

We note that $\text{Cr}(\text{NH}_3)_6^{3+}$ also displays a wavelength dependent phosphorescence intensity (ϕ_p) across the first ligand field absorption band with ϕ_p 514 nm/ ϕ_p 436 nm = 0.60. As previously discussed for $\text{Cr}(\text{en})_3^{3+}$,¹ the observation is consonant with very rapid ${}^4\text{T}_{2g} \rightarrow {}^2\text{E}_g$ ISC. (Very rapid ISC has been recently demonstrated for $\text{Cr}(\text{NCS})_6^{3-}$ and $\text{Cr}(\text{acac})_3^0$ from picosecond flash studies.²¹ However, no direct measure of the relative rates of ISC vs. quartet relaxation is possible from such investigations.) Assuming strict O_h symmetry for the ${}^4\text{T}_{2g}$ and ${}^2\text{E}_g$ states, the quartet and doublet surfaces lack an irreducible representation in common. However, the vibrationally equilibrated ${}^4\text{T}_{2g}$ state is undoubtedly distorted from ground state geometry, C_{4v} , D_{3h} , or D_{5h} symmetry having been suggested.¹⁸⁻²⁰ For either distortion model, provided the "crossing point" between the quartet and doublet surfaces occurs after substantial quartet relaxation, an irreducible representation (E) is again available to the states involved in ISC. Extension of these studies to other Cr(III) systems holds considerable promise for providing a clearer insight into the details of ${}^4\text{T}_{2g}$ excited state relaxation in aqueous solution.

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- Percent reaction quenching was determined from the difference in observed photoracemization yields in aqueous (pH 6) and 0.01 M NaOH solution. It was established from phosphorescence intensity measurements that complete doublet quenching is achieved in 0.01 M NaOH—a situation analogous to that reported for $\text{Cr}(\text{NH}_3)_6^{3+}$.¹⁴
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Carbonyl Compounds as Primary Products in the Reduction of Alkyldioxcobaloximes by Sodium Borohydride

Sir:

Stereochemical studies of oxygen-insertion in the cobalt-carbon bond of alkylcobaloximes have recently been reported.¹⁻³ The procedure used by Jensen and Kiskis^{1,2} con-

Table I. Reduction Products of Alkyldioxcobaloximes **2** by NaBH_4 ^a

Compounds	Yield, %	Products, %	
		R_1COR_2	R_1CHOHR_2
2a	20	100	—
2b	70	60	40
2d	90	100	0
2e	80	100	0
2f	50	100	0
2g	80	50	50

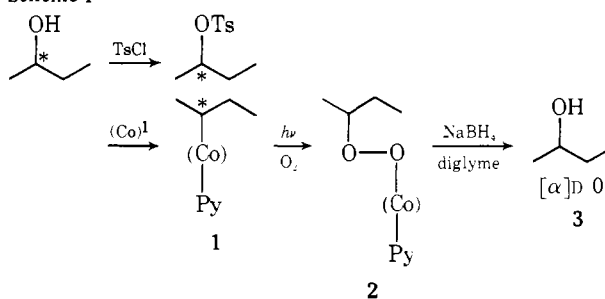
^a The reductions were carried out using an equivalent amount of NaBH_4 .

Table II. Evolution of Products during the Reduction of Compound **2d** by NaBH_4 ^a

<i>t</i> , min	$p\text{-F-C}_6\text{H}_4\text{CCH}_3$ O	$p\text{-F-C}_6\text{H}_4\text{CHCH}_3$ OH
60	33	67
90	20	80
120	0	100

^a A fivefold excess of NaBH_4 was used.

Scheme I



sisted in preparing first an optically active cobaloxime from a readily available chiral alkytosylate and, secondly, in converting the alkyl complex **1** into the corresponding oxygen insertion derivative **2** which was subsequently reduced to the corresponding alcohol **3** by excess sodium borohydride. Obtention of an optically inactive alcohol was considered as a proof of racemization during the oxygen insertion reaction (Scheme I). Shinozaki and Tada³ reached the same conclusions using a similar method which involved the synthesis of two diastereomeric alkylcobaloximes which were submitted to oxygen insertion and then to NaBH_4 reduction.

In the present communication, we report preliminary results which establish that the primary products of reduction of alkyldioxcobaloximes by NaBH_4 are not the alcohols but, for the main part, the corresponding ketones or aldehydes, which are, but subsequently, reduced to the alcohols by excess NaBH_4 .

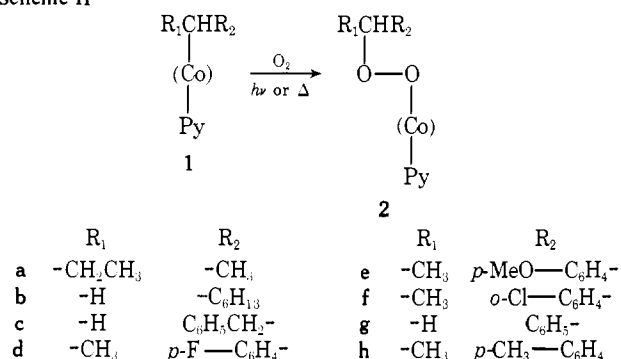
Products **2a-c** were prepared by photochemical oxygenation of the corresponding alkylcobaloximes **1a-c** and purified as previously described.⁴ Complexes **2d-h** were obtained by thermal insertion of oxygen into the cobalt-carbon bond of alkylcobaloximes **1d-h** and purified similarly (Scheme II). When methanolic solutions of alkyldioxcobaloximes were treated with equimolecular amounts of NaBH_4 , the corresponding aldehydes or ketones were isolated (Table I) and characterized by their NMR spectra, or converted into their crystalline 2,4-dinitrophenylhydrazine derivatives.

Table III. Reduction Products of Alkyldioxycobaloximes **2** by NaBD₄ or LiAlD₄^a

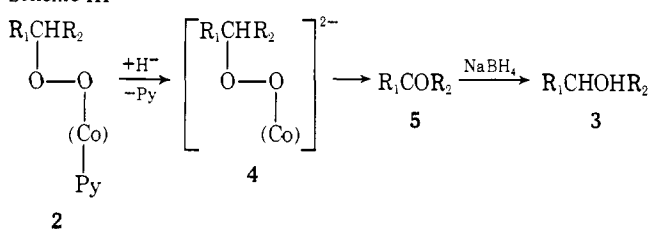
Com- pounds	Reducing agent	Yield, %	% products ^b	
			R ₁ CDR ₂ OH	R ₁ CHR ₂ OH
2b	NaBD ₄	70	80	20
2c	NaBD ₄	70	70	30
2c	LiAlD ₄	80	25	75
2h	NaBD ₄	90	65	35

^a The reductions were carried out in MeOH (NaBD₄) or THF (LiAlD₄) using a fivefold excess of the deuterated hydride. ^b The percentages of deuterated and undeuterated alcohols were determined by NMR and mass spectroscopy.

Scheme II



Scheme III



The reduction of **2d** by excess NaBH₄ was studied as a function of time. The results (Table II) suggest that *p*-fluoracetophenone is the primary reduction product, which is subsequently reduced to *p*-fluorophenyl-1-ethanol.

The results shown in Table III are further proof that alcohols are not the main primary reduction products. Compounds **2b**, **2c**, and **2h** were reduced with excess NaBD₄ and the corresponding alcohols were shown by their NMR and mass spectra to be deuterated to an extent of 65 to 80%. Product **2c** was also reduced by excess LiAlD₄ in THF: NMR and mass spectroscopy reveal that the reaction product contains 30% deuterium in the α -position.

Scheme III gives a possible mechanism for the reduction of alkyldioxycobaloximes by NaBH₄: the first step is a two-electron reduction of the alkyldioxycobaloxime to a Co^I complex **4** which decomposes into the corresponding carbonyl compound **5**. This mechanism is consistent with previous studies on the reduction of cobalt(III) complexes.⁵

The formation of some nondeuterated alcohols by reduction of peroxycobaloximes with NaBD₄ or LiAlD₄ suggests that an alternative pathway leading directly to the alcohols is also operative, possibly via the alkylhydroperoxide.⁶

From these results it is clear that the sequence of reactions (Scheme I) used to establish the stereochemistry of oxygen insertion^{1,2} is not appropriate and can lead to erroneous conclusions due to the lack of information concerning the reactions

involved. For the same reasons, the method described by Shinozaki et al.³ seems to be invalid. We are presently investigating more direct methods to establish the stereochemical course of the insertion reaction.

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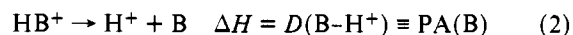
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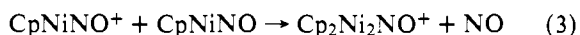
Quantitative Metal-Ligand Bond Dissociation Energies in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Sir:

Any description of the energetic changes associated with reactions catalyzed by transition metal ions suffers from a paucity of quantitative metal-ligand bond dissociation energies. These data are directly accessible in experiments utilizing the techniques of ion cyclotron resonance spectroscopy (ICR).¹ We wish to describe the experimental methodology for these studies and its application to the determination of the binding energies (eq 1) of 30 *n*-donor ligands to the cyclopentadienyl nickel cation, (η^5 -C₅H₅)Ni⁺, and to compare the scale of base strengths thus determined with results previously obtained for proton binding energies (eq 2).^{2,3}



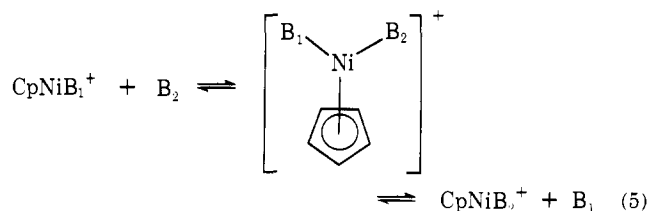
In cyclopentadienyl nickel nitrosyl alone, only the parent ion, CpNiNO⁺, is observed at low electron energies (8.5–10.5 eV), and reacts with the precursor in accordance with process 3 ($k = (7.5 \pm 1.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).



In the presence of excess base, B, fast ligand displacement reactions, such as generalized in eq 4,



are observed (e.g., $k = (1.4 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for B = NH₃). With a mixture of bases, attainment of equilibrium in transfer of CpNi⁺ between B₁ and B₂ (eq 5) is ob-



served to be rapid in comparison to any further reactions of the complexes with the neutrals present. The rapid exchange of monodentate *n*-donor ligands is promoted by the coordination vacancy of the 16-electron complex, CpNiB⁺, which facilitates binding of a second pair donor to form the 18-electron intermediate indicated in eq 5. The displacement of a monodentate ligand by a bidentate or polydentate ligand (e.g., butadiene, benzene, and pyridine) results in the formation of an 18-(or