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**Preliminary communication**

# EVIDENCE FOR THE FLUXIONALITY AND STRUCTURE IN SOLUTION OF INTERMEDIATES OF THE TYPE $W(CO)_4(L)$ (L = LEWIS BASE)

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## Summary

Evidence based on amine substitution reactions in $W(CO)_4$(tmpa) (tmpa = *N,N,N′,N′*-tetramethyl-1,3-diaminopropane) and *cis*-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ with $PPh_3$ and $^{13}CO$ indicates (a) that the square pyramidal $[W(CO)_4PPh_3]$ intermediate arising from amine dissociation is fluxional, and (b) that the intermediate containing $PPh_3$ in the equatorial plane of the square pyramid is thermodynamically more stable than that containing $PPh_3$ in the axial position.

Very recently, Atwood and Brown advanced a "site preference" model to explain a considerable body of kinetic data. This model proposes that in octahedral metal carbonyl derivatives, $M(CO)_5L$, carbonyls *cis* to the substituent are labilized relative to those in the hexacarbonyls themselves, when L is a poorer acceptor of metallic $d_\pi$ electron density than is CO [1]. These observations were attributed to a thermodynamic preference by L to adopt a position in the equatorial plane of the sixteen valence electron, square pyramidal intermediate arising through carbonyl dissociation*. Thus, the transition state leading to formation of the *cis* disubstituted product is stabilized by the presence of an equatorial L. However, experimental evidence for the preferred geometry of the coordinatively-unsaturated intermediates, $[M(CO)_4L]$, resulting from the dissociation of the sixth ligand (CO or L) in substituted Group VIB complexes is lacking. In this regard we wish to report results which indicate, (a) that the $M(CO)_4L$ species arising through dissociation of CO from $M(CO)_5L$ substrates are fluxional, and (b) that as proposed by Atwood and Brown [1], the square pyramidal intermediate containing L in the equatorial plane is thermodynamical-

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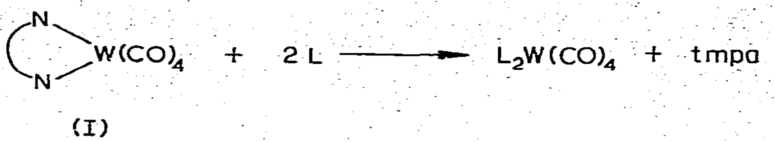
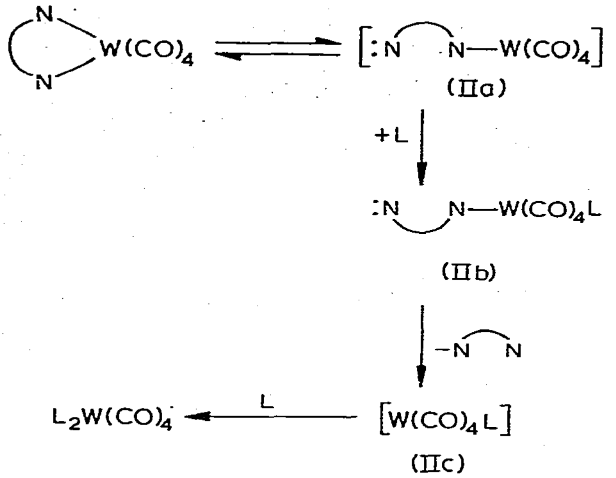
*Substantial evidence has been presented that sixteen valence electron, pentacoordinate metal carbonyls and derivatives exhibit square pyramidal, rather than trigonal bipyramidal geometry, both in solution and in inert matrices [8].



(1)



(2)

ly more stable than the species containing L in the axial position.

Based upon observed rate data, the reaction of (tmpa)W(CO)$_4$ (tmpa = *N,N,N′,N′*-tetramethyl-1,3-diaminopropane) with phosphines and phosphites (L) (eq. 1) proceeds largely via mechanism (2) [2,3].

For L = P(OCH$_2$)$_3$CCH$_3$, intermediate (II b) exhibiting exclusively *cis* stereochemistry has been identified [3]. For L = triphenylphosphine, reaction at 43.0°C in xylene solvent was monitored in the visible region (yellow, 425 nm). Plots of ln $(A_t - A_\infty)$ vs. time ($A_t$ and $A_\infty$ are absorbances at times $t$ and $t_\infty$, respectively) for reactions under pseudo first-order reaction conditions (excess triphenylphosphine) were linear to two or more half-lives*. It was also determined that the final reaction products were both the *trans*- and *cis*-(PPh$_3$)$_2$W(CO)$_4$, with the *trans* isomer predominant (ca. 80%). It is known that the *trans* isomer absorbs significantly at 425 nm**, and thus non-linear plots of ln $(A_t - A_\infty)$ vs. $t$ are to be expected unless the ratio of the concentrations of the product isomers, [*cis*]/[*trans*], remains constant over the course of the reaction. That no isomerization occurs on the time scale of the ligand-substitution process [1] is further substantiated by analysis of the carbonyl stretching spectra (2200—1800 cm$^{-1}$) of reaction solutions as a function of time. Thus, the formation of both the *cis* and *trans* isomeric products must involve a process rapid on the time scale of the substitution reaction. The only such process which would seem to be reasonable under the reaction conditions employed would involve a fluxional,

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*For experimental details, see ref. 2.

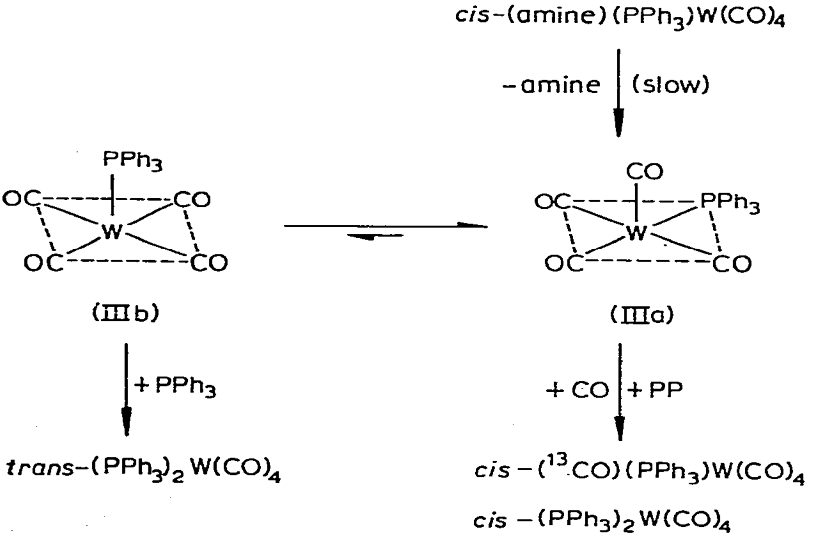
**The *trans* and *cis* isomers exhibit greatly differing molar absorptivities at this wavelength.

five-coordinate intermediate, i.e., $[W(CO)_4(PPh_3)]$*.

These results are of interest in view of another study which demonstrates that *cis*-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ undergoes stereospecific enrichment with $^{13}CO$ to afford *cis*-$(^{13}CO)(PPh_3)W(CO)_4$ under reaction conditions identical to those employed in reaction 1**. On the other hand, *cis*-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ reacts with triphenylphosphine in xylene also affording a mixture of *cis*- and *trans*-$(PPh_3)_2W(CO)_4$ products, with a *cis/trans* ratio similar to that observed for reaction of $(tmpa)W(CO)_4$ with triphenylphosphine. Both processes, the stereospecific enrichment and the ligand substitution, in all probability proceed via the same intermediate, square pyramidal $[W(CO)_4(PPh_3)]$ (IIc), arising from dissociation of the amine, and in which the triphenylphosphine ligand (L) initially must be equatorial. Based upon detailed kinetics results for ligand-replacement reactions of $(amine)Mo(CO)_5$ [4] and *cis*-$(amine)(PPh_3)Mo(CO)_4$ [5] substrates, it is probable that the formation of equatorially-substituted $[W(CO)_4(PPh_3)]$ involves essentially complete breaking of the amine—tungsten bond.

The differing stereochemical behavior of the intermediate in its reaction with $^{13}CO$ and triphenylphosphine can be explained in terms of mechanism 3***.

It is presumed that the equatorially-substituted intermediate IIIa is the predominant fluxional species, affording the observed *cis*-$(^{13}CO)(PPh_3)W(CO)_4$ product, while steric interactions dictate a much greater preference for $PPh_3$ to react with intermediate IIIb. Thus, as was proposed by Atwood and Brown [1], these results are interpretable in terms of a thermodynamically more stable



(3)

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*An intermediate such as (IIa) might also be the fluxional species, although, as noted above, a *cis*-intermediate of the type IIb has been observed for $L = P(OCH_2)_3CCH_3$. The arguments to be presented below are, however, valid whatever the identity of the five-coordinate fluxional species. An alternate mechanism involving the very rapid, intramolecular, non-dissociative isomerization of $L_2W(CO)_4$ can be ruled out in that both *cis*- and *trans*-$[P(C_6H_5)_3]_2W(CO)_4$ have been synthesized in these laboratories (D.J.D.) and have been found not to undergo interconversion on the required time scale under the reaction conditions employed in these experiments.

**See ref. 5 for details of analogous enrichment experiments with *cis*-$(amine)(PPh_3)Mo(CO)_4$ complexes.

***Photochemical isomerizations of the type (IIIa↔IIIb) have been discussed by Black and Bratermann [11].

equatorially-substituted square-pyramidal intermediate*. Similar mechanistic pathways have been invoked to explain the stereochemical outcome of thermal reactions of $Ph_3EMn(CO)_5$ (E = Ge, Sn) with phosphines and amines [6] and photochemical reactions of $XRe(CO)_5$ (X = Cl, Br, I) with triphenylphosphine [7], although no direct evidence for the fluxionality of the presumed five-coordinate intermediates, or for the site of initial carbonyl dissociation was reported**.

## Acknowledgments

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*However, in $M(CO)_4L$ intermediates where L is a better $\pi$-accepting ligand than CO, the predominant square-pyramidal species is expected to contain L in the *axial* position [9].

**Atwood and Brown [10] have independently obtained evidence for the fluxionality of $[BrRe(CO)_4]$.