nearly the same endo selectivities for **1** and **4** in the reactions with a given acrylic or methacrylic compound. Both dienes are electroneutral, and thus the type of interactions operative in the determination of endo–exo stereoselectivity should be analogous for the two dienes. The fact that the exo adducts are the predominant products of the reactions of methacrylic dienophiles with both dienes could best be understood by assuming that, in the transition state, the methyl substituent in the dienophile is subject to greater attraction from the diene sp^2 carbons than the unsaturated polar substituents. The attractive force of the methyl group will be of the van der Waals type (dispersion).

Recently, Houk and Luskus[8] have argued against our proposal of the attractive van der Waals interactions of the methyl group, claiming that the stereoselectivity observed for **1**[1] should be taken as an indication of the steric repulsion between the methyl substituent in dienophiles and the apical hydrogens in **1**. They found that 2,5-dimethyl-3,4-diphenylcyclopentadienone (**9**), which has no such apical hydrogen atom, gives major endo adducts in its reactions with methyl methacrylate and crotonate. However, their substrate must be greatly polarized because of the carbonyl group attached to the reaction center. Apparently, the situation introduces an additional complexity to the otherwise straightforward understanding of the stereochemical factors for the reactions of simple, nonpolar diene moieties. Direct comparison of the endo selectivities between **1** and **9** thus cannot be clear-cut evidence against our hypothesis of the van der Waals attractive interaction. Even though the adverse steric effects can often be an important factor to control stereochemical courses, they certainly cannot be a major factor in the reaction of **4** and probably not in the reaction of **1**, either.

In conclusion, we emphasize that cases can exist in which the endo–exo stereoselectivity of Diels–Alder reactions is governed primarily by local London–van der Waals attraction forces.[9] The methyl substituent in dienophiles exhibits rather greater attractive forces than do the unsaturated polar substituents, *e.g.*, CN, $COOCH_3$, and CHO. Polar dienes might well be influenced by dipole–dipole and dipole–induced dipole interactions and cause changes in potential surface of reaction, analyses of which would need more thorough investigations.[8,10]

endo adducts **5**, in contrast to the exo selectivity of the methacrylate. In the case of **1**, the products were mainly exo adducts for all these three dienophiles. Steric repulsions are thought to be an influencing factor only in the reactions of bulky dienophiles, in which bulky alkyl substituents favor the less crowded side; exo in **4** and endo in **1** (Y. Kobuke, T. Sugimoto, T. Shimizu, and J. Furukawa, unpublished data).

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Photochemistry of Ethylenediaminetetraacetate Complexes. Excited State Reaction Pathways in Cobalt(III) Complexes[1]

Sir:

It has become increasingly evident that triplet sensitizers are powerful tools for characterizing chemically reactive excited states of transition metal complexes.[2–11] Despite the obvious mechanistic potentialities, the photosensitization of oxidation–reduction decomposition of cobalt(III) complexes[2,3,7] has been fraught with sufficient ambiguities[12] that Adamson's radical pair hypothesis[13,14] can still be vigorously defended as the only viable model for cobalt(III) photochemistry.[15,16] A particularly puzzling feature of the photochemistry of cobalt(III) complexes has been the lack of appreciable photochemical reactivity associated with the irradiation of ligand field absorption bands[2,13–15,17–19] contrasted to the significant yields of aquation products frequently observed to accompany irradiation of near-ultraviolet charge transfer to metal (CTTM) absorption bands.[2,13–15] To date, the single quantitative study of the sensitized oxidation–reduction decomposition of a cobalt(III) complex, the reaction which accompanies $Co(NH_3)_6{}^{3+}$ quenching of the biphenyl phosphorescence,[7] has resulted in a limiting sensitized yield (of Co^{2+}) about four times greater than the yield which results from direct excitation.[7,20] This observation suggests that the product yields resulting from the direct excitation of cobalt(III) complexes may be greatly complicated by inefficient intersystem crossing from the initially populated spectroscopic singlet states to chemically reactive triplet states.

In this communication we report on the direct and sensitized photochemistry of some simple acido–ethylenediaminetetraacetate complexes of cobalt(III), $Co(HEDTA)X^-$ ($X = Cl, Br, NO_2$).[21] As sensitizer we have chosen $Ru(bipy)_3{}^{2+}$ whose emission spectroscopy[22] and utility as a sensitizer[9] have been well docu-

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Table I. Product Yields Resulting from Direct and Sensitized Excitation of $Co(EDTA)^-$ and $Co(HEDTA)X^-$ [a]

Complex	Direct photolysis: At 254 nm ϕ_X[b]	$\phi_{Co^{2+}}$	At 450 nm $10^3\phi_X$[b]	$10^3\phi_{Co^{2+}}$	Sensitized photolysis[c]: ϕ_X^{lim} [b]	$\phi_{Co^{2+}}^{lim}$
$Co(EDTA)^-$	*d*	0.05 ± 0.005		<0.1	*d*	0.10 ± 0.01
$Co(HEDTA)Cl^-$	0.04 ± 0.01	0.18 ± 0.02	10 ± 1	25 ± 3	0.40 ± 0.06	0.24 ± 0.03
$Co(HEDTA)Br^-$	0.06 ± 0.01	0.12 ± 0.01	30 ± 4	9 ± 1	0.10 ± 0.02	0.8 ± 0.1
$Co(HEDTA)NO_2^-$	~ 0.01[e]	0.17 ± 0.02	~ 4 ~ 10[e]	~ 4	*f*	0.71 ± 0.09

[a] All studies in water at 25°, pH = 3. [b] Yield for X^- aquation except as indicated. Based on comparison of absorption spectra. [c] The $Ru(bipy)_3^{2+}$ sensitizer was irradiated at 450 nm. [d] No detectable spectral change. [e] Approximate linkage isomerization yield. [f] Not known.

mented. This is a particularly good sensitizer for anionic acceptors and this sensitizer has a sufficiently intense, and characteristic, absorption spectrum that chemical or photochemical decomposition of the sensitizer is easily ruled out. Simple Stern–Volmer dependence[2,23] on [$Co(HEDTA)X^-$] of the quenching of $Ru(bipy)_3^{2+}$ phosphorescence and of product yields has been observed in each case. The quenching rate constants (calculated assuming a lifetime of 2×10^{-6} sec for the $Ru(bipy)_3^{2+}$ triplet)[22] vary, depending on X, in the range 10^8–10^9 M^{-1} sec^{-1}.

We find that a combination, depending again on X, of labilization and oxidation–reduction reactions of $Co(HEDTA)X^-$ accompany direct *and* sensitized excitation. In each case the oxidation–reduction photochemistry involves the production of Co^{2+} and CO_2 as the predominant products. In the case of $Co(HEDTA)NO_2^-$ the spectral changes which accompany direct ligand field excitation (at 400 and 540 nm) or CTTM excitation (at 254 nm; correction made for Co^{2+} formation) are most compatible with a combination of NO_2^- aquation and linkage isomerization. Although $Co(HEDTA)OH_2$ is easily prepared and characterized, we have not yet been able to separate and characterize $Co(HEDTA)ONO^-$; our present identification of this species as a reaction product is by analogy with $Co(NH_3)_5ONO^{2+}$ and will be described in detail elsewhere. It is of considerable significance that, although NO_2^- is appreciably labilized following ligand field excitation, this labilization is not accompanied by the formation of Co^{2+}.

Examination of our observations, summarized in Table I, demonstrates clearly and for the first time that ligand labilization (or aquation) and oxidation–reduction are *not* coupled processes in the photochemistry of cobalt(III). This is also the first demonstration of sensitized ligand labilization reactions in cobalt(III) complexes with relatively low crystal field splitting energy.[24]

It is to be observed that the total limiting yields ($\phi_X^{lim} + \phi_{Co^{2+}}^{lim}$) from our sensitization studies generally are near unity.[25] There seems no reason to question that the mechanism for $Co(HEDTA)X^-$ quenching of the $Ru(bipy)_3^{2+}$ phosphorescence involves triplet-to-triplet energy transfer,[2,22] and thus that the triplet states of cobalt(III), whether CTTM *or* ligand field in character, are chemically very reactive. More specifically the implicated ligand field triplet states must have intrinsic yields for product formation greater than or equal to 0.7, 0.5, and 0.3, respectively, for X = Cl, Br, and NO_2.

We infer that the simplest (and probably most general) model for the photochemistry of cobalt(III) complexes would have aquation (and other ligand labilization) products produced from some ligand field excited states of triplet spin multiplicity and oxidation–reduction products produced from CTTM excited states of triplet spin multiplicity. Since appreciable yields of both kinds of products result from the sensitization studies, CTTM triplet-to-ligand field triplet internal conversion processes cannot be very efficient compared to reaction processes (the lowest energy ligand field triplet in these complexes must have an energy less than 10^4 cm^{-1}).

On the basis of the present study it appears that the most likely reason for the photoinsensitivity of the ligand field absorption bands of most cobalt(III) complexes must arise from the relatively rapid rate of ligand field excited singlet state-to-ground singlet state nonradiative deexcitation compared to ligand field excited singlet state-to-ligand field excited triplet state intersystem crossing. This may be contrasted to the $Rh^{III}(NH_3)_5X$ complexes in which the intersystem crossing rate between ligand field states appears to be relatively efficient.[11,26] This contrast in intersystem crossing efficiencies between cobalt(III) and rhodium(III) complexes is a likely manifestation of the larger spin–orbit coupling parameters of the heavier metal.[27] Many of the qualitative features of the excited states of $Co(HEDTA)X^-$ complexes, as discussed above, are very similar to the analogous models inferred from the photochemistry of $Rh^{III}(NH_3)_5X$ complexes.[26]

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(24) Aquation of CN^- can be sensitized in $Co(CN)_6^{3-}$. See ref 5.
(25) For the $Co(HEDTA)X^-$ complexes ($\phi_X^{lim} + \phi_{Co^{2+}}^{lim}$) averages 0.8. Note that the absorption spectra of $Co(EDTA)^-$ and $Co(HEDTA)OH_2$ are so similar that we would have been unable to detect sensitized aquation of the former.

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Use of the *O*-Trimethylsilyl Group in Conformational Analysis and in Carbon-13 Nuclear Magnetic Resonance Spectroscopy

Sir:

Trimethylsilylation of alcohols is widely used analytically, and the rate of etherification is reported to be