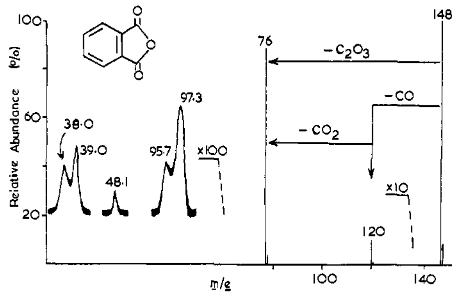

Figure 1. Collision induced negative ion mass spectrum of phthalic anhydride.

therefore of interest to devise a method by which initially unreactive molecular anions gain enough internal energy to enable fragmentation to occur. Collision excitation has recently been used to investigate the properties of collision-induced dissociations in positive ion spectra,[9-11] and adaptation of this technique to negative ions enables collision-induced fragmentation to be achieved. Sample pressures of *ca.* 5 × 10^{-7} Torr in the ion source are used, and collision gas is introduced through a separate inlet system into the first field-free region of the mass spectrometer to give a pressure of 10^{-5} Torr. The collision gas should (a) not produce negative ions under the reaction conditions and (b) not react with negative ions to produce ion–molecule product ions. We have successfully used krypton, nitrogen, benzene, and toluene for this purpose, but the use of aliphatic hydrocarbons (*e.g.*, methane[12]) as collision gases is to be avoided because of the risk of ion–molecule reactions producing anomalous peaks.

The spectra produced by this technique contain new peaks due to both fragmentation in the ion source[13] and to collision-induced dissociations in the field-free regions. Differential pumping of the ion source should be used if a spectrum is required which contains only fragment ions produced by collision-induced dissociations. The spectra reported in this communication were obtained with the differential pumping unit inoperative.

The first three examples to be discussed are those of molecular anions which give no fragmentation in the absence of collision gas. The spectrum[14] (Figure 1) of phthalic anhydride[15] shows the decompositions $M - CO - CO_2$ and $M - C_2O_3$. Collision-induced peaks[16] are observed for these processes and also for processes which do not occur in the ion source. Examples of the latter type are the decompositions $M - CHO\cdot$ (collision induced peak (cip) at *m/e* 95.7) and $M - C_2HO_3\cdot$ (cip at *m/e* 38.0). The spectrum of maleic anhydride shows the following fragment ions: *viz.*, $(M - CO)\cdot^-$ (cip at *m/e* 50.0), $CO_2\cdot^-$, and C_2H^-. The naphthoquinone molecular anion does not fragment in the ion source, but pronounced collision-induced peaks are produced in both field-free regions. These peaks are observed at *m/e* 105.3 and 64.6, produced by the unusual decompositions $M - CHO\cdot$ and $M - (CHO\cdot + CO)$.

The final example is that of a functional group which does not fragment under normal conditions. The conventional negative ion spectrum of *p*-nitroacetophenone[17] shows the decompositions $M - NO\cdot$ and $M \rightarrow NO_2^-$. The collision-induced spectrum shows the following decompositions of the COMe group in the field-free regions: *viz.*, $(M - NO\cdot) - Me\cdot$, $(M - NO\cdot - Me\cdot) - CO$, $(M - NO\cdot) - MeCO\cdot$, and $(M - NO\cdot) - CH_2CO$.

In summary, collision excitation allows the observation of fragmentations of moieties which do not decompose under the normal conditions used for the formation of molecular anions and shows considerable potential for the study of the reactivities of negative ions in the gas phase and for the structure determination of some types of organic compounds.

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(10) W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 4745 (1968).

(11) F. W. McLafferty and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, **91**, 1866 (1969).

(12) The chemical ionization negative ion mass spectra of some chlorinated insecticides using methane as the collision gas have been described: R. C. Dougherty, J. Dalton, and F. J. Biros, *Org. Mass Spectrom.*, **6**, 1171 (1972).

(13) The mechanism for the formation of the ions in the ion source is not known. Collision excitation seems unlikely, and a referee has suggested that charge-exchange processes may be operating: *cf.* R. C. Dougherty and C. R. Weisberger, *J. Amer. Chem. Soc.*, **90**, 6570 (1968), and references cited therein.

(14) Hitachi Perkin-Elmer R.M.U. 7D instrument, sample pressure 5 × 10^{-7} Torr, toluene as collision gas, total pressure 3 × 10^{-5} Torr, electron beam energy 70 eV, and accelerating potential 3600 V. Identical conditions were used for other spectra.

(15) For the conventional negative ion spectra of phthalic anhydrides see T. Blumenthal and J. H. Bowie, *Aust. J. Chem.*, **24**, 1853 (1971).

(16) The reactant and product ions produced in all collision-induced dissociations mentioned in the text have been uniquely defined by application of the "metastable defocusing" technique: M. Barber and R. M. Elliot, paper presented to the 12th Annual Conference on Mass Spectrometry, ASTM E-14, Montreal, 1964; K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965); J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965); and A. H. Struck and H. W. Major, paper presented to the 12th Annual Conference on Mass Spectrometry, ASTM E-14, Dallas, 1969.

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John H. Bowie
Department of Organic Chemistry, University of Adelaide
Adelaide, South Australia 5001

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Influence of Trans Ligands on the Bonding Mode of Thiocyanate in Cobalt(III) Complexes. Evidence for Adjacent and Remote Attack during Electron-Transfer Reactions

Sir:

We report here the stereoselective formation and subsequent linkage isomerization of complexes of the type *trans*-$LCo(DH)_2SCN$, where L = amine, phosphine, or phosphite ligand and DH = monoanion of dimethylglyoxime. These complexes were prepared *in situ* from isomeric mixtures of $CNpyCo(DH)_2SCN$–$CNpyCo(DH)_2NCS$, where CNpy = 4-cyanopyridine, by addition of ligand, L. The reactions are examples of a new class of ligand-exchange reactions[1] which proceed only in the presence of catalytic amounts of $LCo^{II}(DH)_2$ according to eq 1–3. The slow step is

$$\text{slow}\quad LCo(DH)_2X + L'Co(DH)_2 \longrightarrow L'Co(DH)_2X + LCo(DH)_2 \qquad (1)$$

$$\text{fast}\quad LCo(DH)_2 + L' \rightleftharpoons L'Co(DH)_2 + L \qquad (2)$$

$$LCo(DH)_2X + L' \longrightarrow L'Co(DH)_2X + L \qquad (3)$$

believed to involve an inner-sphere electron transfer.

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(1) L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, **11**, 2050 (1972).

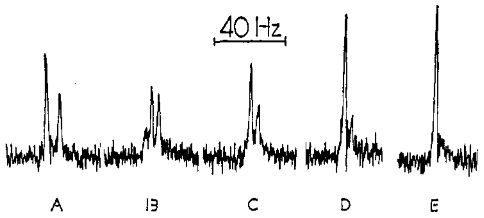

Figure 1. Pmr spectral change of the methyl oxime resonance for the reaction CNpyCo(DH)$_2$NCS-CNpyCo(DH)$_2$SCN (0.038 *M*, nitrobenzene) + 1-methylimidazole (MeIMD, 0.4 *M*) → MeIMDCo(DH)$_2$SCN: A, start (no MeIMD) downfield resonance, S-bonded isomer; B, 1 min after addition of MeIMD, central resonance MeIMDCo(DH)$_2$SCN; C, 2 min, resonance for CNpyCo(DH)$_2$SCN completely gone; D, 15 min, CNpyCo(DH)$_2$NCS half reacted; E, 32 min, CNpyCo(DH)$_2$NCS almost gone, resonance lost in noise in later spectra (the rate of reaction of the S-bonded isomer is *ca.* 200 times that of the N-bonded isomer). If, at this juncture, no cobalt(II) is added, linkage isomerization to the N-bonded complex occurs slowly (the MeIMD complex is more stable than the CNpy complexes, $K \sim 10^5$ for the corresponding Cl complexes).

The reactions reported here are novel in that an isomeric mixture of compounds is converted into only one product, a thermodynamically unstable situation. Several lines of evidence clearly point to the occurrence of *adjacent* attack (eq 4). This evidence includes (1)

$$\begin{aligned}&\mathrm{CNpy(DH)_2CoSCN + Co(DH)_2L \longrightarrow}\\&\qquad\mathrm{CNpy(DH)_2CoS(CN)Co(DH)_2L \longrightarrow}\\&\qquad\qquad\mathrm{CNpy(DH)_2Co + NCSCo(DH)_2L}\quad(4)\end{aligned}$$

the rapid disappearance of CNpyCo(DH)$_2$SCN to form LCo(DH)$_2$SCN and subsequent slower disappearance of CNpyCo(DH)$_2$NCS also to form LCo(DH)$_2$SCN on introduction of L and (2) the preferential broadening of the S-bonded dioxime methyl resonance in the pmr spectra of isomeric mixtures of LCo(DH)$_2$SCN and LCo(DH)$_2$NCS on introduction of LCo^{II}(DH)$_2$ complexes. These phenomena have been observed for a wide variety of L ligands, and examples of pmr spectral changes are given in Figures 1 and 2. The results reported here clearly show that *adjacent* attack is much more rapid than remote attack (eq 5 and 6).

$$\begin{aligned}&\mathrm{CNpy(DH)_2CoSCN + Co(DH)_2L \longrightarrow}\\&\qquad\mathrm{CNpy(DH)_2CoSCNCo(DH)_2L \longrightarrow}\\&\qquad\qquad\mathrm{CNpy(DH)_2Co + SCNCo(DH)_2L}\quad(5)\end{aligned}$$

$$\begin{aligned}&\mathrm{CNpy(DH)_2CoNCS + Co(DH)_2L \longrightarrow}\\&\qquad\mathrm{CNpy(DH)_2CoNCSCo(DH)_2L \longrightarrow}\\&\qquad\qquad\mathrm{CNpy(DH)_2Co + NCSCo(DH)_2L}\quad(6)\end{aligned}$$

The structural assignment in these systems has been discussed.[2] That isomers are easily distinguished and identified by the methyl pmr signal in aromatic solvents only[3] appears to be the consequence of aromatic solvent induced shifts.[4,5] Spectral assignment was also verified by preferential broadening, such as that illustrated in Figure 2.

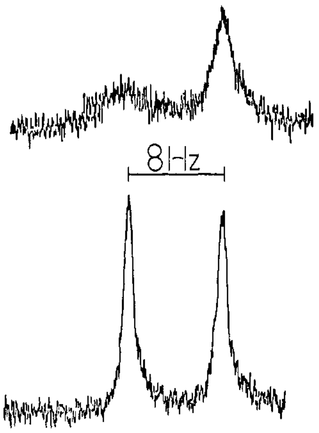

Figure 2. Nuclear magnetic resonance spectrum in the dioxime methyl region ($\tau \sim 7.6$) of isomeric mixture of Bu(py)Co(DH)$_2$SCN (downfield, to left) and Bu(py)Co(DH)$_2$NCS in nitrobenzene, total [Co(III)] = 0.05 *M*. Below, no Co(II) added. Above, in the presence of (C$_6$H$_5$)$_3$PCo(DH)$_2$ (8×10^{-4} *M*). Sweep width = 2 Hz/cm (experiment performed under nitrogen).

Addition of cobalt(II) catalysts, usually P(C$_6$H$_5$)$_3$Co(DH)$_2$, to the stereoselectively formed LCo(DH)$_2$SCN leads to the equilibrium isomeric products. Integration of the dioxime methyl resonance of each isomer allows calculation of the equilibrium constant, Table I. Although it is not possible to interrelate phosphines with phosphites and amine complexes with complexes containing the phosphorus donor ligands, it is clear that within each series good π acceptors (generally weak σ donors) favor the S-bonded isomer. The value of *K* for L = 1-methylimidazole was determined as $\sim$1, but the low solubility of the N-bonded isomer precluded an accurate determination.

Table I. Equilibrium Constants for the Reaction LCo(DH)$_2$NCS $\rightleftharpoons$ LCo(DH)$_2$SCN in Nitrobenzene at 33°

L	pK_a	$\Sigma\chi^c$	K(S/N)
4-CNpy	1.7[a]		1.44
py	5.2[a]		1.35
4-*t*-Bu(py)	6.0[a]		0.90
4-NH$_2$py	9.0[a]		0.63
Ph$_3$P	2.7[b]	12.9	2.47
n-BuPh$_2$P		10.0	1.91
MePh$_2$P		11.2	1.71
n-Bu$_3$P	8.4[b]	4.2	1.18
(PhO)$_3$P		29.1	1.06
EtC(CH$_2$O)$_3$P		~30	0.93
(MeO$_3$)P		23.1	0.79
(*i*-PrO)$_3$P		18.9	0.65

[a] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965. [b] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960); W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960). [c] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

Previous systematic studies of the effect of other ligands on thiocyanate bonding mode have involved primarily second- and third-row transition metal complexes having a square-planar geometry.[6] Recently, from spectroscopic and molecular orbital studies, Gutterman and Gray have suggested that S-bonded SCN acts not as a π acceptor (as has been shown for 4d and 5d complexes) but rather as a *π-donor ligand* when coordinated to first-row transition metals.[7]

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(2) L. A. Epps and L. G. Marzilli, *J. Chem. Soc., Chem. Commun.*, 109 (1972); A. H. Norbury and A. I. P. Sinha, *Inorg. Nucl. Chem. Lett.*, **4**, 617 (1968); A. H. Norbury, P. E. Shaw, and A. I. P. Sinha, *Chem. Commun.*, 1080 (1970); R. L. Hassel and J. L. Burmeister, *ibid.*, 568 (1971).

(3) L. G. Marzilli, *Inorg. Chem.*, 11, 2504 (1972).

(4) J. A. Mosbo, J. R. Pipal, and J. G. Verkade, *J. Magn. Resonance*, **8**, 243 (1972).

(5) R. C. Stewart and L. G. Marzilli, to be submitted for publication.

(6) J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968); D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, **92**, 5351 (1970).

(7) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971); *Inorg. Chem.*, **11**, 1727 (1972).

Our data support this interpretation. Burmeister has suggested that thiocyanate acts as a donor in second- and third-row transition metal complexes in high oxidation states.[8]

Despite numerous electron-transfer studies, it was only recently that the first definitive evidence for adjacent attack on a polyatomic ligand was obtained by Shea and Haim.[9] They found that reduction of $Co(NH_3)_5SCN^{2+}$ by Cr^{2+} and $Co(CN)_5^{3-}$ involved adjacent attack at sulfur. The rates of adjacent and remote attack by Cr^{2+} were comparable. Haim cited arguments[10] which suggest that formation of $CrSCN^{2+}$ (which is unstable) should be *ca.* 10^3 times slower than the formation of $CrNCS^{2+}$ from $Co(NH_3)_5SCN^{2+}$. Therefore, adjacent attack at sulfur is unusually rapid. The great facility of the adjacent mode of attack was attributed to the high electron-mediating ability of sulfur when bound to an oxidizing center such as cobalt(III). Further unpublished studies by Shea and Haim[11] indicate that the rate of reduction by $Co(CN)_5^{3-}$ of $Co(NH_3)_5SCN^{2+}$ is *ca.* 10^3 times that of $Co(NH_3)_5NCS^{2+}$.

Complexes of the type $LCo(DH)_2SCN$ and $LCo(DH)_2NCS$ are of comparable stability in nitrobenzene.[3] Reasoning from Haim's results, one would predict that *adjacent* attack would be a very favorable pathway. Our results lend support to previous conclusions by Haim and Sutin.[12] We are presently studying the effects of ligands on the reaction rates in these systems, as well as extending our studies on the effect of the trans ligand on bonding mode.

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[9] C. Shea and A. Haim, *J. Amer. Chem. Soc.*, **93**, 3057 (1971).

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[11] A. Haim, personal communication.

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Luigi G. Marzilli,* Robert C. Stewart
Leon A. Epps, James B. Allen
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

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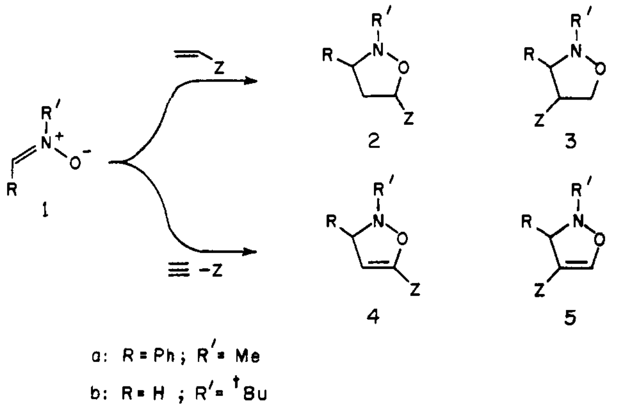
Reversal of Nitrone Cycloaddition Regioselectivity with Electron-Deficient Dipolarophiles

Sir:

A solution to the vexing problem of regioselectivity in concerted cycloadditions[1] has been proposed recently.[2-4] According to the frontier orbital treatment of 1,3-dipolar cycloadditions,[2-5] the unidirectional addition of many 1,3 dipoles to both electron-rich and electron-deficient monosubstituted dipolarophiles should no longer be observed when the dipolarophile is made highly electron deficient.[4] We wish to report confirmations of this prediction.

The reactions of *C*-phenyl-*N*-methylnitrone, **1a**, and other disubstituted nitrones to monosubstituted alkenes give only the 5-substituted isoxazolidines, **2**.[6-10] Reactions of the parent nitrone, a tautomer of formaldoxime, with acrylonitrile or acrylic esters,[11] as well as the reaction of *N*-(1-ethylcyclohexyl)nitrone with styrene gave the 5-substituted adducts, **2**.[12] To verify the unimportance of steric hindrance at the nitrone carbon in producing regioselectivity, we have studied the reactions of *N-tert*-butylnitrone with a variety of monosubstituted alkenes and alkynes, including enamines, enol ethers, alkylethylenes, styrene, acrylonitrile, and methyl acrylate. These reactions gave only the 5-substituted adducts, **2**. With methyl propiolate, Huisgen, *et al.*, observed diminished regioselectivity.[13,14] Nitrone **1a** gave a 42:58 mixture of **4a**-CO_2Me and **5a**-CO_2Me with methyl propiolate in DMF at 85°,[13] while 3,4-dihydroisoquinoline *N*-oxide and isoquinoline *N*-oxide reacted with methyl propiolate to give only the 4-substituted isomers, **5**.[13,14] Low regioselectivity was also observed in reactions of diphenylnitrilimine and benzonitrile oxide with methyl propiolate.[15,16]



Since steric effects appeared to be little different in the acrylate and propiolate, we suggested that the loss or reversal of regioselectivity resulted from the lower HO orbital energy of the propiolate (IP = 11.15 eV)[17] than that of the acrylate (IP = 10.72 eV)[18] so that interaction of the dipole HO orbital with the dipolarophile LU orbital (which favors 4-substituted adducts) was of greater importance with the propiolate than with the acrylate.[4]

Ethyl propiolate reacts rapidly and exothermically

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[1] R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

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[4] K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, in press.

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