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Carbon–hydrogen bond activation in cyclopentadienyl dimethyl tungsten nitrosyl and carbonyl†

Yubo Fan and Michael B. Hall*

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.
E-mail: hall@mail.chem.tamu.edu

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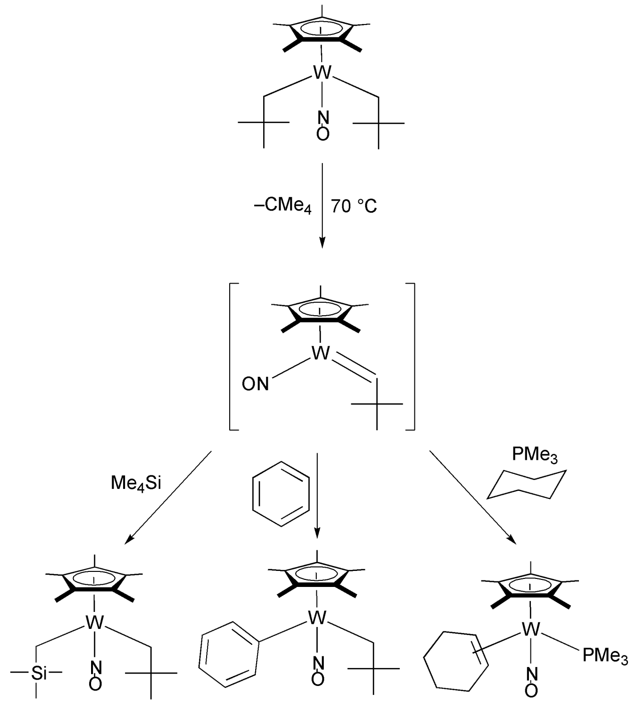
Mechanisms for generating tungsten carbene complexes from $CpW(NO)(CH_3)_2$, $Cp^*W(NO)(CH_3)_2$ and $[CpW(CO)(CH_3)_2]^-$ by methane elimination were studied by density functional (B3LYP) computations. Based on the calculations, a one-step (σ-bond metathesis like) mechanism is preferred in nitrosyl complexes, while a two-step (oxidative addition then reductive elimination) mechanism is preferred in the carbonyl complex. The one-step mechanism is strongly assisted by the metal as the transition state for this mechanism has a W–H distance that is only ≈0.1 Å longer than the W–H single bond in the oxidative addition intermediate. Stronger π backbonding of the NO ligand is responsible for the difference.

Introduction

In recent decades the activation of alkane C–H bonds has become a flourishing field in organometallic chemistry.[2,3] Numerous investigations have been undertaken to synthesize more effective transition metal complexes and to develop more useful reactions.

Although most studies have focused on late transition metals, such as Rh or Ir,[2,3] thermal activation of C–H bonds by tungsten alkylidene complexes, which are generated from $Cp^*W(NO)(CH_2t\text{-}Bu)_2$, have been reported recently.[4] Observed C–H bond activation reactions are summarized in Scheme 1. Because these reactions require heating at 70 °C for 40 hours, the activation energy for the rate-determining step, presumably, the formation of reactive carbene intermediate Cp*W(NO)(CH-*t*-Bu), must be large.

When the C–H activation reaction is effectively an exchange process, a recurring question is whether the reaction proceeds by a σ-bond metathesis or by an oxidative addition (OA) followed by a reductive elimination (RE). Theoretical studies on the low-temperature exchange reaction of $[CpIr(CH_3)(PMe_3)]^+$ established that this exchange proceeds through an OA/RE mechanism and predicted a potentially observable Ir(v) intermediate.[5] A similar question arises here. Does the H transfer from one neopentyl to the other proceed through a σ-bond metathesis with a single transition state (one-step mechanism in Scheme 2) or through OA, an intermediate, and RE (two-step mechanism in Scheme 2)? Recent theoretical calculations on this system[6,7] suggest that the reaction proceeds by the one-step mechanism. Here, with larger basis sets, we examine the alternative path (two-step mechanism in Scheme 2) in more detail and address the factors that influence the choice of paths in these cyclopentadienyl tungsten dialkyl systems.



Scheme 1

Theoretical methods

The theoretical calculations were carried out using the Gaussian 98[8] implementation of B3LYP [Becke three-parameter exchange functional (B3)[9] and the Lee–Yang–Parr correlation functional (LYP)[10]] density functional theory.[11] The basis set for tungsten was the effective core potentials (ECP) of Hay and Wadt (LanL2DZ)[12] as modified by Couty and Hall (341/341/21), where the two outermost p functions were replaced by a (41) split of the optimized tungsten 6p function.[13] The 6-31G* basis sets were utilized for all the carbon, nitrogen and oxygen atoms, the 6-31G** basis set was used for all hydrogen atoms on methyls or for the corresponding hydrogens in transition states, intermediates and products, and the 6-31G basis set was used for all hydrogen atoms on cyclopentadienyl and for the hydrogen and carbon atoms of methyls on pentamethylcyclopentadienyl.[14] All structures were fully optimized, and analytical frequency calculations were performed on each structure to ensure a minimum or *n*th order saddle point was

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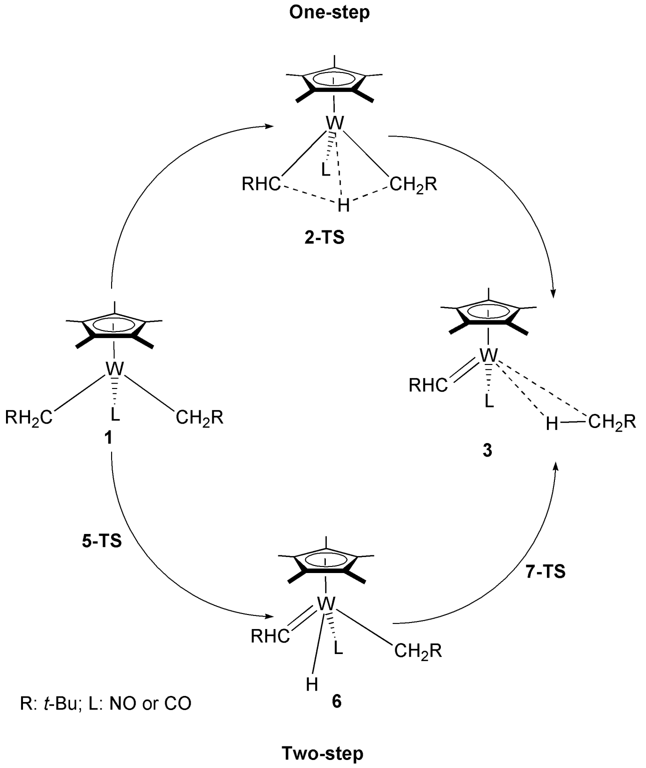
Table 1 Relative energies in the reaction of CpW(NO)(CH$_3$)$_2$

Species	ΔE/kcal mol^{-1}	ΔE_0/kcal mol^{-1}	ΔH/kcal mol^{-1}	ΔG/kcal mol^{-1}	ΔS/cal K^{-1} mol^{-1}
1	0.00	0.00	0.00	0.00	0.00
2-TS	37.11	35.17	34.61	35.93	−4.43
3	27.58	27.54	27.62	27.52	0.31
4	38.45	37.32	37.64	28.83	29.55
5-TS	40.41	38.59	37.83	39.65	−6.08
6	39.56	38.51	38.03	39.47	−4.83

Table 2 Structure parameters for species in Fig. 1

Structure parameters (Å, °)	**1**	**2-TS**	**3**	**4**	**5-TS**	**6**
W–N	1.776	1.786	1.790	1.790	1.822	1.839
N–O	1.202	1.202	1.202	1.201	1.189	1.185
W–C1	2.152	1.976	1.954	1.954	1.991	1.984
W–C2	2.150	2.365	2.664		2.286	2.296
W–H		1.799	2.053		1.729	1.706
W–Cp[a]	2.103	2.110	2.092	2.076	2.101	2.101
C1–C2	3.550	3.115	3.620		3.816	3.957
C1–H		1.723	2.544		2.074	2.386
C2–H		1.433	1.131		2.286	2.313
C1–W–C2	111.2	91.3	102.2		126.1	135.1

[a] Cp-midpoint of cyclopentadienyl.



Scheme 2

achieved. Zero point energy and thermodynamic functions were computed at 298.15 K and 1 atm.

Results

Reaction of CpW(NO)(CH$_3$)$_2$

The optimized structures of the species along the one- and two-step mechanisms for the reaction from CpW(NO)(CH$_3$)$_2$ to CpW(NO)(=CH$_2$) plus free methane are shown in Fig. 1. The relative energies without and with zero point energy (ZPE), enthalpies, Gibbs free energies and entropies of these species are listed in Table 1. Table 2 lists key structural parameters for the species in Fig. 1.

The reactant, **1**, is nearly C_s symmetrical, but the methyls are rotated slightly in the same direction about the C–W bonds. As mentioned in earlier work[7] the reactant shows evidence of slight α-agostic interactions by having slightly tipped methyl groups with one slightly longer (≈0.01 Å) C–H bond, and an unusually large C1–W–C2 angle because such a distortion uses the empty dπ orbital to stabilize the W–C bonds. The agostic complex, pro-product **3**, has a typical agostic W–H bond length of 2.05 Å, while the W–C1 bond length is shortened from 2.152 Å in **1** to 1.954 Å in **3**, as expected for the change to a W=C double bond. Along the one-step mechanism, the H transfers through a "σ-bond metathesis" transition state, **2-TS**. As expected both C1 and C2 are close to the H being transferred, 1.723 Å and 1.433 Å, respectively, but the difference in distance indicates a late transition state. W, C1, C2 and H are almost in the same plane and the dihedral angle of C1–W–H–C2 is 179.2°. Unexpected is the rather short, 1.799 Å, W–H distance calculated for this "σ-bond metathesis" TS (**2-TS**). This W–H distance corresponds to a fairly strong W–H interaction and raises questions about the electronic structure of this TS. The product, **4**, has a geometry about W, which is very similar to that of **3**. For this reaction path, the reactant, **1**, needs to overcome a 37.11 kcal mol^{-1} barrier to form the agostic complex **3**, which then dissociates to products **4**. Although the energy of **4** is ≈10 kcal mol^{-1} higher than that of **3**, **4** is favored entropically.

In contrast to the results of Poli and Smith,[7] we have found a stable intermediate corresponding to α C–H oxidative addition, **6**. The principal structural difference between **6** and **2-TS** is the 44° larger C1–W–C2 angle and the corresponding larger C1 ··· H and H ··· C2 distances. Surprisingly, the W–H bond is only 0.09 Å shorter. An IRC calculation confirmed that **5-TS** is in the reaction pathway directly from **1**. Unfortunately, the expected transition state ("**7-TS**") on the pathway from **6** to **3** was not found after extensive searching with various initial geometries and full frequency calculations. Intermediate **6** is 39.56 kcal mol^{-1} less stable than the reactant **1** and is only 2.45 kcal mol^{-1} higher than **2-TS**. The energy of the very late transition state **5-TS** is only 0.85 kcal mol^{-1} higher than that of **6**. Thus, the region around **6** is very flat for a fairly wide range of C1–H and C2–H distances.

Reaction of Cp*W(NO)(CH$_3$)$_2$

All of the optimized structures in the Cp*W(NO)(CH$_3$)$_2$ reaction system are shown in Fig. 2. The relative energies and

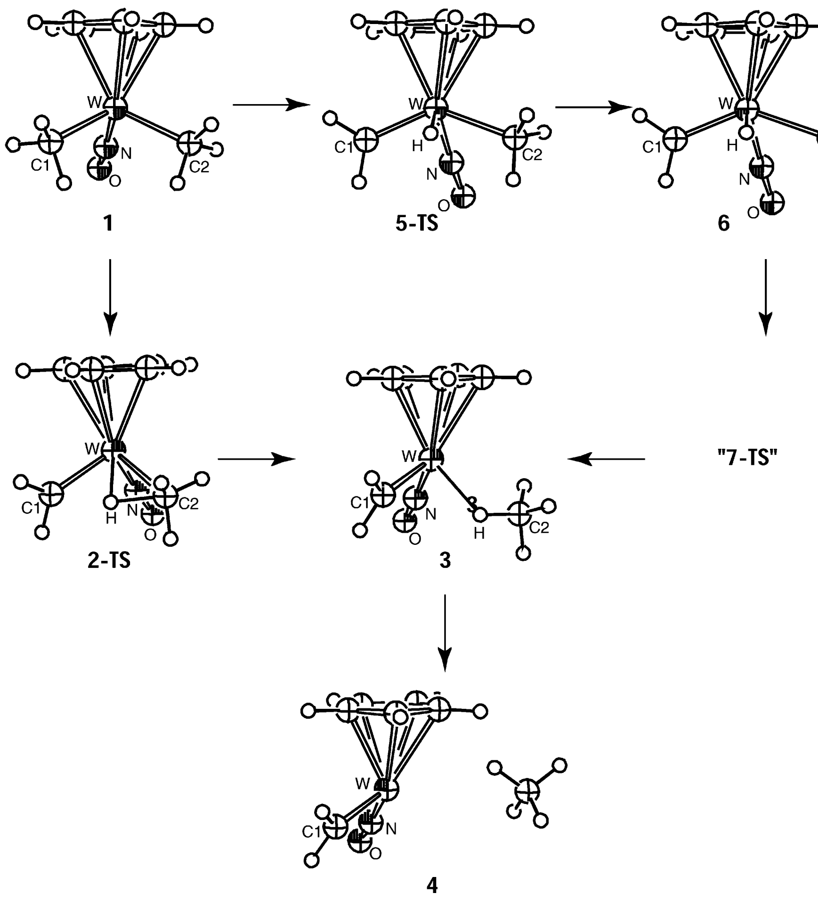


Fig. 1 Optimized geometries in the reaction of CpW(NO)$(CH_3)_2$.

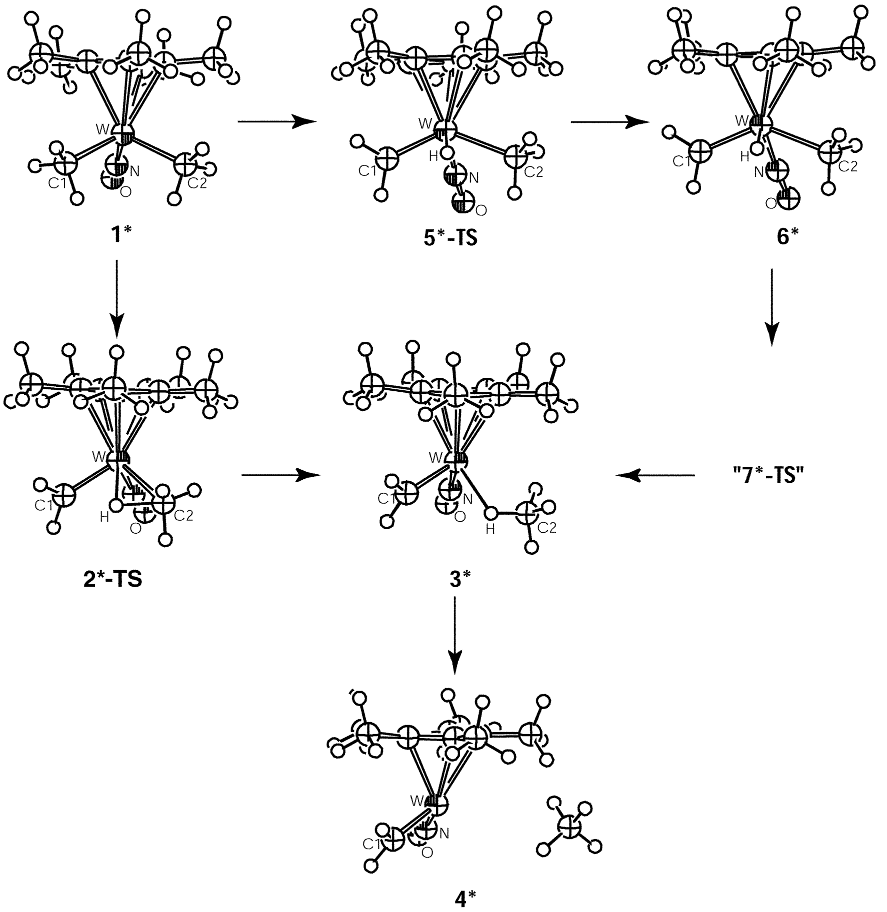


Fig. 2 Optimized geometries in the reaction of Cp*W(NO)$(CH_3)_2$.

Table 3 Relative energies in the reaction of Cp*W(NO)$(CH_3)_2$

Species	ΔE/kcal mol^{-1}	ΔE_0/kcal mol^{-1}	ΔH/kcal mol^{-1}	ΔG/kcal mol^{-1}	ΔS/cal K^{-1} mol^{-1}
1*	0.00	0.00	0.00	0.00	0.00
2*-TS	38.69	36.52	36.09	37.51	−4.76
3*	29.58	29.69	29.69	30.34	−2.20
4*	38.88	37.61	37.97	29.67	27.84
5*-TS	41.86	39.91	39.14	41.75	−8.75
6*	41.32	40.11	39.64	41.62	−6.63

Table 4 Structure parameters for species in Fig. 2

Structure parameters (Å, °)	**1***	**2*-TS**	**3***	**4***	**5*-TS**	**6***
W–N	1.776	1.789	1.792	1.791	1.827	1.843
N–O	1.204	1.199	1.201	1.204	1.186	1.181
W–C1	2.157	1.980	1.958	1.956	1.991	1.985
W–C2	2.155	2.375	2.673		2.291	2.300
W–H		1.806	2.075		1.730	1.713
W–Cp*[a]	2.090	2.094	2.074	2.052	2.095	2.098
C1–C2	3.565	3.108	3.627		3.815	3.932
C1–H		1.724	2.559		2.107	2.372
C2–H		1.422	1.129		2.288	2.303
C1–W–C2	111.5	90.6	102.0		125.8	133.1

[a] Cp*-midpoint of pentamethylcyclopentadienyl.

Table 5 Relative energies in the reaction of $[CpW(CO)(CH_3)_2]^-$

Species	ΔE/kcal mol^{-1}	ΔE_0/kcal mol^{-1}	ΔH/kcal mol^{-1}	ΔG/kcal mol^{-1}	ΔS/cal K^{-1} mol^{-1}
1′	0.00	0.00	0.00	0.00	0.00
2′-TS	39.12	36.92	36.41	37.46	−3.54
3′	29.98	29.99	30.13	29.63	1.68
4′	35.35	34.21	34.65	25.40	31.02
5′-TS	27.84	25.48	24.89	26.25	−4.56
6′	16.44	15.66	15.11	16.56	−4.88
7′-TS	38.25	36.19	35.83	36.10	−0.88

Table 6 Structure parameters for species in Fig. 3

Structure parameters (Å, °)	**1′**	**2′-TS**	**3′**	**4′**	**5′-TS**	**6′**	**7′-TS**
W–C3	1.889	1.900	1.909	1.932	1.918	1.945	1.918
C3–O	1.199	1.199	1.198	1.191	1.192	1.181	1.192
W–C1	2.198	1.999	1.978	1.963	2.001	1.985	1.973
W–C2	2.198	2.414	2.713		2.287	2.296	2.456
W–H		1.816	2.143		1.776	1.725	1.730
W–Cp	2.065	2.100	2.077	2.097	2.097	2.138	2.118
C1–C2	3.648	3.088	3.621		3.771	4.048	3.631
C1–H		1.707	2.562		1.775	2.530	2.686
C2–H		1.406	1.123		2.524	2.396	1.475
C1–W–C2	112.2	88.3	99.9		123.0	141.9	109.7

thermodynamic functions are listed in Table 3. Key structural parameters are listed in Table 4.

Apart from the methyls on the Cp ring, the geometries shown in Fig. 2 and Table 4 are quite close to the Cp counterparts in Fig. 1 and Table 2. **2*-TS** is the transition state from reactant **1*** to agostic product **3*** and the separated product **4***. Intermediate **6*** is formed through transition state **5*-TS** from **1***. Unlike the planar conformation found for cyclopentadienyl, the methyls on Cp* are tilted away from tungsten. Moreover, the relative energies of most species are 1.5~2.0 kcal mol^{-1} higher than those for the Cp counterparts.

Reaction of $[CpW(CO)(CH_3)_2]^-$

The species in the reaction of the isoelectronic carbonyl, $[CpW(CO)(CH_3)_2]^-$ converged to minima and transition states as shown in Fig. 3. The corresponding relative energies, thermodynamic functions and structural parameters are listed in Tables 5 and 6, respectively.

In contrast to the mechanisms for CpW(NO)$(CH_3)_2$, the reaction of $[CpW(CO)(CH_3)_2]^-$ shows two complete, distinct pathways. For the one-step mechanism, the reactant **1′** overcomes a barrier, which corresponds to transition state **2′-TS**, to form the agostic complex **3′**, which dissociates to products **4′**. For the two-step mechanism, **1′** reacts to form intermediate **6′** *via* transition state **5′-TS**, then **6′** goes to the agostic product **3′** through transition state **7′-TS**. Only for this system were we able to optimize the second TS in the two-step mechanism (**7′-TS**).

The energy of the agostic complex **3′** is 29.98 kcal mol^{-1} higher than that of the reactant **1′**, and the activation energy in the one-step mechanism is 39.12 kcal mol^{-1}. In the two-step mechanism, the activation energies for the two consecutive barriers are 27.84 kcal mol^{-1} and 21.81 kcal mol^{-1} respectively. The energy of the intermediate for the two-step mechanism is 16.44 kcal mol^{-1} higher than **1′**. Generally, the energetics of this system are similar to those of the nitrosyl, except that the OA intermediate **6′** is significantly more stable than **6** when compared to their reactants.

Discussion

Overall reactions

Among the structures calculated, **1**, **1*** and **1′** are far more stable than all the other related species. Among the structural elements the bond to the diatomic (EO) ligand, the W–E bond, is the shortest in **1**, **1*** and **1′**. Thus, the reactants have the strongest tungsten to nitrosyl and carbonyl bonds. Moreover, this same bond is the longest, and presumably weakest, in the intermediate **6**, **6*** and **6′**. Together with the charge distributions in Tables 7 and 8 the bond length differences suggest that the backbonding to EO is strongest in **1**, **1*** and **1′** and weakest in **6**, **6*** and **6′**.

Table 7 Mulliken charge distributions for species in Fig. 1

Atom	1	2-TS	3	4	5-TS	6
W	0.45	0.19	0.20	0.39	0.01	0.05
N	−0.01	−0.04	−0.04	−0.04	−0.02	−0.01
O	−0.33	−0.33	−0.33	−0.32	−0.27	−0.25
C1	−0.50	−0.31	−0.28	−0.29	−0.21	−0.24
C2	−0.50	−0.49	−0.49		−0.37	−0.38
H		0.24	0.22		0.12	0.08

The agostic bond in **3**, **3*** and **3′** is fairly strong for a bond between methane and tungsten, especially for the neutral nitrosyl systems. As expected one C–H bond has been elongated by about 0.03–0.02 Å. At 70 °C entropy would favor the dissociation of the methane. Formation of the final products (Scheme 1) drives the overall reaction as the formation of **4**, **4*** and **4′** are unfavorable (ΔG) with respect to **1**, **1*** and **1′**.

For both the one- and two-step mechanisms the barriers are fairly large ≈35 kcal mol^{-1}. This large barrier means that the generation of the tungsten alkylidene requires elevated temperatures. However the "back" reaction, in which the tungsten alkylidene attacks another X–H bond (see Scheme 1), has a relatively small barrier ≈9 kcal mol^{-1} (ΔE).

Reaction mechanism in the nitrosyl systems

The question of whether this reaction proceeds by a one-step mechanism like σ-bond metathesis or a two-step mechanism like oxidative addition then reductive elimination is somewhat problematic for two reasons. The structure of **2-TS** and **2*-TS** are remarkably similar to the structure of the intermediates **6** and **6***. In particular, there seems to be a strong W–H interaction in both. Furthermore, the energies of these transition states are similar to those of the intermediates. We have already

Table 8 Mulliken charge distributions for species in Fig. 3

Atom	1′	2′-TS	3′	4′	5′-TS	6′	7′-TS
W	−0.01	−0.33	−0.37	−0.21	−0.33	−0.23	−0.33
C3	0.20	0.19	0.18	0.13	0.19	0.20	0.17
O	−0.37	−0.37	−0.36	−0.32	−0.32	−0.31	−0.34
C1	−0.49	−0.32	−0.28	−0.33	−0.24	−0.30	−0.26
C2	−0.50	−0.50	−0.53		−0.40	−0.43	−0.44
H		0.24	0.25		0.04	−0.03	0.10

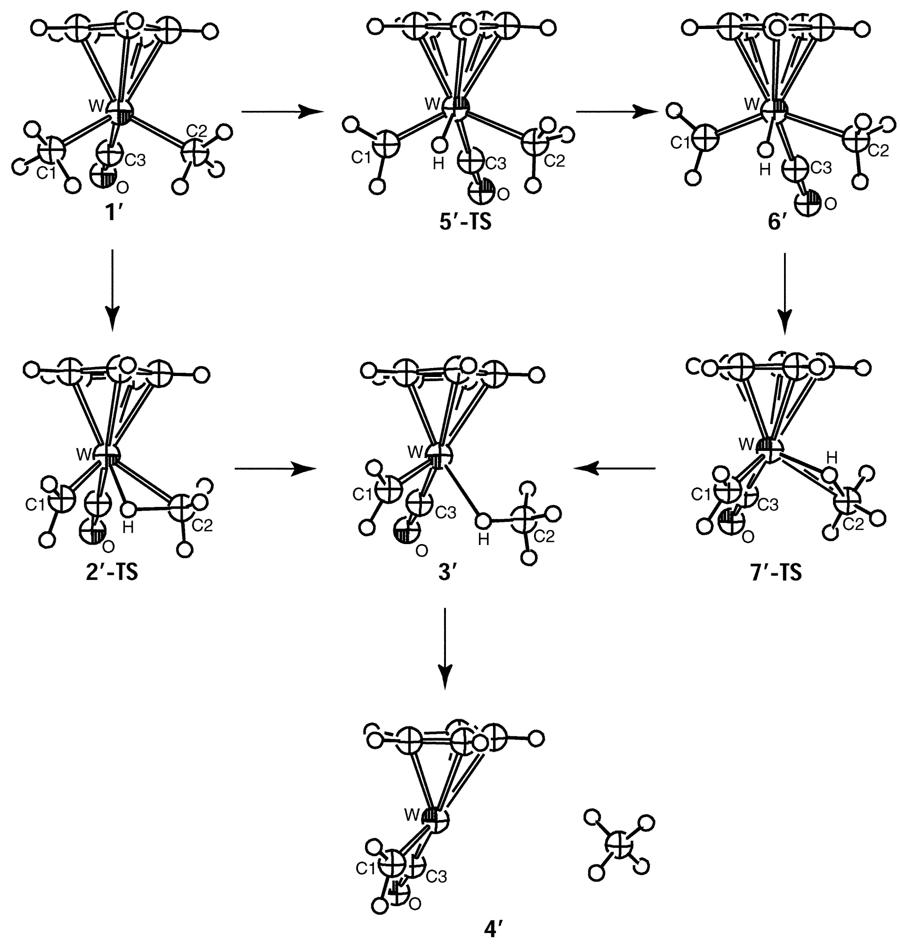


Fig. 3 Optimized geometries in the reaction of $[\text{CpW(CO)(CH}_3)_2]^-$.

established that **1** and **1*** are the most stable because of stronger backbonding to the ligand. The response of this ligand to the reaction may hold some clues to the features described above. In the TS for the one-step mechanism the W–N bond distances are quite similar to those of the reactants, but the intermediates have a much longer W–N bond distance. These differences parallel the charge distribution in Tables 7 and 8. In particular, we note that the intermediate has a much more negative W and a much more negative H (migratory). Thus, the results would appear to imply the situation of the two-step (OA/RE) mechanism involving a more negative (lower oxidation state) W. This dichotomy arises because the strong nitrosyl backbonding, which is so important in stabilizing the reactant, plays a key role in directing the nature of the H transfer mechanism. In the one-step mechanism the H transfers with more protonic character and allows the nitrosyl to maintain strong backbonding. In the two-step mechanism the proton attacks the metal raising the formal oxidation state from W^{II} to W^{IV} and removes a pair of electrons for W–NO backbonding. The change of this electron pair is so drastic that the W actually becomes more negative when transforming from W^{II} to W^{IV}, *i.e.* the nitrosyl removes more electron density from W^{II} in **1**, **1***, **2-TS** and **2*-TS** than the combinations of ligands do in the formally higher oxidation state (W^{IV}) intermediates **6** and **6***. Since we have been unable to locate a transition state connecting the intermediate **6** with the products **3/4**, we cannot rule out the two-step mechanism even though it appears to be slightly disfavored by the relative energy of the first transition states on the two alternative mechanisms, *i.e.* **2-TS** *vs.* **5-TS**.

Cp *vs.* Cp*

Since Cp* is a better donor than Cp one might expect that the replacement might favor the two-step mechanism which formally involves the higher (W^{IV}) oxidation state. However, the relative stability of **2-TS** *vs.* **6** and **2*-TS** *vs.* **6*** are nearly identical. Generally the only difference between Cp and Cp* is a ≈2 kcal mol^{-1} destabilization of all TS and intermediates relative to the reactant. This observation may be due partly to the steric bulk of the Cp* and to the fact that all the TS and intermediates have more negative charge and would be destabilized by the better donor.

NO *vs.* CO

As a reactant, the isoelectronic $[CpW(CO)(CH_3)_2]^-$ anion **1′** is relatively more stable than all other species on the pathways to products than in the nitrosyl systems. Like $CpW(NO)(CH_3)_2$, the bonding of W and CO is strongest in **1′** and W is more positive in **1′** than in the other species in this system. However, because of the anionic nature and the weaker π-acceptor (CO), the W has substantially more electron density in this system than in the nitrosyl systems (see Tables 7 and 8). This additional electron density weakens the agostic interaction **3′** and stabilizes the higher oxidation state (W^{IV}) intermediate **6′**, which unexpectedly has a more negatively charged W than **1′**, as seen for the nitrosyl system.

The increase in stability of the intermediate **6′** results in a lower barrier (by ≈11 kcal mol^{-1}) for its formation than for the formation of the products **3′/4′** through **2′-TS**. In this case, the stability of **6′** has allowed us to find the "missing" transition state **7′-TS** which is still lower in energy (by ≈1 kcal mol^{-1}) than **2′-TS**. Thus, the two-step mechanism has barriers of ≈25 kcal mol^{-1} and ≈21 kcal mol^{-1} *vs.* the one-step mechanism with a barrier of ≈37 kcal mol^{-1}.

In the nitrosyl system **5-TS** is ≈3 kcal mol^{-1} less stable than **2-TS**, and **5-TS** is ≈0.2e lower in W charge than **2-TS**. In the carbonyl system **5′-TS** is ≈11 kcal mol^{-1} more stable than **2′-TS**, and **5′-TS** and **2′-TS** have identical W charges. Thus, the naturally poorer π acceptor, CO, provides less of a barrier to the two-step (OA/RE) mechanism and the charge distribution begins to resemble the expected distribution because the CO cannot "give back" as much electron density as the nitrosyl.

Conclusion

According to the B3LYP (DFT) calculations, the generation of tungsten carbene complexes by methane elimination from $CpW(NO)(CH_3)_2$, $Cp^*W(NO)(CH_3)_2$ and $[CpW(CO)(CH_3)_2]^-$, prefers slightly the one-step mechanism in nitrosyl complexes and the two-step mechanism in the carbonyl complex. Although the one-step mechanism resembles a σ-bond metathesis, it is assisted by a strong W–H interaction. Strong π backbonding by NO contributes to the observed differences.

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