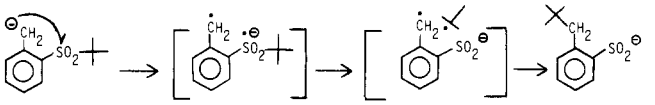
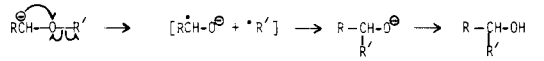
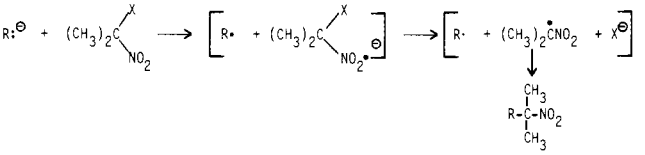


electron from the benzylic carbanion to form a stable benzylic radical and the sulfonyl radical anion. Subsequent or accompanying homolytic cleavage of the sulfur *tert*-butyl bond would generate the sulfinate anion and *tert*-butyl radical. Immediate radical combination, within the solvent cage, would give rise to the observed product.

This mechanism has precedence in the Wittig rearrangement of metalated ethers. Although an early mechanism involved an intramolecular carbanion $S_N2$ displacement, more recent evidence for the Wittig rearrangement favors an electron-transfer-radical-anion mechanism.[3] A related mechanism



has also been suggested in the intermolecular coupling of alkyllithium reagents with 2,2-dinitropropane and 2-nitro-2-halopropane.[4]



Further work on this type of alkyl transfer in Truce-Smiles rearrangements is currently underway in this laboratory and will be reported on at a later date.

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## Unequivocal Determination of the Site of Metal–Carbonyl Bond Breaking in Tetracarbonylchromium(0) Complexes of *o*-Phenanthroline and 2,2'-Dipyridyl

*Sir:*

Since it became evident that five-coordinate intermediates derived through metal–ligand bond breaking in octahedral metal–carbonyl complexes could undergo stereochemical rearrangement on the time scale of the ligand-substitution process,[1] there has been great interest in the determination of the site of such M–L bond fission, where equivocal, so that possible correlation between structure and reactivity both of the substrates and intermediates could be attempted.[2]

In general, isotopic labeling studies have been employed to this end where the ligand is CO. These have involved either determination of the rates of formation and disappearance of labeled species[3] or of the identity of products formed via reaction of stereospecifically labeled substrates.[4]

One method, employed in the analysis of the *cis*-(diphos)-$Mo(CO)_4$ system (diphos = 1,2-bis(diphenylphosphino)-ethane) employed Fourier transform (FT) NMR studies of $^{13}CO$ distribution, but also required a $^{13}C$ "internal standard" to be present in the molecules studied. Solubility and stability problems, as well as the lack of a sufficient amount of natural isotropic abundance noncarbonyl carbon-13 in many stystems of interest, have severely limited the applicability of this approach.

The communication describes an alternative approach, of much broader applicability, through which the site of initial M–CO bond breaking, as well as the degree of fluxionality of the five-coordinate intermediate thus formed *under the normal conditions employed in the ligand-substitution process*, can be determined. The systems chosen for study,

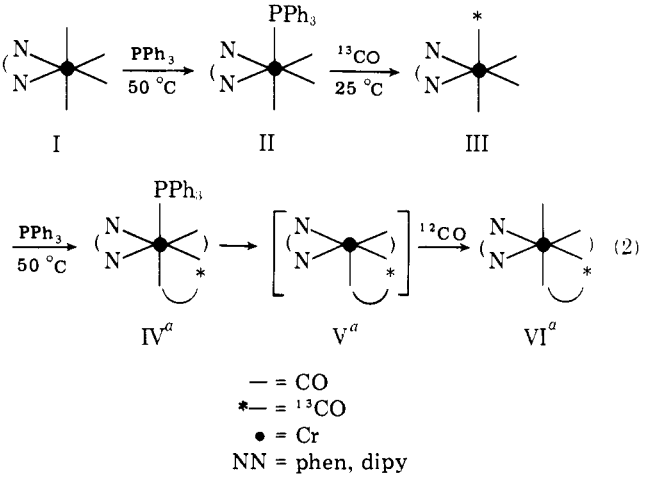
$$cis\text{-}(L_2)Cr(CO)_4 + L' \rightarrow fac\text{-}(L_2)Cr(CO)_3L' + CO \quad (1)$$

$L_2$ = *o*-phenanthroline (phen) and 2,2'-dipyridyl (dpy)

$L'$ = phosphine, phosphite

have been studied in this context in two previous reports;[5,6] the present results, which are unequivocal and are quantitative, reveal loss to occur exclusively at an axial position (cis to $L_2$), with *complete scrambling of label during the ligand-substitution process*.

The preparation of a stereospecifically labeled *cis*-$(L_2)$-$Cr(CO)_4$ molecule and the subsequent ligand-substitution process employed, similar to those employed in the *cis*-(diphos)$Mo(CO)_4$ system,[4] are illustrated in eq 2. The key to the

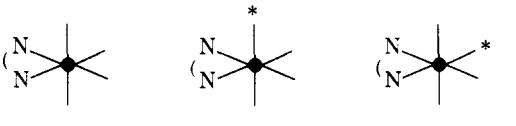


— = CO
*— = $^{13}CO$
• = Cr
NN = phen, dipy

[a] In IV–VI the label need no longer be stereospecific.

application of the chemical transformations outlined there is choice of $(L_2)Cr(CO)_3(L')$ species (II, IV) exhibiting significantly greater instability than the tetracarbonyl complex from which they are formed, e.g., I and III; thus species containing more than one isotopic label are produced only to the extent that enrichment takes place in a molecule containing the natural isotopic abundance label. This greatly simplifies data in comparison with studies in which continuous introduction of a label in a substrate such as I can lead to successive enrichment and the production in significant quantities of as many as 12 species.[3,6]

The question of the site of initial Cr–CO bond breaking and the extent of scrambling during the ligand-substitution process (III to IV) rests with the determination of the quantity of label found in the various positions in VI, i.e., the relative quantities of the three species VIa–c present upon completion of the li-



VIa VIb VIc

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gand-substitution process. This can unambiguously be adduced through determination of the ratio, $r_1$, of equatorial-axial $^{13}CO$ from the $^{13}C$ FT NMR spectrum of VI[8] and the ratio, $r_2$, of the intensities of the carbonyl stretching bands observed at 1829 and at 1801, 1800 $cm^{-1}$, respectively, produced by the antisymmetric stretch of the equatorial carbonyls in the various species.[9]

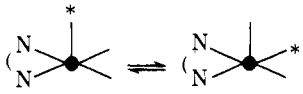
Table I presents an accounting of the relative abundances of various species expected for axial loss and complete scrambling for ligand exchange in III, which has been shown ($^{13}C$ FT NMR) to be stereospecifically labeled axially (90 mol % label employed). This table also presents the equations employed to solve for the fractions of a, b, and c present in VI.[10]

Results are also presented in Table I. They demonstrate that in both substrates Cr-CO bond breaking is >90% axial and that the intermediates V are fluxional under the conditions of ligand exchange of *cis*-$(L_2)Cr(CO)_4$ with triphenylphosphine which were employed; i.e., the label is random at one axial and two equatorial positions in VI.

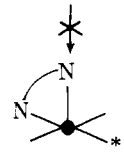
These results are consistent with those obtained by Cohen and Brown,[6] which supported axial loss and some scrambling in the intermediate. In the several studies which now have unequivocally elucidated the site of initial metal-CO bond breaking, for $M(CO)_5Br$ (M = Mn, Re),[3] *cis*-$M(CO)_4(L)Br$,[11] *cis*-(diphos)$Mo(CO)_4$,[4] and for *cis*-(phen)$Cr(CO)_4$ and *cis*-(dpy)$Cr(CO)_4$, results have indicated that in each case loss is of CO trans to CO. These results are consistent with both transition-state stabilization (cis labilization) arguments[12] and with ground-state arguments[2,13] based upon the Fenske "direct-donation" [14] concept and/or of the directional influence of $\pi$-bonding effects.[15]

Under the conditions employed in this study, dissociation of $PPh_3$ from *fac*-$(L_2)Cr(CO)_3(PPh_3)$ is rapid compared with dissociation of CO from *cis*-$(L_2)Cr(CO)_4$;[7] thus the $[(L_2)Cr(CO)_3]$ intermediate V is formed several times during the substitution process. It is therefore possible that the rate of scrambling is relatively slow on the time scale of the reaction of $PPh_3$ or CO with that intermediate.

However, the stereospecificity of formation of *fac*-$(L_2)Cr(CO)_3(^{13}CO)$, despite fluxionality of the $[(L_2)Cr(CO)_3]$ intermediate, is best explained in terms of a scrambling path which does not involve formation of a species in which N occupies an apical position in the intermediate VII.[16] Thus, in



VII



substituted octahedral systems, stereospecific labeling can result from displacement of a weakly bonded substituent whether or not rapid scrambling of carbonyls in the intermediate takes place on the time scale of ligand substitution. This conclusion is consistent with results obtained in a number of systems thus far studied.

The method of determination of the site of CO loss and possible fluxionality of the resulting intermediates thus is generally applicable to octahedral $M(CO)_{6-x}L_x$ systems possessing the following features (cf. eq 2): (a) containment of chemically distinct carbonyls; (b) dissociation of CO more readily than L; (c) possibility that CO can be replaced by L′ more weakly held than CO.[17]

**Table I.** Site of Cr-CO Bond Breaking and Fluxionality in $(L_2)Cr(CO)_4$ Complexes

| isotopic species | fraction present, theory (axial loss, scrambling) | calcd for $L_2$ = phen | calcd for $L_2$ = dpy |
|---|---|---|---|
| a | 0.5266 | 0.496 | 0.531 |
| b | 0.1568 | 0.183 | 0.161 |
| c | 0.3017 | 0.307 | 0.294 |
| d | 0.0017 | | |
| e | 0.0099 | | |
| f | 0.0033 | | |
| g | 0.00007 | | |
| h | 0.00004 | | |

d e f g

Equations

(A) $\begin{cases} a + b + c \approx 1 & \text{phen: } r_1 = 1.65;\ r_2 = 2.35 \\ a + b + c = 0.9850 & \text{dipy: } r_1 = 1.78;\ r_2 = 2.50 \end{cases}$

(B) $\begin{cases} r_1 = (c + e + 2f + g + 2h)/(b + 2d + e + 2g + h) \\ \quad \approx (c + 0.01665/(b = 0.01358) \end{cases}$

(C) $\begin{cases} r_2 = 1.458(a + b + d)/(1.333c + 1.272e + 1.265g) \\ \approx (1.458(a + b) + 0.0024786)/(1.333c + 0.01268) \end{cases}$

Given the large number of systems which can be designed to exhibit these features, patterns of reactivity via CO loss as a function of the steric and electronic properties of $M(CO)_{6-x}L_x$ species should emerge through further investigation.

**Acknowledgments.** The support of this research by the Robert A. Welch Foundation under Grant No. B-434 and the North Texas State University Faculty Research Fund is gratefully acknowledged. We thank Cato R. McDaniel, Jr., for the FT NMR spectra and Dr. D. J. Darensbourg for a manuscript in advance of publication.

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(8) Procedures employed in the recording of $^{13}C$ NMR spectra have been given in ref 4. Spectra were obtained at 0 °C. Chemical shifts vs. $Me_4Si$ for the carbonyls determined from VI: (*o*-phen)$Cr(CO)_4$, axial, $\delta$ 212.8, and equatorial, $\delta$ 228.2; (dpy)$Cr(CO)_4$, axial, $\delta$ 212.7, and equatorial, $\delta$ 227.2.
(9) It is known that substitution of $^{13}CO$ for $^{12}CO$ in a molecule may alter the absolute intensities of carbonyl stretching modes, and thus it is necessary to correct for such effects. For the (phen)$Cr(CO)_4$ and (dpy)$Cr(CO)_4$ molecules, these corrections have been reported and discussed. The appropriate corrections to the $B_2$ carbonyl stretching mode[6] upon axial or equatorial substitution have been incorporated into B in Table I.
(10) Trial solution of the equations for a, b, and c neglecting the contributions of multiply enriched species d–h revealed that, as a first approximation, loss was exclusively axial, with complete scrambling. The modified equations employ contributions from d–h based on this assumption.
(11) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3155 (1976).
(12) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976).
(13) G. R. Dobson, *Ann. N.Y. Acad. Sci.*, **239**, 237 (1974).
(14) R. F. Fenske and R. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).
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however, convenient representations: D. J. Darensbourg and A. H. Graves, *Inorg. Chem.*, **18**, 1257 (1979).
(17) This substitution can readily be effected through efficient removal of CO as it is evolved during the substitution process.

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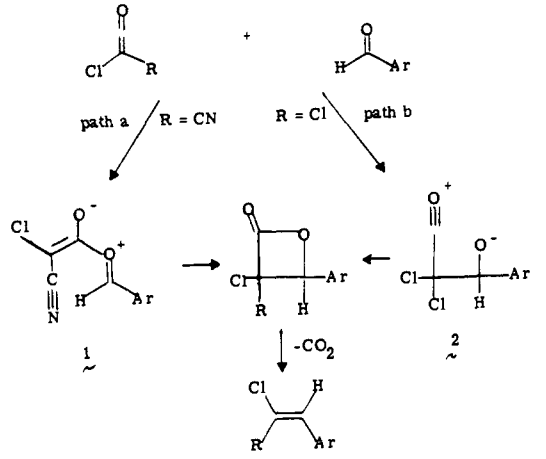
## Cyanoketenes. Cycloadditions of Halocyanoketenes to Benzaldehydes

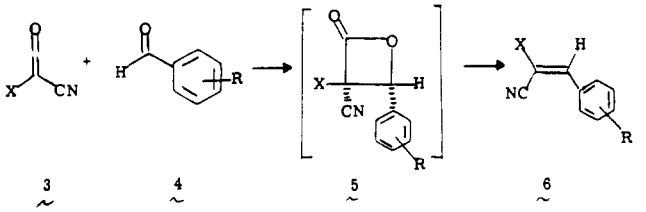
*Sir:*

Reported here is an investigation of the reaction of halocyanoketenes[1] with aromatic aldehydes to give exclusively the *E* isomer of 1-halo-1-cyano-2-phenylethenes (**6a–m**). As anticipated, the penultimate precursors to these alkenes are the corresponding β-lactones (**5a–m**) formed by the cycloaddition of the ketene to the aldehyde carbonyl group; these β-lactones then suffer stereospecific decarboxylation under the reaction conditions to give the alkenes. Even though this stereoselective conversion of an aldehyde into an alkene is of synthetic note, it does not constitute the most significant aspect of this work. Most important is the fact that the initial cycloaddition is a nonconcerted dipolar process in which the cyanoketene uniquely functions as an electrophile and the aldehyde as the nucleophile (zwitterion **1**, Scheme 1). To our knowledge, such an observation is without precedent since all other ketene–aldehyde cycloadditions for which mechanistic data has been reported suggests nucleophilic character to the ketene and electrophilic character to the aldehyde (zwitterion **2**, Scheme 1).[2] Scheme 1 summarizes the mechanistic rationale for the work outlined here using chloro- (or bromo-) cyanoketene (path a) and compares it to results recently reported by Krabbenhoft[2e] for an analogous study with dichloroketene (path b).

**Scheme I**




**Scheme II**



The halocyanoketene cycloadditions were accomplished by generating the cyanoketenes from 4-azido-3-halo-5-methoxy-2(5*H*)-furanone in refluxing benzene in the presence of 1 equiv of the aldehyde. The reactions were complete within 5 hr to give only the *E* isomers of 1-halo-1-cyano-2-phenylethene, **6a–m**, as isolable products (Scheme II and Table I).[4] The reaction conditions preempted isolation of the β-lactones **5a–m**. However, in one case, **5l**, this product was detected by monitoring the reaction with IR and $^1$H NMR spectroscopy; the former showed the formation and subsequent disappearance of the characteristic β-lactone carbonyl absorption at 1860 cm$^{-1}$ and the latter showed the transient absorption of the methine proton in **5l** at δ 5.99. The indicated *E* stereochemistry of the β-lactones is assumed since the thermally induced decarboxylation of β-lactones is known to proceed with retention of stereochemistry.[5]

The structures of the alkenes **6a–m** are based upon spectral and analytical data, and, additionally, in one case, **6h**, upon an independent synthesis involving antarafacial addition of bromine to (*E*)-1-cyano-2-phenylethene followed by antarafacial ($E_2$) dehydrobromination. This transformation gives a product which is identical in all respects to the product obtained by the cycloaddition of bromocyanoketene to benzaldehyde, i.e., **6h**. Thus, the stereochemistry of **6h** can be reasonably concluded to be *E*, and, by implication, analogous stereochemistry for the other alkenes are assigned.

The mechanism of these cycloadditions was established to involve a zwitterionic intermediate such as **1** rather than **2** by the following data. (1) Chlorocyanoketene did not react with the electron-deficient carbonyl of chloral. Many other ketenes, including dichloroketene, are known to cycloadd to this aldehyde.[2e] (2) The product yields (Scheme I) observed in the cycloadditions of the halocyanoketenes to the benzaldehydes

**Table I**

| compd | X | R | yield, % | mp, °C | $^{13}$C NMR, δ(CDCl$_3$) $C_2$ | $^{13}$C NMR, δ(CDCl$_3$) $C_1$ | $^1$H NMR, δ(CDCl$_3$), vinyl H | IR, C≡N |
|---|---|---|---|---|---|---|---|---|
| **6a** | Cl | 2,4-$(OCH_3)_2$ | 92 | 92–94 | 140.0 | 97.0 | 7.67 | 2210 |
| **6b** | Cl | 4-$N(CH_3)_2$ | 78 | 58–60 | 145.5 | 93.4 | 7.16 | 2202 |
| **6c** | Cl | 4-$OCH_3$ | 73 | 53–55 | 144.9 | 97.3 | 7.26 | 2208 |
| **6d** | Br | 4-$OCH_3$ | 79 | 66–67 | 148.5 | 81.3 | 7.50 | 2201 |
| **6e** | Cl | 4-$OCOCH_3$ | 61 | 81–82 | 144.2 | 100.2 | 7.34 | 2208 |
| **6f** | Br | 4-$OCOCH_3$ | 51 | 84–85 | 152.8 | 84.7 | 7.72 | 2198 |
| **6g** | Cl | H | 61 | oil | 145.3 | 100.4 | 7.30 | 2215 |
| **6h** | Br | H | 48 | oil | 148.9 | 84.3 | 7.60 | 2203 |
| **6i** | Cl | 4-$CH_3$ | 54 | oil | 145.3 | 99.2 | 7.30 | 2218 |
| **6j** | Cl | 4-Cl | 32 | 51–52 | 144.0 | 101.1 | 7.33 | 2217 |
| **6k** | Br | 4-Cl | 27 | oil | 147.6 | 85.3 | 7.50 | 2203 |
| **6l** | Cl | 4-$NO_2$ | 8[a] | 85–86 | 148.8 | 104.7 | 7.48 | 2221 |
| **6m** | Br | 4-$NO_2$ | <5[b] | | | | | |

[a] In order to achieve an 8% yield, the ratio of ketene to aldehyde was 2:1. [b] Estimated yield of unisolated product based upon $^1$H NMR analysis.

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