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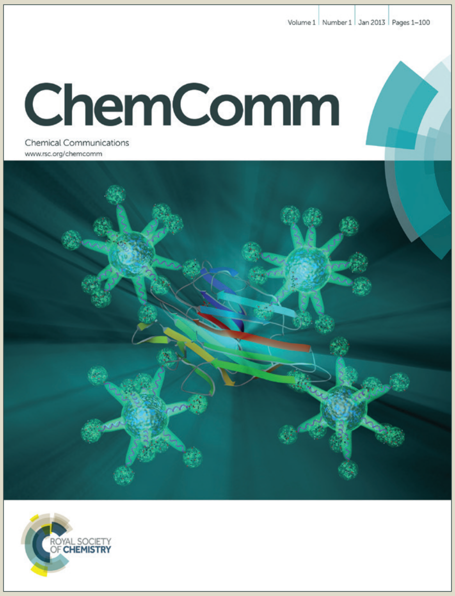

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Evidence for a Zwitterionic transition state in double bond rotations within tungsten-vinyl complexes.

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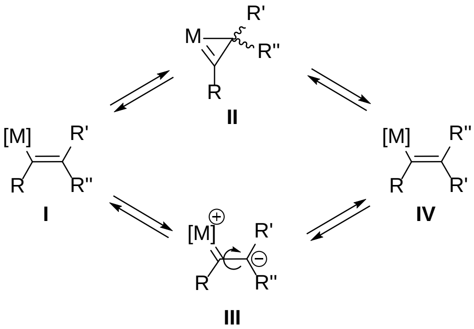
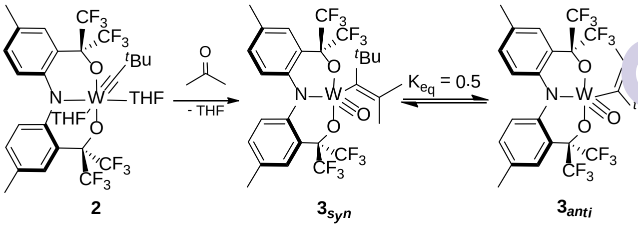
The trianionic pincer supported tungsten-vinyl complex [CF$_3$-ONO]W(O){(CH$_3$)$_3$CC=C(CH$_3$)$_2$} (3$_{syn}$) undergoes facile double bond rotation at ambient temperature. The degenerate methyl exchange rates were measured via selective inversion-recovery experiments. DFT computations in conjunction with experimentally determined rate constants support a double bond rotation that proceeds via a Zwiterionic transition state.

In general, C=C double bonds have a high energy barrier to rotation at ambient temperatures.[1-2] However, E/Z-alkenes do isomerize, and in fact the rate of isomerization for so called “push-pull” alkenes can be fast. “Push-pull” refers to alkenes with electron-donating/-withdrawing substituents at opposite ends of the alkene.[3-4] Proposed mechanisms for the E/Z isomerization in metal-vinyl species involve either formation of a metallacyclopropene intermediate[7] (Scheme 1: **II**), or formation of a Zwitterion[8] (Scheme 1: **III**). Some Ru-, Rh-, and Ir-vinyl complexes exhibit rapid C=C bond rotation.[5-11] The high d-electron count metals participate as the electron-donor in the push-pull partnership. Control of metal-vinyl C=C bond rotation during the hydrosilylation of alkynes[,5-11] is critical to stereochemical selectivity in the reaction and during 1,4-migration of metal centers employed in organic transformations.[12-13] Only one example of a metal ion participating as the electron-withdrawing partner (i.e. low d-electron counts) has been published.[14] Herein, we present a mechanistic study that offers compelling evidence for a facile and degenerate formal C=C bond rotation within a d^0 tungsten-vinyl complex.



Scheme 1. Proposed mechanisms for E/Z isomerization *via metallacyclopropene* (II) and Zwitterion (III) formation.

Previously reported,[15] treating the trianionic pincer ligand[16] precursor [CF$_3$-ONO]H$_3$ (**1**) with (^{t}BuO)$_3$W≡C^{t}Bu leads to the synthesis of [CF$_3$-ONO]W≡C^{t}Bu(THF)$_2$ (**2**). Complex **2** reacts rapidly, in a Wittig-like manner, with a variety of carbon-containing compounds to generate tungsten-oxo-vinyl complexes (Scheme 2). For example, treating complex **2** with acetone in C$_6$D$_6$ yields the oxo-vinyl complex [CF$_3$-ONO]W(O){(CH$_3$)$_3$CC=C(CH$_3$)$_2$} (**3**). Complex **3** forms initially as the *syn*-isomer **3$_{syn}$**, but slow rotation about the W-C bond (k = 2.1(1) x 10^{-5} s^{-1}) yields the *anti*-isomer **3$_{anti}$** and equilibrium establishes at 25 °C in a 2:1 ratio of *syn*:*anti*.[15] However, a second dynamic process occurs rapidly at 25 °C. The methyl groups on the W-vinyl ligand are in rapid exchange (Scheme 3).



Scheme 1. Synthesis of the oxo-vinyl complex **3$_{syn}$** and rotational isomerization to **3$_{anti}$**

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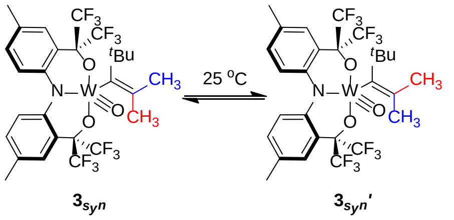


Scheme 2. Degenerate double bond rotation between $\mathbf{3}_{syn}$ and $\mathbf{3}_{syn}$'.

In the ^1H NMR spectrum of $\mathbf{3}_{syn}/\mathbf{3}_{syn}$' the methyl group *trans* (red) to the ^{t}Bu resonates at 2.89 ppm and the *cis*-methyl (blue) appears at 1.78 ppm. The methyl resonances at room temperature are sharp and do not indicate that a rapid dynamic process is occurring in solution. Thus, the unusual double bond rotation was initially overlooked.

Figure 1 presents, in blue, the recovery of the methyl signal at 2.89 ppm after selective inversion. The red squares represent the intensity of the methyl signal at 1.78 ppm at the same points in time. The initial decrease in the intensity of the signal at 1.78 ppm is due to exchange of population with the inverted signal. Eventually, both signals relax to equilibrium.

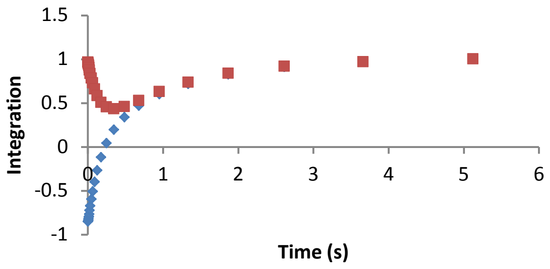
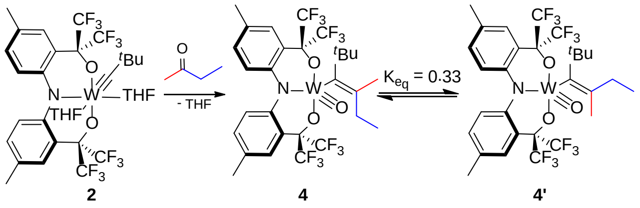


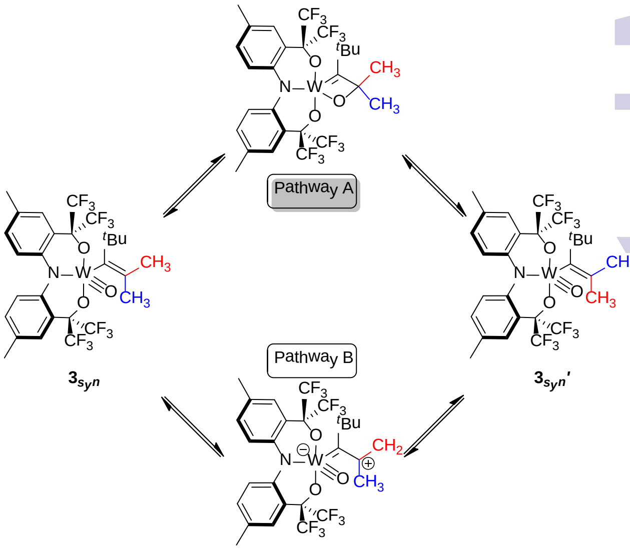
Fig. 1. Evolution of the intensity of the methyl signals at 2.89 ppm (blue) and 1.78 ppm (red) in a selective inversion-recovery experiment.

To ensure the dynamic exchange is not unique to the vinyl-dimethyl complex $\mathbf{3}_{syn}$, the vinyl-ethyl-methyl derivative was synthesized. Complex **2** reacts instantaneously with 2-butanone to generate the tungsten-oxo-vinyl species [CF_3-ONO]W(O){$(CH_3)_3CC=C(CH_2CH_3)(CH_3)$} (**4**) according to Scheme 4. Two isomers **4** and **4'** form in a ratio of 3:1, respectively. The major isomer **4** has the methyl group *cis* to the ^{t}Bu, whereas the minor isomer **4'** has the methyl *trans*. Indeed, **4** and **4'** interconvert rapidly at 25 °C (see Supporting Information).



Scheme 3. Synthesis of the tungsten-oxo-vinyl complex **4** and **4'**.

Analogous to proposed mechanisms for metal-vinyl double bond rotations (Scheme 1), two double bond isomerization mechanisms are proposed for complex $\mathbf{3}_{syn}$ in Scheme 5. Pathway A invokes an oxytungstenacyclobutene intermediate.[17] In this process one π-bond converts into one σ-bond, a process similar to electrocyclization reactions in organic chemistry.[18] During the electrocyclization, the methyl groups exchange either during the ring-closing or during the ring-opening process. In pathway B, as the double bond rotates, at the point of the π-bond rupture, a Zwitterionic intermediate forms generating an anionic tungsten center and a corresponding carbocation. The Zwitterion contains a C-C single bond, thus permitting the complete rotation. Another important feature is the development of W=C double bond character within the transition state.



Scheme 4. Possible pathways for the observed degenerate methyl exchange.

At twelve equally spaced temperatures over a 0 – 55 °C interval, the exchange rates were determined by iteratively fitting the rates in the selective inversion-recovery experiments and the relaxation rates in the non-selective ones. The CIFIT program by Bain and Cramer was employed to fit the data.[19] Plotting ln (k/T) versus 1/T (see Supporting Information for details) provides the thermodynamic parameters ΔH = 18.2(2) kcal·mol^{-1}, ΔS = 5.2(8) cal·mol^{-1}·K^{-1}, and ΔG = 16.6(3) kcal·mol^{-1}.

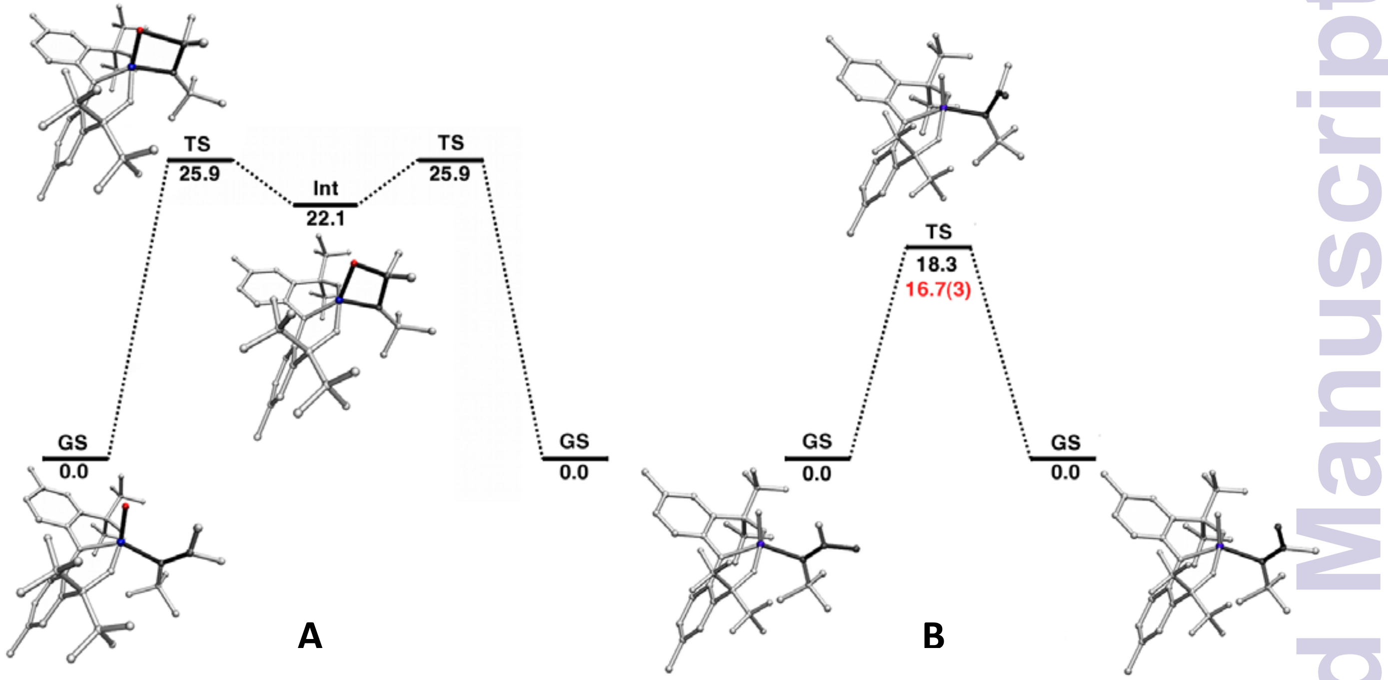


Fig 2. Potential energy diagrams for the methyl exchange through (Pathway A) metallacycle formation, and (Pathway B) a zwitterionic transition state. Relative energies in kcal·mol^{-1}.

DFT calculations help distinguish the two possible mechanisms for double bond rotation in $\mathbf{3}_{syn}$. Figure 2 depicts reaction coordinate versus free energy diagrams for the two different pathways; oxometallacycle (pathway A), and double bond rotation/Zwitterion (pathway B). In pathway A, the oxometallacycle transition state forms at 25.9 kcal·mol^{-1} and a slightly lower energy intermediate forms at 22.1 kcal·mol^{-1}. The free energy of both the transition state and intermediate are significantly higher than the experimentally determined barrier of ΔG = 16.6(3) kcal·mol^{-1}. A better fit to the experimental data comes within pathway B. Rotating the W-C=C-CH_3 dihedral angle incrementally provides intermediate energies as the double bond weakens. When the dihedral angle reaches 90°, the π-bond cleaves providing a transition state energy of 18.3 kcal·mol^{-1}, which is only 1.6 kcal·mol^{-1} above the experimentally determined value. Furthermore, inspection of the molecular orbital diagram generated from the transition state species reveals a HOMO-1 orbital that contains significant W=C double bond character, a hallmark for the Zwitterionic pathway (Figure 3).

It is plausible that methyl exchange can also occur within $\mathbf{3}_{anti}$. Indeed, the selective inversion recovery experiments reveal the exchange at 95 °C, but the elevated temperatures required prevent the determination of activation parameters in this case. However, DFT calculations reflect the need for higher temperatures with a computed barrier for the methyl exchange within $\mathbf{3}_{anti}$ of 24.8 kcal·mol^{-1} (see Supporting Information). A reason for the lower barrier for methyl exchange within $\mathbf{3}_{syn}$ versus $\mathbf{3}_{anti}$ is the relative orientation and distance of the developing carbocation to the W-oxo. In the ground state of $\mathbf{3}_{syn}$ the distance between the vinyl $[=C(CH_3)_2]$ carbon and the oxygen atom is 3.42 Å, whereas in the transition state the distance between the developing carbocation and the oxygen atom is only 2.79 Å. In contrast within $\mathbf{3}_{anti}$, due to its inherent *anti*-orientation it is impossible for the developing carbocation to associate with the W-oxo.

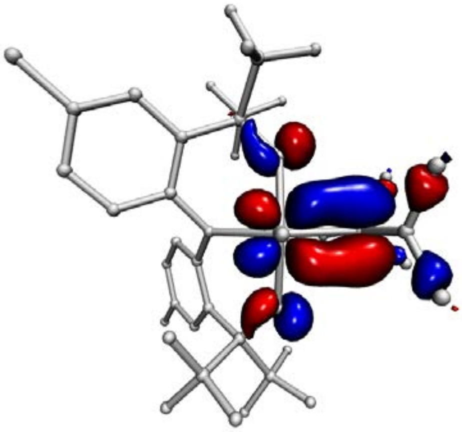


Fig. 3. HOMO-1 orbital of transition state species in Pathway B highlighting the formation of a W=C π-bond. Isovalue: 0.05.

In summary, double bond rotation within the W-vinyl complex $\mathbf{3}_{syn}$ is facile at ambient temperatures. Interestingly, kinetic data, in conjunction with DFT calculations, are consistent with a Zwitterionic transition state for the double bond rotation. Relative to "push-pull" electron rich Ru-, Rh and Ir-vinyl complexes that participate as the electron-donors complex $\mathbf{3}_{syn}$ contains an electron deficient d^0 metal ion that in contrast participates as the electron-withdrawing component. Metal-vinyl double bond rotation is important from the perspective of controlling stereochemical outcomes in metal-catalyzed hydrosilylation of alkynes.

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