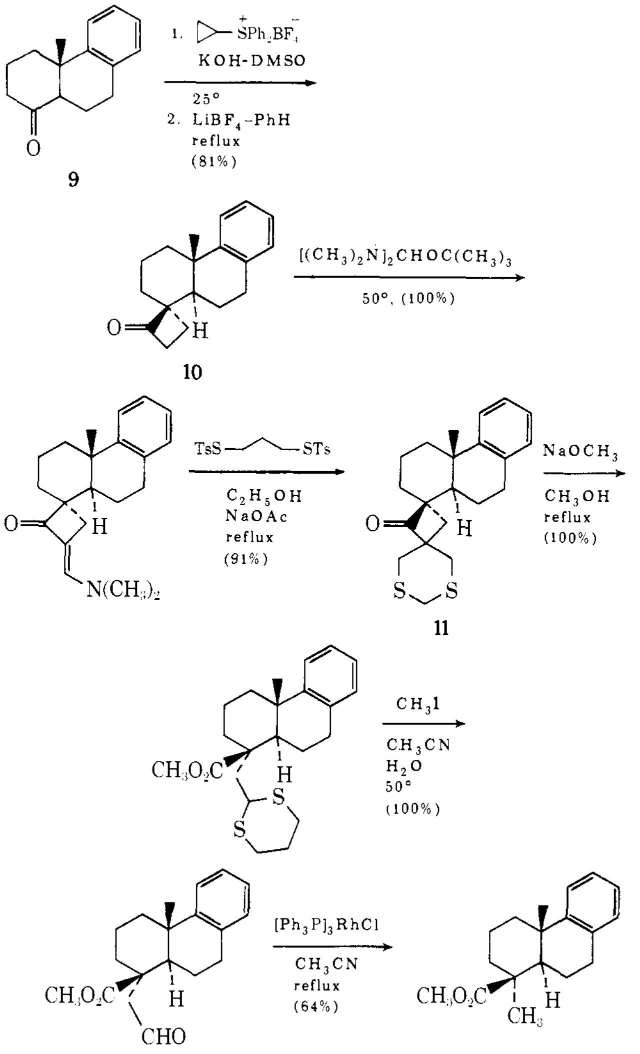
Scheme I. Stereoselectivity of Modified Geminal Alkylation, Synthesis of Methyl Desoxypodocarpate



prisingly, even with such a hindered carbonyl system, cleavage to **12** (mp 135.0–135.5°) occurred smoothly with methanolic sodium methoxide at reflux. Following a sequence patterned after the recently reported work of Wenkert, *et al.*,[12] would lead into the stereochemistry of the abietic acid series from **11**. Alternatively dithiane hydrolysis and decarbonylation utilizing Wilkinson's catalyst completes the sequence in the podocarpate series. Comparison of ir, nmr, and tlc properties with an authentic sample confirmed the identity of the compound and consequently the stereochemistry of **10**.

The development of this alternative approach to geminal alkylation should ensure the generality of the approach for a wide range of structural types.

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Ligand and Geometry Effects in the Quenching of the Tris(2,2′-dipyridyl)ruthenium(II) Phosphorescence by Some Chromium(III) Complexes

Sir:

The quenching of the excited states has extensively been studied in the field of organic chemistry.[1] When energy and spin requirements are satisfied, these processes are generally diffusion controlled in fluid solution at room temperature.[1,2] This "rule," however, does not apply when coordination compounds are involved.[3-13] It has been reported that the quenching efficiency in the collision encounter is strongly affected by the charge[7,10,11,13] and the geometry[12] of the complex and by the nature of the ligands.[4-6,10] However, systematic studies are needed in order to establish what is the actual role played by these and other factors in determining the quenching efficiency. We wish to report here the results of an investigation which was carried out using Ru(dipy)$_3{}^{2+}$ as a donor and several Cr(III) complexes as quenchers.

The experiments were carried out in aqueous solutions at 22°. The ionic strength was adjusted by adding KCl. The quenching of the Ru(dipy)$_3{}^{2+}$ phosphorescence intensity was measured with a Perkin-Elmer MPF3 spectrofluorimeter. In some cases, the quenching of the phosphorescence lifetime was measured with the equipment previously described.[14] The τ^0/τ values were practically equal to the corresponding I^0/I values, showing that no static quenching occurred.[15] In the case of *trans*-Cr(en)$_2$(NCS)$_2{}^+$, the quenching of the Ru(dipy)$_3{}^{2+}$ phosphorescence was accompanied by the sensitized emission of the quencher.[16]

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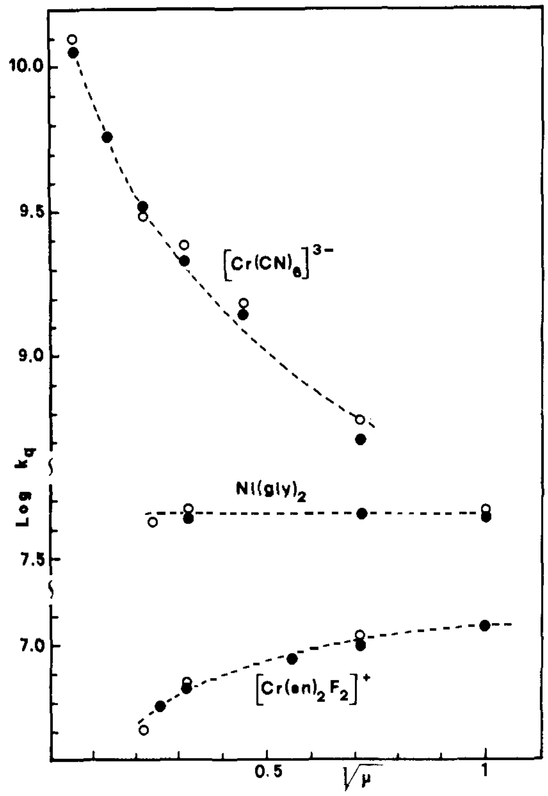

Figure 1. Quenching of the Ru(dipy)$_3^{2+}$ phosphorescence by complexes of different charge as a function of the ionic strength: ○, from lifetime measurements; ●, from intensity measurements.

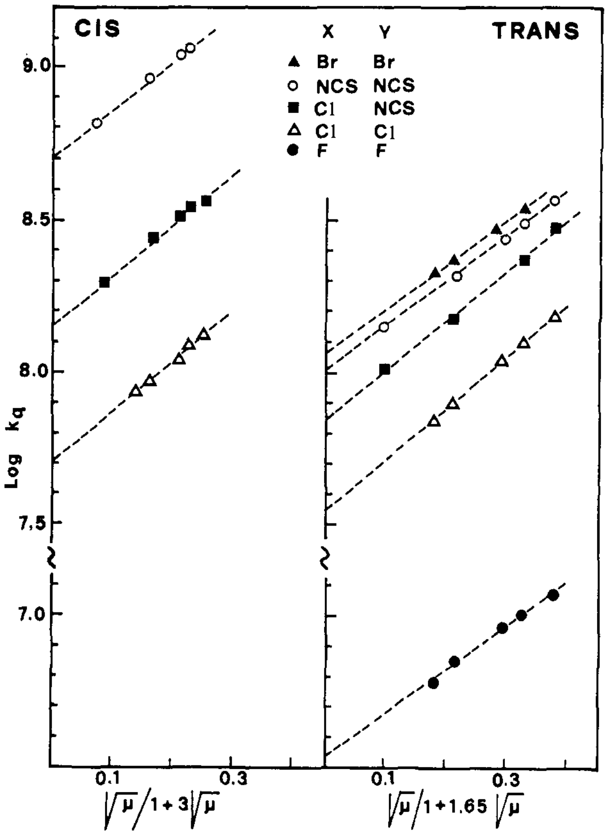

Figure 2. Quenching of the Ru(dipy)$_3^{2+}$ phosphorescence by complexes of the Cr(en)$_2$XY$^+$ type as a function of the ionic strength.

Since the diffusion of the excited state and the quencher is a necessary (although not sufficient) condition for a dynamic quenching, an ionic strength influence on the bimolecular quenching constant (k_q) is to be expected whenever the excited state and the quencher are charged species.[18-20] The plots shown in Figure 1 are in agreement with such an expectation. Therefore, in order to compare the quenching ability of the various complexes, the experimental quenching constants should be extrapolated to zero ionic strength (k_q^0). It is known that the salt effects for diffusion controlled reactions can be fitted by Brønsted-Debye equations.[19-21] For Cr(CN)$_6^{3-}$, a linear plot of log k_q against $\sqrt{\mu}/(1 + 2\sqrt{\mu})$ was obtained, whose slope was near the theoretical value. The extrapolated k_q^0 value ($\sim 2 \times 10^{10}$ M^{-1} sec^{-1}) was in good agreement with the diffusion controlled rate constant (3.2×10^{10} M^{-1} sec^{-1}).[14] For the positively charged Cr(III) complexes, almost linear plots for k_q against $\sqrt{\mu}/(1 + \alpha\sqrt{\mu})$ were obtained, but their slope was about 20% lower than the theoretical value (Figure 2). Moreover, whereas for the trans isomers the α value was reasonable, it was exceedingly high for the cis isomers. Thus, whatever the reason may be for such a behavior, the extrapolated values that can be obtained from the plots of Figure 2 might not represent the "true" quenching constants at zero ionic strength. However, it can be safely assumed that the extrapolation gives upper limiting values for the "true" quenching constants, which must thus be lower than the diffusion controlled rate constant (3×10^9 M^{-1} sec^{-1}).[21]

Since the complexes of the same family are affected by the ionic strength exactly in the same way (see Figure 2), the relative quenching abilities of the various complexes belonging to the same family may be represented by k_q values taken at the same ionic strength. Therefore, it is clear from Figure 2 that the nature of the ligands has a great influence on the quenching ability of the complex and that the contribution of the various ligands to the quenching ability increases in the series $F^- < Cl^- < NCS^- < Br^-$. This behavior cannot be due to energy reasons since all of our complexes have doublet states at lower energy than that of the excited donor (17.1 kK[22]).[23] It seems more likely that the above series is determined by the "conductor" ability of the ligands.[6,10] We would like to note, however, that this series does not coincide[6] with the nephelauxetic series.[24]

As previously mentioned, there is some difference in the effect of the ionic strength on the quenching

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(16) Among the quenchers used, *trans*-Cr(en)$_2$(NCS)$_2^+$ is the only one which is able to emit phosphorescence under our experimental conditions.[17]

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(23) Energy reasons would be important if the excited quartets of Cr(III) complexes played a primary role in the quenching. This, however, does not seem to be the case since the Cr(en)$_2$(NCS)$_2^+$ complexes, whose lowest quartet-quartet vertical excitation energy is >20 kK, exhibit very high quenching constants (Figure 2).

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constants of the cis and trans isomers.[25] Although this fact prevents any quantitative comparison, from Figure 2 it is apparent that the quenching ability of the cis isomers is higher than that of the corresponding trans isomers. Moreover, a change in the ligands seems to cause a larger effect in the cis family.

In conclusion, our data show that the nature of the ligands and the geometrical configuration are very important factors in determining the quenching ability of coordination compounds. Whether the ionic charge also plays an important role should be established by similar, systematic investigations. These, however, are made difficult by the fact that a change in the ionic charge is accompanied by a change in the nature of the ligands.

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[25] Whether this difference originates during the diffusion or the encounter is to be established.

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The Karplus Relationship and the Correlation of Two Anomalous ^{13}C-Vicinal ^{1}H Coupling Constants with Bonding Electron Density Distribution Found by Accurate X-Ray Analysis

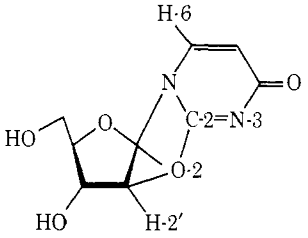
Sir:

Recently,[1] a Karplus-type[2] relationship between the coupling constants for ^{13}C-2 and vicinal ^{1}H nuclei and the magnitudes of the respective torsional angles defined by these two atomic species in uridine, 2,2′-anhydro-1-β-D-*arabino*-furanosyluracil, (**1**) and 2,5′-anhydro-2′,3′-isopropylidenecyclouridine (**2**), was demonstrated. The latter two cyclonucleosides possess conformationally rigid structures as a consequence of their polycyclic fused ring systems and one can therefore be confident in comparing their conformations as observed in the crystalline state with those deduced in solution. To this end X-ray crystallographic analyses of these two cyclonucleosides were carried out so that accurate values for the torsional angles which had previously been estimated from molecular models would be available. In addition to providing the above information these two structural determinations have provided insight into two anomalous coupling constants observed in the ^{13}C nmr spectrum of **2** (with the 2 position of the uracil ring ^{13}C enriched). Finally, this work has provided evidence of a shift of electron density from two bonding orbitals on N-3 of the uracil ring in **1** to the lone-pair orbital of this atom when a hydrogen bond is formed.

Compound **1** crystallizes in space group $P2_12_12_1$ with unit cell dimensions a = 13.687 (2), b = 18.241 (3), and c = 7.439 (1) Å. Compound **2** crystallizes in space group $P2_1$ with the unit cell dimensions a = 10.344 (1), b = 6.407 (1), and c = 9.077 (1) Å, and β = 93.69 (1)°. Intensity data in the range 3° < 2θ < 60° for the two compounds were collected on a Picker FACS-1 diffractometer with Mo Kα (λ = 0.71069 Å) radiation and a graphite monochromator. The solution of the crystal structure of **1** was accomplished by the straightforward application of the tangent formula[3] whereas that of **2** required the additional use of a translation function.[4,5] The final R indexes were 0.033 and 0.034 for **1** and **2**, respectively.

The relevant torsional angles found by these X-ray analyses are given in Table I along with the corresponding ^{13}C to vicinal ^{1}H coupling constants and the previously estimated torsion angles.[1] Figure 1 shows that, with two exceptions, a Karplus-type relation does exist; the $^{3}J_{^{13}\text{C-2,H-5}'}$ for **2** lies 2.8 Hz above and the $^{3}J_{^{13}\text{C-2,H-1}'}$ for **2** falls 1.0 Hz below the curve in Figure 1. The occurrence of these two values may be denoted as anomalies to this Karplus curve.

Table I. Relationships of Vicinal ^{13}C–^{1}H Coupling Constants to Torsion Angle



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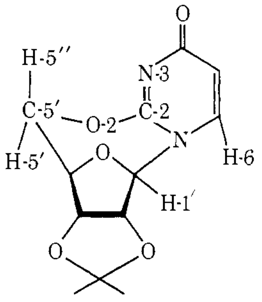

2

Vicinal atoms	$J_{^{13}\text{C},^{1}\text{H}}$, Hz[a]	Torsion angle, deg[b]	Previously estimated[a]	Solvent
C-2–H-6	8.0 (**1**)	180, 177		D_2O
	7.2 (**2**)	−174	~175	$CDCl_3$
C-2–H-1′	3.6 (**1**)	−134, −138	−125	D_2O
	6.6 (**2**)	−175	170	$CDCl_3$
C-2–H-2′	2.0 (**1**)	120, 112	120	D_2O
C-2–H-5′	8.7 (**2**)	−158	175	$CDCl_3$
C-2–H-5″	2.0 (**2**)	−38	50	$CDCl_3$

[a] Reference 1. [b] The estimated standard deviation of these torsional angles is ±2°.

The conformation and dimensions of compounds **1** and **2** differ. The glycosidic torsion angles, O-1′–C-1′–N-1–C-6,[6] are 294.5 and 290.0° for the two independent molecules of **1** and 246.4° for molecule **2**. In general, the chemically equivalent bond distances are similar in **1** and **2**, but many chemically equivalent bond angles differ greatly, particularly in the regions of the uracil–sugar linkages. The distances C-2′–O-2 in the two molecules of compound **1** are 1.460 (2) and 1.462 (2) Å. The similar distance in compound **2**, C-5′–O-2, is 1.458 (3) Å and is therefore equivalent. The exocyclic distances C-2–O-2 in the two molecules of compound **1** are 1.337 (2) and 1.333 (2) Å, whereas this distance has

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