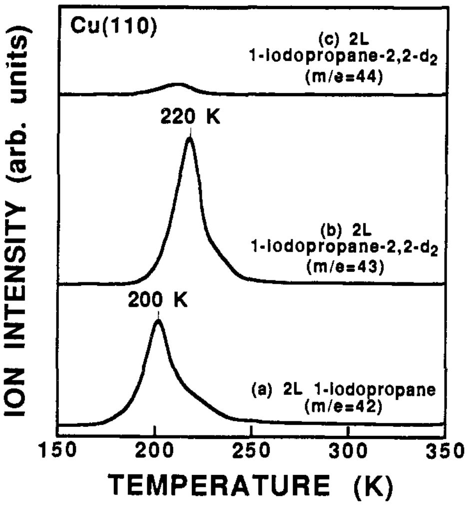

Figure 3. Thermal evolution from Cu(110) of (a) propylene ($m/e = 42$) after adsorption of 2.0 L of 1-iodopropane at 110 K and (b,c) propylene-*d* ($m/e = 43$) and propylene-d_2 ($m/e = 44$), respectively, following the adsorption of 2.0 L of 1-iodopropane-*2,2*-d_2 at 110 K. The high-temperature shoulders are due to surface defects.[5b] The heating rate is 2.5 K/s.

and iodine atoms. In addition, studies in which the iodine coverage is varied show that, at least for the low coverages discussed in this paper, the alkyl reaction products and kinetics are not significantly affected by the coadsorbed iodine. These results are discussed in detail elsewhere.[5,10] We report here on the mechanisms and rates of the C–H bond breaking reactions that occur subsequent to C–I bond scission. This chemistry is illustrated with results from studies with iodomethane and 1-iodopropane.

Methyl groups formed by CH_3I dissociation on Cu(110) are stable until temperatures above 400 K as evidenced by the lack of H_2 desorption at 330–360 K, the temperature range for hydrogen recombination on iodine-covered Cu(110). Above 400 K, methyl groups react to form methane and ethylene, and as shown in Figures 1a and 2a, both products evolve at 425 K. These results are consistent with data previously reported without mechanistic interpretation for the photolysis and thermal annealing of CH_3Br monolayers on copper films.[9] Coverage-dependence studies as well as analyses of the peak shapes indicate first-order reaction kinetics, suggesting that unimolecular C–H bond breaking in the methyl group is rate limiting. Consistent with this inference, studies with CD_3I yield a deuterium isotope effect of 3.1 ± 0.8 at 400 K.[5a] In addition, calibrated mass spectrometry shows that the methane/ethylene ratio is 2, while AES studies indicate that all detectable carbon is removed from the surface by these two products. Taken together, these observations suggest that methane and ethylene are formed by the following coupled reactions:

$$\mathrm{CH_3(a)} \xrightarrow[\text{step}]{\text{rate-determining}} \mathrm{CH_2(a) + H(a)} \qquad \alpha\text{-elimination}$$

$$\mathrm{CH_3(a) + H(a)} \longrightarrow \mathrm{CH_4(g)} \qquad \text{reductive elimination}$$

$$\mathrm{CH_2(a) + CH_2(a)} \longrightarrow \mathrm{C_2H_4(g)} \qquad \text{methylene coupling}$$

We have confirmed that α-elimination is rate determining by studying the subsequent reductive elimination and methylene coupling reactions separately. In particular, as shown in parts b and c of Figure 1, when Cu(110) is precovered with a partial monolayer of deuterium atoms, reductive elimination to form methane-*d* occurs at temperatures as low as 350 K. Similarly, as shown in Figure 2b, the coupling of methylene groups, formed by thermal dissociation of CH_2I_2, produces ethylene with a peak temperature, T_p, of 300 K.

While α-elimination from methyl groups occurs above 400 K, β C–H bond scission in longer alkyls occurs below 250 K. For example, as shown in parts a and b of Figure 3, 1-iodopropane decomposes to produce propylene ($T_p = 200$ K), while 1-iodopropane-*2,2*-d_2 decomposes to produce propylene-*d* ($T_p = 220$ K). The other product at low coverage is correspondingly H_2 or D_2 ($T_p = 335$–360 K). The lack of significant propylene-d_2 ($m/e = 44$) formation from 1-iodopropane-*2,2*-d_2, as illustrated in Figure 3c, confirms the β-elimination pathway, while the deuterium isotope effect evident in parts a and b of Figure 3 implicates C–H bond breaking as the rate-determining step. Consistent with this conclusion, it is found that propylene adsorbed on Cu(110) thermally desorbs below 200 K.[5b]

Applying several methods for extracting kinetic parameters from thermal desorption spectra,[11] we find that the ratio of the rate of β-elimination from propyl groups to the rate of α-elimination from methyl groups at 300 K on iodine-covered Cu(110) is $\sim 10^{10}$. Even if one assumes preexponential factors as low as 10^7 s^{-1}, this ratio is still 10^6. This observation is particularly interesting in light of recent results for the decomposition of alkyl halides on Pt(111) where α-elimination from methyl groups[12] and β-hydride elimination from ethyl groups[4c–f] occur at quite similar temperatures (260 K vs 200 K). Furthermore, since β-hydride elimination on both Pt(111) and Cu(110) occurs at about 200 K, the major difference between platinum and copper is the differing rate of α-elimination on these metals. Studies are in progress to address this issue.

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(10) Jenks, C. J.; Paul, A.; Bent, B. E., manuscript in preparation.

(11) (a) Redhead, P. A. *Vacuum* **1962**, *12*, 203–211. (b) Chan, C.-M.; Aris, R.; Weinberg, W. H. *Appl. Surf. Sci.* **1978**, *1*, 360–376. (c) Habenschaden, E.; Kuppers, J. *Surf. Sci.* **1984**, *138*, L147–L150.

(12) While α-elimination has not been explicitly demonstrated, methyl group decomposition at 260 K on Pt(111) presumably occurs by this pathway: Liu, Z.-M.; Costello, S. A.; Roop, B.; Coon, S. R.; Akhter, S.; White, J. M. *J. Phys. Chem.* **1989**, *93*, 7681–7688. See also ref 8.

Unambiguous Demonstration of Vacant-Site Inversion in a *cis*-$P_2M(CO)_3$ Intermediate

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Ligand substitution reactions of octahedral metal carbonyl complexes have been intensely studied over the past 25 years. A wealth of evidence suggests the formation of reactive five-coordinate intermediates in these reactions.[1] Matrix isolation studies and elegant kinetic and flash photolysis studies by Dobson indicate rapid solvolysis of these species even in poorly coordinating solvents such as toluene.[2] Collapse of the nonsolvated five-coordinate intermediates to fluxional TBP species is often proposed to account for isotopic scrambling of ^{13}CO observed in these substitution reactions.[1] It has also been noted that many ligand substitution

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(1) For a review, see: Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

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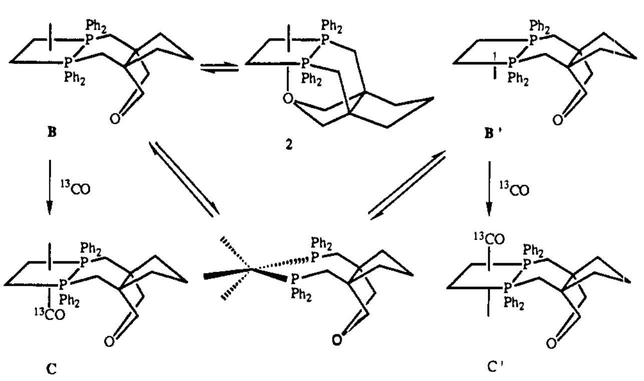
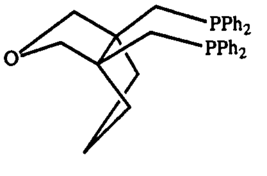
Scheme I

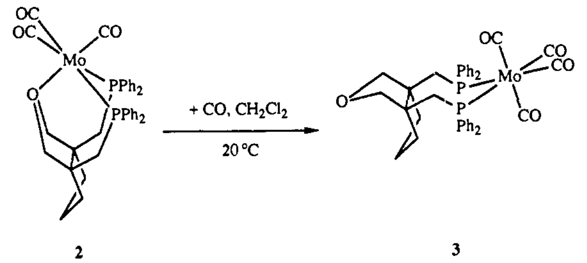


reactions of octahedral metal carbonyl complexes are stereospecific with a strong preference for the formation of *fac* products from *fac* reactants.[3] Despite this observed stereospecificity, it has not been demonstrated whether the incoming ligand coordinates to the axial site vacated by the departing ligand and/or to the one trans to this site, since these axial sites have been equivalent in all previously studied cases. For example, studies by Dobson[2a] and Angelici[4] have shown that reactions of *fac*-(py)(diphos)-Mo(CO)$_3$ with phosphites and the reaction of [(Ph$_2$PCH$_2$CH$_2$)$_2$NEt]Mo(CO)$_3$ with ^{13}CO, respectively, yield only *fac* products upon displacement of the coordinated py and nitrogen in the corresponding starting materials. Even though the site trans to the departing nitrogen ligand presumably also became available in both cases via fluxionality of the five-coordinate intermediate, the mirror symmetry of the chelating ligand with respect to the P$_2$M plane precluded confirmation of the hypothesis that both axial sites are involved. We report here that, by utilizing ligand **1**, diastereomeric *fac* products are obtained in which one diastereomer contains the attacking ligand in the site vacated by the departing ligand, whereas in the other the new ligand occupies the site trans to the departing ligand.



1

We recently synthesized the new ligand **1**, which reacts with (cycloheptatriene)Mo(CO)$_3$ to yield *fac*-(**1**-*P*,*P'*,*O*)Mo(CO)$_3$ (**2**) in which all three donor atoms are coordinated.[5] Solutions of complex **2** in CH$_2$Cl$_2$ react with CO to yield *cis*-(**1**-*P*,*P'*)Mo(CO)$_4$ (**3**) via displacement of the coordinated ether (eq 1). A ^{13}C NMR spectrum[6] of **3** clearly shows two nonequivalent axial[7] carbonyls due to the symmetry of **1**. The ratio of intensities of the equatorial to axial carbonyl resonances is approximately 2:1:1. In the presence of ^{13}CO, **2** forms two diastereomers of *fac*-(**1**-*P*,*P'*)(O^{13}C)Mo(CO)$_3$ with no ^{13}C NMR evidence for the formation of a *mer* complex in which ^{13}CO has been incorporated into an equatorial site.[8] The initial *fac* diastereomer ratio of 4:1 remained stable over a period of 17 days, indicating that no isomerization process was occurring.



(1)

The rationale we offer to account for the formation of two diastereomeric *fac* products is illustrated in Scheme I. Dissociation of the ether donor of **1** from **2** yields the five-coordinate intermediate B of approximately square pyramidal geometry.[9] Unsaturated five-coordinate intermediates, such as [Cr(CO)$_5$], have been shown to be solvated within picoseconds after their formation.[2e,f] On the basis of calculations by Davy and Hall,[10] this process is too rapid to allow isomerization of B to provide an equatorial vacancy. Thus, no *mer* products should be formed in accord with the observed stereospecificity in this type of substitution reaction. Lichtenberger and Brown[11] have proposed a mechanism whereby, in a five-coordinate intermediate, the vacant site may be interchanged between two sites cis to a non-carbonyl ligand, but trans to each other, without the intermediate formation of a vacant site trans to the non-carbonyl ligand. In Scheme I, inversion of the vacant site to the position trans to itself would involve the migration of the axial carbonyl, trans to the vacant site, to an equatorial site with the simultaneous migration of the equatorial carbonyl to the initially vacant axial site. Calculations by Davy and Hall[10] show that such a rearrangement has an activation barrier of less than 1 kcal/mol for Cr(CO)$_4$PH$_3$ and can occur within the time frame of solvation. In our case, this rearrangement would isomerize the two five-coordinate intermediates B and B'. These two intermediates are diastereomeric and should not be degenerate in energy. Thus, the rate of interconversion of B and B' relative to their rates of reaction with ^{13}CO may account for the 4:1 ratio of diastereomeric products observed.

Our observation of two diastereomers of *fac*-(**1**-*P*,*P'*)(O^{13}C)-Mo(CO)$_3$ constitutes the first direct evidence that, in substitution reactions of *fac* complexes, the incoming ligand may occupy the site initially trans to the departing ligand as well as the same site vacated by the departing ligand. The stereochemical course of the reactions of **2** with other ligands is presently under investigation.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank R. J. Angelici for valuable discussions.

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[6] **3**: ^{13}C NMR (CD$_2$Cl$_2$, 75.4 MHz) δ 215.9 (m, CO$_{eq}$), 212.2 (t, $^2J_{PC}$ = 9.5 Hz, CO$_{ax}$), 206.0 (t, $^2J_{PC}$ = 7.5 Hz, CO$_{ax}$). Approximate ratio of 2:1:1.

[7] In this context axial refers to a site cis to both phosphorus donors and equatorial refers to a site trans to a phosphorus donor.

[8] A deep yellow solution of **2**[5] (21 mg) in ~0.5 mL of CD$_2$Cl$_2$ was prepared in a 5-mm NMR tube under argon. ^{13}CO (99%, Cambridge Isotope Laboratories) was bubbled through the solution for 5 min, resulting in a colorless solution. A small quantity of decomposition product precipitated initially, but ^{1}H and ^{13}C NMR spectra of the supernatant liquid showed only the presence of two diastereomers of *fac*-(**1**-*P*,*P'*)Mo(CO)$_3$(^{13}CO) in an approximately 4:1 ratio. As an internal standard, the intensity of the CO$_{eq}$ resonance remained approximately the same as that for the *ipso*-Ph resonances, just as is observed in the natural-abundance spectrum of **3**. The NMR tube was then sealed and the reaction monitored by ^{13}C NMR spectroscopy over the course of 17 days.

[9] We propose square-pyramidal intermediates on the basis of the conclusions of Dobson[2a–c] and the results of molecular orbital calculations (Elian, M.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 1058), which suggest that the ground state for a d^6 M(CO)$_5$ complex should be a square pyramid. Alternatively, preferential attack at two positions adjacent to the equatorial phosphorus in a distorted TBP intermediate can also account for our results. The energy difference between these two geometries is expected to be small.

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