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Octahedral Metal Carbonyls.

61*. The Mechanism of *cis–trans* Isomerization During Ligand-substitution Reactions Affording *cis*-Bis(triphenylphosphine)tetracarbonyltungsten(0)

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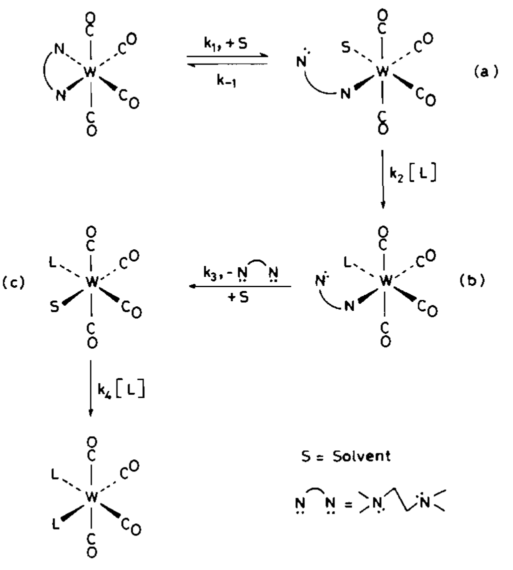
It has been reported that during thermal ligand substitution in (tmpa)W(CO)$_4$ (tmpa = N,N,N',N'-tetramethyl-1,3-diaminopropane) proceeding by stoichiometry (1) and mechanism (2) (L = phosphine,

$$\text{(tmpa)W(CO)}_4 + 2\text{L} \longrightarrow \text{L}_2\text{W(CO)}_4 + \text{tmpa} \qquad (1)$$

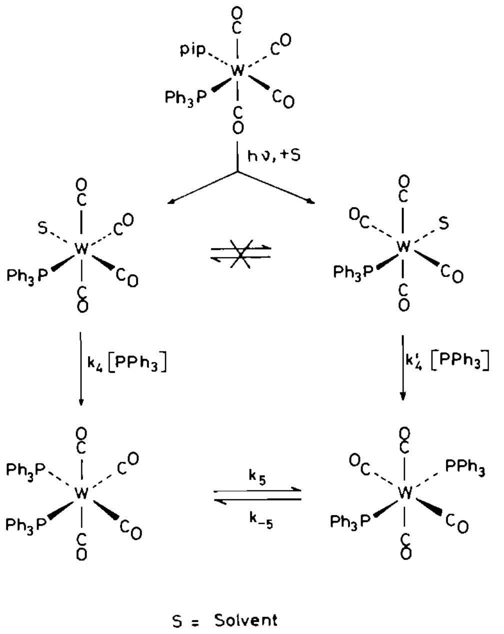
phosphite) [1], stereochemical rearrangement takes place in the five-coordinated intermediate (2c) [2].



(2)

This rearrangement thus would account for the creation of the two observed isomeric reaction products, *cis*- and *trans*-L$_2$W(CO)$_4$, and it could be inferred that the five-coordinate species undergo stereochemical rearrangement on the time-scale of ligand-substitution. We report several lines of evidence which demonstrate that this proposal is not correct but, rather, that the isomerization takes place through a well-documented [3] non-dissociative scrambling process. Evidence further indicates that where a five-coordinate intermediate *is* produced, no stereochemical rearrangement takes place.

(a) Pulsed laser flash photolysis at 43.0 °C in xylene or chloroform of *cis*-(pip)(PPh$_3$)W(CO)$_4$ (pip = piperidine) was carried out as previously described [4, 5]. The complex, synthesized via the method of Darensbourg and Kump [6], reacts upon photolysis via W–N bond fission [5]. At 430 nm two independent exponential decays are observed in the presence of PPh$_3$. The faster decay (k_4, eqn. (3)) $\approx 10^7$ M^{-1} s^{-1} in xylene and 8.9(5) × 10^4 M^{-1} s^{-1} in chloroform) has been shown [5] to involve bimolecular reaction of the specifically solvated *cis*-[Ph$_3$PW(CO)$_4$] transient with PPh$_3$. The slower decay ($k_4' = 6.8 \times 10^5$ M^{-1} s^{-1} in xylene and 8.4(1) × 10^3 M^{-1} s^{-1} in chloroform) has been attributed to the reaction of the corresponding *trans* isomer [4]. Only one decay would be observed if these species were undergoing rapid intramolecular interconversion. Thus the overall photolysis mechanism is that in eqn. (3).



(3)

(b) ^{31}P NMR studies of chelate ring-displacement (eqn. (2)) by PPh$_3$ (0.305 M, Jeol FX90Q spectrometer) in CHCl$_3$/CDCl$_3$ at 52.3 °C clearly demonstrate that the peak at 27.529 ppm (downfield from a PPh$_3$ internal standard), attributable to the *cis*-(Ph$_3$P)$_2$W(CO)$_4$ product, grows in intensity at the reaction's earlier stages but that the corresponding *trans* peak (at 32.678 ppm) appears only after an

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induction period. The chemical shifts of the two isomers were identified through comparison with those of authentic samples*. These observations indicate that the *cis*-$(Ph_3P)_2W(CO)_4$ reaction product is produced first, with subsequent rearrangement to the *trans* isomer. Mosbo and coworkers have made similar observations for analogous systems for L = $PPhMe_2$ and PPh_2Me [3g].

(c) The rates of the thermal *cis*-to-*trans* isomerization of *cis*-$(Ph_3P)_2W(CO)_4$ were studied spectrophotometrically at 400 nm in toluene at 52.5 °C in the absence and in the presence of $P(OEt)_3$. The results demonstrate that the process is unimolecular and that the derived rate constant ($k_5 + k_{-5}$, eqn. (3)) is independent of the concentration of $P(OEt)_3$ (k in the absence of $P(OEt)_3 = 6.06(3) \times 10^{-4}$ s^{-1}; in its presence (three concentrations over the range 0.1–0.5 M) $k_5 + k_{-5} = 5.79(9) \times 10^{-4}$ s^{-1})). Further, in the presence of added L (=$P(OEt)_3$, pip), no $(L)(PPh_3)W(CO)_4$ products are observed to form during the isomerization process. Thus, a five-coordinate species formed via W–PPh_3 bond-fission is not produced, since pulsed laser flash photolysis studies indicate that L readily trap $[Ph_3PW(CO)_4]$ [5].

Thus it may be concluded that *cis*-$(Ph_3P)_2W(CO)_4$ undergoes isomerization exclusively via a slow, intramolecular scrambling process probably involving a trigonal twist [3].

The results may be contrasted to those for the analogous Mo complex, for which thermal isomerization *does* take place via a mechanism involving Mo–P bond-fission; it has been suggested that isomerization of the *cis*-$[PPh_3Mo(CO)_4]$ intermediate to afford *trans*-$(PPh_3)_2Mo(CO)_4$ may be a concerted process [7].

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*The *cis* complex was prepared photolytically employing a 2:1 ratio of $W(CO)_6$ to PPh_3 dissolved in hexane (400 w medium pressure Hg lamp for 20 min). The precipitated product was washed with hexane until the peak characteristic of $(Ph_3P)W(CO)_5$ at *ca.* 2075 cm^{-1} has disappeared. The *trans* isomer was synthesized via displacement of tmpa from $(tmpa)W(CO)_4$ in chlorobenzene at 52 °C over three hours.