does not change the absorption spectra of the ground-state complexes nor the wavelength profiles of the emission spectra from ^2E. At constant [substrate], the presence of Cl^- does cause a change in emission intensity commensurate with the change in τ.

It has been established[12] that pairing between $Fe(bpy)_3{}^{2+}$ or $Fe(phen)_3{}^{2+}$ and Cl^- is quite extensive; ion pairing for the tripositive Cr(III) complexes, in both the ground and excited states, would be expected to be even more extensive.[13] In previous publications[2,5-7] we have shown that this ion pairing results in the prolongation of the lifetime of ^2E; this effect is seen here from the comparison of the values of τ in the limit of infinite substrate dilution in the presence and absence of Cl^- (Table III). The lack of observable ground-state quenching for $Cr(bpy)_3{}^{3+}$ in 1 M HCl is attributed simply to the failure of that medium to decrease k_0 sufficiently for the quenching phenomenon to be observed outside of the experimental scatter.

One effect of ion pairing is the reduction of the overall positive charges of the ground- and excited-state complexes with concomitant reduction of the mutual electrostatic repulsion.[12] Thus, the values of k_g, which are virtually the same for both complexes in Cl^- medium, reflect the encounter of ion-paired ground-state $[Cr(III)\cdots Cl^-]$ and excited-state $[{}^*Cr(III)\cdots Cl^-]$ species; in the absence of Cl^-, k_g could well be many orders of magnitude lower so that no quenching is observed. The quenching reaction cannot be due to excited-state electron transfer to form Cr(II) and Cr(IV); the energetics of such a reaction are completely unfavorable. The reaction must proceed via collision-induced nonradiative deactivation of the excited-state species. It is easy to visualize, for example, the formation of an "ion-bridged excimer", $^*[Cr(III)\cdots Cl^-\cdots Cr(III)]$, as the result of this encounter (Scheme I). Excimer formation is a fairly common phenomenon for aromatic molecules and is generally manifested in lowered excited-state lifetimes with increasing ground-state concentrations of the substrate.[15] In the absence of any emission that can be attributed to the "ion-bridged excimer" we cannot know the lifetime of $^*[Cr(III)\cdots Cl^-\cdots Cr(III)]$, but it is probably very short owing to rapid nonradiative deactivation through the coupling of the vibrational modes of the aggregate. In any event, it should be noted that ground-state quenching of the excited states of Cr(III) complexes in solid matrices, attributable to aggregate formation, has been reported.[16,17]

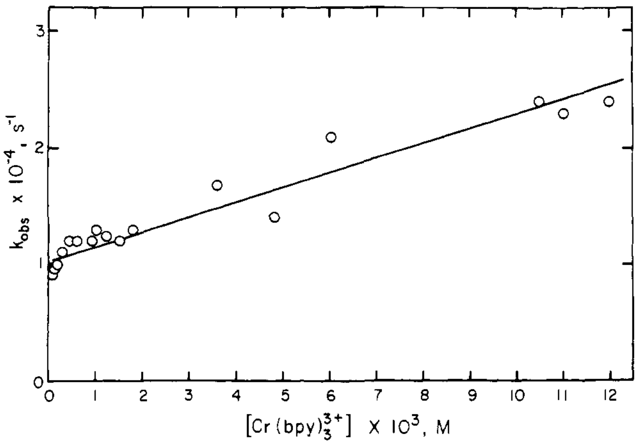


Figure 2. Quenching plot of the data for $(^2E)Cr(bpy)_3{}^{3+}$ in deaerated aqueous 5 M HCl solutions at 22 ± 1 °C; points at [substrate] $<2 \times 10^{-4}$ M cannot be shown owing to the scale used. Correlation coefficient of least-squares plot of all the points = 0.962.

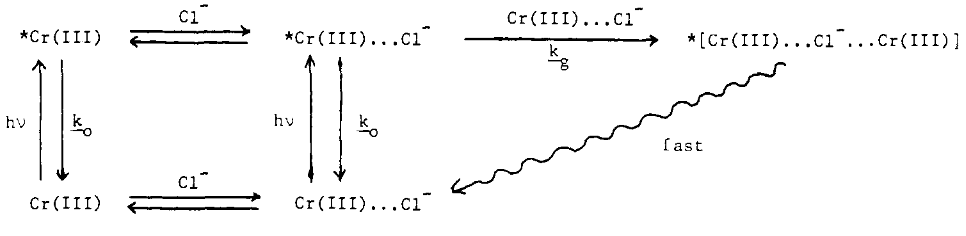
Table III. Rate Constants in the Ground-State Quenching of (^2E)-$Cr(NN)_3{}^{3+}$ [a]

	*Cr(III)	*Cr(III)···Cl$^-$	
	k_0, s^{-1} (τ, ms)	k_0, s^{-1} (τ, ms)	k_g, $M^{-1}\,s^{-1}$
$Cr(bpy)_3{}^{3+}$	1.4×10^4 (0.068)	1.0×10^4 (0.10)	1.3×10^6 [b]
$Cr(phen)_3{}^{3+}$	4.0×10^3 (0.25)	3.0×10^3 (0.33)	2.3×10^6 [c]

[a] 22 ± 1 °C, deaerated aqueous solutions. [b] 5 M HCl. [c] 1 M HCl.

The results reported here serve as a further indication of the dependence of the photophysics and photochemistry of Cr(III) complexes on solution medium and remind investigators to control those conditions and report them explicitly. It is entirely possible that the ground-state quenching of the excited states of cationic coordination complexes mediated by anions in fluid

Scheme I



solution at room temperature is a general phenomenon. Its observation depends on the values of k_0 and k_g, specifically, low values of k_0 and high values of k_g. These conditions are evidently satisfied by $Cr(NN)_3^{3+}$ and further studies are underway to define the structural and solution medium parameters that regulate these rate constants.

References and Notes

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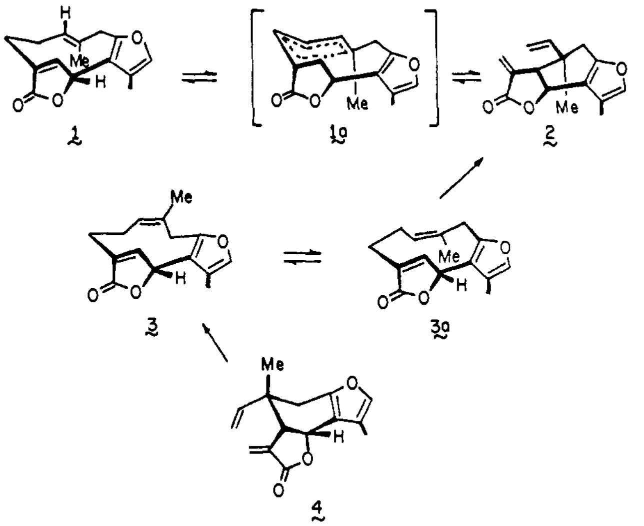
Synthesis of (±)-Linderalactone, (±)-Isolinderalactone, and (±)-Neolinderalactone

Sir:

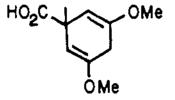
The germacrane furanosesquiterpenes, linderalactone (**1**), isolinderalactone (**2**),[1] and neolinderalactone (**3**)[2] were isolated by Takeda from the root of the shrub *Lindera strychnifolia* Vill. Their structures are based upon chemical degradation, and for linderalactone **1** an X-ray crystal structure is available.[3]



Linderalactone (**1**) has generated considerable interest because of its facile Cope rearrangement to isolinderalactone (**2**) (antipodal to the elemane sesquiterpenes); NOE studies have concluded that the stereochemical outcome of such rearrangements is dependent upon the conformation of the ten-membered ring.[4] Neolinderalactone exists at room temperature as a mixture of conformers **3** and **3a** in the ratio 4:1.[2b] Cope rearrangement of neolinderalactone gave isolinderalactone **2**, which therefore must proceed from the conformer **3a** rather than **3**.[4]

Here we report the total synthesis of **1**, **2**, and **3** by an approach that, because of its strategy, does not need to rely upon any stereochemical or regiochemical controls.

Birch reduction of 3,5-dimethoxybenzoic acid and in situ alkylation with methyl iodide gave **5** (87%), which on treatment with lithium aluminium hydride gave the known alcohol **6**.[6]



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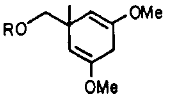
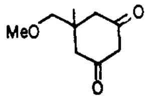


6, R = H
7, R = Me



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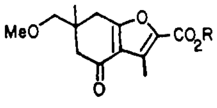
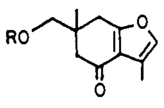


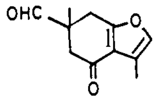
9, R = Et
10, R = H

After trying many protecting groups for the primary alcohol in **6**, and also attempting to avoid the use of protecting groups altogether, we converted **6** into the *O*-methyl ether **7** (NaH, MeI, THF), 95%.[7] Mild acid hydrolysis of **7** (4 N HCl, THF, 6 h at room temperature) gave the symmetrical *β*-diketone **8** (76%, mp 92-93 °C).[7] Condensation of **8** with ethyl 2-chloroacetoacetate in methanolic potassium hydroxide[8] gave the tetrasubstituted furan **9** (57%)[7] along with small amounts of the acid **10**. Because of the symmetry of **8** there are no regiochemical considerations in making **9**. The ester **9** was further hydrolyzed with methanolic potassium hydroxide to give pure **10**, mp 140-142 °C (85%). Decarboxylation of **10** proceeded best using the classical procedure Cu, pyridine, and diethylene glycol at 160-165 °C to give **11** (85%).[7] Demethylation of **11** using boron tribromide-dichloromethane −70 to +20 °C gave the alcohol **12** (96%),[7] which was oxidized directly to the aldehyde **13** using pyridinium chlorochromate (74%).[7] Methylenation of **13** using methylenetriphenylphosphorane in THF gave the vinyl derivative **14** (67% after bulb to bulb distillation).[7]

Introduction of the fused *γ*-lactone ring onto **14** poses no stereochemical problems since, as we will see, it does not matter if alkylation of **14** produces a mixture of epimers. Indeed it is



11, R = Me
12, R = H



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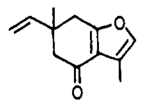
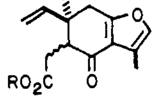
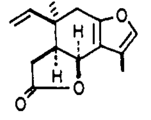
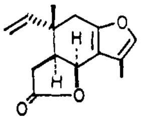


14



15, R = Et
16, R = H





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