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Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 1. Cis Labilization in Carbonyl Substitution Reactions of Hexacoordinate Chromium(0) and Manganese(I) Pentacarbonyl Complexes

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Hartree-Fock-Roothaan calculations are reported for the pentacarbonyls $M(CO)_5L$ ($M = Cr$, $L = PH_3$, NH_3; $M = Mn$, $L = Cl$, H) and for the fragments formed by carbonyl loss. Analytical gradient techniques were used to completely optimize the geometries. The loss of a carbonyl cis to the heteroligand is favored over trans loss by 3-9 kcal/mol. For most complexes this difference is split between ground-state effects and relaxation effects in the intermediate. The importance of relaxation effects increases as the π-donor ability of L increases. Direct conversion of the trans-loss to cis-loss intermediate is calculated to require approximately 10 kcal/mol in the gas phase. However, an indirect mode of trans-carbonyl incorporation has a calculated activation energy of only 1 kcal/mol.

Introduction

Carbonyl dissociation is the first step in many ligand substitution reactions in organometallic chemistry. Therefore, much attention has been given to the relative lability of carbonyls in different complexes, or inequivalent carbonyls in a given complex.[1]

Prior to 1970, Angelici had classified various ligands as either labilizing or nonlabilizing relative to carbonyl.[2] The earliest studies to show cis labilization were those of Basolo and Wojcicki, on $Mn(CO)_5X$ (X = Cl, Br, I),[3] and those of Hieber and Wollmann on the same complex (X = Cl, Br).[4] On the basis of ^{14}CO exchange these studies concluded that the four carbonyls cis to X exchange at a faster rate than the trans carbonyl. Johnson et al., however, followed $C^{18}O$ exchange for $Mn(CO)_5X$ (X = Cl, Br) by means of IR spectroscopy and concluded that the rates of cis and trans incorporation were the same.[5]

In 1975 Atwood and Brown[6] monitored the substitution of ^{13}CO for CO in $M(CO)_5Br$ complexes (M = Re, Mn) by means of infrared spectroscopy. They determined that CO dissociation was the rate-determining step in the substitution and that the rate constant for cis dissociation was 10 times that of trans. In subsequent papers Atwood and Brown postulated a site-preference model for this cis labilization.[7,8] According to this model the loss of a cis CO is favored because the labilizing ligand prefers to occupy a basal site in the "square-pyramidal" intermediate. They concluded that ligands which are weak σ donors and poor π acceptors will prefer the basal site of the square pyramid and will be cis labilizing and that this preference would decrease as the σ-donor and π-acceptor ability of the ligand increases.

The reason for the site preference, however, is not completely clear. The site preference could be due to a stronger M-C bond trans to the heteroligand or greater relaxation of the fragment afforded by cis loss. Lichtenberger and Brown published Fenske-Hall calculations on $Mn(CO)_5Br$ that indicated little strengthening of the trans M-C bond relative to the cis bond in the ground state of the molecule.[9] A partial optimization (Br-M-C angles) of the fragments due to both cis and trans loss showed substantially greater relaxation energy for cis loss. They proposed that the site preference was due to transition-state relaxation, rather than ground-state strengthening of the trans M-C bond. They also proposed a C_{2v} structure for the cis-loss fragment and a mechanism for its fluxionality.

More recently, however, work by Atwood and co-workers on $Cr(CO)_4L_2$ (L = phosphine, phosphite) has led them to modify the earlier conclusions.[10,11] They affirm that labilization is a transition-state effect; the transition state of an unsaturated intermediate is lowered by the replacement of a CO ligand by a better donor such as a phosphine. The preference for cis loss, however, is attributed to the strenghtening of the trans M-C bond apart from any relaxation effects in the intermediate. The trans M-C bond is stronger because the trans carbonyl competes with the weaker π acid in both of its π planes, whereas a cis carbonyl still competes with all carbonyls in one plane. This argument is supported by crystal structures of several $M(CO)_5L$ complexes in which the $M-C_{trans}$ bonds are shorter than the $M-C_{cis}$ bonds.[8]

The possibility of fluxionality in the five-coordinate intermediate has been a source of complication and controversy in substitution reaction studies. The early studies found two very different rates of cis and trans incorporation of labeled CO, which implies a nonfluxional intermediate.[3] Atwood and Brown, however, found evidence of fluxionality.[6] Lichtenberger and Brown proposed a scheme whereby a labeled CO is initially incorporated cis but moves to the trans position during the exchange of a second CO. This gives rise to trans incorporation without direct trans CO loss.

Several studies carried out by Dobson and co-workers have indicated that the five-coordinate $L_2M(CO)_3$ complex generated by CO loss is fluxional.[12-15] They monitored (via NMR spectroscopy) the scrambling of the labeled carbonyl in *fac*-L_2-$(^{13}CO)M(CO)_3$ during a CO-exchange reaction. The pattern of scrambling indicated that CO loss was exclusively axial (cis to both of the bidentate ligand coordination sites) and that the scrambling occurred without opening a coordination site in the equatorial plane. Thus, at no time was a coordination site trans to a heteroligand open.[15] This is similar to the scheme of Lichtenberger and Brown, which also allowed trans incorporation without opening the trans coordination site.[9]

Darensbourg and co-workers used ^{13}C NMR spectroscopy to examine the ligand dissociation reactions of group 6B carbonyls. They found that substitution of ^{13}CO for L (L = phosphine, phosphite) in both *cis*- and *trans*-$Mo(CO)_4L_2$ gave *cis*-(^{13}CO)-$Mo(CO)_4L$.[16] Darensbourg et al. also reported that the reaction of *trans*-$Cr(CO)_4(PPh_3)_2$ with ^{13}CO initially produces only *cis*-$Cr(CO)_4(^{13}CO)(PPh_3)$, but eventually a statistical distribution of cis and trans product is formed.[17] They concluded that the five-coordinate intermediate $M(CO)_4L$ rearranges from the trans-vacancy isomer to the cis-vacancy isomer in these complexes

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and that the $Cr(CO)_5L$ complex is fluxional in the ground state. Darensbourg and co-workers have done a series of studies on nondissociative fluxionality in octahedral species.[17-19] They showed that $Cr(CO)_5(PPh_3)$ and the complexes $Mo(CO)_4(PR_3)_2$ (R = Et, *n*-Bu) are fluxional. Thus, it is possible that some rearrangements attributed to intermediates could be occurring in the fully ligated ground state.[20]

In a very recent publication Jackson[21] has challenged some of the conclusions of Brown and co-workers and reiterated that a disagreement exists between the early experiments and later IR and NMR studies. However, Brown has recently rebutted this challenge.[22]

In order to clarify the energetics of CO dissociation and fluxionality of monosubstituted group 6B carbonyls, we have calculated the energies and geometries of both the ground states and the five-coordinate intermediates formed by carbonyl loss. It is possible to theoretically determine bond strengths and geometries for the ground state, intermediate, and the experimentally less accessible transition states. Transition-metal complexes are often too large to permit theoretical determinations that are accurate enough to make a priori predictions of bond strength. Theory can, however, determine accurate relative energies and provide a basis for interpreting experimental results. For this study, complete geometry optimizations have been carried out at the Hartree–Fock–Roothaan level for ground states, intermediates, and transition states for carbonyl loss from $M(CO)_5L$ complexes. In a theoretical study one can separate effects and evaluate their relative importance. This ability will provide answers to several questions. What is the relative importance of ground- and transition-state effects for stereospecific cis labilization? What is the importance of π effects? Do calculations support the fluxionality of the five-coordinate intermediate, and is the calculated mechanism consistent with the many experimental studies?

Theory

All calculations were performed at the restricted Hartree–Fock (RHF) level of approximation. In general, electron correlation is essential to describe bond dissociation. The thermal dissociation of CO, however, leaves two closed-shell fragments; therefore, for these complexes a reasonable estimate of the dissociation energy can be obtained at the RHF level. The purpose of this paper is not the calculation of the exact dissociation energies for CO loss but of the relative energies of dissociation of inequivalent carbonyls of the same complex. In other words, the questions depend on relative energies of different geometries of a given $M(CO)_4L$ complex and the energy of interconversion between different geometries. Correlation and basis set errors should remain nearly constant for these comparisons, and the results obtained at the RHF level with a modest basis set should be qualitatively reliable. Recent calculations by Daniel and Veillard have noted that adding electron correlation to a Hartree–Fock calculation on $Mo(CO)_4(NH_3)$ leaves the relative stability of different singlet-state geometries practically unchanged.[23]

The basis sets on the metal are the modifications of the Huzinaga basis sets of Williamson and Hall.[24] The final basis set on each metal is (432-421-31), where the spherical parts of the d functions have been retained. All other basis sets are due to Huzinaga.[25] The basis sets on C, O, and N are the (33-3) basis sets split to (321-21), and those for Cl and P are the (333-33) sets split to (3321-321). The basis set for the H atom was Huzinaga's contraction of three Gaussians for the NH_3 and PH_3 groups but was split (21) for $Mn(CO)_5H$. All optimized geometries were obtained by analytical gradient methods. Except where noted, all structures are fully optimized within the constraint of their point group symmetry. Although the stationary points obtained have not been fully characterized, they are similar to those one would expect on the basis of experimental observations. Convergence in the geometry was defined by a maximum gradient of 0.002 25 hartree/rad (or au) and an average gradient of 0.000 15 hartree/rad (or au). All calculations were carried out by using the GAMESS program.[26]

Table I. Geometry Parameters for Ground States of Model Complexes (Bond Lengths in Å and Angles in deg)

	$Cr(CO)_5PH_3$[a]		$Cr(CO)_5NH_3$
	calcd	exptl	calcd
M–L	2.51	2.422 (1)	2.27
$M-C_{cis}$	1.90	1.880 (5)	1.91
$M-C_{trans}$	1.88	1.845 (5)	1.86
$C-O_{cis}$	1.143	1.147 (6)	1.143
$C-O_{trans}$	1.144	1.154 (5)	1.147
L–M–C	89.8	95.0 (5)	91.1
X–C–O	89.9	85.8 (3)	89.7
L–H	1.41		1.02

	$Mn(CO)_5Cl$[b]		$Mn(CO)_5H$[c]	
	calcd	exptl	calcd	exptl
M–L	2.46[d]	2.367 (4)	1.60	1.601 (16)
$M-C_{cis}$	1.97	1.893 (6)	1.90	1.852 (12)
$M-C_{trans}$	1.93	1.807 (9)	1.90	1.822 (12)
$C-O_{cis}$	1.127	1.109 (8)	1.133	1.130 (9)
$C-O_{trans}$	1.131	1.122 (11)	1.134	1.143 (9)
L–M–C	84.9	88.3 (2)	82.3	83.0 (8)
X–C–O	85.8	88.0 (6)	83.8	87.3 (7)

[a] Reference 29. [b] Reference 30. [c] Reference 31. [d] With a polarizatrion function on Cl the value is 2.43.

Results and Discussion

The results fall into two parts, and each part addresses a question raised by experimental studies. In the first section we will examine the optimal geometries of both the ground states and intermediates and relate them to the energetics of cis and trans carbonyl loss. In this section the ground-state and relaxation effects will be evaluated separately, in order to determine their relative importance for each complex. In the second section the energetics of interconversion of the intermediates due to cis and trans dissociation will be presented. These results should give a clearer theoretical understanding of the pattern of multiple substitutions of labeled CO molecules and will allow us to address the questions raised by Jackson about the incompatibility of a rapidly interconverting intermediate with the early experimental results.[21,22]

Two matters of terminology should be noted. The term "ground-state effects" describes effects that can be seen in ground-state properties, such as differences in bond lengths and vibrational frequencies. The term "relaxation effects" describes those effects that are shown by the relaxation of a five-coordinate fragment from a frozen ground-state geometry. This is a more precise term for describing the results presented here than "transition-state effects", which has been previously used in the literature. Our calculations indicate no energy barrier for the recombination of CO with the $M(CO)_4L$ fragment in the gas phase. Therefore, according to these calculations, any barrier to recombination that is found by experiment is due to the energy required for the carbonyl to displace a weakly bound solvent molecule. This is in agreement with the flash photolysis studies of Simon et al.,[27] which indicated that the photofragment $[Cr(CO)_5]$ is deactivated by solvent within 0.8 ps. Since we calculate the barrier to recombination to be essentially zero, the calculated energy of the fragment is indistinguishable from that of the gas-phase transition state. The optimized fragments may be classified as intermediates, because they are stable for the time required for a CO to diffuse close enough to recombine; therefore, they will be refered to as either intermediates or, simply, optimized fragments.

Optimal Geometries and Their Energies. The optimal geometries of the ground states are given in Table I and are shown in Figure

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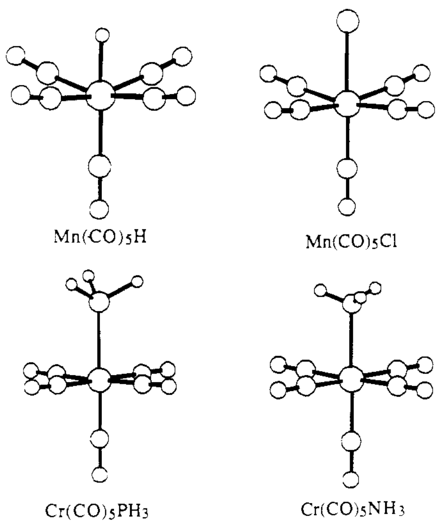

Figure 1. Calculated optimal ground-state geometries.

Table II. Calculated Energies (in kcal/mol) for CO Dissociation

	trans loss			cis loss		
	fix.	rel	Δ	fix.	rel	Δ
$Mn(CO)_5Cl$	20.8	19.9	0.9	18.5	14.4	4.1
$Mn(CO)_5H$	18.3	17.4	0.9	15.5	14.4	1.1
$Cr(CO)_5PH_3$	31.1	30.9	0.2	28.7	26.9	1.8
$Cr(CO)_5NH_3$	32.5	31.9	0.6	26.8	23.1	3.7

	trans–cis				trans–cis		
	fix.	rel	Δ		fix.	rel	Δ
$Mn(CO)_5Cl$	2.3	5.5	3.2	$Cr(CO)_5PH_3$	2.4	4.0	1.6
$Mn(CO)_5H$	2.8	3.1	0.3	$Cr(CO)_5NH_3$	5.7	8.8	3.1

1. The calculated geometries are for the most part in good agreement with experiment. The notable exception is the $Mn(CO)_5Cl$ complex. It has been previously noted[24,28] that correct absolute values for metal–Cl bond lengths are difficult to obtain theoretically and require basis sets larger than those used here. The relative strength of the interaction between the cis and trans carbonyl and the metal, however, agrees more closely with experiment than the absolute values of the bond lengths, and only these relative values are crucial to this study. The effect of a polarization function was tested by adding a single d function (exponent 0.514)[25] to the chloride and reoptimizing the ground state. The Mn–Cl bond shortened by 0.03 Å, but none of the metal–carbonyl bond parameters, which are of interest here, changed significantly.

In each complex the $M-C_{cis}$ bond is longer than the $M-C_{trans}$ bond. This is consistent with the usual π-back-bonding arguments; the extent of π back-bonding to a CO group increases as the π-acceptor ability of a heteroligand competing for back-bonding electrons decreases. The trans bond is strengthened relative to the cis because both π orbitals of the trans carbonyl, but only one of the two cis carbonyl π orbitals, are of appropriate symmetry to compete with the π orbitals of the heteroligand. The differences between $M-C_{cis}$ and $M-C_{trans}$ and between $C-O_{cis}$ and $C-O_{trans}$ are smallest for $Cr(CO)_5PH_3$ and $Mn(CO)_5H$. This is what one would expect, on the basis of the π-accepting order $Cl^- < NH_3 < H < PH_3 < CO$. As the π-accepting ability of a heteroligand approaches that of CO, the difference between cis and trans carbonyl bonding should decrease. Thus, the chloride ion causes a greater difference between cis and trans bonds than hydride, and NH_3 causes a greater difference than PH_3.

Table III. Calculated Optimal Geometries for Cis-Loss Fragments (Bond Lengths in Å and Angles in deg)[a]

	$Cr(CO)_4PH_3$	$Cr(CO)_4NH_3$	$Mn(CO)_4Cl$	$Mn(CO)_4H$
M–L	2.54	2.23	2.37	1.63
M–C				
cis,cis	1.90	1.90	1.98	1.89
cis,trans	1.88	1.86	1.94	1.90
trans,cis	1.87	1.85	1.94	1.91
C–O				
cis,cis	1.144	1.144	1.127	1.134
cis,trans	1.147	1.150	1.130	1.135
trans,cis	1.148	1.150	1.129	1.134
L–M–C				
cis,cis	89.5	90.0	87.9	87.9
cis,trans	168.4	154.3	154.6	174.4
trans,cis	97.8	110.8	108.6	87.1
X–M–C				
cis,cis	90.0	90.8	85.8	81.5
M–C–O				
cis,trans	180.0	177.4	179.1	181.6
trans,cis	178.1	176.3	174.7	170.8
tilt	181.6	181.8	178.6	179.4
wag	180.8	182.0	175.4	172.4
L–H	1.42	1.02		
M–L–H	120.0	109.8		

[a] The variables are labeled as shown in Figure 1.

Table IV. Calculated Optimal Geometries for Trans-Loss Fragments (Bond Lengths in Å and Angles in deg)

	$Cr(CO)_4PH_3$	$Cr(CO)_4NH_3$	$Mn(CO)_4Cl$	$Mn(CO)_4H$
M–L	1.88	1.86	2.46	1.63
M–C	1.91	1.91	1.98	1.90
C–O	1.145	1.145	1.128	1.134
L–M–C	90.1	89.7	87.0	84.1
M–C–O	178.1	178.1	175.4	172.3
L–H	1.41	1.02		
M–L–H	118.8	109.9		

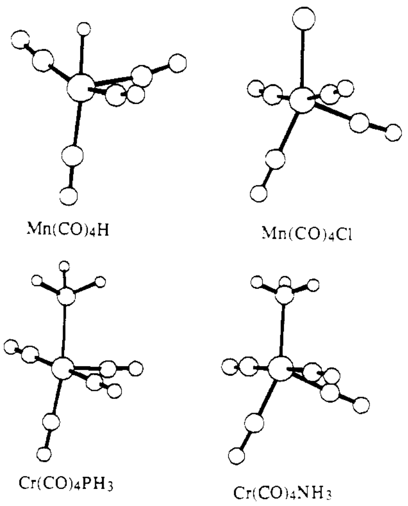

Figure 2. Calculated optimal geometries for cis-loss intermediates.

The effect of the ground-state differences between cis and trans bonding on the energetics of CO dissociation can be evaluated theoretically, apart from any relaxation effects, by calculating the energy of the cis- and trans-loss fragments that have been frozen in the ground-state geometries. The contribution of relaxation to the cis/trans energy difference may then be determined by optimizing the geometries of the pentacoordinate fragments. The energies of cis and trans loss are given in Table II. Optimized fragment geometries are given in Tables III and IV and shown in Figures 2 and 3. The labeling scheme is shown by **1**.

The optimized fragments for trans loss are nearly square pyramidal with almost 90° angles in all four complexes. The optimized cis-loss geometries show some variety in their relaxed geometries. The complexes $Mn(CO)_4Cl$ and $Cr(CO)_4NH_3$ differ most from a square pyramid upon cis loss. They do not, however,

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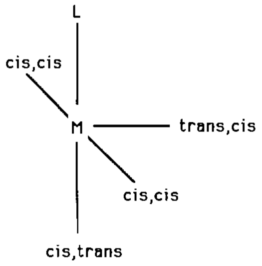

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assume a trigonal-bipyramidal structure. The $C_{\mathrm{cis,trans}}$–M–$C_{\mathrm{trans,cis}}$ bond angle remains smaller than 120°, in agreement with the calculations of Daniel and Veillard.[23]

The energy differences in Table II are small, but they establish trends that can be used to estimate the relative importance of ground-state and relaxation effects and indicate under what circumstances relaxation effects will be important. It is encouraging to note that the general difference between the energies of CO loss for the chromium and manganese complexes agrees with the experimental data compiled by Brown.[8] One would expect the neutral chromium complexes to have stronger π donation to the carbonyls and require more energy to dissociate either the cis or trans carbonyl. The experimental data show a difference of 10^6 between the rate constants for CO loss from $Cr(CO)_5PPh_3$ and $Mn(CO)_5Cl$ at 30 °C. This corresponds to a difference in activation energies of about 8–9 kcal/mol (assuming an Arrhenius expression for the rate constant, and similar preexponential factors), which is in good agreement with the 12 kcal/mol difference calculated here. Our calculations underestimate the strength of the Mn–carbonyl interaction, in part, because Hartree–Fock calculations overestimate the ionic nature of Mn^+ and do not allow enough π back-bonding to the carbonyls.

Brown notes that $Mn(CO)_5H$ does not undergo dissociative CO loss and suggests that it may undergo hydride migration instead.[8] The barrier to hydride migration at the RHF level in our basis set is about 18 kcal/mol, which is higher than the barrier to cis carbonyl loss. As noted above, however, the absolute value of the calculated Mn–carbonyl interaction is probably too weak by 3–4 kcal/mol, which would make the barrier to hydride migration similar to that for cis carbonyl loss. In the present study only the hydride's effect on cis and trans carbonyl loss is of interest; therefore, the presence of a lower energy pathway to an open coordination site will not affect our conclusions.

Table II and the optimized geometries of the fragments provide clues to the relative importance of ground- and transition-state effects. It should be emphasized that the energy differences calculated here are small, and one must use both the geometry and the energies as indicators of the importance of relaxation effects. If only ground-state effects are involved, then all of the energy difference between cis and trans CO loss should be apparent even when the fragment is not allowed to relax. If only relaxation effects are important, the relative energies of the frozen cis- and trans-loss geometries should be nearly equivalent. As shown in Table II, the relaxation energies of the trans-loss fragments are small and nearly equal among the complexes. Relaxation is most important for the cis-loss fragments, and they show significant differences in relaxation energies and optimized geometries. Therefore, we will concentrate on the relaxation energy of the cis-loss fragment. As one might expect, most cases lie between the two extremes of all ground-state or all relaxation effects. Only for $Mn(CO)_4H$ is the difference between cis and trans loss almost entirely a ground-state effect. When allowed to relax, the cis-loss fragment of $Mn(CO)_4H$ shows almost no change in geometry from the ground state. For $Mn(CO)_4Cl$ relaxation makes up a slightly greater portion of the overall energy difference between cis and trans loss. For both of the chromium complexes a slightly greater portion of the cis/trans energy difference is present prior to relaxation.

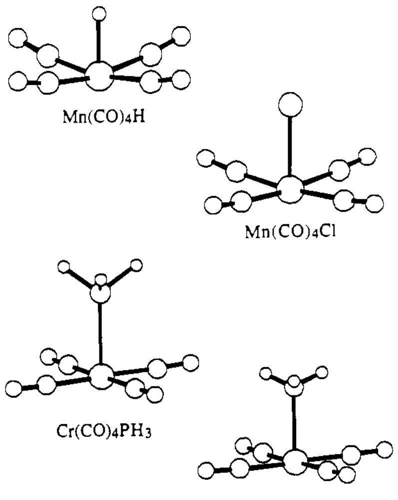

Figure 3. Calculated optimal geometries for trans-loss intermediates.

Although calculations do not show a clear predominance of either ground-state or relaxation effects in all cases, they do show the importance of π-donor and -acceptor interactions. For each metal, the heteroligand that is the stronger π donor (NH_3 on Cr and Cl^- on Mn) shows a greater cis/trans energy difference in both the frozen and optimized fragments. The ground-state effects of the various heteroligands, as shown by the relative energies of the frozen cis- and trans-loss fragments, are in agreement with previously given rationales (vide supra). The optimized fragment geometries and energies, however, are, in some respects, surprising. Although the NH_3 group can be considered a π donor, it is very weak compared to Cl^-; however, the cis-loss fragment geometries and relaxation energies of $Mn(CO)_5Cl$ and $Cr(CO)_5NH_3$ are quite similar. Even a very weak π donor is calculated to cause rearrangement of the cis-loss fragment, but the PH_3 group and the hydride ion cause little geometry change and provide little relaxation energy upon cis loss.

Mulliken population analysis shows that, for the two π-donor ligands Cl^- and NH_3, donation increases upon cis loss, whereas it decreases for PH_3 and H^-. The changes in donation in all cases are small, but they consistently show that the relaxation effects are tied to the π-donor ability of the heteroligand. For the low-valent complexes considered here, the relaxation energy for cis loss is greater for π donors than for π acceptors because the donor can effectively coordinate the cis vacancy. Lichtenberger and Brown reached similar conclusions using Fenske–Hall calculations.[9] When the cis carbonyl is lost, the fragment rearranges to allow the halide ion to donate to the newly vacant metal orbital. Although Lichtenberger and Brown provisionally wrote a trigonal-bipyramidal fragment geometry, the trigonal bipyramid remains a maximum connecting two C_s symmetry minima (vide infra). The increase in π donation brought about by the geometry relaxation does not necessarily affect the charge on the metal, but it strengthens both the M–L bond and the metal–carbonyl bonds that lie in the C_s plane. The bond strengthening can be seen by comparing the ground-state geometry with the cis fragment geometry for the chromium ammine and manganese chloride complexes. The M–$(CO)_{\mathrm{trans}}$ interaction weakens slightly, as indicated by the longer M–C bond and the shorter C–O bond. The M–$(CO)_{\mathrm{cis}}$ interaction in the symmetry plane, however, becomes substantially stronger. Some references[32] show the heteroligand along the axis of the trigonal bipyramid, but for the d^6 complexes studied here it prefers the equatorial plane by 3–9 kcal/mol, and this preference increases as the ability of the ligand to π donate increases.

The importance of the π interaction to cis labilization can be seen in the cis-labilizing sequence given by Atwood and Brown:[8] $H^- < P(OPh)_3 < PPh_3 < Cl^-$. Our results indicate that ligands which are π donors stabilize the cis loss relative to trans by both strengthening the trans bond in the ground state and providing more relaxation energy for cis loss than trans. For ligands that

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(32) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; p 114.

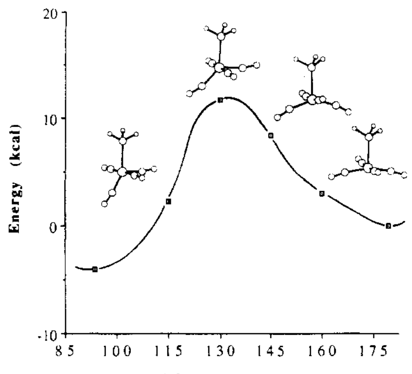

Figure 4. Potential energy curve for the trans-vacancy to cis-vacancy rearrangement of $Cr(CO)_4PH_3$. The optimal geometries of the fragment at each fixed C–M–C angle are shown. The end points are the cis- and trans-loss geometries.

are only weak π acceptors, the overall cis labilization should more closely resemble the ground-state strengthening alone. Our calculations support the conclusions of Atwood et al. that, for the weak π-acceptor ligands PR_3 and $P(OR)_3$, most of the labilizing influence of these ligands is independent of relaxation.[10,33] However, our calculations also show that the relative importance of ground-state effects is less for good π-donor ligands such as Cl^-. In general, both ground-state and relaxation effects are important in cis labilization; the nature of L determines which will be most important.

Cis–Trans Rearrangement. Figure 4 shows the energies and structures for the conversion between the optimized cis- and trans-loss fragments of $Cr(CO)_4PH_3$. The calculated barrier for trans to cis conversion is about 10 kcal/mol without zero-point corrections. Typical C–M–C bending vibrations in carbonyls, however, are in the range of 80–100 cm^{-1};[34] therefore, a zero-point correction would be less than 2 kcal/mol. The barrier's maximum occurs where the carbonyl must move past a filled orbital. As the complex climbs the barrier, the metal–carbon bonds in the symmetry plane lengthen, and the M–C–O bond bends in order to reduce the repulsion between the CO 5σ orbital (C lone pair) and the occupied metal orbital. Our results for the cis-loss to trans-loss conversion of $Mn(CO)_4Cl$ are similar.

Clearly the calculated energy required to dissociate a cis carbonyl and continue over the cis–trans rearrangement barrier is much greater than the energy required for simple trans CO loss. Therefore, opening a coordination site by loss and rearrangement should be slow compared to direct loss of either cis or trans carbonyls. Recent studies by Dobson et al.[35] on $L'LW(CO)_4$ (L′ = piperidine; L = phosphine, phosphite) also indicate a large cis–trans rearrangement barrier. Photolysis produces both the cis- and trans-loss isomers, and separate decay rates are observed for their recombination with CO. This rules out rapid, direct interconversion between the isomers.

Darensbourg et al.,[16,17] however, have shown that substitution of ^{13}CO for PPh_3 in *trans*-$Cr(CO)_4(PPh_3)_2$ initially gives only *cis*-$(^{13}CO)Cr(CO)_4(PPh_3)$. They conclude that a trans-vacancy to cis-vacancy rearrangement occurs with a rate constant of at least 3×10^4, because the rate of rearrangement must be faster than the rate of recombination with CO. Thus, calculations on chromium complexes with small ligands (PH_3) and experiments on tungsten complexes would indicate no rearrangement, but rearrangement is observed for chromium complexes with bulky ligands. The different results could be due to steric factors. A bulky phosphine ligand will destabilize the trans-loss intermediate and therefore lower the activation energy for trans-vacancy to cis-vacancy conversion. Our calculations use the model ligand PH_3; therefore, they underestimate steric effects. Complexes of tungsten will also show less steric effect than complexes of the much smaller chromium.

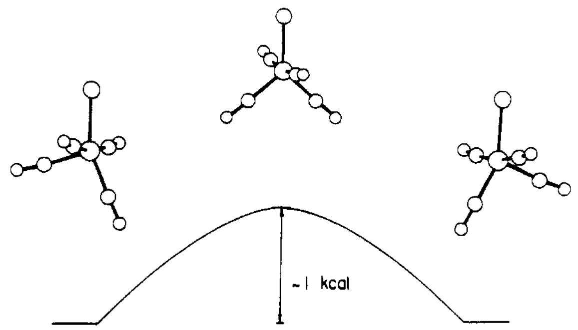

Figure 5. Potential energy curve for a cis-vacancy to cis-vacancy rearrangement. The optimal cis-loss geometry is shown on either end; at the barrier maximum the $C_{cis,trans}$–M–$C_{trans,cis}$ angle was constrained.

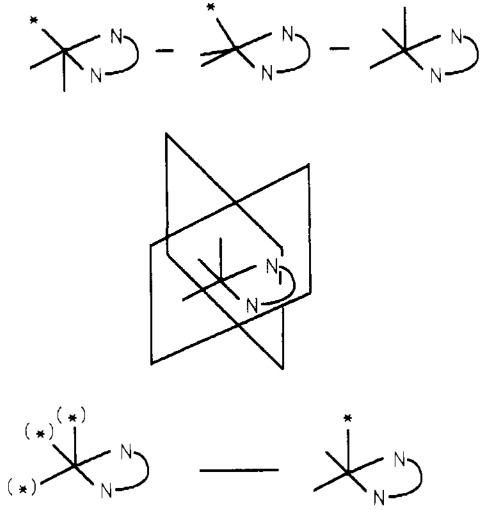

Figure 6. Scrambling process observed by Dobson (shown at the top). This scrambling can be accomplished by consecutive "cis to cis" rearrangements in the two planes that contain a heteroatom, the metal, and the vacant coordination site.

Although a large barrier is calculated for direct conversion from the cis to the trans geometry, Lichtenberger and Brown proposed an indirect mechanism for trans incorporation in multiple substitution processes.[9] Their mechanism is based on the movement of a cis carbonyl into the trans position upon loss of the carbonyl directly across from it, as shown in Figure 5. This mechanism involves a cis-to-cis conversion in which the trans coordination site is never avaiable for an incoming ligand. This conversion is also very similar to that postulated by Hoffman and Caulton from their experimental study of pentacoordinate d^6 complexes in solution.[36] The barrier to this transition is very small, less than 1 kcal/mol, and it should be noted that the transition state for this interconversion is nearly identical with the lowest energy geometry in the study of Lichtenberger and Brown; they could not have found the minimum predicted here because they forced C_{2v} symmetry on their transition state.

One might imagine creating a trans vacancy by beginning at the top of this barrier and continuing along a C_{2v} symmetry reaction coordinate until one reached the trans-loss fragment. This reaction coordinate is formally forbidden since it involves an orbital crossing. Our calculation indicates that this process would be much higher in energy than the conversion shown in Figure 4.

The indirect mechanism for trans incorporation also agrees with the experiments of Dobson and co-workers.[12-15] Their experiments indicated a fluxional process in which the sites trans to heteroatoms were never open for substitution. The five-coordinate intermediate

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[33] Wovkulich, M. J.; Atwood, J. D. *Organometallics* **1982**, *1*, 1316.

[34] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978.

[35] Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M.; Turner, J. J.; Stephen, F.; Khalil, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218.

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in their study is shown in Figure 6.[13] A "cis-to-cis" rearrangement like that shown in Figure 5 can occur in either of the two planes that contain a heteroatom, the metal, and the vacant site, as is also shown in Figure 6. These cis-to-cis rearrangements would scramble the labeled carbonyl but would never allow direct trans incorporation. Our calculations indicate that this process has a very small energy barrier.

Conclusion

From the calculations presented here, one may conclude that both ground-state and relaxation effects are important in cis labilization. Relaxation effects are more important for those heteroligands that are not merely weaker π acceptors but are π donors. In the fragments $M(CO)_4L$, direct trans-vacancy to cis-vacancy conversion is a higher energy process than simple trans loss for thermal dissociation of CO from $M(CO)_5L$. If a ligand that is more labile than CO is dissociated from the trans position, then a trans-vacancy to cis-vacancy conversion is possible but has a calculated barrier for small L (in the gas phase) of about 10 kcal/mol. Indirect trans incorporation via a mechanism similar to that of Lichtenberger and Brown[9] is predicted to be a very low energy process and should be observed in multiple substitution processes.

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Registry No. $Mn(CO)_5Cl$, 14100-30-2; $Mn(CO)_5H$, 16972-33-1; $Cr(CO)_5PH_3$, 18116-53-5; $Cr(CO)_5NH_3$, 15228-27-0.

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[μ-1,1′-Bis(diphenylphosphino)ferrocene]bis(chlorogold): Synthesis, Iron-57 and Gold-197 Mössbauer Spectroscopy, X-ray Crystal Structure, and Antitumor Activity

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The title compound **2**, $Fdpp(AuCl)_2$, synthesized via the addition of Fdpp (**1**) to an aqueous solution of $[(HOCH_2CH_2)_2S]AuCl$ generated in situ by the thiodiglycol reduction of $HAuCl_4$ showed a $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR chemical shift at δ 27.39, which was downfield from that of **1** at δ −17.34 relative to $(CH_3O)_3PO$. The ^{57}Fe Mössbauer spectrum of **2** is a doublet with parameters (IS = 0.50 mm/s relative to Fe, QS = 2.33 mm/s) similar to those of ferrocene. The ^{197}Au Mössbauer spectrum of **2** is an asymmetric doublet (QS = 6.93 mm/s) with an IS of 3.81 mm/s relative to Au metal. $Fdpp(AuCl)_2$ crystallized in space group $P\bar{1}$ with lattice constants a = 16.192 (4) Å, b = 16.921 (4) Å, and c = 10.878 (5) Å with Z = 3. Two crystallographically independent molecules, A and B, were observed in the structure of **2** with a chloroform solvate molecule per 1.5 formula units of the gold complex. For A, the P atoms are 180° opposed and the rings exactly staggered, while in B the P atoms are 150° apart and the rings are partially staggered. The P–Au–Cl linkage is nearly linear, and the bond distances fall within normal ranges. Evaluation in an ip P388 leukemia mouse model showed **1** and **2** to have only marginal activity with an increased life span (ILS) relative to untreated controls of 30% at a maximally tolerated dose (MTD) of 231 μmol/kg and 40% ILS at 4 μmol/kg, respectively.

Introduction

The antitumor activity of bis(diphenylphosphines) and their bis(gold(I)) complexes has been of recent interest.[1,2] The spacer connecting the phosphine moieties has been varied, and a number of ligands and their gold complexes have been prepared and evaluated in a P388 leukemia mouse model.[1] Although some of the ligands have significant activity in this model, the corresponding gold complexes appear to have increased potency on a molar basis. Maximal activity was found when the phosphines were bridged by cis-ethylene or ethane, e.g. 1,2-bis(diphenylphosphino)ethane (dppe). Recently, several ferrocenium salts have been reported to be active against Ehrlich ascites tumor, producing cure rates of 70–100% over a broad dose range.[3,4] In addition, these ferrocenium compounds inhibited several solid tumors including B_{16} melanoma, colon 38 carcinoma, and Lewis lung carcinoma.[5] Together these findings suggested that the incorporation of the essential structural features of the bis(phosphinogold) complexes with a ferrocene might provide compounds with antitumor activity.

A ligand incorporating the necessary structural elements suitable as a gold(I) complexing agent is the readily available phosphinoferrocene: 1,1′-bis(diphenylphosphino)ferrocene (Fdpp, **1**).[6] This bidentate ligand is capable of both bridging and chelation and can form complexes with ratios of metal atom to ligand of 1 or 2, behaving in a manner similar to that of dppe.[7] Complexes of **1** with a variety of metals including Co,[7] Ni,[7] Hg,[8] Mo,[9] W,[9] Pd,[10] Pt,[11] and Rh[12] have been described. Solutions of Fdpp (**1**)

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