$W_2Cl_4(NHCMe_3)_2(PR_3)_2$ Molecules (R_3 = Me_3, Et_3, Pr^n_3, Me_2Ph). 2. $^{31}P\{^1H\}$ NMR Studies of *Cis–Trans* Isomerizations and Evidence That Suggests an Internal Flip of the W_2 Unit

Hong Chen, F. Albert Cotton,* and Zhengui Yao

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843-3255

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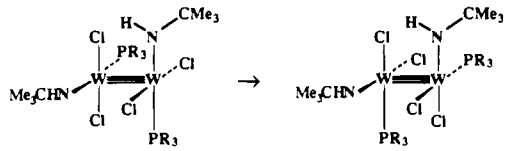
$^{31}P\{^1H\}$ NMR spectroscopy has been used to study the interconversion of *trans*-$W_2Cl_4(NHCMe_3)_2(PR_3)_2$ and *cis*-$W_2Cl_4(NHCMe_3)_2(PR_3)_2$ (R_3 = Me_3, Me_2Ph). The coupling constants between ^{183}W and ^{31}P are about 110 and 300 Hz for the *trans* and *cis* isomers, respectively, which is consistent with the differences in W—P bond distances. The *cis* and *trans* isomers come to equilibrium in solution, with detectable amounts of both present. The [*trans*]/[*cis*] equilibrium constant at 50 °C for the PMe_2Ph system is 0.40 ± 0.05. The rates of the isomerization for the PMe_2Ph system is greatly slowed down by free phosphine in solution, but they are basically unchanged when free phosphine concentrations increase from 0.0021 to 0.415 M. Competing mechanisms, one involving phosphine dissociation as the rate determining step and the other a unimolecular one are proposed. It is suggested that the unimolecular mechanism may be one involving internal flip processes and that the flip barrier has a value in the range of 25–30 kcal/mol^{-1}.

Introduction

In an earlier paper,[1] Part 1, we have reported in detail on the preparation and structures of the isomeric title compounds, **I** and **II**, with particular attention to (a) the experimental condi-



I. Trans **II. Cis**

tions required to obtain crystalline samples of the pure *cis* or the pure *trans* isomer, (b) the existence of polymorphs of several of the compounds, and (c) the occurence of disorder in some of the crystals and the effect of such disorder on the apparent lengths of certain bonds.

Underlying point (a) are the questions of what ratio of isomers is present in solution as a function of time and how do the isomers interconvert. Because of a marked and characteristic difference in the ^{31}P—^{183}W coupling constants for the *cis* and *trans* isomers, $^{31}P\{^1H\}$ NMR spectroscopy affords an efficient and unambiguous means of dealing with these underlying questions. We report here the results of such a study.

Experimental Section

All manipulations were carried out under an atmosphere of dry, oxygen-free argon with Schlenk techniques. Solvents were dried and deoxygenated by refluxing over appropriate reagents before use. The phosphine ligands, PMe_3, PEt_3, PPr^n_3, and PMe_2Ph, were purchased from Strem Chemicals and used as received. *tert*-Butylamine and sodium triethylborohydride (1.0 M in toluene) were purchased from Aldrich, Inc., and used as received. $W_2Cl_4(NHCMe_3)_2(NH_2CMe_3)_2$ was synthesized according to the published procedure[2] using either Na—Hg or $NaBEt_3H$ (1.0 M in toluene) as reducing agent. Methods for the synthesis of the phosphine compounds are given in the preceding paper[1] and are compared with earlier work.[3]

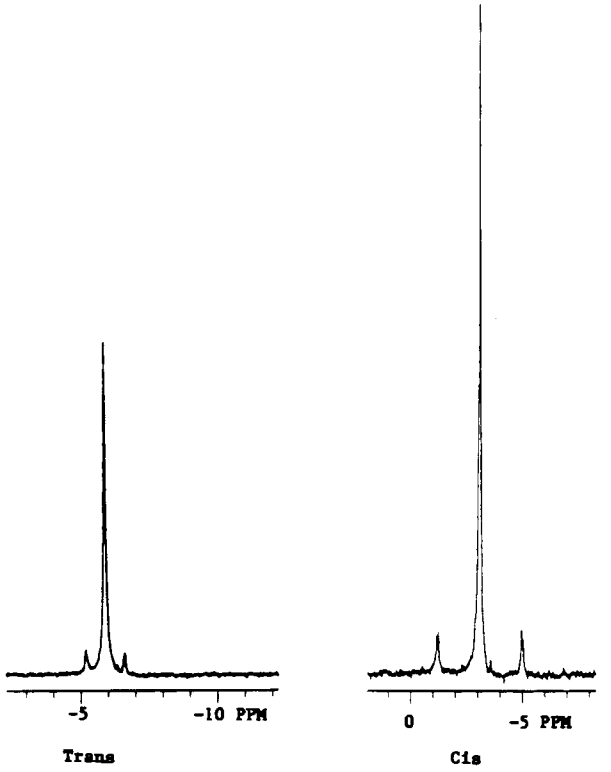


Figure 1. $^{31}P\{^1H\}$ NMR spectra of *trans*- (left) and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_3)_2$ (right) at room temperature.

The $^{31}P\{^1H\}$ NMR spectra were recorded at 81 MHz in 10 mm NMR tubes on a Varian XL-200 spectrometer. Chemical shifts were referenced externally and are reported relative to 85% H_3PO_4. The variable temperature $^{31}P\{^1H\}$ NMR studies were carried out on approximately 50 mg of powder or crystalline samples dissolved in toluene and deuterated benzene (about 1/3 C_6D_6 and 2/3 C_7H_8). A delay of at least 10 min was allowed whenever the temperature was changed.

* Author to whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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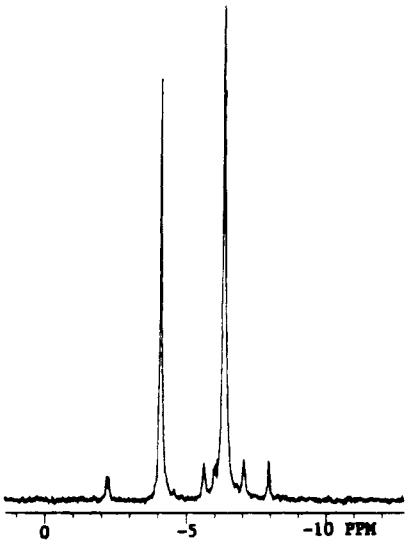

Figure 2. $^{31}P\{^1H\}$ NMR spectrum of *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_3)_2$ after heating to 50 °C.

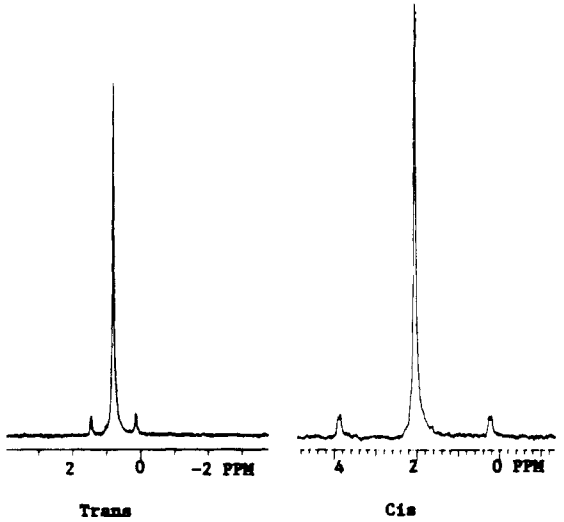

Figure 3. $^{31}P\{^1H\}$ NMR spectra of *trans*- (left) and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ (right) at room temperature.

The kinetic measurements were carried out at 50 °C with about 50 mg of *trans*-$W_2Cl_4(NHCMe_2)_2(PMe_2Ph)_2$ in 3 mL of a 1:2 mixture of C_6D_6 and C_7H_8. To each solution except one was added some additional PMe_2Ph. Before the temperature was raised to 50 °C, spectra measured at room temperature were integrated to obtain the ratio of free to bonded phosphine. The temperature was then raised as quickly as possible to 50 °C and the spectra were measured at 10 min intervals. Rate constants were calculated based on a first-order reversible rate law, namely, $k = \ln((A - A_e)/(A_o - A_e))$.

Results and Discussion

***trans*- and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_3)_2$.** The $^{31}P\{^1H\}$ NMR spectra of *trans*- and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_3)_2$ in toluene are shown in Figure 1. The chemical shift for the *trans* isomer is −5.91 ppm with $^1J_{W-P} = 114$ Hz. The chemical shift for the *cis* isomer is −3.13 ppm with $^1J_{W-P} = 301$ Hz and $^3J_{P-P} = 5.2$ Hz. The coupling constants are consistent with the average W—P bond distances in the *trans* and *cis* isomers, which are 2.603(4) and 2.523(1) Å, respectively. Because of the stronger W—P bond in the *cis* isomer, we can observe the P—P through-three-bond coupling, whereas in the *trans* isomer this coupling is too small to be observed.

When a toluene solution of the *trans* isomer was heated to 50 °C, the peaks corresponding to the *cis* isomer and also a small peak due to $W_2Cl_4(PMe_3)_4$ with chemical shift at −7.99 ppm appeared. The $^{31}P\{^1H\}$ NMR spectrum is given in Figure 2.

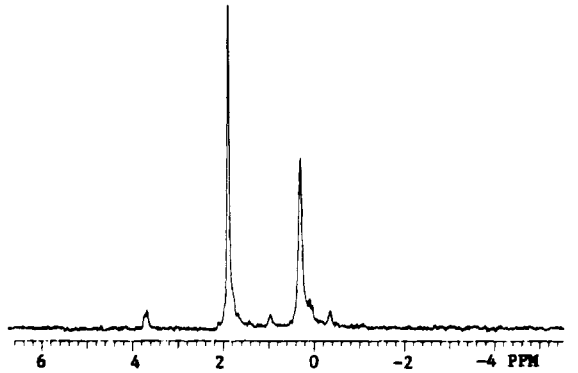

Figure 4. $^{31}P\{^1H\}$ NMR spectrum for *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ after heating to 80 °C.

Table 1. NMR Data for the *Trans* and *Cis* Isomers of the $W_2Cl_4(NHCMe_3)_2(PR_3)_2$ Compounds

	trans		*Cis*		
PR_3	^{31}P shift[a]	$^1J_{W-P}$[b]	^{31}P shift[a]	$^1J_{W-P}$[b]	$31J_{W-P}$[b]
PMe_3	−5.91	114	−3.13	301	5.2
PMe_2Ph	0.77	106	2.04	296	4.5
PEt_3	12.18	107	15.10	294	3.6
PMe_3	11.62	107	15.07	296	5.6

[a] Relative to 85% H_3PO_4. [b] In Hz.

***trans* and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$.** A sample of *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ was dissolved in toluene, and a $^{31}P\{^1H\}$ NMR spectrum at room temperature was taken. It is shown in Figure 3. The appearance of only one peak at 0.77 ppm with a $^{183}W—^{31}P$ coupling constant of 106 Hz, confirms that the reaction product as isolated (at least in our hands) is the pure *trans* isomer, and not a mixture of both *trans* and *cis* isomers as stated by Bradley.[3] The chemical shift for the *cis* isomer is 2.04 ppm with $^1J_{W-P} = 296$ Hz and $^3J_{P-P} = 4.5$ Hz. The spectrum of pure *cis*-$W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2$ in toluene at room temperature is also shown in Figure 3 for comparison. When a solution of *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ was heated to 80 °C, peaks corresponding to the *cis* isomer appeared, as seen in the $^{31}P\{^1H\}$ NMR spectrum shown in Figure 4.

$W_2Cl_4(NHCMe_3)_2(PEt_3)_2$ and $W_2Cl_4(NHCMe_3)_2(PPr^n_3)_2$. The $^{31}P\{^1H\}$ NMR spectrum of *trans*-$W_2Cl_4(NHCMe_3)_2(PEt_3)_2$ in toluene at room temperature is similar to that of the *trans* isomer of the PMe_3 compound. The chemical shift is 12.18 ppm with $^1J_{W-P} = 107$ Hz. When this solution was heated to 80 °C, a new peak appeared due to the *cis* isomer at 15.10 ppm with satellite peaks indicative of $^1J_{W-P} = 294$ Hz and $^3J_{P-P} = 3.6$ Hz. Another small peak at 5.9 ppm corresponds to $W_2Cl_4(PEt_3)_4$. Unlike the PMe_3 and PMe_2Ph compounds, the *cis* isomer of the PEt_3 compound is very soluble in hexanes, and when formed, it does not crystallize out, although some crystals of the less soluble $W_2Cl_4(PEt_3)_4$ are obtained.[1]

In the $^{31}P\{^1H\}$ NMR spectrum of *trans*-$W_2Cl_4(NHCMe_3)_2(PPr^n_3)_2$ in toluene at room temperature, there is only one peak at 11.62 ppm with $^1J_{W-P} = 107$ Hz. Again, when the solution is heated, both isomerization and decomposition occur. The chemical shift for the *cis* isomer is 15.07 ppm with the coupling constants $^1J_{W-P} = 296$ Hz and $^3J_{P-P} = 5.6$ Hz. There is another peak at 7.55 ppm which is presumably due to $W_2Cl_4(PPr^n_3)_4$.

Origin of the $W_2Cl_4(PR_3)_4$ Compounds. In the experiments just discussed it was found that for $PR_3 = PMe_3$, PEt_3, and PPr^n_3, but not for PMe_2Ph, small amounts of the $W_2Cl_4(PR_3)_4$ compounds were formed. The spontaneous conversion of a

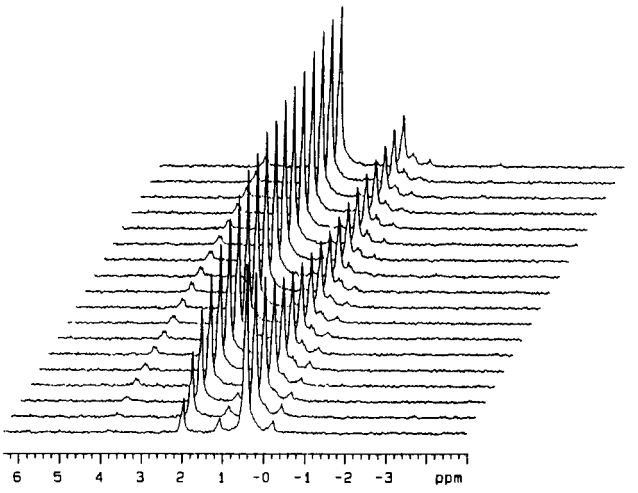

Figure 5. $^{31}P\{^1H\}$ NMR spectra showing conversion of *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ to *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ as a function of time at 50 °C.

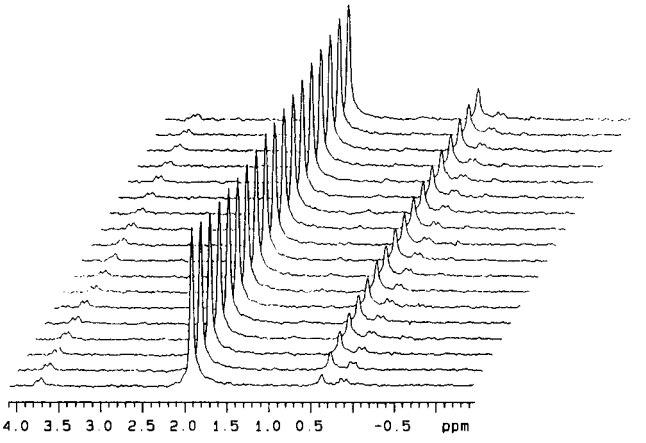

Figure 6. $^{31}P\{^1H\}$ NMR spectra showing conversion of *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ to *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ as a function of time at 50 °C.

W_2^{6+} to a W_2^{4+} complex is a little surprising and might well be worthy of further investigation. Two possible explanations come to mind. In view of the fact that only the three trialkylphosphines, which are the better reducing agents, give this result, it might be attributed to the presence of excess PR_3, as indicated in the following reaction:

$$W_2Cl_4(HNCMe_3)_2(PR_3)_2 + 3PR_3 \rightarrow$$

$$W_2Cl_4(PR_3)_4 + R_3P(HNCMe_3)_2 \xrightarrow{?}$$

$$R_3P(NCMe_3) + H_2NCMe_3$$

Alternatively, there might be a disproportionation reaction, viz.,

$$W_2Cl_4(NHCMe_3)_2(PR_3)_2 \rightarrow W_2Cl_4(PR_3)_4 + \text{“}W_2Cl_4(NHCMe_3)_4\text{”}$$

The true nature of the product (or products) containing the tungsten(IV) is unknown. Since no other ^{31}P signal was seen in the NMR spectrum, the first explanation seems less likely than the second.

Overview of the NMR Spectra. The $^{31}P\{^1H\}$ NMR spectra of all the *cis* and *trans* isomers of the $W_2Cl_4(NHCMe_3)_2(PR_3)_2$ molecules consist, as expected, of strong central singlets flanked by satellites due to the presence of ^{183}W nuclei (^{183}W is 14.3% abundant with $S = 1/2$). The data are collected in Table 1. The satellites are interesting and informative, and correlate well with the structures and bonding. Because the $NHCMe_3$ ligands exert a stronger *trans* influence than do Cl ligands, the P—W bonds are appreciably stronger in the *cis* than in the *trans* isomer, and this in turn makes the $^1J_{P-W}$ coupling constants significantly larger, namely, about 300 Hz vs 110 Hz, for the *cis* isomer vs the *trans* isomer.

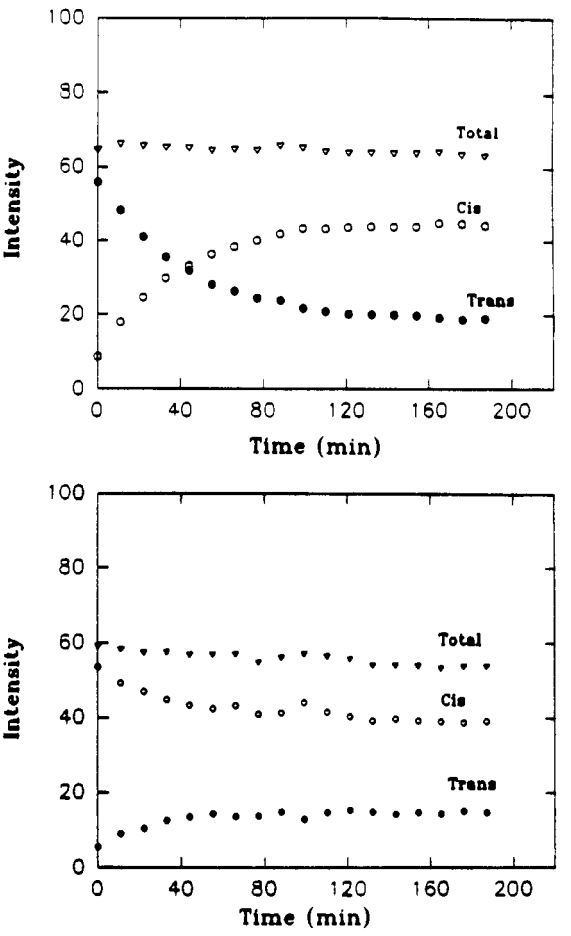

Figure 7. Diagrams of the intensity of *trans*- and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ versus time at 50 °C starting from the *trans* isomer (top) and starting from the *cis* isomer (bottom).

In addition, the *cis* compound is readily distinguishable from the *trans* by the appearance of the satellites as doublets for the former and singlets for the latter. In both cases the molecules with one ^{183}W nucleus are the only ones that cause observable satellites, and they constitute ABX spin systems, each in the extreme region where $\delta_A \approx \delta_B$ and $J_{AX} \gg J_{BX}$. Under these circumstances,[4] the splitting observed in the satellites will be proportional to J_{AB} (which is $^3J_{P-P}$). For the *cis* isomers, $^3J_{P-P}$ is large enough to produce a resolved splitting of the satellites, while in the *trans* isomer it is not, being perhaps 2—4 times smaller. A case similar to the present one with the *cis* isomers was previously reported by Chisholm.[5]

***Cis*—*Trans* Equilibrium.** In the case of the PMe_2Ph system, the value of the *trans*—*cis* equilibrium constant at 50 °C was found to be 0.40 ± 0.05. In the other cases, it was merely shown that at equilibrium (50 °C) readily detectable amounts of both isomers were present at equilibrium, but quantitative results were not obtained. The important general point is that

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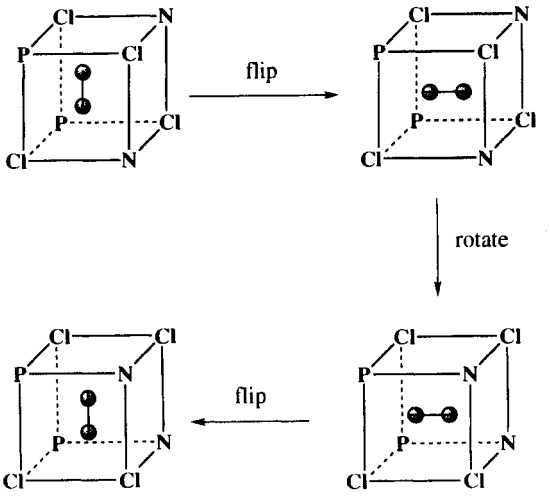

Figure 8. Intramolecular process for the observed *trans* to *cis* isomerization.

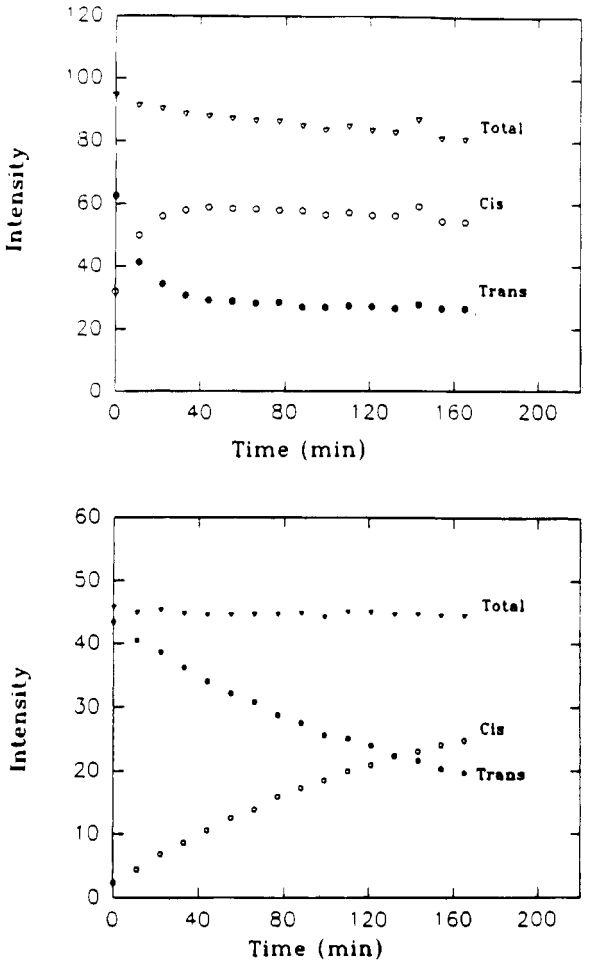

Figure 9. Diagrams of the intensity of *trans*- and *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ versus time at 60 °C without free PMe_2Ph (top) and with 1.6 equivalent of PMe_2Ph (bottom).

the *cis* and *trans* isomers differ little in stability in solution in a nonpolar solvent. Thus, the synthetic procedures[1] leading to the preferential isolation of one isomer or the other are mainly dependent on the temperature, the time allowed for equilibration, and solubilities rather than on inherent stabilities.

Rate and Mechanism of the *Trans*−*Cis* Isomerization. All the compounds of the *cis*- or *trans*-$W_2Cl_4(NHCMe_3)_2(PR_3)_2$ type we have studied undergo isomerization to produce a mixture of the isomers **I** and **II** in solution at room temperature. For the PMe_3, PEt_3, and PPr^n_3 compounds, there is usually also some

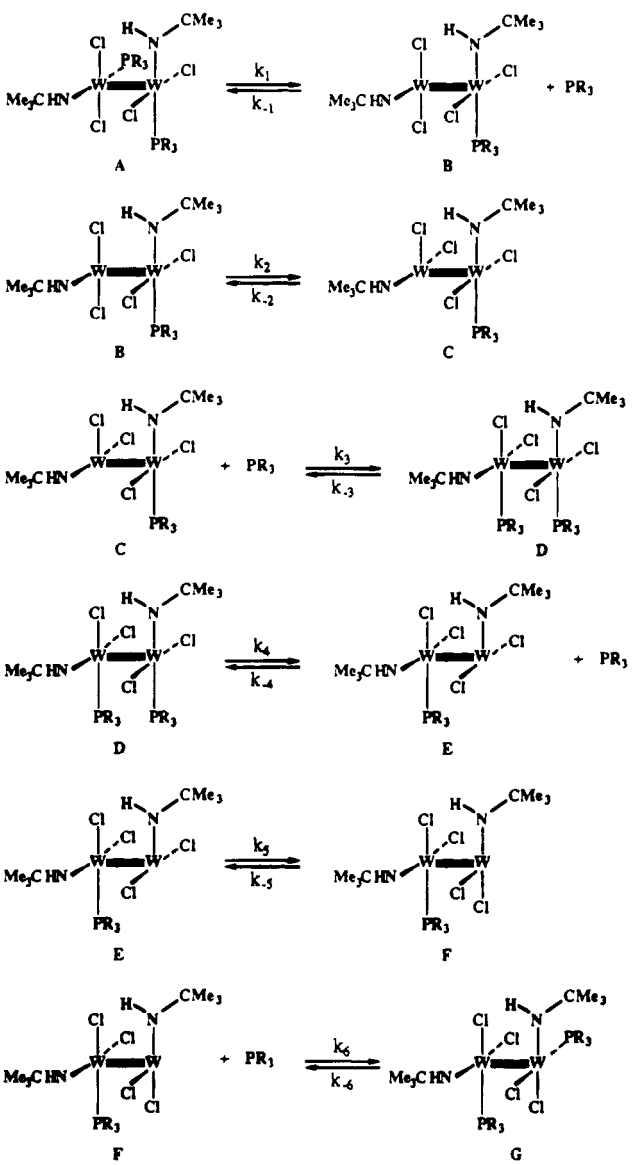

Figure 10. Dissociation mechanism for the *trans* to *cis* isomerization.

decomposition to $W_2Cl_4(PR_3)_4$. For the PMe_2Ph compound, however, only the *trans* and *cis* peaks were present in the spectrum, and therefore this compound was chosen for kinetic measurements. The results of a run in which the *trans* compound was converted to a *cis*/*trans* mixture in toluene at 50 °C are shown in Figure 5, while comparable data for the *cis* to *trans* process are presented in Figure 6. Figure 7 shows plots of both these runs, and it can be seen that equilibrium is reached in 2 h or less and is the same in both cases.

It was our hope in undertaking this work that the isomerization reactions, *cis* ⇌ *trans*, might occur by way of internal flips of the W_2 unit within the ligand cage. Since there is no δ bond, the barrier to internal rotation should be virtually zero, and thus the total activation energy for the process shown in Figure 8 would be about that required for the internal flip steps. If this

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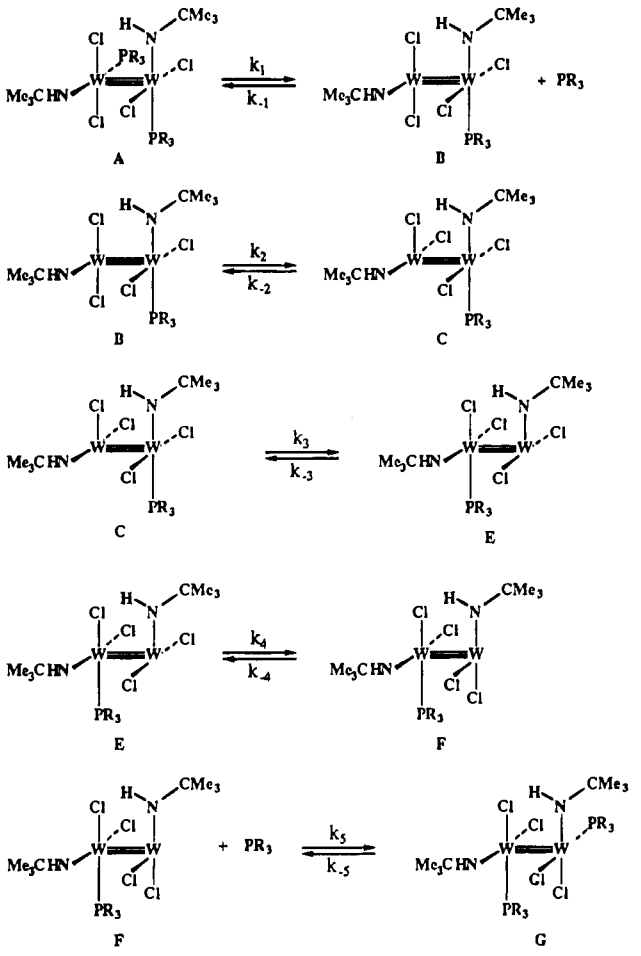
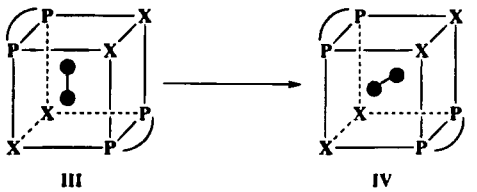


Figure 11. Dissociation mechanism for the *trans* to *cis* isomerization.

were to be the mechanism, then by measuring the activation energy of the isomerization, one would obtain an estimate of the activation energy for the internal flip process. It should be noted that while the internal flip as a concept has been discussed for species of this type generally,[6] it has only been observed and its energy barriers measured for the α to β isomerization of $Mo_2X_4(P\text{-}P)_2$ compounds,[7-12] shown schematically as **III** → **IV**.



III **IV**

An indispensible criterion to be satisfied for the flip mechanism to be viable would be that the isomerization process be unimolecular with a rate independent of the presence of additional ligands in solution. It seems safe to assume that when the process occurs in solvents of very low dielectric constant, such as toluene or hexane, the possibility that the Cl^- or

Table 2. Rate Constants for the *trans*- to *cis*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ Isomerization

10^3[complex][a] (M)	10^3[PMe_2Ph][b] (M)	[PMe_2Ph][b]/[complex][a]	10^3k (min^{-1})
17.3	0.0	0.0	36 (4)
18.1	2.1	0.12	9.3 (2)
16.8	6.3	0.38	5.9 (2)
17.5	10.6	0.61	6.1 (2)
17.7	39.2	2.21	9.1 (4)
18.4	73.2	3.98	8.1 (3)
19.3	415	21.5	8.9 (5)

[a] The initial concentration of *trans*-$W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$. [b] The concentration of free PMe_2Ph.

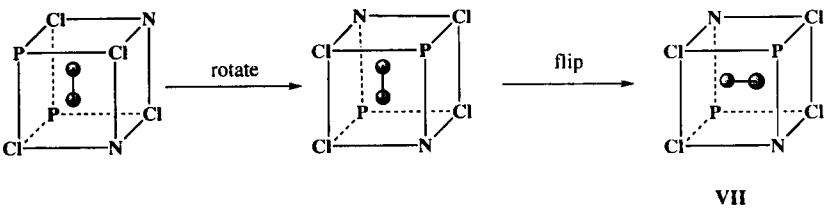
$NHCMe_3^-$ ligands would dissociate, as an initial step, is very remote, but dissociation of a phosphine ligand had to be checked. When this was done, initially in a qualitative way, it was found that the addition of excess phosphine measurably lowered the isomerization rates in both directions. The results for the trans → cis reaction are shown in Figure 9.

Clearly then, there is an important reaction pathway that entails the dissociation of a phosphine ligand as either the rate determining step or as a necessary preequilibrium. One such pathway is shown in Figure 10. In this mechanism, after loss of a PR_3, the Cl atom on the same W atom that does not participate in hydrogen bonding to the $NHCMe_3$ ligand on the other end shifts to the position vacated by the PR_3. This PR_3 then returns to the same metal atom, but it now finds itself directly opposite the PR_3 group on the other metal atom. This is a sterically unfavorable situation that can lead to loss of PR_3 from the other metal atom, after which there is a Cl shift and recapture of the PR_3.

An attractive variant of this mechanism is shown in Figure 11. In this case, after the first PR_3 dissociation and the shift of the non-hydrogen-bonded Cl, there is a transfer of the PR_3 ligand from the other metal atom. This is followed by a Cl shift on the other metal atom, and the process is then completed by recapture of the PR_3 group whose dissociation began the whole chain of events.

It should be noted that in either of the above forms, this dissociation mechanism is capable of accounting for an inverse dependence of rate, in both directions, on the concentration of added PR_3. However, the next step, a quantitative experimental study led to further complications. Table 2 shows the effect of successive additions of PMe_2Ph on the rate constant for the *trans* to *cis* conversion. After a substantial decrease upon addition of 0.0021 M PMe_2Ph, the rate did not show any further persistent decrease, but instead remained constant at a value 7.6(1.3) over a range of phosphine concentrations from 0.0063 to 0.415 M.

The interpretation of these results seems unambiguous. There must be some other mechanism that does not depend on the concentration of excess phosphine, that is, a unimolecular mechanism. This second mechanism is only slightly slower than the dissociative mechanism in the absence of added phosphine, so that, when the dissociative pathway is slowed by the addition of excess phosphine, the second mechanism takes over. This, of course, raises the intriguing question of what

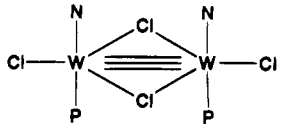


VII

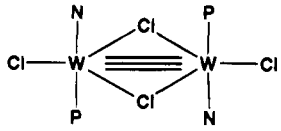
Figure 12. Another unimolecular isomerization that could occur by way of a rate-determining internal flip.

this second mechanism could be. Clearly, a valid possibility is the internal flip mechanism already mentioned and shown in Figure 8.

The important question now is whether there is any other acceptable unimolecular mechanism. The only answer we can give is that we have not been able to invent one. The only ligand migration process that seems reasonable would begin by having two Cl atoms slip into bridging positions, thus generating either **V** or **VI**. However, we can see no way that this would



V



VI

lead to the observed isomerization. If the bridging Cl atoms each pass on to the other metal atom, the *trans* configuration is recovered, albeit with a scrambled set of Cl ligands. While both of these bridged structures entail trigonal bipyramidal configurations at the metal atoms, the recognized modes of rearrangement for such tbp species, that is a Berry or turnstile process, are both ruled out. The tying together of two Cl atoms by the bridging role they play and the unlikelihood of the other ligands assuming a bridging role make the Berry and the turnstile, respectively, unacceptable events.

If we therefore adopt the internal flip process as the second mechanism, with a rate of *ca.* 8×10^{-3} min^{-1} at 50 °C (1.3×10^{-4} s^{-1} at 323 K) we can estimate the activation energy for the rate-determining internal flip as 24.5 kcal/mol ($\Delta G^{\ddagger}$ from the absolute rate theory) or 25−29 kcal/mol (E_a in the Arrhenius equation) taking the pre-exponential factor as $10^{13}-10^{16}$.

A Caveat. It must be noted that there is a very puzzling aspect to the observations reported here, namely, the absence in any of the four systems studied of the remaining possible *cis* isomer, shown as **VII** in Figure 12. It is non-chiral since it has C_i symmetry. There is no reason evident to us why this isomer should not be thermodynamically competitive with **I** and **II**. Moreover, as shown in Figure 12, it could be obtained by a mechanism entailing only one internal flip. However, lest it be concluded, incorrectly, that the internal flip pathway shown in Figure 8 must be excluded on this basis, it will be noted that the pathways shown in Figures 10 and 11 could give rise to a rotomer of **VII** if the Cl atom switch in step 4 were to go in the other possible direction. Thus, while these molecules may be the first ones to provide examples of the internal flip process in a molecule having eight separate unidentate ligands about a central M_2^{n+} unit, there is still much that is not clear about both the kinetic and the thermodynamic aspects of their behavior. We intend to study these and related systems more closely, including, if they are obtainable, the Mo_2 analogs. It is also pertinent to mention that the internal flip process discussed here with an M_2 cluster should be viewed as related to the processes investigated by Johnson and co-workers, in which M_3 and M_4 clusters undergo flips within the cavity created by a set of CO ligands.[13]

Acknowledgment. We thank the National Science Foundation for financial support.

(13) Johnson, B. F. G.; Roberts, Y. V.; Parisini, E. *J. Chem. Soc., Dalton Trans.* **1992**, 2573 and references therein.