Cis−*Trans* Isomerization in Triply-Bonded Ditungsten Complexes: A Multitude of Possible Pathways

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Received May 2, 2001

We have investigated different possible mechanisms for the cis−trans isomerization in triply bonded ditungsten complexes with stoichiometry $W_2Cl_4(NHEt)_2(PMe_3)_2$ using static density functional calculations as well as Car-Parrinello simulations. Our studies reveal an unexpected richness of possible reaction pathways that include both unimolecular and bimolecular mechanisms. Among the possible routes that have been identified are processes involving successive dissociation/reassociation of phosphine ligands, intramolecular chloride hopping, intertungsten phosphine exchange as well as numerous combinations of these basic reaction types. All pathways involve maximal activation barriers of less than 35 kcal/mol and include phosphine concentration dependent and independent routes. The energetically most favorable phosphine-dependent pathway is based on the dissociation/reassociation of phosphine ligands. This path is characterized by a maximal dissociation barrier of 18 kcal/mol. The fastest alternative unimolecular route (with a maximal activation barrier of 24 kcal/mol) is based on a direct exchange of phosphine between the two metallic coordination centers. All the identified pathways, with the exception of a previously proposed internal flip mechanism that can be ruled out on energetic grounds, are competitive and may contribute in various combinations to the overall reaction rate. The identified isomerization mechanisms are fully consistent with the experimentally observed 3-state-kinetics and the dependence of the overall reaction rate on the excess concentration of phosphine which is demonstrated with a simplified kinetic model of the process.

1. Introduction

Molecules with stoichiometry $(PR'_3)(NHR)Cl_2W-WCl_2(NHR)(PR'_3)$ can form three isomeric compounds, a *trans* and two *cis* isomers with C_i and C_2 symmetry (Figure 1), that fulfill two stability governing principles: (i) they form two intramolecular hydrogen-bonds between chloride and amido ligands in opposite coordination spheres and (ii) the bulky phosphine ligands do not occupy adjacent coordination sites. In fact, among all the possible permutational isomers, these three forms are the only ones that are consistent with these two rules. For several systems (e.g., for complexes with R = CMe_3 and R′ = Me, Et, Pr^n, Me_2Ph,[1,2] and related compounds[3] such as $W_2Cl_4(NHCMe_3)_2(L-L)$ (with L−L = dmpm, dmpe, dppm, dppe),[4] it was possible to observe the *trans* and the *cis*-C_2 isomers experimentally. The third possible isomer with *cis*-C_i symmetry, on the other hand, has proven to be more elusive. In fact, up to date there exists only one system, $W_2Cl_4(NHR)_2(PMe_3)_2$ (with R = Et, Pr^n, and Bu^n), for which this form has been detected.[5]

These triply bonded tungsten complexes exhibit also a particularly interesting interconversion behavior. The *trans* compound is formed as initial product of the synthetic process, while the *cis*-C_i isomer appears as intermediate and the cis-C_2 as final product. Some suggestions about possible *cis*−*trans* isomerization mechanisms in these systems have been put forward,[1,3b,5−7] but the detailed mechanisms of the interconversion processes are still unknown. From experimental observations it has been interferred that at least two independent pathways for isomerization exist.[1,5] Measurements of the overall rate constant of the reaction as a function of the excess phosphine concentration show an initial drop and level off subsequently to a constant, phosphine independent rate. Cotton et al. suggested[1,5] that the initial rate dependence is due to an isomerization mechanism involving phosphine ligand dissociation and that the phosphine concentration independence originates from a slower unimolecular pathway that possibly involves an internal flip of the W−W unit as depicted schematically in Figure 2.[1,3b,5]

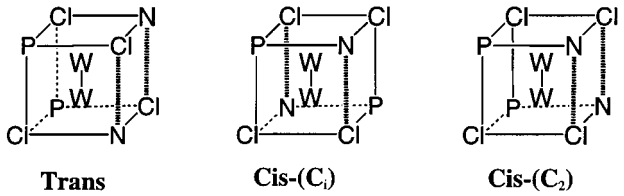

Figure 1. Schematic representation of the three isomeric forms of $W_2Cl_4(NHEt)_2(PMe_3)_2$. Intramolecular hydrogen bonds between the amido and the chloride ligands are indicated by thick dashed lines.

The fast pathway can be blocked by a larger excess concentration of PMe_3 whereas the presence of the slower, phosphine concentration-independent route is consistent with the constant, non vanishing value of the reaction rate at high PMe_3 excess. The experimental estimate of the free energy barrier for the slower unimolecular pathway is 25−30 kcal/mol.[1]

(1) Chen, H.; Cotton, F. A.; Yao, Z. *Inorg. Chem.* **1994**, *33*, 4255.
(2) Cotton, F. A.; Yao, Z. *J. Clus. Sci.* **1994**, *5*, 11.
(3) A similar transition between rotational isomers has also been observed in quadruply bonded dimolybdenum complexes: (a) Fraser, I. F.; McVitie, A.; Peacock, R. D. *J. Chem. Res.* **1984**, 420. (b) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1986**, *25*, 15. (c) Cotton, F. A.; Dikarev, E. V.; Gu, J.; Herrero, S.; Modec, B. *J. Am. Chem. Soc.* **1999**, *121*, 11758.
(4) Cotton, F. A.; Dikarev, E. V.; Wong, W. Y. *Inorg. Chem.* **1997**, *36*, 80.
(5) Cotton, F. A.; Dikarev, E. V.; Wong, W. Y. *Inorg. Chem.* **1997**, *36*, 2670.
(6) Magistrato, A.; VandeVondele, J.; Rothlisberger, U. *Inorg. Chem.* **2000**, *39*, 5553.
(7) Jean, Y.; Lledos, A. *Chem. Commun.* **1998**, 1443.

10.1021/ic010470+ CCC: $20.00
Published on Web 10/11/2001

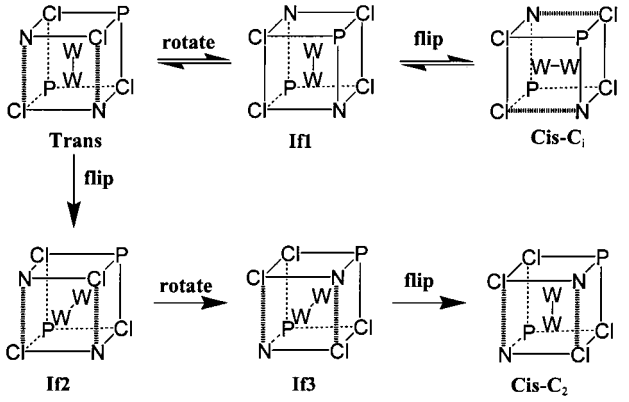

Figure 2. Schematic representation of the internal flip mechanism according to Cotton et al.[1,3b,5] Intramolecular hydrogen bonds between the amido and the chloride ligands are indicated by thick dashed lines. Note the absence of any intramolecular hydrogen bond in structure **If1**.

We have recently characterized the structural, electronic and dynamic properties of the three stable isomeric forms using ab initio molecular dynamics simulations[8,9] based on density functional theory (DFT). Our calculations[6] were able to reproduce the structural and energetic properties of these systems surprisingly well. In particular, DFT calculations with two different models for the exchange and correlation energy predicted both the *cis*-C_2 isomer as the most stable form in agreement with the experimental findings. In our previous study, we were also able to establish that the initial dissociation of one or two phosphine ligands can occur as a low-energy reaction channel. This suggested that phosphine dissociation could indeed be involved in the isomerization, but several indications pointed to the fact that the real process is more complex.[1,5,6]

Herein, we use the same technique for a detailed study of the possible interconversion mechanisms. Surprisingly, in view of the deceiving simplicity of the system, we find that the reaction mechanism is amazingly complex and involves a multitude of possible reaction pathways including channels based on dissociation/association of phosphine, internal hopping of chloride ligands and intermetallic exchange of phosphine between the two coordination centers. All pathways involve maximal activation barriers in the range of 18−35 kcal/mol consistent with the experimental estimates of the involved barriers of ca. 25−30 kcal/mol.[1] These basic reaction types can combine in various ways generating a whole manifold of possible interconversion paths. The overall energetics of many routes is comparable so that it is likely that a multitude of channels participates in the actual isomerization process. The only mechanism that can be excluded is the previously suggested internal flip mechanism, which seems to involve too high a barrier to be competitive with the other pathways. The lower-energy channels that we have identified here include both routes that are dependent and independent of phosphine concentration and we are also able to rationalize possible channels to the transient intermediate *cis*-C_i. Our results are thus consistent with the main qualitative features of the observed kinetics as demonstrated with the explicit solution of a simplified kinetic model in Section 3.5.

2. Details of the Computational Scheme

For the identification of possible isomerization pathways, we have performed ab initio molecular dynamics (Car-Parrinello) simulations[8,9] at elevated temperatures. The quantitative characterization of metastable intermediates and transition states were achieved via constrained molecular dynamics (MD) runs along appropriately chosen reaction coordinates[10] in combination with local optimization techniques based on preconditioned conjugate gradient minimization and direct inversion of the iterative subspace algorithms.[11] All the calculations were performed with the program CPMD,[12] which is an implementation of the original Car-Parrinello scheme based on density functional theory (DFT), periodic boundary conditions, plane wave basis sets and a pseudo potential formalism. If not mentioned otherwise, our computational setup is identical to the one in ref 6 where full details are given and the adequacy of our computational scheme has been demonstrated thoroughly. As in our previous study, we use again two different descriptions for the exchange-correlation functional, BP[13,14] and BLYP.[13,15] Whereas the former results in an improved description for these systems,[16] the latter was used in order to assess the sensitivity of our calculations with respect to the chosen model for correlation which can be particularly delicate in the description of transition metal complexes.

All our calculations refer to gas-phase complexes whereas the kinetic measurements[1] were performed in THF/C_6D_6. We expect that the presence of a relatively apolar environment such as the one of THF/C_6D_6 does not lead to any major changes in the relative stabilities of the different species but subtle variations cannot be excluded. The same is likely to hold for the influence of entropic effects. Possible small alterations of our calculated values due to the neglect of solvent and entropy are pointed out for specific cases in Section 3.

3. Results and Discussion

A series of short (1−2 ps) Car-Parrinello runs at low and elevated temperatures (from 400 to 1500 K with increments of approximately 200 K) were used to explore an extended part of the potential energy surface and to trace down possible reactive pathways. These studies lead in particular to the identification of phosphine dissociation as the initial lowest-energy channel for all three isomeric forms. The fact that this process was observed at very different temperatures (around ∼600K for the *trans*, ∼1200K for the *cis*-C_i and around ∼1500K for the *cis*-C_2 compound) suggested that the three isomeric forms might exhibit large differences in the activation barriers for phosphine dissociation.[6] These initial studies motivated a detailed quantitative characterization of possible isomerization mechanisms based on successive dissociation and reassociation of phosphine ligands.

3.1. Dissociation/Association of Phosphine Ligands. Two different possible pathways are conceivable that yield qualitatively different reaction kinetics. The first route from the *trans* to the *cis* isomers (shown schematically in Figure 3a) involves two successive dissociations of phosphine ligands followed by two successive association reactions.

(8) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
(9) (a) Car, R.; Parrinello, M., Proceedings of NATO ARW: *Simple Molecular System at very High Density*; Les Houches, France, 1988; NATO ASI Series; Plenum Press: New York. (b) Galli, G.; Parrinello, M. *Computer Simulation in Material Science*; Meyer, M., Pontikis, V., Eds.; Fluwer: Dordrecht, The Netherlands, 1991, 238. (c) Remler, D. K.; Madden, P. A. *Mol. Phys.* **1990**, *70*, 691. (d) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045. (e) Marx, D.; Hutter, J. *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; Forschungszentrum Juelich, NIC Series, 2000; Vol.1, 301.
(10) Sprik, M.; Ciccotti, G. *J. Chem. Phys.* **1998**, *109*, 7737.
(11) Hutter, J.; Lüthi, H. P.; Parrinello, M. *Comput. Mater. Sci.* **1994**, *2*, 244.
(12) Hutter J.; Ballone P.; Bernasconi M.; Focher P.; Fois E.; Goedecker S.; Parrinello M.; Tuckerman M. Max-Planck-Institut für Festkörperforschung and IBM Zurich Research Laboratory 1995−96.
(13) Becke, A. D. *Phys. Rev. A* **1998**, *38*, 3098.
(14) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(16) Ziegler, T. *Density Functional Methods in Chemistry and Material Science*; Wiley: New York, 1997; p 69.

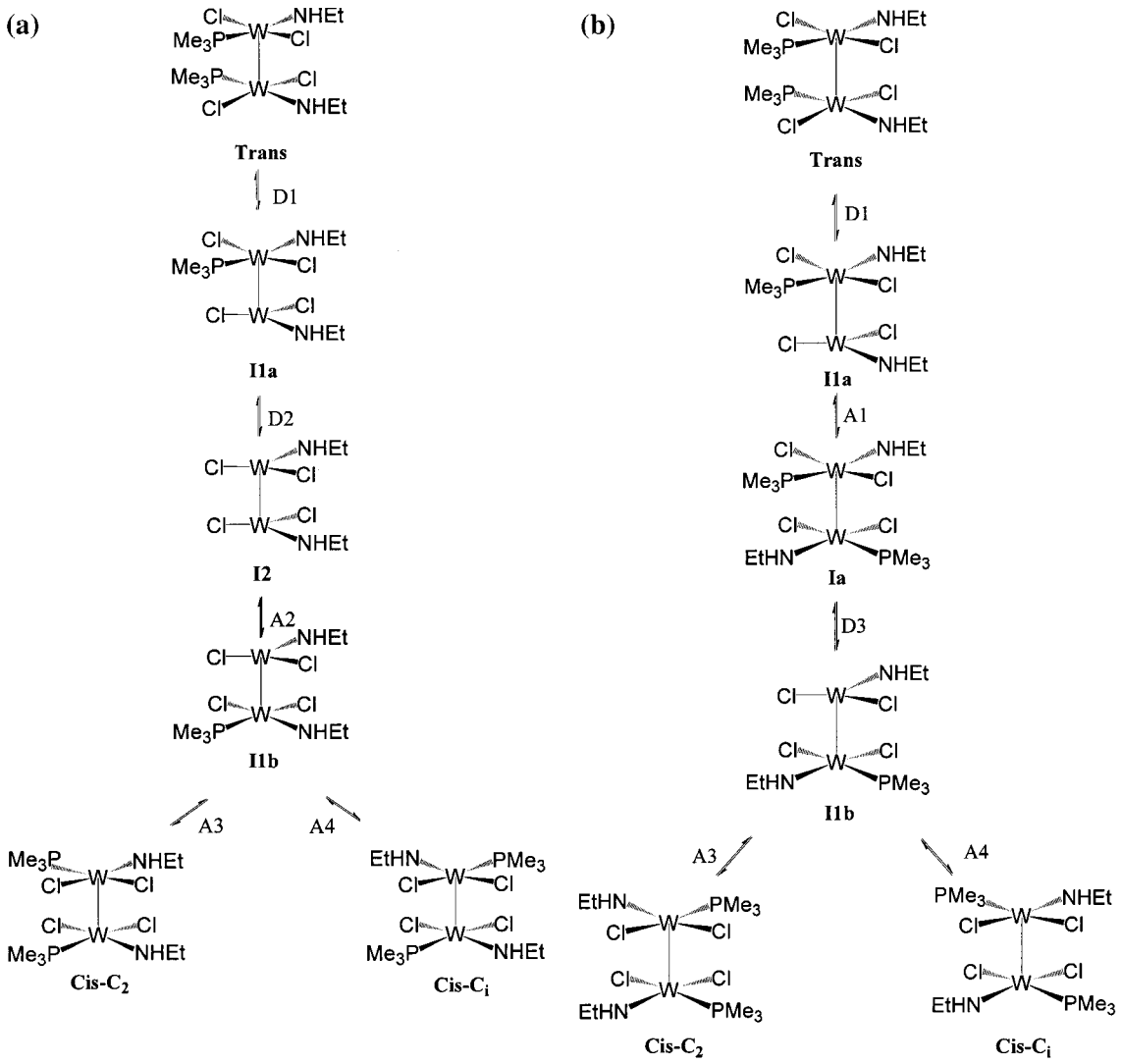

Figure 3. Schematic representation of the two possible *cis*−*trans* isomerization pathways via dissociation/reassociation of phosphine ligands. (a) Mechanism involving consecutive loss of both phosphine ligands and (b) Mechanism involving sequential dissociation/reassociation events. Stable intermediates are indicated with **I** and transition states are indicated with **A** for associative and **D** for dissociative steps.

There are three stable intermediates involved, the first having one phosphine and the amido ligand in *trans* position (**I1a**), the second having no phosphine ligands (**I2**), and the third having one phosphine and one chloride ligand in *trans* position (**I1b**). The second pathway (Figure 3b) involves two consecutive dissociation/reassociation events of only one phosphine ligand. Also this mechanism proceeds via three stable intermediates, **I1a**, **I1b** and a new form, **Ia**, which has one phosphine ligand on each tungsten atom, but one coordination center has the chloride ligands in *cis* and the other in *trans* position. Both pathways can lead to either of the two *cis* isomers, since the final association step to the intermediate **I1b** is common to both pathways, and can yield both *cis*-C_i and *cis*-C_2. It is thus the relative difference in activation barrier for association to the two *cis* isomers that determines if an intermediate *cis*-C_i can be observed during the reaction. It is also apparent that the overall rate constant for the two pathways depends differently on the initial excess concentration of PMe_3. The first interconversion route (Figure 3a) will be slowed if the initial concentration of phosphine is increased, whereas the second one (Figure 3b) is independent of the phosphine concentration. In fact, even though the concentration of the dissociated intermediate **I1a** is decreased upon addition of PMe_3 (as the equilibrium is shifted toward the undissociated form), the forward association step to **Ia** is equally accelerated. This independence on PMe_3 concentration can be demonstrated, using the assumption that the concentration of the intermediates (**I1a**, **I1b**, **Ia, I2**) is steady and small. Within this assumption the kinetic equation for the second dissociation/association pathway is given by

$$\frac{d[trans]}{dt} = -\frac{(k^b_{1a}k^b_a k^b_{1b}k^b_c + k^f_{1a}k^f_a k^f_{1b}k^f_t)[trans] - k^b_{1a}k^b_a k^b_{1b}k^b_c[T_0]}{k^b_{1a}k^b_a k^b_{1b} + k^f_{1a}k^f_a k^f_{1b} + k^b_{1a}k^b_a k^f_{1b} + k^b_{1a}k^f_a k^f_{1b}} \quad (1)$$

where the lower index (1a,a,1b,2,c,t) of the rate constant k specifies the state (**I1a**, **Ia**, **I1b**, **I2, *cis, trans***), the upper index (*b,f*) stands for backward and forward, and $[T_0]$ is the initial concentration of the *trans* complex. The same does not hold for the first interconversion route (Figure 3a):

$$\frac{d[trans]}{dt} = -\frac{(k^b_{1a}k^b_2 k^b_{1b}k^b_c + k^f_{1a}k^f_2 k^f_{1b}k^f_t)[trans] - k^b_{1a}k^b_a k^b_{1b}k^b_c[T_0]}{k^b_{1a}k^b_a k^b_{1b} + k^f_{1a}k^f_a k^f_{1b} + (k^b_{1a}k^b_2 k^f_{1b} + k^b_{1a}k^f_2 k^f_{1b})[PMe_3]} \quad (2)$$

Table 1. Relative Energies of Intermediates (kcal/mol)[a]

Ex-Corr	*trans*	*cis*-C_i	*cis*-C_2	**Ia**	**Ib**	**Ic**	**I1a**	**I1b**	**I2**
BP	0.0	1.0	−1.4	9.9	12.1	17.9	15.7	16.3	31.9
BLYP	0.0	2.5	−0.3	10.2	12.2	17.1	9.4	10.4	20.1

[a] Relative energies of intermediates (kcal/mol). All energies are relative to the *trans* isomer. For the species involving dissociated phosphine ligands the energy of the free phosphine molecule is taken into account. Labels are as in Figures 3−6.

Table 2. Activation Energies for Dissociation (kcal/mol)[a]

Ex-Corr	**D1**	**D2**	**D3**	**A1**	**A2**	**A3**	**A4**
BP	18.2	36.5	21.4	32.7	40.3	21.3	25.3
BP^{for}	18.2	20.8	11.5	17.0	8.4	5.0	9.0
BLYP	12.6	26.4	17.2	27.4	29.8	17.1	21.1
BLYP^{for}	12.6	17.0	7.0	18.0	9.7	6.7	10.7

[a] Relative energies of the transition states for phosphine dissociation (kcal/mol). All energies are relative to the *trans* isomer. For the species involving dissociated phosphine ligands the energy of the free phosphine molecule is taken into account. Activation energies for the forward reaction (from *trans* to *cis*) are indicated with a superscript "*for*". Labels are as in Figure 3.

Note that eq 2 depends explicitly on [PMe_3] whereas eq 1 does not.

We have performed a detailed characterization of all intermediates using local optimization techniques; and transition states of both pathways have been determined using the W−P distance as a reaction coordinate. The resulting relative energies of the intermediates are given in Table 1. In view of its superior performance for the description of transition metal complexes,[16] the values obtained with the BP functional are the best estimates we can give at the current state.

Corresponding values with the BLYP functional have been included as an indication of the sensitivity of the obtained results with respect to the specific correlation functional. The BLYP functional generally underestimates the relative energy differences significantly, but both descriptions predict the same relative trends. We have previously demonstrated that the *cis*-C_2 isomer is predicted to be the most stable form while the *trans* isomer is 1.4 kcal/mol and the *cis*-C_i isomer 2.4 kcal/mol higher in energy.[6] The relative stabilities of the *trans* and the *cis*-C_i isomer are reversed with respect to the experimental findings.[1] However, relative energy differences as small as 1 kcal/mol are certainly at the limit of accuracy of our computational method and small deviations can also be expected when entropic contributions or solvent effects are taken into account.

All the other intermediates of the dissociative/associative pathways (**Ia**,**I1a**,**I1b**, and **I2**) lie at high energies, in the range of 10−32 kcal/mol above the energy of the *trans* isomer. The concentrations of these species during the reaction are therefore minute and most probably beyond the limit of experimental detection. The involved activation energies for dissociation/association steps are given in Table 2.

These values demonstrate that the dissociation of at least one of the phosphine ligands is a rather fast reaction with an activation energy of the order of 18 kcal/mol. Furthermore, due to entropic contributions, the free energies of dissociation can be expected to be substantially lower than these values. Indeed, in our ab initio molecular dynamics runs of a few picoseconds, it is possible to observe spontaneous dissociation of phosphine from the *trans* isomer at temperatures as low as 600 K. We have previously shown that the initial barriers for phosphine dissociation are distinctly different for the three isomeric forms and vary in the order *trans* (18kcal/mol) < *cis*-C_2 (21 kcal/mol) < *cis*-C_i (25 kcal/mol).[6] The markedly lower activation energy of the *trans* isomer can be rationalized in terms of a classic *trans* effect of the amido ligand and is consistent with the observed thermal instability toward isomerization to the *cis* forms. The same holds for the relative variations of all the other barrier heights for dissociation/association. The maximal barrier for the pathway involving two successive dissociations is about 21 kcal/mol, while the one involving sequential dissociation/association steps is only 18 kcal/mol. These data thus suggest that the phosphine concentration-dependent pathway (Figure 3a) is somewhat higher in energy. However, we should stress again that the calculated values are only internal energies, and no entropic contributions have been taken into account. The barriers and relative stabilities at finite temperature can be slightly different, in particular, an entropic contribution favors dissociated states and therefore lowers the dissociation barriers with respect to the corresponding calculated values. Additionally, the relation between the overall rate constant and the highest barrier in a given pathway is not straightforward and might depend in particular on the excess concentration of phosphine that is present, e.g. at very low concentrations of phosphine the double dissociation path (Figure 3a) is favored (as we shall show in Section 3.5).

The association to **I1b** is the step that determines the intermediate concentrations of the *cis*-C_i and the *cis*-C_2 isomer. The calculated values given in Table 2 show that the barriers for this step are within 4 kcal/mol the same for both isomers, being slightly larger for the association to the *cis*-C_i isomer. However, since these barriers are particular sensitive to the specific description of exchange and correlation, we cannot definitively establish which of the two channels is faster. In addition, subtle solvent effects might be sufficient to induce a relative reversal in barrier heights. This delicate balance between a 2-state (with only the *trans* and the *cis*-C_2 forms) or a 3-state kinetic model (with the *cis*-C_i form as an additional transient intermediate) is in general agreement with the available experimental data. It is important to notice that both dissociation/association models are in principle capable of rationalizing the interconversion from the *trans* form to the *cis*-C_2 isomer and the possible occurrence of a *cis*-C_i intermediate. Furthermore, as the two possible reaction pathways in Figure 3a and b constitute both a phosphine concentration dependent and independent path, they are also consistent with the observed behavior of the overall rate constant as a function of excess concentration of phosphine.[1] Indeed, a simplified kinetic model based solely on such events only is sufficient to reproduce the qualitative features of the observed isomerization kinetics (vide infra). We would therefore like to point out, that in principle, the observed experimental data can be interpreted consistently based on a dissociative mechanism only without the need for an additional intramolecular pathway as originally interfered from the experimental measurements.[1,5]

However, as the existence of unimolecular, phosphine concentration independent isomerization mechanisms cannot be excluded we have investigated this possibility in great detail. The results of our search for alternative interconversion routes are presented in the following Sections.

3.2. Internal Flip of the Tungsten−Tungsten Unit. A first suggestion for a second, slower unimolecular reaction channel has been made by Cotton et al.[1,3b,5] This hypothetical isomerization mechanism is shown schematically in Figure 2. It involves a rotation of one of the coordination planes by 90° and internal flips of the W−W bond within the ligand cage. Our short (1−2 ps) molecular dynamics simulations at elevated temperatures (600−1500 K) confirm that configurations with 90° rotated coordination planes are formed relatively easily. However, the specific rotated form (**If1**) involved in the

conversion from the *trans* to *cis*-C_i isomer (Figure 2) implies the loss of both intramolecular hydrogen-bonds and turns out to be a relatively high lying transition state with an energy of at least 16 kcal/mol (BLYP) with respect to the *trans* form. Therefore this is not a stable intermediate as previously suggested.[5] We have made several attempts to localize a possible transition state for the internal flip of the W−W unit that leads to **If2**, but all the paths that we have investigated lie invariably at very high energies (≥ 50 kcal/mol[17]). It seems that the simultaneous cleavage of all four coordination bonds between each tungsten atom and its ligands, as implied by the internal flip mechanism, is energetically highly disfavored. This is in agreement with a recent theoretical study of the isomerization processes in quadruply bonded dimolybdenum complexes for which the internal flip mechanism also turns out to be a high energy route.[7]

3.3. Internal Hopping of Chloride Ligands. Since an internal flip mechanism can be essentially ruled out on energetic grounds, we started an intensive search for possible energetically more relevant alternatives. A careful inspection of the finite temperature trajectories showed that the chloride ions are rather mobile and in particular the W−W−Cl angle is highly flexible.[6] This lead to the investigation of an alternative unimolecular isomerization mechanism that involves a hopping of the chloride ligands within the coordination plane of the tungsten atoms.

In contrast to the internal flip mechanism, this pathway (Figure 4a) involves no bond breakage and constitutes therefore a more promising candidate for a low energy route. It consists of a hopping of the chloride ions over either the phosphine or the amido ligand. The isomerization process is initiated by an out-of-plane movement of a chloride ion to a position in which the W−W−Cl angle becomes nearly 180°. Then either the phosphine or the amido ligand turns, via an intermediate trigonal geometry, around the W−W bond axis to take the vacant coordination site and finally the chloride ligand returns to the former coordination site of the migrated phosphine, respectively amido ligand. During this rearrangement all ligands remain coordinated as indicated by a bond shortening of the phosphine ligand, and only a limited bond elongation of 12% of the chloride ligand near the transition state. In this way, one of the coordination planes of the molecule can transform from a *trans* to a *cis* arrangement.

Several possible pathways based on such a hopping event exist to convert the *trans* isomer into either the *cis*-C_i or the *cis*-C_2 isomer. The isomerization reaction via chloride hopping is an intramolecular process. However, hopping can also occur after initial dissociation, linking the intermediates **I1a** and **I1b** (Figure 4b). Chloride hopping can therefore take part in both phosphine dependent and independent pathways. Additionally, since **Ia** and **Ib** can convert into one another by a rotation of 90 degrees of one coordination plane, both the *cis*-C_i and *cis*-C_2 are accessible from these common intermediates. As a consequence, the relative barrier height for the hop to either *cis* isomer can become decisive for the appearance of a *cis*-C_i isomer as a transient intermediate. For the calculation of the barriers for hopping, intermediates that can be formed by 90° rotations of the ligands around the W−W bond have also been considered. In particular, the intermediate **Ia** and its rotated analogue **Ib** both take part in the reaction. As mentioned

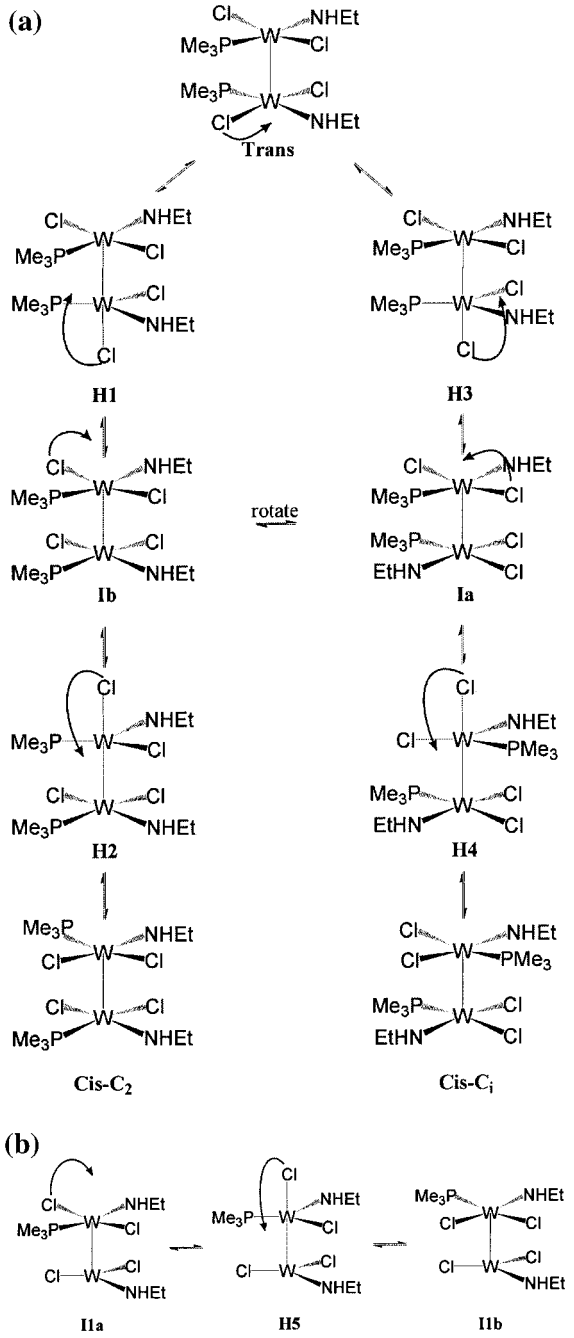

Figure 4. Schematic representation of the *cis*−*trans* isomerization pathways involving internal hopping of a chloride ligand. (a) The unimolecular pathways leading to cis-C_i and to cis-C_2, (b) the pathway involving the intermediates with only one coordinated phosphine. Stable intermediates and transition states are indicated with **I** and **H**, respectively.

previously, these configurations are rather easily interconvertable since e.g. the transformation from **Ia** into **Ib** involves only a rotation of the ligands within one of the coordination planes and no bond breaking. The calculated barriers for chloride hopping, based on the P−Cl−Cl−N dihedral angle as reaction coordinate, demonstrate that this mechanism implies maximal activation barriers of the order of 35 kcal/mol (shown in Table 3). This is close to the range of the experimentally estimated overall reaction barriers of the order of 25−30 kcal/mol.

Chloride hopping could therefore be a possible alternative mechanism that has been overlooked so far. Particularly noteworthy is the fact that the *cis*-C_i isomer can be reached with a much lower barrier than the *cis*-C_2 isomer. This reaction

(17) This rough estimate of the approximate energy involved in an internal flip of the W−W unit was calculated by choosing the torsional angle defined by the two midpoints of the coordination planes and the two tungsten atoms as reaction coordinate. The value given in the text has been calculated with the BLYP model for exchange and correlation and thus is likely to be a lower limit of the actual activation barrier.

Table 3. Activation Energies for Chloride Hopping (kcal/mol)[a]

Ex-Corr	H1	H2	H3	H4	H5
BP	35.1	36.7	34.9	30.8	43.4
BP^{for}	35.1	24.6	34.9	20.9	27.7
BLYP	35.0	36.7	34.7	31.2	37.1
BLYP^{for}	35.0	24.5	34.7	21.0	27.7

[a] Relative energies of the transition states for chloride hopping (kcal/mol). All energies are relative to the *trans* isomer. For the species involving dissociated phosphine ligands the energy of the free phosphine is taken into account. Activation energies for the forward reaction (from *trans* to *cis*) are indicated with a superscript "*for*". Labels are as in Figure 4.

Table 4. Activation Energies for Phosphine Exchange (kcal/mol)[a]

Ex-Corr	E1	E2	E3
BP	23.5	24.0	28.3
BP^{for}	23.5	6.1	12.6
BLYP	24.0		
BLYP^{for}	24.0		

[a] Relative energies of the transition states for phosphine exchange (kcal/mol). All energies are relative to the *trans* isomer. For the species involving dissociated phosphine ligands the energy of the free phosphine is taken into account.. Activation energies for the forward reaction (from *trans* to *cis*) are indicated with a superscript "*for*". Labels are as in Figure 5.

route provides therefore an additional channel for the transient stabilization of this intermediate. However, we note that the barrier for dissociation from the isomer **Ia** is lower than that for the hop by approximately 9 kcal/mol.

3.4. Intertungsten Phosphine Exchange. A further possibility that we have considered as potential unimolecular route consists of the direct exchange of a phosphine ligand between the two tungsten atoms. This mechanism is represented schematically in Figure 5a. Starting from the *trans* form, one phosphine ligand is transferred from one coordination center to the other via an intermediate configuration in which it is positioned about midway between the two tungsten atoms. This transition state, located using the distance of the phosphine to the other coordination center as a reaction coordinate, involves an activation barrier of ∼24 kcal/mol and is similar to the activated complex that has been previously reported for an unimolecular isomerization mechanism in quadruply bonded dimolybdenum complexes.[7] Barrier crossing leads to a metastable intermediate (**Ic**) with three ligands on one tungsten center and five on the other.

The steric crowding caused by the enhanced coordination is released by moving one of the chloride ligands to an almost perpendicular position above the coordination plane (similar to the transition state structure involved in chloride hopping). The undercoordinated tungsten center, on the other hand, assumes an approximately trigonal arrangement. This intermediate lies at an energy of about 17 kcal/mol with respect to the *trans* form. The isomerization cycle can be concluded by a reexchange of a phosphine ligand from the 5-fold to the 3-fold coordinated center. The involved activation barrier is essentially identical to the one of the forward reaction (∼24 kcal/mol with respect to the *trans* form and ∼6 kcal/mol with respect to the stable intermediate **Ic**). If the two exchange processes of phosphine ligands take place with the least possible geometrical rearrangements this process results in a direct route from the *trans* to the *cis*-C_2 isomer. Possible pathways to the *cis*-C_i isomer require much more drastic structural changes and are likely to lie at high energies. Phosphine exchange constitutes thus a prominent direct pathway to the *cis*-C_2 form. With a maximum barrier of 24 kcal/mol this process is again a possible competitive

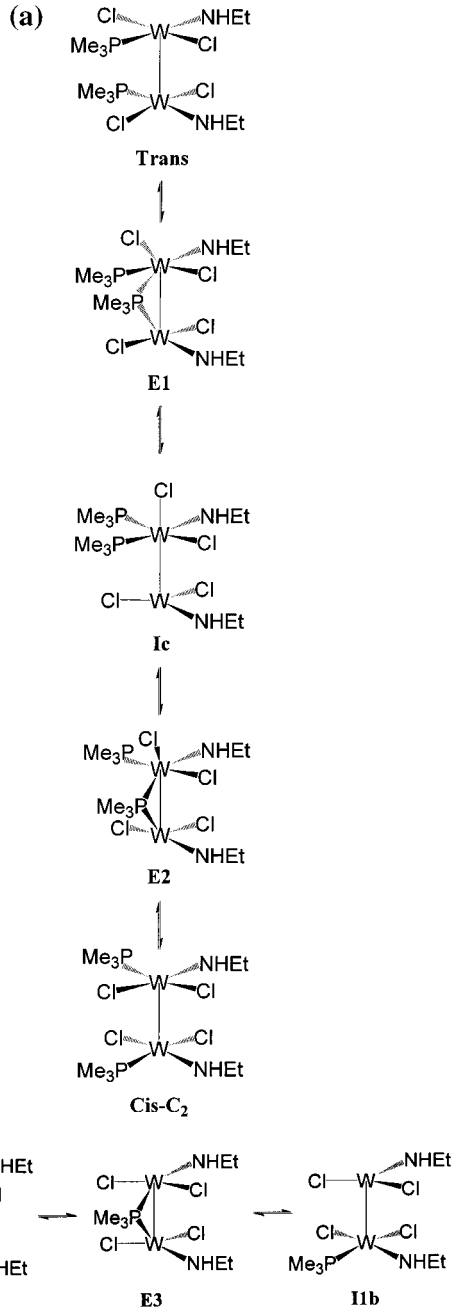

Figure 5. Schematic representation of the *cis*−*trans* isomerization pathway via exchange of phosphine ligands between the two tungsten centers. (a) The unimolecular pathway, (b) the pathway involving the intermediates with only one phosphine. Stable intermediates and transition states are indicated with **I** and **E**, respectively.

alternative to the dissociation/association and the chloride hopping models.

Additionally, this process can also occur between the dissociated intermediates **I1a** and **I1b** as shown in Figure 5b. Phosphine exchange therefore provides both phosphine concentration dependent and independent pathways.

3.5. Synopsis and Simplified Kinetic Model. The dissociation/reassociation mechanism and the pathways based on chloride hopping and intertungsten phosphine exchange all constitute energetically feasible routes for the *cis*−*trans* isomerization reaction of complexes of the form $W_2Cl_4(NHEt)_2(PMe_3)_2$. The overall kinetic scheme is even more complicated as all of these processes can also be combined with one another as different elementary reaction steps. An approximate overview of the existing routes is shown schematically in Figure 6.

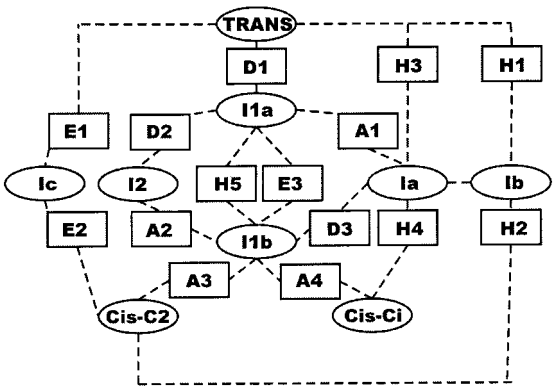

Figure 6. Schematic diagram of the different isomerization routes. Oval shapes represent stable intermediates and square boxes transition states. Dashed lines connect possible isomerization routes. **I** is a generic label for intermediates and **D**, **A**, **E**, and **H** refer to transition states of dissociation, association, tungsten exchange, and chloride hopping reactions. Detailed labels are the same as in Figures 3−5.

Clearly, a comprehensive kinetic scheme for this process is prohibitively complex. To make direct contact with the experimentally observed kinetic behavior we have therefore performed a series of simulations with a simplified kinetic model.

The kinetic equations for the associative/dissociative mechanism involving simultaneously the two pathways (Figure 3a and b) from *trans* to *cis*-C_2 have been solved, assuming a rate constant of the form

$$k = k_0 e^{\Delta E/kT} \rightarrow k = k_0 e^{-\Delta E/kT} \qquad (3)$$

where ΔE is the calculated value (BP) for the energy barrier, and k_0 was estimated to be in the range of 10^{13} s^{-1} to 10^{16} s^{-1}. [1] Here, we have chosen 10^{16} s^{-1} for uni-molecular and 10^{13} $Mol^{-1}s^{-1}$ for bi-molecular reactions, to account for entropic effects. The time dependence of the concentration of the *trans* compound is shown in Figure 7 for several values of the initial phosphine concentration.

Two observations can be made: (a) the rate constant decreases with increasing initial phosphine concentrations; (b) in agreement with the experimental observations[1] the rate saturates for high concentrations. As a consequence we can conclude that at low concentrations the mechanism involving two successive dissociation steps dominates, whereas at high concentrations the mechanism involving two successive association/dissociation steps is prominent. This is not in contradiction with the high energy of the intermediate **I2**, since for very low initial concentrations of phosphine the formation of this intermediate can be considered to be irreversible.

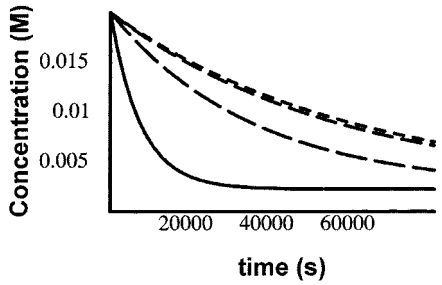

Figure 7. The concentration of the *trans* compound as a function of time, for several initial phosphine concentrations, as predicted by the simplified kinetic model (see text). The initial concentrations of phosphine are 0.002, 0.02, 0.2, and 2 M for the solid, long dashed, dashed, and short dashed line, respectively.

4. Conclusions

We have performed a detailed investigation of the mechanisms for *cis*−*trans* isomerization in triply bonded ditungsten complexes of the form $W_2Cl_4(NHEt)_2(PMe_3)_2$. Our static and dynamic density functional calculations reveal an unexpected high complexity of the kinetic properties of these molecules. At least three basic reaction types involving (i) the dissociation/reassociation of phosphine ligands; (ii) a hopping of chloride ions and (iii) an intertungsten phosphine exchange were identified that can all lead to an interconversion of the different structural isomers. All of the three basic reaction mechanisms are energetically rather competitive in the sense that they all involve maximal activation barriers in a range of 18−35 kcal/mol. The single steps of the three elementary reactions can be combined in an almost unlimited amount of ways resulting in a plethora of possible isomerization pathways. This high complexity prohibits the development of a fully comprehensive kinetic model for the isomerization process. However, all of the basic reaction pathways that have been identified in this work are consistent with the essential features of the experimentally observed kinetics. Formally, they can all lead either to a 2-state kinetic model involving the *trans* and the *cis*-C_2 form, or to a 3-state kinetic scheme with the *cis*-C_i isomer as an additional transient intermediate of the interconversion process. Furthermore, the multitude of isomerization pathways includes both phosphine concentration dependent and independent routes that are able to rationalize the experimentally observed variation of the overall reaction rate as a function of excess phosphine.

Acknowledgment. We thank F.A. Cotton for suggesting this study. J.V. and A.M. acknowledge funding from ETH internal grants.

IC010470+