

- wavelength (λ) and temperature (t), l is measured in decimeters, and c is in grams per milliliter. All solutions had a concentration of 5 mg/ml and corrections were applied for the water blanks.
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Cis Labilization of Ligand Dissociation. 4. Kinetics and Mechanism of ¹³CO Exchange with Cr(CO)₄(chelate) Complexes¹

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Received November 11, 1975

AIC50817V

The kinetics and stereochemistry of ¹³CO incorporation upon exchange with Cr(CO)₄phen and Cr(CO)₄bpy at 40 °C in 1,2-dichloroethane have been evaluated. The results are in best accord with a mechanism which involves preferential loss of CO from the cis position ($k_{cis} \geq 10k_{trans}$) and a partially fluxional five-coordinate intermediate, Cr(CO)₃(chelate). Exchange of ¹³CO with Cr(CO)₄diphos at 110 °C in decalin and with Cr(CO)₄dpp at 90 °C in decalin proceeds preferentially at the cis positions, but it was not possible to ascertain anything of the fluxional character of the presumed five-coordinate intermediate. Reaction of ¹³CO with Cr(CO)₄nbd at 40 °C in 1,2-dichloroethane yields cis and trans dilabeled Cr(CO)₆. The above results are consistent with the site preference model which ascribes preferential loss of ligand from the cis position to stabilization of the transition state resulting from preferential siting of ligands.

In the previous papers of this series,²⁻⁴ it has been shown that ligands which are weaker π acceptors than CO may labilize a substituted metal carbonyl complex toward dissociative ligand loss and that when labilization occurs, the ligand is lost preferentially from a position cis to the labilizing ligand. To investigate further the phenomenon of cis labilization, we have studied ¹³CO exchange with Cr(CO)₄(chelate) complexes, in which chelate = 1,10-phenanthroline (phen), 2,2'-bipyridine (bpy), 1,2-bis(diphenylphosphino)ethane (diphos), 1,3-bis(diphenylphosphino)propane (dpp), 1,2-bis(diphenylarsino)ethane (dae), or 2,5-norbornadiene (nbd).

There have been several investigations of the kinetics and mechanisms of ligand substitution by various L' into group 6 metal carbonyl chelate complexes M(CO)₄(chelate) (M = Cr, Mo, W).⁵⁻²⁴ The rate law shown in eq 1 is applicable.

$$\frac{d[M(CO)_4(\text{chelate})]}{dt} = \{k_1 + k_2[L']\}[M(CO)_4(\text{chelate})] \quad (1)$$

Depending on the chelating ligand, several products have been observed; these include M(CO)₃(chelate)L', M(CO)₄L'₂, and M(CO)₃L'₃. Three mechanisms^{24,25} have been postulated to explain the observed rate law and products: (a) an associative pathway, the application of which has been limited to Mo and W complexes, and a mechanism which is therefore not applicable to the present work; (b) CO dissociation as the rate-determining step, accounting for the k_1 term in the rate law; (c) a chelate ring opening pathway as shown in Figure 1. The rate-determining step is dissociation of one end of the chelate. Dobson²⁰ has shown that this mechanism can yield

a rate law term which is first order in both starting complex and entering ligand.

Comparisons previously made^{5,7} indicate that dissociative loss of CO is facile in Cr(CO)₄(chelate) complexes relative to Cr(CO)₆. However, the site of ligand dissociation cannot be inferred rigorously from substitution reactions; the incoming ligand, by virtue of its different steric requirements or interactions with the chelate might not enter the site of CO dissociation. This difficulty is circumvented in ¹³CO exchange studies. However, in any attempts to make stereochemical inferences from ¹³CO exchange studies, account must be taken of the nature of the five-coordinate intermediate generated by either CO dissociation or chelate ring opening. Is the intermediate rigid, as is sometimes implicitly assumed, or fluxional? We report here a study of the kinetics and stereochemistry of ¹³CO exchange in several complexes of the type Cr(CO)₄(chelate).

Experimental Section

Preparation of Compounds. All reactions, preparations, and manipulations were performed under N₂ protection. All compounds have previously been reported; Cr(CO)₄phen,²⁶ Cr(CO)₄bpy,²⁷ Cr(CO)₄nbd,²⁸ and Cr(CO)₄diphos²⁹ were prepared as reported; Cr(CO)₄dpp and Cr(CO)₄dae were prepared using the method of Chatt.²⁹ Satisfactory elemental analyses and infrared spectra were obtained for the various species.

Preparation of *fac*-Cr(CO)₃(¹³CO)phen. A saturated 1,2-dichloroethane solution of *fac*-Cr(CO)₃phenPPh₃ was placed in an exchange vessel² and thermostated to 40.0 °C. ¹³CO (90% enriched) was circulated through the solution for 35 min and the reaction then quenched by immersing the vessel into liquid N₂. The solvent was

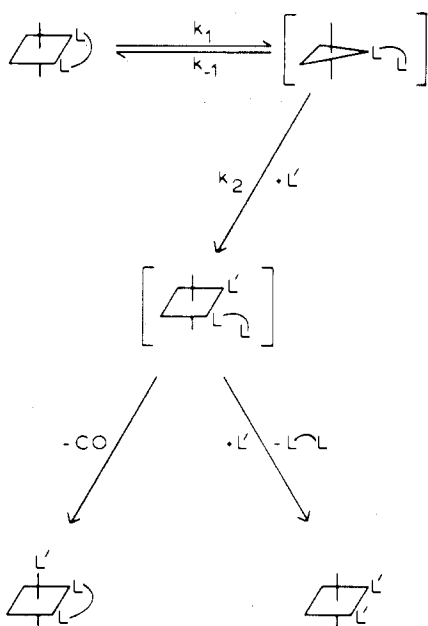


Figure 1. Chelate ring-opening pathway for substitution into a $M(\text{CO})_4(\text{chelate})$ complex.

removed directly from the vessel warmed to $\sim 0^\circ\text{C}$ with a salt/ice bath. No attempt was made to remove the free PPh_3 since the reaction of $\text{Cr}(\text{CO})_4\text{phen}$ with PPh_3 and also isomerization are expected to be slow at 0°C and below. The ^{13}C NMR spectrum of the product in CDCl_3 at -13°C was obtained using a Varian Associates XL-100FT NMR instrument.

Kinetics Experiments. The ^{13}C CO exchange reactions were performed using the techniques previously described,^{2,3} except that the entire reaction apparatus was continually kept under an N_2 atmosphere by using a polyethylene glovebag. In this way, the competing decomposition reaction previously noted⁵ for $\text{Cr}(\text{CO})_4\text{bpy}$ was avoided. The compound under study was dissolved in an appropriate solvent in an inert-atmosphere box and thermostated under an N_2 atmosphere, and the reaction was initiated by circulating CO of 90% ^{13}C CO enrichment through the solution. Each reaction was monitored using ir spectroscopy until equilibrium was attained. All ir spectra were obtained using 1-mm path length NaCl window solution cells, with a Beckman IR-7 or IR-9 spectrophotometer operating in the absorbance mode.

Treatment of Data. Figure 2 illustrates two portions of the ir spectrum of $\text{Cr}(\text{CO})_4\text{phen}$ in the region of the CO stretching modes. The B_1 (1900 cm^{-1}) and low-frequency A_1 (1880 cm^{-1}) modes overlap extensively. The bands derived from these upon ^{13}C CO incorporation

Table I. Calculated Simplified Force Field Parameters for $\text{Cr}(\text{CO})_4(\text{chelate})$ Compounds

	F_c	F_t	f_{cc}	f_{ct}	f_{tt}
$\text{Cr}(\text{CO})_4\text{phen}$	15.23	14.06	0.64	0.55	0.41
$\text{Cr}(\text{CO})_4\text{bpy}$	15.47	14.46	0.68		0.24
$\text{Cr}(\text{CO})_4\text{diphos}$	15.63	14.60	0.60		0.18

are not resolvable. The two modes which do afford useful indicators of CO incorporation are the high-frequency A_1 (2008 cm^{-1}) and B_2 (1828 cm^{-1}) modes. The high-frequency A_1 mode is weighted heavily in the symmetry coordinate corresponding to the symmetric stretching of cis CO groups. The B_2 mode, on the other hand, is dominated by the asymmetric stretch of the trans carbonyl groups.

To use the ir spectrum properly as a quantitative measure of ^{13}C CO incorporation, it is necessary to identify the frequency shifts associated with all possible degrees and positions of ^{13}C CO incorporation. Vibrational analyses using the Cotton-Kraihanzel approximations^{30,31} were performed on the all- ^{12}C CO molecule to obtain two stretching parameters F_c and F_t and two interaction parameters f_{cc} and f_{tt} (Figure 3). Ordinarily, it is assumed that $f_{ct} = f_{tc}$. However, for $\text{Cr}(\text{CO})_4\text{phen}$ and $\text{Cr}(\text{CO})_4\text{bpy}$ it was necessary to differentiate between f_{ct} and f_{tc} to obtain physically reasonable solutions to the vibrational problem. Figure 4 shows all nine possible labeled molecules. The choice of an appropriate value for f_{cc} was made on the basis of how well the resulting set of parameters reproduced the highest frequency CO stretching mode for all the various possible substituted molecules A-I, Figure 4. To do this a value for f_{cc} was assumed, and values for the remaining four parameters were calculated from the four frequencies for the all- ^{12}C CO molecule, using the VIB II program of Schachtschneider.^{32,33} Then, using VIB I,^{32,33} the resulting set of five parameters was employed to calculate the frequencies of the CO stretching modes for all of the various isotopically substituted molecules A-I. This type of calculation was carried out for a range of possible values of f_{cc} . Of course, as the value for f_{cc} is changed, the values of the other parameters which give a fit with the observed frequencies also change. It proved convenient to graph the values for the highest frequency CO stretch as a function of the resulting value for F_c , as illustrated in Figure 5. By choosing the place along this graph at which the observed and calculated frequencies seem to be in best agreement, shown by the dotted line, it was thus possible to select an appropriate value for f_{cc} . The set of parameters which gave the most reasonable fit with the experimental data are listed in Table I. Agreement between the calculated and observed frequencies using these parameters, Table II, is satisfactory; all calculated frequencies are within 2 cm^{-1} of those observed. The vibrational analysis also provided L matrix elements, necessary for the application of corrections to the intensities of the bands of the isotopically labeled molecules.

Figure 2 shows the time dependence of the ir spectrum for the thermal exchange reaction of $\text{Cr}(\text{CO})_4\text{phen}$ with ^{13}C CO (40.0°C , $\text{CICH}_2\text{CH}_2\text{Cl}$). There is a rapid appearance of ^{13}C CO incorporation

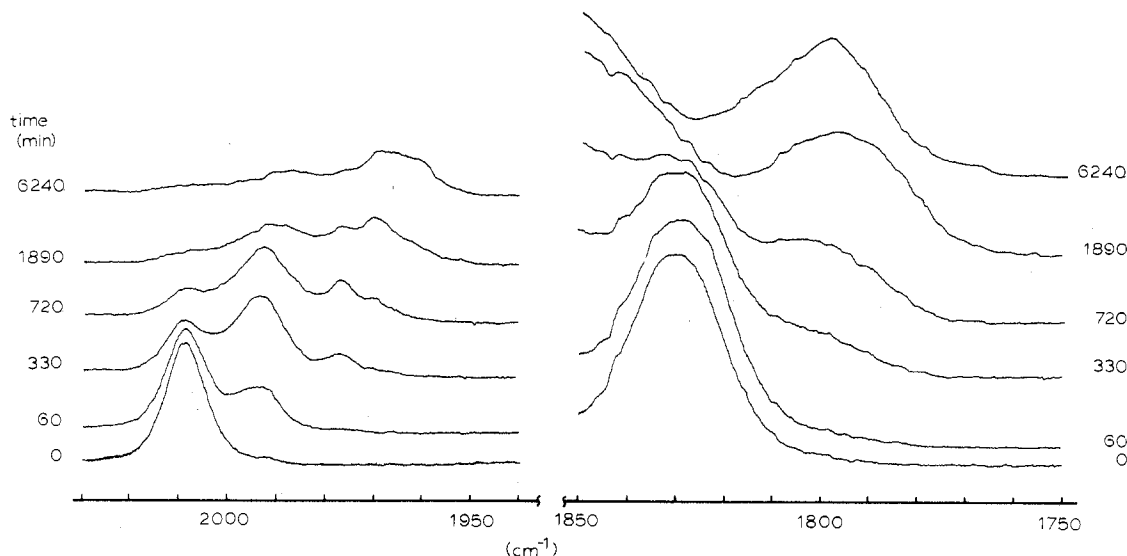


Figure 2. Infrared spectra of $\text{Cr}(\text{CO})_4\text{phen}$ in 1,2-dichloroethane at 40°C in the presence of ^{13}C CO as a function of time.

Table II. Calculated and Observed CO Stretching Frequencies for ^{13}CO -Labeled $\text{Cr}(\text{CO})_4$ phen Molecules

Obsd freq, cm^{-1}	2008	High-Frequency A_1 Mode					1975	1970	1965
		2006	2005	1991	1990	1988			
Calcd freq, cm^{-1}	2008	2006	2005	1991	1990	1988	1975	1970	1965
Possible position of ^{13}CO incorporation	None	3	3, 4	1	1, 3	1, 3, 4	1, 2	1, 2, 3	1, 2, 3, 4
Species	A	C	F	B	E	H	D	G	I

Obsd freq, cm^{-1}	B_2 Mode		
	1829	1800	1788
Calcd freq, cm^{-1}	1829	1801	1788
Possible position of ^{13}CO incorporation	None; 1; 1, 2	3; 3, 1; 3, 1, 2	3, 4; 3, 4, 1; 3, 4, 1, 2
Species	A; B; D	C; E; G	F; H; I

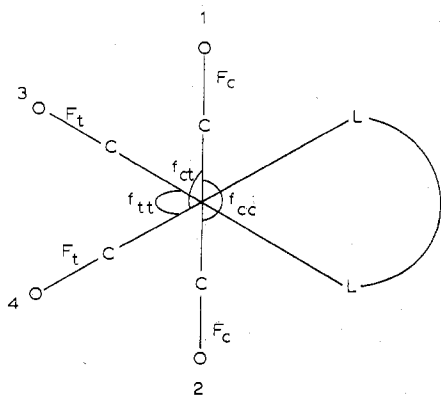


Figure 3. Force constants of the energy-factored force field and labeling system for CO groups.

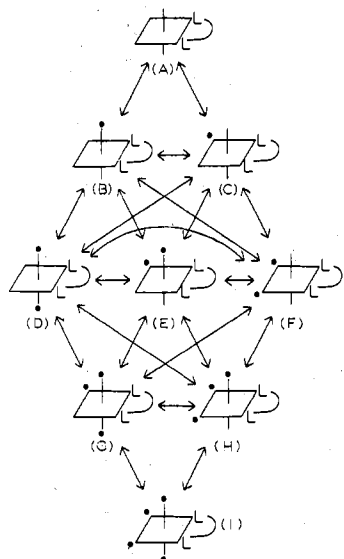


Figure 4. Kinetics scheme for ^{13}CO exchange with $\text{M}(\text{CO})_4^-$ (chelate), assuming a fluxional five-coordinate intermediate. The labels identify all the nine possible isotopically labeled species. The rate constants for conversion from one species to another are all expressed in terms of k_c , k_t , and f . The rate constant expressions are given in Appendix A.

into positions 1 and 2 (those cis to phen) as evidenced by the appearance of absorptions in the 2000–1950- cm^{-1} region. However, incorporation into positions trans to phen does not occur in the early stages of the reaction, as evidenced by the invariance of the spectra in the region around 1800 cm^{-1} . Also noted was an induction period for a decrease in the absorbance of the 1828- cm^{-1} band characteristic of the all- ^{12}CO trans CO group. By analogy with earlier studies,^{2,3} these observations suggest that incorporation of ^{13}CO into positions 3 and 4 occurs via intramolecular rearrangement during the lifetime of a fluxional five-coordinate intermediate. Figure 4 illustrates the kinetics scheme for ^{13}CO exchange corresponding to the assumption of a fluxional intermediate. The dissociative rate constant for position 1 or 2 is k_c , while the dissociative rate constant for position 3 or 4 is k_t . The expressions for the concentrations of all species in this

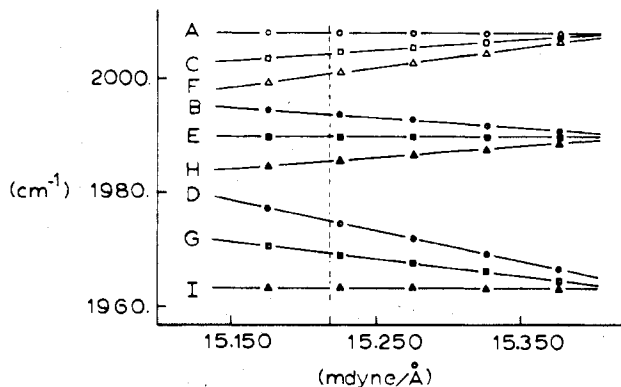


Figure 5. Frequency of highest frequency CO stretching mode for each of the nine possible isotopically labeled $\text{Cr}(\text{CO})_4$ phen species (see Figure 4) as a function of F_c .

reaction scheme, in terms of k_c , k_t , and f , the fractional abundance of ^{13}CO in the exchanging gas, are given in Appendix A. In Appendix B are the similar expressions for the case in which the intermediate is assumed to be rigid. (See paragraph at end of paper regarding supplementary material.)

To determine the rate of cis CO dissociation, the relative integrated absorbances of the bands occurring in the region 2010–1960 cm^{-1} were measured. The bands which appear in the region 2000–1950 cm^{-1} are due to molecules with either one or two ^{13}CO in positions 1 and 2. There are three major groupings of absorptions in the region from 2010 to 1950 cm^{-1} , corresponding to zero, one, or two ^{13}CO molecules in positions 1 and 2. Molecules with a given number of ^{13}CO groups in positions 1 and 2 may have zero, one, or two ^{13}CO molecules in positions 3 and 4. The vibrational analysis based on the best set of parameters yielded the grouping of molecules into three groups; the frequencies are given by the intersections with the dotted line in Figure 5. For no ^{13}CO groups in positions 1 and 2, the highest frequency band occurs in a narrow range of frequency, for different degrees of incorporation of ^{13}CO into positions 3 and 4. Similarly, for one ^{13}CO in positions 1 and 2, absorption occurs in a narrow range around 1990 cm^{-1} , regardless of the degree of incorporation of ^{13}CO into positions 3 and 4. However, when there are two ^{13}CO groups in positions 1 and 2, the band frequency shows a larger degree of dependence on the degree of ^{13}CO incorporation into positions 3 and 4. This effect is quite evident from Figure 2, in which three overlapping bands are seen in the 1980–1950- cm^{-1} region. It was possible to resolve the absorptions occurring at 1975, 1970, and 1964 cm^{-1} using a Du Pont Model 210 curve resolver. Analysis of the spectra in the region from 2010 to 1950 cm^{-1} therefore yielded five relative integrated absorbances as a function of time; the molecules in each set are listed in Table II.

A similar analysis was made for the bands occurring in the region 1830–1760 cm^{-1} , to obtain data for incorporation of ^{13}CO into the trans positions. Again, there are three main groupings of bands, corresponding to zero, one or two ^{13}CO molecules in positions 3 and 4.

The frequency of the band corresponding to a particular number of ^{13}CO groups in positions 3 and 4 is in each case only slightly sensitive to incorporation of ^{13}CO in positions 1 or 2. Each observed band is in effect a group of absorptions corresponding to molecules with varying degrees of ^{13}CO incorporation into positions 1 and 2, but with a particular degree of incorporation into positions 3 and 4.

As is evident from Figure 2, severe overlapping of bands occurs in the 1850–1750- cm^{-1} region. Using the curve resolver it was possible

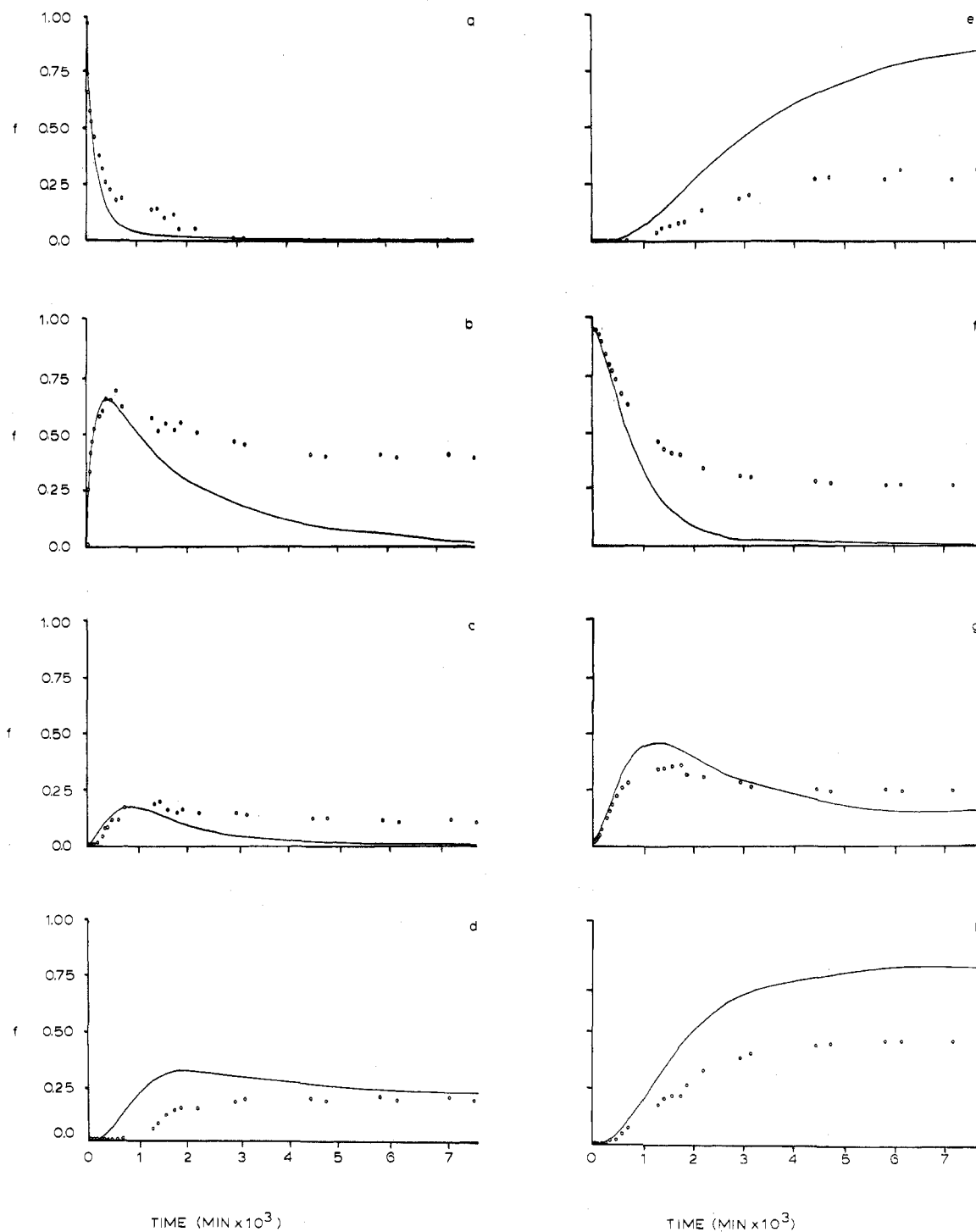


Figure 6. Comparison of calculated and observed fractional integrated absorbances for ^{13}CO exchange with $\text{Cr}(\text{CO})_4\text{phen}$: (a) molecules A, C, and F (see Figure 4) which contain no ^{13}CO in position 1 or 2; (b) molecules B, E, and H, which contain a single ^{13}CO in positions 1 and 2; (c) molecule D; (d) molecule G; (e) molecule I; (f-h) incorporation of zero, one, or two ^{13}CO groups, respectively, into position 3 or 4. The calculated results, represented by the lines, are based on the kinetics scheme shown in Figure 4. The points represent fractional absorption based on analysis of the ir spectra.

to make rough estimates of the fractional absorbances of the three band groupings. Although these data are not quantitatively very precise, they serve to show that incorporation of ^{13}CO into positions 3 and 4 occurs only after a substantial induction period (vide infra).

From the L matrix elements of the vibrational analyses it is possible to calculate the relative intensities of the CO stretching modes for all the various isotopically substituted molecules. In these calculations we assumed idealized 90° angles about Cr and assumed further that all MCO group dipole moment derivatives are equal.^{2,3} Having these intensities, the total absorbance at a given frequency as a function of time can be obtained from the model by calculating the fractional

abundances of all species present at a given time, assuming the kinetics scheme shown in Figure 4. The contribution of each species to a given absorption is then computed and these are summed to give the total fractional absorbance within each group of overlapping absorptions. These calculated fractional absorbances are compared with the fractional absorbances obtained from the spectra following resolution of the bands and integration. The results of such an analysis for the exchange of ^{13}CO with $\text{Cr}(\text{CO})_4\text{phen}$ are shown in Figure 6. The circles show the fractional abundances derived from the ir spectra; the solid lines, the calculated quantities, assuming the kinetics scheme of Figure 4 (a fluxional intermediate) and assuming $k_c \gg k_i$. Entirely

Table III

Rates of Decomposition			
Compd	$T, ^\circ\text{C}$	Solvent	$k_{\text{obsd}}, \text{s}^{-1}$
Cr(CO) ₄ nbd	40.0	CICH ₂ CH ₂ Cl	7.4×10^{-7}
Cr(CO) ₄ dae	90.0	BrCH ₂ CH ₂ Br	6.0×10^{-6}
Rates of ¹³ CO Exchange			
Compd	$T, ^\circ\text{C}$	Solvent	$k_{\text{e}}, \text{s}^{-1}$
Cr(CO) ₄ phen	40.0	CICH ₂ CH ₂ Cl	4.2×10^{-5}
Cr(CO) ₄ bpy	40.0	CICH ₂ CH ₂ Cl	7.6×10^{-5}
Cr(CO) ₄ diphos	110.0	Decalin	1.7×10^{-7}
Cr(CO) ₄ dpp	90.0	Decalin	1.9×10^{-7}

analogous results were obtained for Cr(CO)₄bpy.

Results and Discussion

The reaction of Cr(CO)₄(chelate) with ¹³CO has been observed to have three possible outcomes. First, the parent compound may decompose under the conditions of the reaction without giving a simple and readily identifiable product. This was observed to occur with Cr(CO)₄dae. The apparent first-order rate constant for decomposition, obtained by following the loss of parent peak at 2008 cm⁻¹, is listed in Table III. Secondly, reaction with ¹³CO may lead to replacement of ligand to yield labeled Cr(CO)₆. This was observed to occur with Cr(CO)₄nbd. The first-order rate constant for disappearance of starting Cr(CO)₄nbd is given in Table III. Analysis of the ir spectrum of the Cr(CO)₆ formed in this case indicated that both the cis and trans dilabeled species are present in the product, in comparable amounts.

The most likely mechanism by which the chelate nbd ligand is replaced is a ring-opening process, in which one of the chelate coordination positions is substituted by ¹³CO in the rate-determining step. The loss of chelate ligand then follows in a (probably) faster step,³⁴ yielding the dilabeled Cr(CO)₆ as product. A mechanism of this type has been proposed for chelate ring replacement in Cr(CO)₄dae¹⁷ and Mo(CO)₄(cyclooctadiene).^{9,10}

The fact that both cis and trans dilabeled Cr(CO)₆ are formed suggests that the five-coordinate intermediate Cr(CO)₄(¹³CO) formed upon loss of the chelate ligand is fluxional. Assuming that the first ¹³CO is incorporated in the position cis to the monoligated ligand, a position cis to a ¹³CO is vacated when the ligand is lost completely from the metal. If the five-coordinate intermediate so generated were not fluxional, the incoming ¹³CO would be incorporated into a position cis to the first ¹³CO. The fact that both cis and trans dispositions of the two ¹³CO groups are observed suggests that the five-coordinate intermediate is in fact fluxional during its lifetime. This conclusion is consistent with the conclusions arrived at in several other instances involving five-coordinate species.^{2,3,35,36}

A third possible outcome of the reaction of ¹³CO with Cr(CO)₄(chelate) is ¹³CO incorporation, with retention of chelate coordination. This reaction might occur via a ring-opening process in which one end of the chelate comes off the metal, ¹³CO incorporation occurs, and then the free end of the chelate displaces one of the other CO groups in a position cis to the bound end of the chelate, to form again the bidentate binding to the metal. There are strong lines of evidence against this pathway. Knebel and Angelici have shown^{21,22} for Cr(CO)₅(P-N) [(P-N) = Ph₂P(CH₂)_nC₅H₄N ($n = 1, 2, \text{ or } 3$) or Ph₂P(CH₂)_nNR₂ ($n = 2, 3$)], in which the potentially bidentate ligand is bound to Cr via phosphorus, that displacement of a CO by the free end of the ligand is very slow. Similarly, Connor and co-workers³⁷⁻³⁹ have shown that for several complexes of the form Cr(CO)₅(PR₂(CH₂)_nPR₂), with $n = 1-3$, formation of chelate binding to the metal is quite slow. Thus there is not apparently a facile, ligand-assisted

dissociative pathway available for bidentate phosphorus ligands. On the basis of a cis-labilization mechanism,^{2,3} more facile displacement of CO might be expected when the monoligated system involves a coordinated amine. Dobson and co-workers have argued that the ring-opening pathway under consideration is operative in Cr(CO)₄bpy reactions with phosphites.²³ However, the present results suggest that for ¹³CO as ligand, the ring-opening pathway is not important, for the reasons which are given below.

The most reasonable pathway for substitution or exchange in the compounds under investigation is CO dissociation. On the basis of previous studies of substitution of CO by other ligands at the group 6 metal in compounds of the form M(CO)₄(chelate),⁵⁻⁸ it has been proposed that the first-order term in the rate law corresponds to CO dissociation. Furthermore, the CO dissociation has been presumed to occur from the position cis to the chelate, since the substituting ligand is found in that position in the product. The use of ¹³CO as substituting ligand ensures that the incoming CO will take up a position cis or trans to the chelate ligand with the same degree of preference as that shown by the CO groups in departing from those positions.⁴⁰ In an earlier study of C¹⁸O exchange with Cr(CO)₄phen,¹⁸ it was concluded that CO loss from the cis position is 3 times more rapid than from the trans. However, no account was taken of the possibility that the five-coordinate intermediate formed by loss of CO might be fluxional.

The curves shown in Figure 6 represent the calculated time dependences of the various labeled species (or groups of related species) formed by ¹³CO exchange with Cr(CO)₄phen in 1,2-dichloroethane at 40 °C, assuming that the exchange occurs by CO dissociation exclusively from the position cis to the chelate and assuming that the five-coordinate intermediate is fluxional. The rate constant for CO dissociation from a given cis position which is obtained from this fit of the data is $4.2 \times 10^{-5} \text{ s}^{-1}$. Since this value corresponds to dissociation from a single position, it should be doubled for comparison with the value of $8.1 \times 10^{-5} \text{ s}^{-1}$ obtained by Angelici and Graham⁷ for the first-order rate constant for substitution at the same temperature. The agreement is very good. However, it is clear from inspection of Figure 6 that the calculated and observed quantities are not in good agreement at times beyond the first half-life or so. No doubt some of the disagreement originates in the difficulties associated with resolving the bands in the 1850-1770-cm⁻¹ region. For example, the lack of agreement between calculated and observed results f and h (Figure 6) must be ascribed to our failure to correct properly for overlaps in absorptions. However, the fact remains that there is literally no change in this spectral region until some time has elapsed. The sigmoidal shape is evident in the data shown in g and h of Figure 6. In addition there is evidence, especially in d and e of Figure 6, that bands due to ¹³CO incorporation into positions 3 and 4 do not grow in as rapidly as expected. It should be kept in mind that the *only* means by which a label can find its way into the 3 or 4 position with the presumed mechanism is the intramolecular rearrangement of a molecule in which one or more CO groups have already been replaced by ¹³CO. The fact that we have excellent agreement between the rate constant for exchange and the rate constant observed for substitution indicates that the initial incorporation of ¹³CO into the cis positions is correctly reproduced. That this enrichment appears to remain in this location, rather than move in part into the trans positions suggests that the five-coordinate Cr(CO)₃phen intermediate cannot be completely fluxional.

An alternative model is one in which the five-coordinate intermediate is assumed to be totally nonfluxional. In such a model the incorporation of label into the cis and trans

positions occurs entirely in accord with the relative rate constants for dissociation of CO from the cis and trans positions. This model is not in accord with the observations, because it predicts no induction period in the appearance of label in the trans positions. Similarly, a ring-opening mechanism is ruled out as an important pathway. In such a mechanism the ring closure to form $\text{Cr}(\text{CO})_3(^{13}\text{CO})$ (chelate) (lower left in Figure 1) could occur with equal a priori probability at each of the three ^{13}CO positions cis to the monoligated ligand in the intermediate. This could result in formation of a labeled product molecule with a 1:2 ratio of trans to cis location for ^{13}CO . No induction period for incorporation of ^{13}CO into the trans positions would be observed, contrary to the observations. We therefore conclude that the most reasonable model is one in which $k_c \gg k_t^{41}$ and in which there is some fractional probability that the five-coordinate intermediate will undergo rearrangement during its lifetime, before it recaptures a CO group.

It is not unreasonable that this sort of behavior should be observed for $\text{Cr}(\text{CO})_4\text{phen}$ and $\text{Cr}(\text{CO})_4\text{bpy}$ (which shows essentially identical behavior). Although the five-coordinate intermediates postulated in earlier studies in this series have so far all appeared to be entirely fluxional in character, the effect of the bidentate group may be to restrict intramolecular motion, thus making it possible for the five-coordinate intermediate to combine with a ^{13}CO before rearrangement occurs.

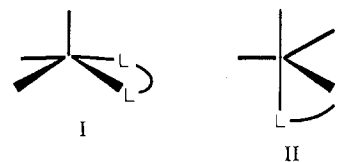
The compound *fac*- $\text{Cr}(\text{CO})_3(\text{PPh}_3)\text{phen}$ reacts readily with ^{13}CO at 40.0 °C in 1,2-dichloroethane to yield $\text{Cr}(\text{CO})_3(^{13}\text{CO})\text{phen}$. (An analogous result was observed with *fac*- $\text{Cr}(\text{CO})_3(\text{PPh}_3)\text{bpy}$,⁵ using ^{12}CO , to produce $\text{Cr}(\text{CO})_4\text{bpy}$.) The ir spectrum of the product in our case indicates that ^{13}CO has been incorporated exclusively into the cis position. Verification of this conclusion comes from the ^{13}C NMR spectrum of the product in CDCl_3 at -13 °C. A single resonance was observed at 216 ppm from TMS as internal standard with a signal to noise ratio of about 9. Although chemical shift values have not been assigned to the CO groups cis and trans to the chelate, the fact that the ir spectra show the presence of only the *fac* isomer strongly indicates that the single ^{13}C carbonyl resonance seen is that of the cis ^{13}CO .⁴² The intermediate formed by loss of PPh_3 from *fac*- $\text{Cr}(\text{CO})_3(\text{PPh}_3)\text{phen}$ is the same as that formed from loss of CO from $\text{Cr}(\text{CO})_4\text{phen}$. The preferential uptake of ^{13}CO into the cis position in this case thus provides additional support for the conclusion that loss of CO from $\text{Cr}(\text{CO})_4\text{phen}$ occurs preferentially from the cis position. It is worth noting also that the rate constant for loss of CO from $\text{Cr}(\text{CO})_4\text{phen}$ or $\text{Cr}(\text{CO})_4\text{bpy}$ is larger by several orders of magnitude at the same temperature than for loss of CO from $\text{Cr}(\text{CO})_6$.^{4,5,7} Thus phen and bpy may be classified as cis-labilizing ligands.²⁻⁴

The exchange of ^{13}CO with $\text{Cr}(\text{CO})_4\text{diphos}$ and $\text{Cr}(\text{dpe})$ was more difficult to study. The reactions are considerably slower. Decomposition of the complex prevented acquisition of reliable data beyond about 50% reaction. As a result it was not possible to test the model for incorporation of ^{13}CO corresponding to the assumptions that $k_c \gg k_t$ and that the five-coordinate intermediate is fluxional. However, it is quite clear from the manner in which the spectra change during the early stages of the reaction that $k_c > k_t$. Thus, both diphos and dpp appear to cause preferential loss of cis CO, although there is no substantial labilization of the complexes as compared with $\text{Cr}(\text{CO})_6$, at any rate for $\text{Cr}(\text{CO})_4\text{diphos}$.

It is interesting that CO loss is significantly faster for dpp than for diphos. The two ligands appear to have about the same effect on the metal in the ground state, as evidenced by the nearly identical CO stretching frequencies. The difference

in rates of CO loss is probably due to a difference in stabilities of the transition states, relating to strain in the six-membered chelate ring as compared with the five-membered ring.

The present work does not shed light on the geometry of the transition state or the closely related five-coordinate $\text{Cr}(\text{CO})_3$ (chelate) intermediate. If it is assumed that the intermediate possesses an idealized square-pyramidal geometry, then the chelate ligands must be supposed to occupy preferentially the basal positions; as in I. On the other hand, if



the geometry of the intermediate is idealized trigonal bipyramidal, the chelate may be supposed to occupy an axial and equatorial site, as in II. If I is the more stable arrangement for the intermediate and if intramolecular rearrangement proceeds via a Berry type of process,⁴⁴ then the rearrangement would need to proceed through a structure such as II. On the other hand, if II is the lower energy form, rearrangement via a Berry process would need to proceed via I. In either case, it is reasonable to suppose that the presence of a chelate group could increase the free energy barrier to rearrangement sufficiently so that the average time for rearrangement would be considerably longer than the average lifetime of the intermediate itself.

In terms of the site preference model described earlier,⁴ such labilization as occurs in the $\text{Cr}(\text{CO})_4$ (chelate) systems may be ascribed to stabilization of the transition state. This stabilization results from preferential siting of the ligands as illustrated in I and II, as compared with CO in those same positions. In certain cases, substantial labilization of the complex as a whole in comparison with $\text{Cr}(\text{CO})_6$ does not occur, as in $\text{Cr}(\text{CO})_4\text{diphos}$, but there still exists evidence for preferential loss of CO from positions cis to the ligands. In these cases, the transition state I or II, while not especially stable, is preferred to the one which would be formed by trans CO loss.

Registry No. $\text{Cr}(\text{CO})_4\text{nbd}$, 12146-36-0; $\text{Cr}(\text{CO})_4\text{dac}$, 26111-08-0; $\text{Cr}(\text{CO})_4\text{phen}$, 14168-63-9; $\text{Cr}(\text{CO})_4\text{bpy}$, 15668-63-0; $\text{Cr}(\text{CO})_4\text{diphos}$, 15712-88-6; $\text{Cr}(\text{CO})_4\text{dpp}$, 40545-09-3; *fac*- $\text{Cr}(\text{CO})_3(^{13}\text{CO})\text{phen}$, 58717-86-5; *fac*- $\text{Cr}(\text{CO})_3\text{phenPPh}_3$, 15492-75-8; ^{13}CO , 1641-69-6.

Supplementary Material Available: Appendixes A and B listing the rate expressions for the time dependence of all of the isotopically labeled species shown in Figure 4 for the assumption of a fluxional five-coordinate intermediate and for an assumed rigid five-coordinate intermediate, respectively, and Appendix C containing an account of the corrections applied to the ir intensities of the CO stretching modes in the isotopically labeled molecules (14 pages). Ordering information is given on any current masthead page.

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 (41) The calculated spectra are essentially insensitive to an increase in the ratio k_c/k_t beyond about 10. This ratio might in fact be (and indeed we believe it is) much larger than this.
 (42) It has recently been reported⁴³ that *fac*-(glyoxal bis(*tert*-butylimine))tricarbonyl(acetonitrile)chromium loses CH_3CN at 20 °C in the presence of ^{13}C O to yield both *cis* and *trans* ^{13}C O labeled (glyoxal bis(*tert*-butylimine))tetracarbonylchromium. This suggests that the bidentate nitrogen ligand in this case is nonstereospecific in directing dissociative CO loss. A more likely explanation is that chelate ring opening occurs.
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Mononuclear and Binuclear Carbonyl Complexes of Chromium, Molybdenum, and Tungsten with 2,3-Diazabicyclo[2.2.1]hept-2-ene

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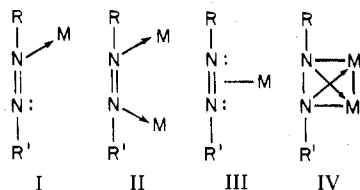
Received August 20, 1975

AIC50621V

Three series of carbonyl complexes of the group 6B metals with the azo ligand 2,3-diazabicyclo[2.2.1]hept-2-ene, $\text{C}_5\text{H}_8\text{N}_2$ (DBH), have been synthesized. In the compounds *cis*-(CO)₄M(C₅H₈N₂)₂ (M = Cr, Mo, W) the azo group is coordinated by only one of the nitrogen lone pairs. Both nitrogen lone pairs are coordinated in the dibridging derivatives (CO)₄M-(C₅H₈N₂)₂M'(CO)₄ (M, M' = Cr, Mo, W) and in the tribridging (CO)₃M(C₅H₈N₂)₃M(CO)₃ (M = Cr, Mo, W). The dibridging compounds include the first examples of mixed-metal azo-bridged complexes. For a given structural type the reactivity is in the order Mo > Cr > W; the stability trend for the three structures is (CO)₃M(C₅H₈N₂)₃M(CO)₃ > (CO)₄M(C₅H₈N₂)₂M(CO)₄ > *cis*-(CO)₄M(C₅H₈N₂)₂. Force constants calculated by the Cotton-Kraihanzel method for *cis*-(CO)₄M(C₅H₈N₂)₂ and (CO)₃M(C₅H₈N₂)₃M(CO)₃ are interpreted as supporting π -acceptor ability by the azo group in DBH.

Introduction

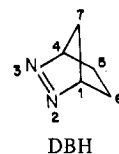
Organometallic complexes containing a coordinated azo linkage ($\text{--}\ddot{\text{N}}=\ddot{\text{N}}\text{--}$) have attracted considerable recent attention.^{1,2} The two nitrogen lone pairs and the $\text{N}=\text{N}$ π bond provide for a rich variety of coordination modes for the azo grouping. Four types of complexes have been identified in which the N--N bond remains intact. These involve coordination through one or both nitrogen lone pairs (I, II), co-



ordination through the $\text{N}=\text{N}$ π bond (III), and coordination through both lone pairs and the π bond simultaneously (IV). Type III coordination, which appears to be the least frequently encountered, is quite sensitive to the nature of the metal center and the identity of other ligands coordinated to it.¹⁻³ Likewise type IV coordination which retains the N--N σ bond only is limited to systems in which M--M is the $\text{Fe}_2(\text{CO})_6$ unit. Coordination types I and II are most widely encountered with examples known for a variety of azo ligands and metal systems.

Even diazene, $\text{HN}=\text{NH}$, the parent azo compound has been stabilized in type II complexes.⁴ Type I and type II complexes may be models for possible metal-diazene intermediates in the biological fixation of nitrogen.^{5,6}

At the time we began our work no careful investigation of types I and II coordination with any single metal system had been reported, although a brief report of type I benzo[*c*]cinnoline complexes, $\text{LM}(\text{CO})_5$ (M = Cr, Mo, W), appeared shortly thereafter.⁷ Hence we initiated such a study focusing on group 6B metal carbonyl compounds with the ligand 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) which had previously



been demonstrated to coordinate to metal carbonyl systems.^{8,9} We now report on a series of group 6B coordination compounds with DBH involving three different modes of types I and II coordination. Included in this set are the first examples of mixed-metal bridging systems. When this work was nearly complete and a preliminary report was already in press,¹⁰ an independent synthesis of the chromium compounds was reported.¹¹ However, no previous report of the molybdenum,