Synthesis and Reactions of *cis*- and *trans*-$W(CO)_4(^{13}CO)(L)$ Compounds

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Abstract: Reaction of $Bu_4N[trans\text{-}W(CO)_4(CS)(I)]$ with silver(I) salts under a ^{13}CO atmosphere gives *trans*-$W(CO)_4(^{13}CO)(CS)$ in high yield. Reactions of $[cis\text{-}W(CO)_4(X)(L)]^-$ complexes ($X^- = Cl^-, I^-$; L = phosphine or isocyanide) with Ag^+ and ^{13}CO yield *cis*-$W(CO)_4(^{13}CO)(L)$ compounds. Similarly, preferentially cis ^{13}CO-enriched $[W(CO)_4(^{13}CO)(Cl)]^-$ reacts with Ag^+ and L to yield $W(CO)_4(^{13}CO)(L)$ compounds which largely retain the preferential cis label. These reactions were performed in coordinating solvents, which may cause retention of geometry by stabilizing the pentacoordinate intermediates before rearrangement can occur. A number of reactions of *trans*-$W(CO)_4(^{13}CO)(CS)$ were investigated. Thus, *trans*-$W(CO)_4(^{13}CO)(C{\equiv}NR)$ and $[trans\text{-}W(CO)_4(^{13}CO)(NCS)]^-$ compounds were prepared by reaction of the complex with H_2NR and N_3^-, respectively. The intramolecular isomerization of *trans*-$W(CO)_4(^{13}CO)(CS)$ to a mixture of the cis and trans isomers was studied in decalin solution and the gas phase. The rate of CO dissociation has been studied by CO exchange and $P(C_6H_5)_3$ substitution; it was found to be about 20 times slower than the rate of isomerization. The activation parameters for isomerization and CO dissociation are very similar, suggesting that the two processes are closely related. The *trans*-$(^{13}CO)W(CO)_4(CS)$ compound reacts with Bu_4NI to give $Bu_4N[trans\text{-}IW(CO)_4(CS)]$, with predominant or complete replacement of the trans, labeled carbonyl ligand. The mechanistic implications of this specificity are also discussed.

Several recent reports in the literature describe reactions in which labeled carbon monoxide may be incorporated, with varying degrees of specificity, into one bonding site of a metal carbonyl complex.[1-9] Most of these preferentially labeled products result from differences in rates of exchange of chemically nonequivalent carbonyl ligands in a complex with ^{13}CO or $C^{18}O$.[1-6] Other labeling reactions involve replacement of a weakly bound ligand with labeled CO,[7,8] and the decarbonylation of $Mn(CO)_5(^{13}C(O)CH_3)$.[9]

We now report some observations on highly stereospecific reactions in which the halide ion in certain tungsten carbonyl halide complexes is abstracted by Ag^+ and replaced by ^{13}CO. This method of introducing a labeled CO ligand into a carbonyl complex has two advantages over the CO exchange reaction: its high stereochemical specificity and the incorporation of only one labeled CO. In order to gain information about the stereochemical specificity of this process, related reactions were performed with ^{13}CO-labeled complexes to determine whether or not the pentacoordinate intermediates in these reactions are fluxional. Studies of isomerization and ligand substitution in one of these labeled complexes, *trans*-$W(CO)_4(^{13}CO)(CS)$, are also reported.

Results and Discussion

Reactions Yielding Preferentially Cis or Trans ^{13}CO Labeled Complexes. The thiocarbonyl iodide complex, $Bu_4N[trans\text{-}W(CO)_4(CS)(I)]$,[10] reacts with $AgBF_4$ or $AgCF_3SO_3$ in acetone or tetrahydrofuran (THF) solution under ^{13}CO to give greater than 80% yields of the isolated *trans*-$W(CO)_4(^{13}CO)(CS)$ product (eq 1).

$$[trans\text{-}W(CO)_4(CS)(I)]^- \xrightarrow[-AgI]{Ag^+,\ ^{13}CO} trans\text{-}W(CO)_4(^{13}CO)(CS) \qquad (1)$$

The trans position appears to be labeled with very high specificity, based on the ir spectrum of the product (Table I). The good agreement between the observed and calculated infrared carbonyl frequencies for the trans isomer and the cis product, obtained by isomerization (see below), supports the band assignments.[11] Use of a variety of other ligands, L, in place of ^{13}CO in the above reaction has been found to afford exclusively *trans*-$W(CO)_4(L)(CS)$ complexes.[12]

To determine whether other $[W(CO)_4(L)(X)]^-$ complexes would also undergo specific ^{13}CO introduction after halide ion abstraction, similar experiments were performed with $[cis\text{-}W(CO)_4(CNC_6H_{11})(Cl)]^-$ and $[cis\text{-}W(CO)_4\{P(4\text{-}ClC_6H_4)_3\}(I)]^-$. In both cases, reaction with Ag^+ in a coordinating solvent under ^{13}CO (eq 2) gave $W(CO)_4(^{13}CO)(L)$ products (L = CNC_6H_{11}, $P(4\text{-}ClC_6H_4)_3$) (Table II) which were found by ^{13}C NMR (Table III) to be almost exclusively (>95%) the cis-labeled isomers (Figure 1).

$$[cis\text{-}W(CO)_4(X)(L)]^- \xrightarrow[-AgX]{Ag^+,\ ^{13}CO} cis\text{-}W(CO)_4(^{13}CO)(L) \qquad (2)$$

Thus, reaction of $[cis\text{-}W(CO)_4(I)\{P(4\text{-}ClC_6H_4)_3\}]^-$ and $[cis\text{-}W(CO)_4(Cl)(CNC_6H_{11})]^-$ with Ag^+ and ^{13}CO leads to the corresponding cis products, while $[trans\text{-}W(CO)_4(I)(CS)]^-$ gives the trans product.

Two mechanistic situations may be envisioned which could account for the observed retention of geometry during halide substitution by ^{13}CO. First, the removal of a halide ligand from a complex could yield a square pyramidal intermediate which reacts with ^{13}CO or solvent before it can rearrange to another isomer (i.e., kinetic control). Secondly, a stereochemically fluxional pentacoordinate $W(CO)_4L$ intermediate could be formed which is free to rearrange, but prefers a particular square pyramidal geometry with the L ligand either cis or trans to the open coordination site (i.e., thermodynamic control). The preference for a $W(CO)_4(CS)$ geometry in which the strongly π-bonding CS ligand is trans to the vacant site might be supported by matrix isolation photolysis studies of $W(CO)_5(CS)$, which show that $W(CO)_4(CS)$ forms predominantly this C_{4v} structure.[13] In the other $W(CO)_4L$ intermediates (where L = PR_3 or CNC_6H_{11}) the best π-bonding ligand is CO which may prefer the position trans to the vacant site, leaving the phosphine or isocyanide group cis to that site. Thus, either a fluxional or a nonfluxional intermediate could account for the geometries of the observed products.

An experiment designed to ascertain whether or not the $W(CO)_4(^{13}CO)$ moiety is fluxional under similar conditions was carried out by treating $[cis\text{-}W(CO)_4(^{13}CO)Cl]^-$ with $P(4\text{-}ClC_6H_4)_3$ and Ag^+. If the $W(CO)_4(^{13}CO)$ intermediate is rigid, only *cis*-$W(CO)_4(^{13}CO)[P(4\text{-}ClC_6H_4)_3]$ would result. If it is fluxional, a statistical mixture of the cis and trans isomers would be formed. To perform the experiment, preferentially cis ^{13}CO-labeled $[W(CO)_5Cl]^-$ was prepared by stirring

Table I. Infrared ν(CO) Data for $W(^{12}CO)_5(CS)$ and $W(^{12}CO)_4(^{13}CO)(CS)$ Isomers in Decalin Solvent

Compound[d]	Band assignment	Frequencies (cm^{-1}) Obsd[a]	Calcd[b]
$W(^{12}CO)_5(CS)$	A_1	2096 (4200)	2096.0
	B_1	*c*	2014.5
	A_1	2007 (6500)	2006.9
	E	1989 (35 000)	1988.6
trans-$W(CO)_4$-$(^{13}CO)(CS)$	A_1	2091 (1800)	2091.0
	B_1	*c*	2014.5
	E	1989 (35 000)	1988.6
	A_1	1967 (6500)	1967.0
cis-$W(CO)_4$-$(^{13}CO)(CS)$	A′	2089 (3000)	2089.0
	A′	2010 (~1000)	2010.0
	A′	2005 (6000)	2005.2
	A″	1988 (10 000)	1988.6
	A′	1957 (10 000)	1956.9

[a] Approximate molar extinction coefficients (M^{-1} cm^{-1}) given in parentheses. [b] An initial set of force constants obtained from $W(^{12}CO)_5(CS)$ frequencies using the Cotton–Kraihanzel approximation was refined by a least-squares method (R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975)). Frequencies given were calculated from force constants $k_{ax} = 16.495$, $k_{eq} = 16.457$, $k_c = 0.2687$, $k'_c = 0.2804$, $k_t = 0.4900$ mdyn Å^{-1}. [c] Ir inactive. [d] The ν(CS) absorption occurred at 1258 cm^{-1} in all three compounds in CS_2 solvent.

Table II. Infrared ν(CO) Data[a]

Compound	ν(CO)
$W(CO)_5(CNC_6H_{11})$[b]	2065 w, 1953 vs
trans-$W(CO)_4(^{13}CO)(CNC_6H_{11})$	2058 w, 1953 vs, 1912 m
cis-$W(CO)_4(^{13}CO)(CNC_6H_{11})$	2056 w, 1980 w, 1953 s, 1924 m
$W(CO)_5(CNCH_3)$[c]	2069 w, 1956 vs
trans-$W(CO)_4(^{13}CO)(CNCH_3)$	2064 w, 1956 vs, 1916 m
$W(CO)_5[P(4\text{-}ClC_6H_4)_3]$[d]	2073 w, 1953 m, 1945 s
cis-$W(CO)_4(^{13}CO)[P(4\text{-}ClC_6H_4)_3]$	2066 w, 1975 vw, 1953 m, 1945 s, 1914 m, br
$[(Ph_3P)_2N][W(CO)_5Cl]$[e,f]	2063 w, 1914 vs, 1838 m
$[(Ph_3P)_2N]$[*cis*-$W(CO)_4(^{13}CO)Cl$][f]	2054 w, 1967 w, 1914 s, 1892 s, 1838 m
$[(Ph_3P)_2N][W(CO)_5(NCS)]$[f,g]	2066 w, 1921 vs, 1861 m
$[(Ph_3P)_2N]$[*trans*-$W(CO)_4(^{13}CO)$-(NCS)][f]	2061 w, 1921 vs, 1822 m

[a] Recorded in *n*-hexane unless specified otherwise. [b] Reference 36. ν_{CN} 2154 cm^{-1}. [c] Reference 23. ν_{CN} 2177 cm^{-1}. [d] Prepared from $Et_4N[W(CO)_5I]$, $AgCF_3SO_3$, and $P(4\text{-}ClC_6H_4)_3$ in acetone. Anal. Calcd for $W(CO)_5[P(4\text{-}ClC_6H_4)_3]$: C, 40.03; H, 1.74. Found: C, 40.53; H, 1.76. [e] Reference 35. [f] Recorded in CH_2Cl_2 solvent. [g] A. Wojcicki and M. Farona, *J. Inorg. Nucl. Chem.*, **26**, 2289 (1964). ν_{CN} 2102 cm^{-1}.

Table III. ^{13}C NMR Data

Compound	δ_{CO}(cis)[a]	δ_{CO}(trans)[a]
$W(CO)_5[P(4\text{-}ClC_6H_4)_3]$	−196.4[b,c]	−197.9[d]
$W(CO)_5(CNC_6H_{11})$	−194.0[b]	−196.2[e]
$[(Ph_3P)_2N][ClW(CO)_5]$	−198.7[f]	−201.6

[a] Parts per million downfield from Me_4Si in $DCCl_3$. [b] $J_{^{183}W-^{13}C} = 128$ Hz. [c] $J_{PWC} = 6$ Hz. [d] $J_{PWC} = 22$ Hz. [e] $J_{^{183}W-^{13}C} = 137$ Hz. [f] $J_{^{183}W-^{13}C} = 129$ Hz.

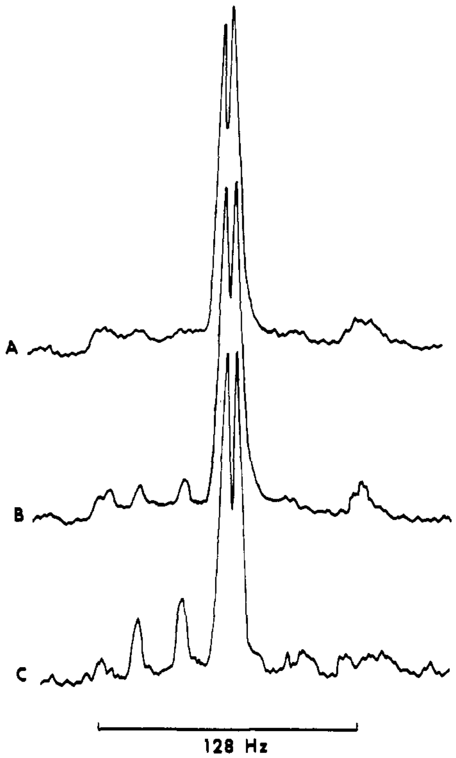


Figure 1. Carbonyl carbon resonances in the ^{13}C NMR spectrum of $W(CO)_5[P(4\text{-}ClC_6H_4)_3]$: (A) ^{13}CO-enriched sample prepared from [*cis*-$W(CO)_4I\{P(4\text{-}ClC_6H_4)_3\}]^-$, $AgCF_3SO_3$, and ^{13}CO; (B) ^{13}CO-enriched sample prepared from preferentially cis ^{13}CO-labeled $[W(CO)_5Cl]^-$, $AgCF_3SO_3$, and $P(4\text{-}ClC_6H_4)_3$; (C) natural abundance ^{13}C sample. The strong doublet is the cis carbonyl resonance; the less intense doublet to the left is the trans resonance. Positions and coupling constants are given in Table III.

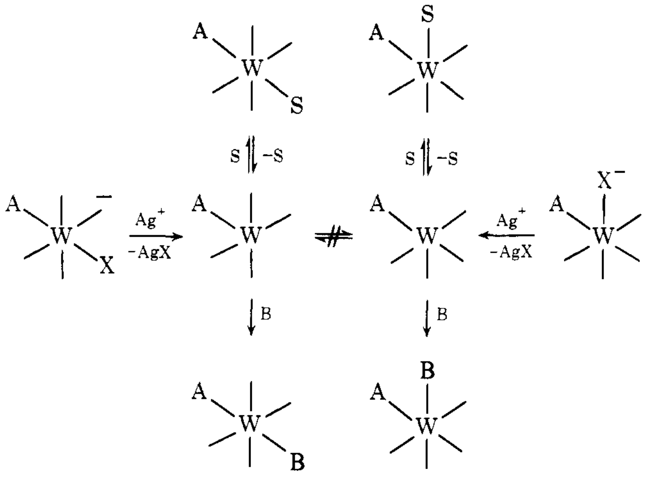
$[(Ph_3P)_2N][W(CO)_5Cl]$ under about 1.5 atm of 90% ^{13}CO in CH_2Cl_2 for 2 h. The product was estimated to contain approximately 40% of the monolabeled $[W(CO)_4(^{13}CO)Cl]^-$ product, based on the infrared spectrum. The isotopically labeled product was found by ^{13}C NMR spectroscopy to be a mixture of cis and trans ^{13}CO-labeled isomers, with about 92% of the label in the cis position, as compared to the 80% expected on a statistical basis. Recent studies of $Mn(CO)_5Br$ and $Re(CO)_5Br$ have shown that the equatorial carbonyls in these complexes also exchange more rapidly than the axial CO.[14]

The $[W(CO)_4(^{13}CO)Cl]^-$ mixture was dissolved in acetone at 25° and the chloride ion was abstracted with $AgCF_3SO_3$. Addition of a ligand and stirring for 2 h gave ^{13}CO-enriched $W(CO)_5(L)$ complexes (eq 3).

$$[cis\text{-}W(CO)_4(^{13}CO)(Cl)]^- + Ag^+ + L \rightarrow cis\text{-}W(CO)_4(^{13}CO)(L) + AgCl \quad (3)$$

The $W(CO)_4(^{13}CO)[P(4\text{-}ClC_6H_4)_3]$ complex thus formed *retained preferential enrichment* in the cis positions as shown by ^{13}C NMR (Figure 1). Approximately 90% of the label is observed in the cis sites. A reaction in which $W(CO)_4(^{13}CO)(CNC_6H_{11})$ was prepared as in eq 3 also showed a similar retention of the cis label. These experiments indicate that the Ag^+ promoted substitution reactions proceed through intermediates in which rearrangement is difficult. A possible reaction sequence is shown in Scheme I (S = coordinating solvent).

Scheme I



A = CS; B = ^{13}CO, phosphine, isocyanide, etc.

A = phosphine or isocyanide
B = ^{13}CO

A = ^{13}CO; B = phosphine or isocyanide

The silver ion-assisted replacement of coordinated halide by a solvent molecule or ligand may be considered to be a dissociative process with no attack by the incoming ligand, and replacement of a weakly bound solvent molecule by another ligand probably also proceeds by a dissociative mechanism.[15] For example, alkenes, being weak nucleophiles, have been observed to replace acetone in $W(CO)_5$(acetone) exclusively by a dissociative (SN1) process.[16]

The five-coordinate intermediates formed in this scheme are presumed to be square pyramidal; this geometry is supported by matrix isolation studies which indicate that the group 6 $M(CO)_5$ complexes have C_{4v} symmetry.[17,18] These pentacoordinate intermediates (Scheme I) may react with a solvent molecule or ligand, or could possibly rearrange to the other square pyramidal isomer. That reaction 3 yields predominantly *cis*-$W(CO)_4(^{13}CO)(L)$ indicates that very little rearrangement actually occurs, and suggests that the rate of reaction of the $C_sW(CO)_4(^{13}CO)$ intermediate with L or S is rapid as compared with its rearrangement to the C_{4v} isomer. In the presence of a high concentration of coordinating solvent, the lifetime of the $W(CO)_4(^{13}CO)$ intermediate may thus be too short to allow the complex to rearrange.

The combination reaction of $Cr(CO)_5$ and acetone in cyclohexane solution has been previously studied, and a rate constant $k = 1.3 \times 10^8$ M^{-1} s^{-1} was reported.[19] Assuming that $W(CO)_5$ combines with L or S at a rate comparable to this, the rate constant for isomerization ($k_f + k_r$) of $W(CO)_4(^{13}CO)$ in acetone solution (13.6 M acetone) then must be smaller than approximately 1×10^7 s^{-1}. A rate constant larger than this would permit substantial isomerization. Clearly the $Cr(CO)_5$ and $W(CO)_5$ reaction rates could be quite different; the calculated rate of isomerization is only presented here as a possible approximate value.

A reaction related to these has been reported by Darensbourg, Darensbourg, and Dennenberg,[2] who found that SN1 substitution of the amine in preferentially labeled *cis*-$Mo(CO)_4(^{13}CO)$(piperidine) by $AsPh_3$ (1.5×10^{-2} M) gave $Mo(CO)_4(^{13}CO)(AsPh_3)$ with the labeled carbonyl statistically scrambled between the cis and trans positions. It was concluded that under the conditions of the experiment (38° in hexane), the equatorial and axial carbonyls equilibrate in the pentacoordinate $Mo(CO)_5$ intermediate. The differences between our results and those of Darensbourg et al.[2] might be due to the natures of the different complexes involved (different metal and leaving group). It seems probable, however, that the major difference is the solvent, which would rapidly react with the $M(CO)_5$ intermediate in the case of acetone. In hexane the intermediate might be expected to be longer-lived, allowing extensive scrambling to occur.

Retention of geometry by the $W(CO)_4(^{13}CO)$ intermediate in Scheme I apparently results from a relatively slow rate of rearrangement as compared to the rate of ligand addition. For the other intermediates, however, the possibility remains that the C_{4v} (for A = CS) and C_s (for A = phosphine or isocyanide) geometries are the most stable forms of these intermediates, which would dictate against rearrangement on thermodynamic grounds also. Recent studies have shown that ligand electronegativity and π-bonding capacity should be important in determining which isomers of substituted pentacoordinate compounds are the most stable.[20,21]

Except in the case of [*trans*-$W(CO)_4(CS)(I)]^-$, these reactions yield products in which the cis positions are enriched by ^{13}CO. In many studies, trans enrichment would be desirable. Therefore, we have converted *trans*-$W(CO)_4(^{13}CO)(CS)$ to other specifically trans-labeled derivatives. For example, the *trans*-isothiocyanato complex (Table II) has been prepared by reaction with azide ion,

$$trans\text{-}W(CO)_4(^{13}CO)(CS) + N_3^- \rightarrow trans\text{-}W(CO)_4(^{13}CO)(NCS)^- + N_2 \quad (4)$$

a reaction that is analogous to that of $(\eta\text{-}C_5H_5)Fe(CO)_2(CS)^+$ with azide ion.[22] Also, trans-isocyanide complexes (where R = CH_3 and C_6H_{11}) have been prepared,

$$trans\text{-}W(CO)_4(^{13}CO)(CS) + H_2NR \rightarrow trans\text{-}W(CO)_4(^{13}CO)(C{\equiv}NR) + H_2S \quad (5)$$

following the method used previously for the unlabeled thiocarbonyl complex.[23]

Isomerization of *trans*-$W(CO)_4(^{13}CO)(CS)$. The availability of this trans-labeled complex prompted an investigation of the conditions required to randomize the label. Heating a decalin solution of *trans*-$W(CO)_4(^{13}CO)(CS)$ at 100° for several hours under N_2 gives an equilibrium mixture of the cis and trans complexes ([cis]/[trans] = 4).

$$trans\text{-}W(CO)_4(^{13}CO)(CS) \rightleftarrows cis\text{-}W(CO)_4(^{13}CO)(CS) \quad (6)$$

Very little disproportionation to $W(^{12}CO)_5(CS)$ and $W(^{12}CO)_3(^{13}CO)_2(CS)$ is observed. Also, performing the isomerization in ^{12}CO-saturated decalin (under 1 atm of total pressure) yields only a small increase in the amount of $W(^{12}CO)_5(CS)$ under the conditions of the isomerization. (Experiments described later show that in decalin solution the rate of CO exchange is indeed much slower than the rate of isomerization.) These observations indicate that isomerization is not accompanied by CO dissociation and suggest that the process is intramolecular. A mechanism involving CS dissociation is very unlikely because no $W(CO)_6$ was ever observed in these solutions. Also, other studies indicate that the CS ligand is even more strongly bound to the metal than is CO.[23-26]

Definitive studies of intramolecular isomerizations in nonchelate octahedral complexes have been published for only three classes of compounds: H_2ML_4 (M = Fe, Ru; L = phosphine or phosphite),[27] $M(CO)_4(M'R_3)_2$ (M = Ru, Os; M' = Si, Sn; R = CH_3, Cl),[28] and $(CO)_4Cr(PR_3)[C(OCH_3)CH_3]$ (R = C_2H_5, C_6H_{11}).[29] Therefore, a kinetic investigation of the isomerization of *trans*-$W(CO)_4(^{13}CO)(CS)$ was undertaken to gain further information about this process.

Reactions carried out in decalin solution under N_2 at temperatures from 80.0 to 100.5° were followed by recording the rate of appearance of the 2005-cm^{-1} ir carbonyl band (Table I) of the cis isomer. As expected, the reaction was observed to

Table IV. Rate Constants for the Isomerization of *trans*-(^{13}CO)-W(CO)$_4$(CS) in Decalin Solvent[a]

Temp, °C	k_f, s^{-1}
80.0	2.07×10^{-5}
90.0	8.05×10^{-5}
100.5	2.60×10^{-4}

[a] $\Delta H^{\ddagger} = 31.5 \pm 1.9$ kcal/mol and $\Delta S^{\ddagger} = 9.1 \pm 5$ cal/(deg mol).

be first order in the complex. The data were analyzed using the McKay equation for isotopic exchange[30,31] (for ^{13}CO exchange between the cis and trans sites). Thus a plot of ln [A(cis$_e$) − A(cis)] vs. t gives a straight line of slope $-\frac{5}{4}k_f$, where A(cis) is the absorbance of the 2005-cm^{-1} band of the cis-labeled isomer at time t, A(cis$_e$) is the absorbance at equilibrium, and k_f is the rate constant of the forward reaction. Activation parameters $\Delta H^{\ddagger} = 31.5 \pm 1.9$ kcal/mol and $\Delta S^{\ddagger} = 9.1 \pm 5$ cal/(deg mol) were calculated from the rate constants in Table IV.

In order to determine the rate of CO dissociation from W(CO)$_5$(CS), the disappearance of *cis*-W(CO)$_4$(^{13}CO)(CS) in an equilibrium mixture of the cis and trans isomers under 1 atm of ^{12}CO at 100.5° in decalin was followed by ir spectroscopy (at 1957 cm^{-1}). Since CO exchange is observed to be slower than the cis–trans isomerization, an equilibrium mixture of the isomers was maintained throughout the reaction. Assuming that the rate of CO exchange is independent of the CO concentration, as is observed in the gas phase (see below), an approximate rate constant (1×10^{-5} s^{-1}) for the dissociation of one CO from W(CO)$_5$(CS) was determined by multiplying the k_{obsd} value by a statistical factor of five. Thus for W(CO)$_5$(CS), CO dissociation is more than 20 times slower than intramolecular isomerization under the same conditions.

This rate of CO dissociation was confirmed by the following studies. The substitution reaction of W(CO)$_5$(CS) with PPh$_3$ in decalin at 120.0–146.0° to give W(CO)$_4$(CS)(PPh$_3$) showed both phosphine-dependent and phosphine-independent terms in the rate equation.[12] Extrapolation to 100.5° of an Arrhenius plot of the phosphine-independent rate constants gives a CO dissociation rate constant of 1.25×10^{-5} s^{-1}, in good agreement with the approximate value (1×10^{-5} s^{-1}) determined by CO exchange. Comparison of the activation parameters of the W(CO)$_4$(^{13}CO)(CS) isomerization with those of the dissociative substitution process ($\Delta H^{\ddagger} = 31.5 \pm 1$ kcal/mol; $\Delta S^{\ddagger} = 3.1 \pm 3$ cal/(deg mol))[12] reveals a striking similarity in the values. Unless this agreement is simply fortuitous, it suggests that the isomerization and CO dissociation processes are closely related. Perhaps isomerization requires considerable lengthening of a W–CO bond in the activated complex in order for rearrangement to occur. From this activated complex relatively little additional free energy is necessary to bring about complete dissociation of the CO group. Although only tentative, this explanation does account for the similar activation parameters observed for these processes.

As an alternative to intramolecular isomerization, the possibility was considered that CO dissociation, rearrangement of the pentacoordinate fragment, and recombination could occur within a "solvent cage" thereby giving a rate of CO exchange which was slower than the rate of isomerization. Such a mechanism could also account for the similarity between the activation parameters for CO dissociation and isomerization. As a test of this hypothesis, the isomerization of *trans*-W(CO)$_4$(^{13}CO)(CS) was investigated in the gas phase, where there is no possibility of solvent participation. Ampules containing the solid complex in amounts corresponding to approximately 2×10^{-4} M gas-phase concentrations were evacuated and filled with CO (140 Torr) at room temperature. After sealing with a flame, the ampules were submerged in an oil bath at 100.5°. After 75 min, the vessels were immediately cooled and the contents dissolved in a measured quantity of decalin. No decomposition was detected. The quantities of trans and cis isomers present were determined from the intensities of the 1967- and 1957-cm^{-1} ir bands, respectively (see Table I). These bands are of equal intensity after the 75-min time period. Since samples isomerized in decalin solution reach this point at 44 min, it is apparent that the gas-phase isomerization rate constant is approximately 0.6 times the rate constant in decalin solution. The isomerization had proceeded through roughly 1.3 half-lives at this stage.

Gas-phase isomerizations carried out under 280 Torr CO gave identical results, indicating that the rate of isomerization was independent of the CO concentration. However, reactions performed under vacuum (no added CO) gave large amounts of decomposition for unknown reasons. (Possibly a small amount of decomposition yields a species which autocatalyzes the decomposition of the complex. Such a species might be captured in the presence of CO.) Since this could be indicative of a rapid dissociation reaction, experiments were performed with W(CO)$_5$(CS) in an atmosphere of 90% atom-enriched ^{13}CO under the same conditions (140 Torr, 100.5° for 75 min) as the isomerizations, to determine the extent of CO exchange during this period. Relative increases in the 1967- and 1957-cm^{-1} ir bands (due to ^{13}CO in trans and cis positions, respectively) from their natural abundance values (cis = 4.4%, trans = 1.1%) provided a measure of the exchange which had taken place. The exchange reaction is apparently a dissociative process, since the exchange rate is independent of CO pressure; identical results were obtained under 280 Torr ^{13}CO. A total cis enrichment of about 1% is observed, while the trans enrichment is approximately 5%. (The previously described experiment with *trans*-W(CO)$_4$(^{13}CO)(CS) showed that after this same period the isomerization was 60% complete.)

Thus the total amount of CO substitution occurring during the isomerization of *trans*-W(CO)$_4$(^{13}CO)(CS) is small, and the amount of ^{13}CO replacement in *cis*-W(CO)$_4$(^{13}CO)(CS) is negligible. Therefore, of the observed decrease in *trans*-W(CO)$_4$(^{13}CO)(CS) during the isomerization reaction in the presence of ^{12}CO, a *maximum* of 15% can be attributed to trans exchange with ^{12}CO, with the balance due to isomerization to the cis isomer.

It is thus apparent that isomerization in the gas phase is predominantly intramolecular. The similarity between isomerization rates in the gas phase and in decalin solution suggests that the mechanism of isomerization is intramolecular in solution as well.

A high preference for trans CO exchange over cis exchange is observed in the gas-phase exchange reaction, which, as noted above, is found to be a dissociative substitution. A conservative estimate of the trans/cis exchange ratio, after accounting for the statistical factor, is 20. This number may be substantially larger, since much of the observed cis enrichment is undoubtedly due to isomerization from the trans-labeled isomer. It is possible to observe this faster trans exchange in the early stages of reactions between W(CO)$_5$(CS) and ^{13}CO because the rate of formation of *trans*-W(CO)$_4$(^{13}CO)(CS) is faster than its rate of isomerization to the cis isomer, as a result of the high W(CO)$_5$(CS) concentration and the low *trans*-W(CO)$_4$(^{13}CO)(CS) concentration. It is clear, however, from the previous reactions where equal concentrations of these two complexes were used, during observation of CO exchange and isomerization, that the *rate constants* of the two reactions are in the order: k_f(isomerization) > k_{trans}(dissociation).

Stereochemistry of Ligand Substitution in W(CO)$_5$(CS) and *trans*-W(^{13}CO)(CO)$_4$(CS). In contrast to the reactions in decalin solution and in the gas phase, isomerizations carried out in

1,4-dioxane give large amounts of $W(^{12}CO)_5(CS)$ and $W(^{12}CO)_3(^{13}CO)_2(CS)$, indicating that CO dissociation is occurring in this solvent. Dioxane has previously been observed to greatly enhance "SN1" substitution rates of metal carbonyls,[32] an effect that may be attributed to nucleophilic displacement of carbonyl ligands by the dioxane. Thus, it was found that in dioxane solutions under an atmosphere of ^{13}CO at 100°, $W(CO)_5(CS)$ incorporates the labeled ligand much more rapidly than in decalin solution. Although the reactions in decalin give a statistical distribution of the labeled ligand between cis and trans sites, ir spectra of the dioxane solutions indicate that the rate of formation of *trans*-$W(CO)_4(^{13}CO)(CS)$ under these conditions is approximately four times the rate of formation of the cis isomer. Thus, the rate of trans CO exchange in this solvent is considerably faster than both the rate of cis exchange and the rate of isomerization.

If nucleophilic carbonyl displacement by dioxane is responsible for preferential trans carbonyl exchange in $W(CO)_5(CS)$, other donor ligands might also be expected to show a similar specificity for trans substitution. To determine whether it is the trans carbonyl which is specifically replaced in such a reaction, *trans*-$W(CO)_4(^{13}CO)(CS)$ in THF solution was treated with Bu_4NI at 55°, a temperature sufficiently low that isomerization of the complex before reaction is negligible.

$$\textit{trans}\text{-}W(CO)_4(^{13}CO)(CS) + I^- \rightarrow [\textit{trans}\text{-}W(CO)_4(CS)(I)^-] + {}^{13}CO \quad (7)$$

In chlorobenzene solvent at 38–58°, this substitution reaction has been found to be first order in complex and iodide ion and presumably proceeds by I^- attack on the complex.[12] Continuous N_2 purging of the solution was necessary to minimize exchange of liberated ^{13}CO with the relatively labile carbonyls in the $[\textit{trans}\text{-}W(CO)_4(CS)(I)]^-$ product, a process found in other experiments to be quite rapid.

After conversion of the $[\textit{trans}\text{-}W(CO)_4(CS)(I)]^-$ product to $W(CO)_5(CS)$ by reaction with $AgCF_3SO_3$ and ^{12}CO in acetone, a reaction which as noted above gives only trans substitution, it was observed by ir spectroscopy[33] (Table I) that more than 80% of the ^{13}CO had been replaced in the iodide substitution (eq 7). Thus the iodide ion replaces the trans carbonyl in $W(CO)_5(CS)$ with high or complete specificity. This interesting result indicates that a carbonyl trans to CS is chemically quite different from a cis CO, as was also suggested by the observations of gas-phase CO exchange. Furthermore, carbonyls in the two positions do not exchange during the SN2 substitution process. Possible mechanisms to account for this specificity may involve attack by the I^- ion at the metal atom accompanied by simultaneous dissociation of the trans carbonyl, or attack by the I^- ion at the carbon atom of the trans carbonyl followed by rearrangement and loss of the trans CO. Related mechanisms have been considered for the substitution of CO in $W(CO)_6$ with I^-.[34]

Experimental Section

General. Reactions were performed under an atmosphere of dry, prepurified N_2 unless noted otherwise. Dioxane was distilled from CaH_2, and tetrahydrofuran (THF) was distilled from lithium aluminum hydride before use. Decalin solvent was purified by stirring overnight at 130° with Na and distilling under reduced pressure. Slightly modified literature methods were used to prepare $[(Ph_3P)_2N][W(CO)_5Cl]$[35] and $[(Ph_3P)_2N][\textit{cis}\text{-}W(CO)_4(CNC_6H_{11})(Cl)]$.[36] The trans-labeled $W(CO)_4(^{13}CO)(CNCH_3)$, $W(CO)_4(^{13}CO)(CNC_6H_{11})$, and $[(Ph_3P)_2N][W(CO)_4(^{13}CO)(NCS)]$ were prepared from *trans*-$W(CO)_4(^{13}CO)(CS)$ by reactions with CH_3NH_2, $C_6H_{11}NH_2$, and $[(Ph_3P)_2N][N_3]$ in hexane or THF solutions at room temperature, identical with corresponding reactions with $W(^{12}CO)_5(CS)$.[12] Other reagent grade chemicals were used without further purification. Carbon monoxide of 90% ^{13}CO enrichment was obtained from Monsanto Research Corporation.

The isomerization of *trans*-$W(CO)_4(^{13}CO)(CS)$ in decalin solution (5.40×10^{-4} to 2.70×10^{-3} M) was studied in 25-ml flasks capped under N_2 with rubber serum stoppers and immersed in a constant-temperature oil bath. Samples were periodically withdrawn by syringe, and the appearance of the 2005-cm^{-1} infrared ν(CO) band of the cis isomer was monitored. At least three samples were run at each temperature.

Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer. Positions of the peaks were determined with an expanded scale recorder calibrated in the carbonyl region with gaseous CO and DCl. A Bruker HX-90 spectrometer operating in the Fourier transform mode was used to obtain ^{13}C NMR spectra. Samples were run in $DCCl_3$ in the presence of the shiftless paramagnetic relaxing agent, Cr(acetylacetonate)$_3$ (0.05 M).[37]

Preparation of *trans*-$W(CO)_4(^{13}CO)(CS)$. A 100-ml bottle[38] containing $Bu_4N[\textit{trans}\text{-}W(CO)_4(CS)(I)]$[10] (0.71 g, 1.0 mmol) and a magnetic stir bar was securely capped and evacuated through a syringe, and an atmosphere of ^{13}CO was admitted. A solution of $AgCF_3SO_3$ (0.26 g, 1.0 mmol) in 3 ml of acetone was added with vigorous stirring. The ^{13}CO pressure was increased to approximately 25 psi, and stirring was continued for 8 h. The solution was then filtered through Celite and evaporated to dryness. The residue was extracted with warm hexane, filtered, concentrated, and passed through a 1.5 × 30 cm Florisil column with hexane eluent. Evaporation of the product band under reduced pressure gave 0.62 g (84%) of the product. Reactions performed with a lower ^{13}CO pressure or with slow stirring yielded products which contained more $W(^{12}CO)_5(CS)$.

$Et_4N[\textit{cis}\text{-}W(CO)_4\{P(4\text{-}ClC_6H_4)_3\}(I)]$ and *cis*-$W(CO)_4(^{13}CO)[P(4\text{-}ClC_6H_4)_3]$. A modification of the method of Allen and Barrett[39] was employed in the first step of this procedure. A dioxane solution (10 ml) of $Et_4N[W(CO)_5I]$ (0.25 g, 0.42 mmol) was stirred with $P(4\text{-}ClC_6H_4)_3$ (0.16 g, 0.435 mmol) at 100° with continuous purging of the solution by N_2. Infrared spectroscopy showed nearly complete consumption of the starting complex after 1.5 h. Some formation of $W(CO)_5[P(4\text{-}ClC_6H_4)_3]$ was evident, but the major product was identified as $Et_4N[\textit{cis}\text{-}W(CO)_4\{P(4\text{-}ClC_6H_4)_3\}(I)]$, based on the similarity of its ir spectrum to those reported for similar Cr and Mo complexes:[39] ir (CH_2Cl_2) 2007 m, 1893 s, 1876 s, sh, 1818 s cm^{-1}.

The above solution was cooled and saturated for a short time with ^{13}CO, and the flask was securely stoppered with a serum cap. A solution of $AgCF_3SO_3$ (0.107 g, 0.415 mmol) in 3 ml of acetone was added dropwise with stirring. The pressure of ^{13}CO over the solution was increased to about 1.5 atm, and vigorous stirring was continued for 1 h. The solution was then filtered through Celite and evaporated to dryness. The residue was extracted with several 10-ml portions of warm hexane. The combined extracts were concentrated and placed on a 1.5 × 30 cm Florisil column. Developing with 1:1 hexane–CH_2Cl_2 brought down a very pale yellow band, which was collected, concentrated, and cooled to −20°. Cream-colored crystals (0.125 g, 43%) containing *cis*-$W(CO)_4(^{13}CO)[P(4\text{-}ClC_6H_4)_3]$ were obtained.

***cis*-$W(CO)_4(^{13}CO)(CNC_6H_{11})$.** A procedure similar to that above was employed. A 200-ml bottle containing $[(Ph_3P)_2N][\textit{cis}\text{-}W(CO)_4(CNC_6H_{11})(Cl)]$ (1.0 g, 1.02 mmol) in 50 ml of acetone was treated with $AgCF_3SO_3$ (0.263 g, 1.02 mmol) and stirred under 1.5 atm of ^{13}CO for 8 h. After filtration through Celite, the solution was evaporated to dryness and the residue extracted with warm hexane. Concentration and cooling gave colorless crystals (0.25 g, 56%) of *cis*-$W(CO)_4(^{13}CO)(CNC_6H_{11})$.

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References and Notes

(1) M. Dokiya, R. D. Johnston, and F. Basolo, *Inorg. Chem.*, **9**, 996 (1970).
(2) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Am. Chem. Soc.*, **93**, 2807 (1971).
(3) G. Schwenzer, M. Y. Darensbourg, and D. J. Darensbourg, *Inorg. Chem.*, **11**, 1967 (1972).
(4) D. J. Darensbourg and H. H. Nelson, *J. Am. Chem. Soc.*, **96**, 6511 (1974).
(5) R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Am. Chem. Soc.*, **94**, 272 (1972).

(6) M. A. Cohen and T. L. Brown, Abstracts of Papers, 170th National Meeting of the American Chemical Society, 1975.

(7) W. J. Knebel, R. J. Angelici, O. A. Gansow, and D. J. Darensbourg, *J. Organomet. Chem.*, **66,** C11 (1974).

(8) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12,** 1286 (1973).

(9) (a) K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10,** 101 (1967); (b) K. Noack, *ibid.*, **12,** 181 (1968).

(10) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.,* **97,** 1261 (1975).

(11) A complete analysis of the vibrational spectrum is currently in progress elsewhere. I. S. Butler and C. F. Shaw III, to be submitted for publication.

(12) B. D. Dombek and R. J. Angelici, submitted for publication.

(13) M. Poliakoff, private communication.

(14) (a) A. Berry and T. L. Brown, *Inorg. Chem.*, **11,** 1165 (1972); (b) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **97,** 3380 (1975).

(15) R. J. Angelici, *Organomet. Chem. Rev.*, **3,** 173 (1968).

(16) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93,** 6048 (1971).

(17) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14,** 262 (1975).

(18) J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner and R. F. Turner, *J. Am. Chem. Soc.*, **97,** 4805 (1975), and references therein.

(19) J. M. Kelley, D. V. Bent, H. Hermann, D. Schulte-Frohlinde, and E. K. von Gustorf, *J. Organomet. Chem.*, **69,** 259 (1974).

(20) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94,** 3035 (1972).

(21) (a) R. Hoffman, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94,** 3047 (1972); (b) A. R. Rossi and R. Hoffman, *Inorg. Chem.*, **14,** 365 (1975).

(22) L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, **10,** 78 (1971).

(23) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95,** 7516 (1973).

(24) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **96,** 7568 (1974).

(25) I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **66,** 161 (1974).

(26) G. Michels and H. Svec, to be submitted for publication.

(27) (a) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, **92,** 1068 (1970); (b) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, **92,** 3482 (1970); (c) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93,** 4701 (1971).

(28) R. K. Pomeroy and W. A. G. Graham, *J. Am. Chem. Soc.*, **94,** 274 (1972).

(29) (a) E. O. Fischer, H. Fischer, and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **11,** 644 (1972); (b) H. Fischer, E. O. Fischer, and H. Werner, *J. Organomet. Chem.*, **73,** 331 (1974).

(30) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed, Wiley, New York, N.Y., 1961, p 192.

(31) (a) H. A. C. McKay, *Nature* (*London*), **142,** 997 (1938); (b) *J. Chem. Soc.*, **65,** 702 (1943).

(32) H. Werner and R. Prinz, *Chem. Ber.*, **99,** 3582 (1966).

(33) The broadness of the absorptions of $W(CO)_4(CS)I^-$ dissolved in polar solvents prevented a reliable determination of its ^{13}CO content. Hence the compound was converted to $W(CO)_5(CS)$ and studied in a hydrocarbon solvent where the absorptions are very sharp.

(34) J. E. Pardue, M. N. Memering, and G. R. Dobson, *J. Organomet. Chem.*, **71,** 407 (1974).

(35) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).

(36) H. D. Murdoch and R. Henzi, *J. Organomet. Chem.*, **5,** 166 (1966).

(37) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).

(38) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969, p 157.

(39) A. D. Allen and P. F. Barrett, *Can. J. Chem.*, **46,** 1649 (1968).

The Mechanism of Carbonylation of Halo(bis ligand)organoplatinum(II), -palladium(II), and -nickel(II) Complexes

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Abstract: Rates of reaction of a variety of halo(bisphosphorus ligand)organoplatinum(II), -palladium(II), and -nickel(II) complexes with carbon monoxide to form acylmetal derivatives have been measured. Pseudo-first-order kinetics were observed in most instances from ca. 15 to 85% reaction. The effects of changing ligands and the metal upon the observed rate constants and $\Delta S^{\ddagger}$ are noted. In all cases the reaction rates decreased when excess ligand was present. The rate depressions reached a maximum value and thereafter remained constant with further increases in ligand concentration. Triarylphosphine ligands with electron donating substituents produced stepwise reactions and in the most favorable cases four separate steps were distinguishable. Rate constants and $\Delta S^{\ddagger}$ values were obtained where possible. These data are interpreted in terms of formation of an initial five-coordinate intermediate, $(XL_2R(CO)M)$, detectable in several cases and isolable in one, which reacts by two possible paths: (1) a dissociation route forming $XL(CO)RM$ inhibited by excess ligand and (2) a migratory route forming $XL(RCO)M$ which is not inhibited by excess ligand. The mechanism proposed is related to the ligand replacement reaction of square planar complexes. The kinetic analysis indicates the complicated nature of the observed (overall) rate constants and related $\Delta S^{\ddagger}$'s and why these data by themselves are very difficult to interpret.

Numerous carbonylation reactions are known which are catalyzed by platinum, palladium, and nickel complexes.[1] A typical example is the palladium catalyzed conversion of aryl halides into esters.[2] Although no previous, detailed studies have been reported, a possible mechanism for this reaction consists of the following four major steps: (A) Oxidative addition of ArX to a palladium(0) complex previously formed by in situ reduction of a palladium(II) complex initially added; (B) insertion of CO into the aryl–palladium bond forming an acylpalladium complex; (C) alcoholysis of the latter product to ester and a hydridopalladium species; (D) regeneration of the catalyst by decomposition of the hydridopalladium complex back to the palladium(0) species and HX. The HX is then neutralized by the tertiary amine also present. The scheme below is the suggested reaction course.[2]

$$[(X)_2(PPh_3)_2Pd + CO + 2n\text{-}BuOH \rightarrow (n\text{-}BuO)_2CO + 2HX + (CO)(PPh_3)_2Pd]$$

$$(CO)(PPh_3)_2Pd + RX \rightarrow (X)(PPh_3)_2(R)Pd + CO \quad (A)$$

$$(X)(PPh_3)_2(R)Pd + CO \rightarrow (X)(PPh_3)_2(RCO)Pd \quad (B)$$

$$(X)(PPh_3)_2(RCO)Pd + n\text{-}BuOH \rightarrow RCOOBu\text{-}n + (H)(X)(PPh_3)_2Pd \quad (C)$$

$$(H)(X)(PPh_3)_2Pd + CO \rightarrow (CO)(PPh_3)_2Pd + HX \quad (D)$$

$$[HX + n\text{-}Bu_3N \rightarrow n\text{-}Bu_3NH^+X^-]$$

$$X = \text{halide}$$