A Computational Study of Two-State Conformational Changes in 16-Electron [CpW(NO)(L)] Complexes (L = PH_3, CO, CH_2, HCCH, H_2CCH_2)

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Abstract: Electronically and coordinatively unsaturated [Cp*W(NO)(L)] complexes have been postulated as intermediates in several related systems. Model [CpW(NO)(L)] compounds (L = PH_3, CO, CH_2, H_2CCH_2, HCCH) have been investigated theoretically by means of density functional theory computational techniques. The structural parameters calculated for saturated [CpW(NO)(PH_3)(L)] complexes are in good agreement with the solid-state molecular structures determined crystallographically for the corresponding [Cp*W(NO)(PMe_3)(L)] compounds. The 16-electron, singlet [CpW(NO)(L)] species have geometries comparable to those of the same fragment in the phosphine adducts and include a highly pyramidal conformation at W. The energy of the triplet spin state is calculated to be close to or even lower than that of the singlet state for these unsaturated compounds, and depends largely on the π-bonding capabilities of L ($\Delta E_{s-t} = \Delta E_t - \Delta E_s = -3.3$ kcal mol^{-1} (PH_3), +2.8 (CO), +2.4 (CH_2), +6.3 (H_2CCH_2), −2.3 (HCCH)). The optimization of partially constrained structures in both spin states allows for a conformational analysis of the [CpW(NO)(L)] species. The inversion of the conformation of the pyramidal singlet [CpW(NO)(L)] complexes via the planar-at-W triplet species (two-state pathway) is calculated to be competitive with the equivalent process solely along the singlet spin hypersurface. Rotation of the W–CH_2 bond in the singlet carbene species is also found to proceed more readily via a two-state pathway. The preferred alkyne conformation, the unusually stable triplet states, and the strong W-to-L π-donation observed in these systems may all be rationalized by the relatively high energies of the occupied orbitals of the formally W^0 compounds.

Keywords: density functional calculations • ligand effects • pi interactions • spin crossover • tungsten

Introduction

The outcome of organometallic reactions often appears to be dictated by a delicate balance of steric and electronic effects. Seemingly minor variations can lead to disconcertingly disparate modes of reactivity. When the key intermediate in the reaction of interest cannot be directly observed by spectroscopy, even identifying which factors may be important can be difficult. In such cases, a combined experimental and theoretical approach may provide valuable insights. Recent developments in advanced computational techniques have facilitated the study of transition metal containing complexes by the use of models that accurately mimic the actual compounds.[1] The theoretical analysis can help to identify critical effects, which can then be probed experimentally.

One such variable in organotransition-metal chemistry that has recently been studied with this type of combined computational and synthetic investigation is spin state.[2, 3] Unsaturated, open-shell compounds capable of existing in more than one spin state are often implicated as intermediates in organometallic reactions, yet the relative energies of the possible electronic configurations are only rarely considered.[4–7] The relationships between spin state and other crucial factors, such as steric interactions, π-bonding effects, and overall geometry of the complex, have also only begun to be examined experimentally and theoretically.[8–13]

The computational studies described in this paper explore these effects for [CpW(NO)(L)] compounds, where L = PH_3, CO, CH_2, H_2CCH_2, and HCCH. The phosphine, alkyne, and carbene complexes are models for postulated yet unobserved [Cp*W(NO)(L)] species generated by the thermolytic reductive elimination of $SiMe_4$ or CMe_4 from [Cp*W(NO)(PMe_3)(CH_2SiMe_3)H],[14] [Cp*W(NO)(CH_2SiMe_3)(CPh=CH_2)],[15, 16] [Cp*W(NO)(CH_2CMe_3)$_2$],[17] or from the deorthometallation of [Cp*W(NO)(η^2-$Ph_2PC_6H_4$)H].[18] Although analogous alkene compounds have not been generated directly, they have been proposed as intermediates in the intermolecular C–H

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bond activation reactions of the carbene and alkyne complexes.[15, 17] The [CpW(NO)(CO)] model complex was examined in order to extend the range of π-bonding properties of L, as well as to investigate the possible utility of the photolysis of [Cp*W(NO)(CO)$_2$] as an alternative route to reactive [Cp*W(NO)(L)] species.[7]

The [CpW(NO)(PH$_3$)(L)] compounds were investigated first in order to compare ligand effects in a relatively uncomplicated context. Subsequently, the geometries and energies of [CpW(NO)(L)] species were optimized without constraints in both the singlet and triplet spin states. The energies and bonding character of the frontier orbitals of each of these species were examined to rationalize the relative energies and varying structural parameters of the two spin states. Calculations were then performed on various partially constrained structures in order to evaluate the effects of ligand rotation and different degrees of pyramidalization at the metal center, and the barriers to interconversion of the singlet and triplet spin states were estimated. By this combination of geometric and energetic optimization, conformational examination, and frontier orbital analysis, a more complete understanding of the bonding in the critical [Cp*W(NO)(L)] intermediates was obtained, which may ultimately be employed to devise new synthetic strategies for the selective tuning of the reactivity of these species. Preliminary results on the [CpW(NO)(PH$_3$)] system have been recently communicated.[13]

Computational Details

All the electronic structure and geometry optimization calculations were performed with Gaussian 94[19] on an SGI Origin 200 workstation. The LanL2DZ basis set was employed to perform geometry optimizations with a density functional theory (DFT) approach. The B3LYP functional (B3LYP = the three-parameter form of the Becke, Lee, Yang, and Parr functional)[20] was employed. The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H and C[21] and the relativistic core potential sets of Hay and Wadt for the heavy atoms.[22–24] Electrons outside the core were all those for H, C, N, and O, the 5s, 5p, 5d, and 6s electrons for W and the 3s and 3p electrons for P. The mean value of the first-order electronic wavefunction, which is not an exact eigenstate of S^2 for unrestricted calculations on the triplet systems, was considered suitable for the unambiguous identification of the spin state. Spin contamination was carefully monitored and the value of $<S^2>$ for the UB3LYP (UB3LYP = unrestricted B3LYP) calculations on the triplet [CpW(NO)(L)] systems at convergence (L = PH$_3$, 2.0262; CO, 2.0171; CH$_2$, 2.0112; H$_2$CCH$_2$, 2.0075; HCCH, 2.0071) indicated minor spin contamination. The energies shown in the Results and Discussion section correspond to UB3LYP calculations for the triplet [CpW(NO)(L)] species, and to restricted B3LYP calculations for the singlet [CpW(NO)(L)] and [CpW(NO)(PH$_3$)(L)] species.

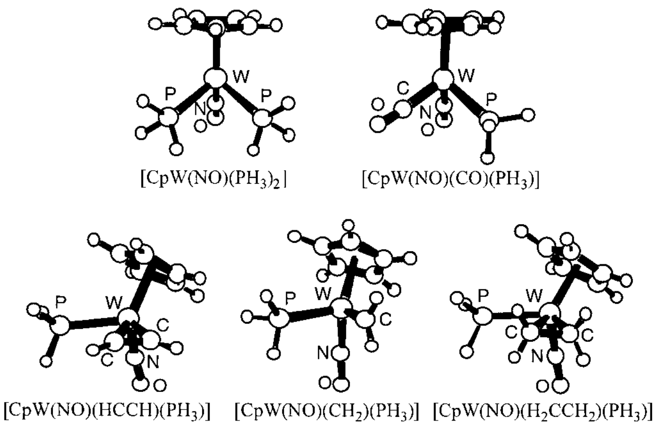
Ground-state energies for both singlet and triplet states were based on complete geometry optimizations. For each complex, the geometry was optimized starting from several different initial structures in order to avoid convergence to a false minimum. For the ligand rotation studies of [CpW(NO)(CH$_2$)] and [CpW(NO)(HCCH)], the H-C-W-N or C-C-W-N dihedral angle, respectively, was fixed and the remainder of the structure was permitted to optimize freely. For the conformation-at-W studies of [CpW(NO)(PH$_3$)], [CpW(NO)(CO)], and [CpW(NO)(CH$_2$)], several approaches were evaluated. The geometries of the planar-at-W singlet [CpW(NO)(L)] species were optimized with imposed C_s symmetry, and converged successfully. For nonplanar singlet and triplet [CpW(NO)(L)] complexes, however, single-point calculations based on appropriately modified ground-state geometries gave unrealistically inflated energies: for example, the inversion barrier for singlet [CpW(NO)(PH$_3$)] was calculated to be 20.0 kcal mol^{-1}, a value almost four times greater than that obtained by the use of a less restrictive approach (vide infra). Next, the C_5 ring of the Cp ligand was fixed as a regular pentagon with a dummy atom set at CNT (CNT = midpoint of the Cp ring), the degree of pyramidalization was set at a specific N-W-CNT-L angle (ϕ), and the geometry was optimized with no other restrained parameters. After our preliminary report on the [CpW(NO)(PH$_3$)] energies calculated with this fixed pentagonal Cp method,[13] lower energies were obtained by imposing a local C_s symmetry on the [CpW(NO)] fragment, fixing the L-CNT-W-N angle (ϕ), and allowing the remaining structural parameters to optimize freely. Even this final, more flexible scheme imposes sizable restrictions on the compounds which occasionally prevented the attainment of complete geometric convergence. However, since these values were necessary in order to estimate the spin-crossover geometries and were not otherwise used in the analysis of the [CpW(NO)(L)] species, this admittedly imperfect technique was employed as the best available option.

The energies, occupancies, and spatial plots of the molecular orbitals were obtained from the B3LYP calculations with Molden *v3.2*.[25] For the triplet [CpW(NO)(L)] species, the orbital energies were taken as an average of the α and β orbitals. For consistency, the bonding character of these orbitals was assessed on the basis of the β orbital in each case for the triplet model compounds.

Results and Discussion

[CpW(NO)(PH$_3$)(L)]: 18-e phosphine adducts: Although [Cp*W(NO)(L)] species have yet to be spectroscopically observed, in several cases they have been trapped, isolated, and structurally characterized as PMe$_3$ adducts.[17, 18, 26] Two decades ago, Hoffmann and co-workers described the theoretical basis for the conformational preferences exhibited by such [CpM(L)(L′)X] compounds.[27, 28] These preferences have been extensively studied for [CpRe(NO)(PPh$_3$)(L)]$^+$ complexes,[29–31] and have recently been observed for [Cp*W(NO)(PPh$_3$)(L)] compounds.[18] Calculations were therefore performed on [CpW(NO)(PH$_3$)(L)] in order to make comparisons with the previous crystallographic, theoretical, and spectroscopic results. Employing 18-electron [CpW(NO)(PH$_3$)(L)] models also allows the bonding properties of the various L groups to be directly compared in the absence of additional complicating factors due to the spin state or the conformation at the metal (vide infra). Other [CpM(NO)]-containing compounds (M = Mo, W) have previously been examined with Fenske–Hall molecular orbital calculations.[32–35]

The optimized geometries of the singlet [CpW(NO)(PH$_3$)(L)] species are depicted in Figure 1. Only a minimal variation in the geometry of the [CpW(NO)(PH$_3$)] fragment is observed between the various complexes, as shown by the structural parameters given in Table 1. The structural parameters of the phosphine, carbene, and alkene complexes are quite close to those found in the corresponding [Cp*W(NO)(PMe$_3$)(L)] compounds which have been structurally characterized by X-ray crystallography.[17, 18, 26] The W–L, W–P, and W–NO bond lengths are within ±0.052 Å of the experimental values, while the bond angles are within ±6°. The larger variation observed for the bond angles is likely to be the result, at least in part, of the greater steric demands of the ligands in the experimental [Cp*W(NO)(PMe$_3$)(L)] compounds, compared to the [CpW(NO)(PH$_3$)(L)] model complexes.



$[CpW(NO)(PH_3)_2]$ $[CpW(NO)(CO)(PH_3)]$

$[CpW(NO)(HCCH)(PH_3)]$ $[CpW(NO)(CH_2)(PH_3)]$ $[CpW(NO)(H_2CCH_2)(PH_3)]$

Figure 1. Optimized geometries of $[CpW(NO)(PH_3)(L)]$ ($L = PH_3$, CO, CH_2, H_2CCH_2, HCCH).

Table 1. Selected bond lengths [Å] and angles [°] for $[CpW(NO)(PH_3)(L)]$.

	$L = PH_3$	$L = CO$	$L = CH_2$	$L = HCCH$	$L = H_2CCH_2$
CNT–W	2.055	2.088	2.137	2.137	2.113
$W-PH_3$	2.455	2.493	2.503	2.507	2.496
W–L	2.455	1.950	1.952	2.037	2.101
W–NO	1.803	1.808	1.787	1.787	1.784
N–O	1.250	1.239	1.252	1.255	
C–O		1.198			
C–C′				1.313	1.461
$CNT-W-PH_3$	121.78	120.92	120.53	116.55	116.75
CNT-W-NO	128.03	129.17	130.81	123.99	126.70
CNT-W-L	121.78	120.74	118.08	120.21	121.89
PH_3-W-L	88.82	90.68	92.66	97.93	96.62
PH_3-W-NO	93.19	92.75	88.91	88.75	90.31
L-W-NO	93.19	92.91	96.61	102.56	96.85
W-N-O	175.49	175.96	177.86	176.69	175.77
N-W-CNT-L	– 124.6	124.1	129.3	– 134.1	– 129.7
N-W-CNT-P	124.6	– 124.0	– 118.7	107.9	112.5
H-C-W-N			– 166.9		
C-C′-W-N				84.5	83.4

Of particular note is the relative orientation of the CH_2 and C_2H_n ($n = 2$, 4) ligands with respect to the W–NO axis, as indicated by the H-C-W-N and C-X-W-N dihedral angles, respectively (X = midpoint of C–C vector). The preferred orientations are the result of competition between ligands for the available π-symmetry orbitals.[27, 28, 36] The energies and bonding character of the frontier orbitals of the $[CpW(NO)(PH_3)(L)]$ compounds are depicted in Figure 2. The three filled orbitals (represented schematically as A, B, and C in Figure 3) are of π-symmetry with respect to the NO, PH_3, and L ligands, and are analogous to the t_{2g} orbitals of octahedral $[ML_6]$ compounds. All the 18-e $[CpW(NO)(PH_3)(L)]$ complexes display a large HOMO–LUMO gap, typical of stable, d^6, pseudooctahedral $[CpM(L)_3]$ compounds.

The THOMO (THOMO = third-highest occupied molecular orbital) and SHOMO (SHOMO = second-highest occupied molecular orbital) of $[CpW(NO)(PH_3)_2]$ are the mutually orthogonal W–NO π-back-bonding orbitals (B and C in Figure 3) lying in and perpendicular to the pseudo-C_s plane of the complex, respectively. The corresponding W–NO π-antibonding orbitals are the LUMO and SLUMO (SLUMO = second-lowest unoccupied molecular orbital) of the complex. The HOMO of $[CpW(NO)(PH_3)_2]$ lies on the plane orthogonal to the W–NO axis (A in Figure 3), and has the highest energy of all the $[CpW(NO)(PH_3)(L)]$ HOMOs in Figure 2. Although the HOMO is of π-symmetry with respect to both phosphine ligands, the PH_3 groups are incapable of forming an effective π-bonding interaction with the metal and thus the orbital remains metal-centered, nonbonding, and relatively high in energy.

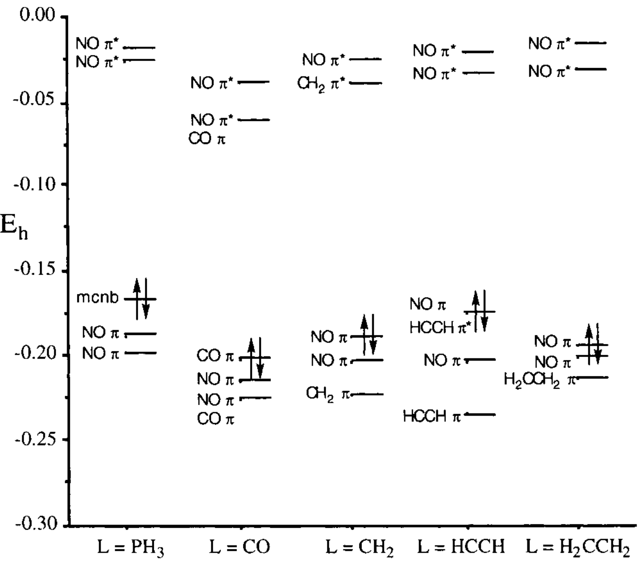


Figure 2. Frontier orbital energies of $[CpW(NO)(PH_3)(L)]$ ($L = PH_3$, CO, CH_2, H_2CCH_2, HCCH).

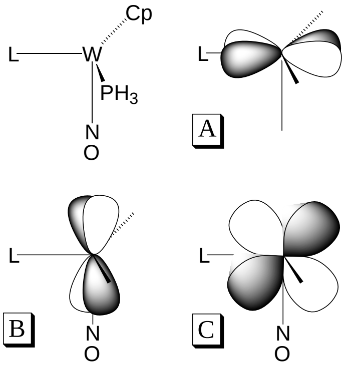


Figure 3. Schematic representation of frontier orbitals of $[CpW(NO)(PH_3)(L)]$ (L = CO, CH_2, H_2CCH_2, HCCH) (metal-based component only).

$[CpW(NO)(CO)(PH_3)]$ lacks the C_s symmetry of $[CpW(NO)(PH_3)_2]$ and, as expected, the orbitals of the carbonyl species adopt a different orientation in response to this electronic asymmetry.[28, 37] The HOMO still corresponds to A, but is now engaged in π-bonding to the CO ligand. The SHOMO and THOMO correspond to B and C, respectively. All three occupied orbitals are lower in energy than the bonding orbitals in $[CpW(NO)(PH_3)_2]$, as a result of stabilizing π-backbonding interactions with both the nitrosyl and carbonyl ligands. However, since the CO group has two orthogonal π-acceptor orbitals, the LUMO is also lowered in energy as it is W–CO π bonding in character in addition to being W–NO π-antibonding (Figure 4). As a result, $[CpW(NO)(CO)(PH_3)]$ has a smaller HOMO–LUMO gap than the other $[CpW(NO)(PH_3)(L)]$ complexes.

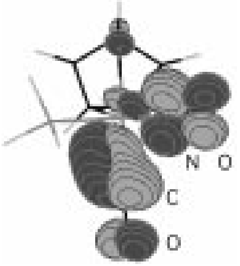


Figure 4. LUMO of $[CpW(NO)(CO)(PH_3)]$.

This overabundance of ligand π-bonding capability is not present in $[CpW(NO)(CH_2)(PH_3)]$, as the carbene group possesses only one π-symmetry orbital. The observed near-planarity of the H_2C-W-NO unit allows the CH_2 ligand to interact with orbital A. This π interaction is apparently quite strong and results in a very low energy W–CH_2 π-bonding combination (the THOMO of $[CpW(NO)(CH_2)(PH_3)]$ in Figure 2). The SHOMO and HOMO are π-bonding to NO, and have approximately the same energy as the corresponding nitrosyl π-backbonding orbitals in the 18-e diphosphine (the THOMO and SHOMO of $[CpW(NO)(PH_3)_2]$). The W–CH_2 π-antibonding orbital forms the LUMO of $[CpW(NO)(CH_2)(PH_3)]$, while the SLUMO is W–NO π antibonding in character.

A similarly neat division of the available π-symmetry orbitals is also observed for $[CpW(NO)(H_2CCH_2)(PH_3)]$. As in the carbene species, the HOMO and SHOMO are W–NO π-bonding while the LUMO and SLUMO are W–NO π-antibonding. Again, the close energy match between the alkene acceptor orbital and orbital A leads to an efficient π-bonding interaction, to form the THOMO of the complex (Figure 5). $[CpW(NO)(H_2CCH_2)(PH_3)]$ has the greatest HOMO–LUMO gap of all the compounds in Figure 2.

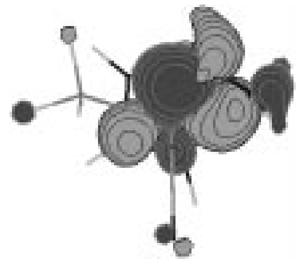


Figure 5. THOMO of $[CpW(NO)(H_2CCH_2)(PH_3)]$.

The bonding situation is more complicated for $[CpW(NO)(HCCH)(PH_3)]$ as a consequence of the filled alkyne orbital, the $\pi_\perp$ orbital, which is of π symmetry with respect to the tungsten–alkyne bond.[38] As in $[CpW(NO)(H_2CCH_2)(PH_3)]$, the W–L π-backbonding interaction is the THOMO of the alkyne compound and has the lowest energy of all the W–L π orbitals in Figure 2. Although the SHOMO and HOMO are both W–NO π-bonding in character, the HOMO (which corresponds to orbital C in Figure 3) is destabilized by a π-antibonding interaction with the filled alkyne $\pi_\perp$ orbital, which leads to a comparatively small HOMO–LUMO gap. As both bonding and antibonding combinations are occupied, no net alkyne-to-W π-donation occurs.

$[CpW(NO)(L)]$ ($L = PH_3$, CO): Conformation at W: The optimized geometries and relative energies of singlet and triplet $[CpW(NO)(L)]$ ($L = PH_3$, CO) are shown in Figure 6, and the structural parameters for these species are listed in Table 2. For each $[CpW(NO)(L)]$ complex, the difference in energy between the singlet and triplet states is remarkably small, with the triplet $[CpW(NO)(PH_3)]$ calculated to be 3.3 kcal mol^{-1} more stable than the singlet, while the paramagnetic electronic configuration is 2.8 kcal mol^{-1} higher in energy than the diamagnetic state for $[CpW(NO)(CO)]$. The singlet $[CpW(NO)(L)]$ structures closely resemble the corresponding PH_3 adducts after removal of the PH_3 group (Tables 1 and 2). The most significant difference between the singlet and triplet $[CpW(NO)(L)]$ structures is the geometry at the metal center. While the triplet $[CpW(NO)(L)]$ species are planar at W, as described by the N-W-CNT-L dihedral angle ϕ (i.e. the angle between the planes defined by N-W-CNT and W-CNT-L, as illustrated in Figure 7), both singlet complexes are distinctly pyramidal at W ($\phi = 125.0°$ and 121.1° for the diamagnetic PH_3 and CO compounds, respectively). The same relationship between conformation-at-metal and spin state has recently been

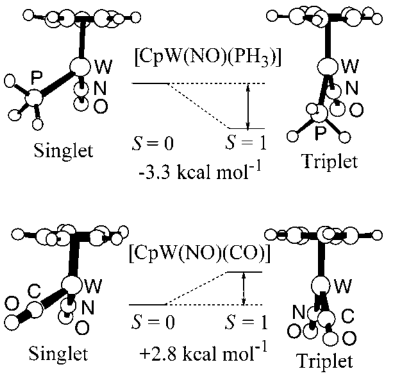


Figure 6. Optimized geometries and relative energies of singlet and triplet $[CpW(NO)(L)]$ ($L = PH_3$, CO).

Table 2. Selected bond lengths [Å] and angles [°] for $[CpW(NO)(L)]$ ($L = PH_3$, CO).

	$L = PH_3$	$L = PH_3$	$L = CO$	$L = CO$
Singlet	Triplet	Singlet	Triplet	
CNT–W	2.108	2.093	2.054	2.091
W–L	2.482	2.522	1.954	1.999
W–NO	1.791	1.794	1.804	1.809
N–O	1.251	1.252	1.236	1.235
C–O			1.195	1.190
CNT-W-L	121.38	132.82	120.0	133.42
CNT-W-NO	128.55	133.55	126.66	129.80
L-W-NO	93.33	93.63	93.43	96.79
W-N-O	175.34	176.71	173.98	174.98
N-W-CNT-L	125.0	180.0	121.1	–179.9

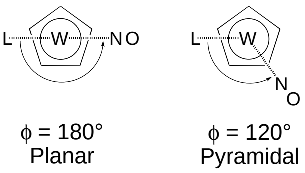


Figure 7. Degree of pyramidalization-at-W in $[CpW(NO)(L)]$, as described by the N-W-CNT-L dihedral angle (ϕ).

calculated for singlet and triplet [CpMn(CO)$_2$] and [CpRe(CO)$_2$].[7] The W–P and W–CNT bond lengths extend slightly from singlet to triplet and the CNT-W-L angle is also significantly greater in the paramagnetic species. While the W–NO structural parameters are essentially invariant with spin state, the triplet [CpW(NO)(CO)] has a longer W–C bond than that calculated for singlet [CpW(NO)(CO)] (Table 2).

Examination of the energies and bonding character of the frontier orbitals of [CpW(NO)(PH$_3$)] and [CpW(NO)(CO)] (Figure 8) can help account for the observed differences between singlet and triplet species. As noted for the corresponding PH$_3$ adducts (Figure 2), each of the orbitals of [CpW(NO)(PH$_3$)] are higher in energy than the corresponding orbitals of [CpW(NO)(CO)]. For both CO and PH$_3$ compounds, the W–NO π-bonding orbitals are slightly lower in energy for the triplet compared to the singlet, and these orbitals remain doubly occupied in both spin states. This latter feature explains the constant W–NO structural parameters, in contrast to M^{II}, d^4 [CpM(NO)Cl$_2$] compounds (M = Mo, Cr), which have greater triplet M–N bond lengths on account of the depopulation of the metal–nitrosyl π-backbonding orbitals in the high-spin configuration.[11]

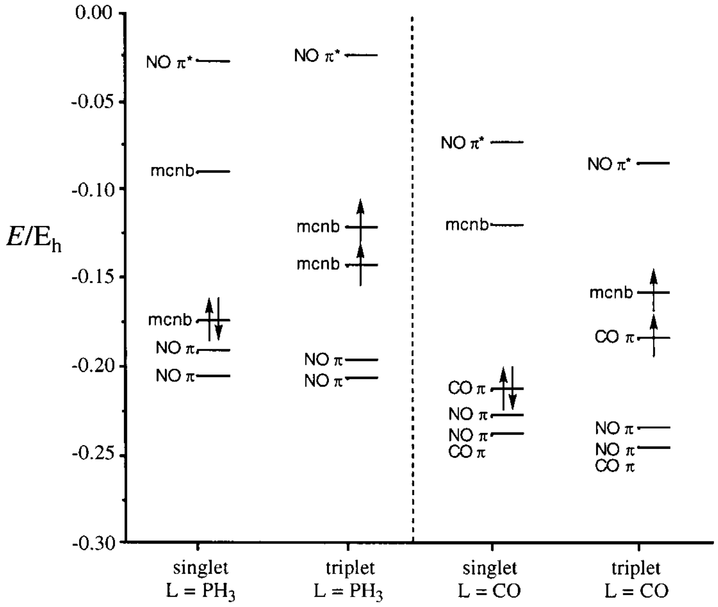


Figure 8. Frontier orbital energies of singlet and triplet [CpW(NO)(L)] (L = PH$_3$, CO).

The difference in conformation-at-W between the two spin states can be traced to the two next highest energy orbitals, that is the HOMO and LUMO for singlet complexes and the two SOMOs (SOMO = singly occupied molecular orbital) for triplet compounds. In pyramidal-at-W complexes, mixing between these two orbitals is allowed. For singlet [CpW(NO)(L)] species, this process constitutes a second-order Jahn–Teller distortion that lowers the HOMO in energy and raises the LUMO (an example of the result of such a distortion is illustrated in Figure 9).[39, 40] For triplet species, however, the planar-at-W geometry is preferred since this reduces the orbital splitting between the two SOMOs, decreases the energy of the highest (singly) occupied molecular orbital, and allows both unpaired electrons to occupy essentially undistorted d-type orbitals.

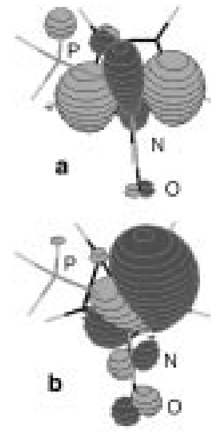


Figure 9. a) HOMO and b) LUMO of singlet [CpW(NO)(PH$_3$)].

The energies, occupancies, and bonding character of the orbitals in Figure 8 may also be used to explain how the electronic and steric properties of L can affect the relative energies of the singlet versus the triplet spin state for [CpW(NO)(L)] complexes. If L is a π acceptor, then the relative stability of the pyramidal-at-W geometry is improved, since W–L π-backbonding is enhanced in this conformation compared to the planar geometry.[39, 40] Additionally, the triplet state will be disfavored by π-acceptor L groups because the triplet contains one fewer electron in the W–L π-bonding orbital (as reflected in the W–CO bond lengths shown in Table 2). Intramolecular steric repulsions caused by the use of large L ligands and/or substituted Cp derivatives would be expected to favor larger CNT-W-L angles and the planar-at-W conformation, thereby decreasing the relative stability of the singlet spin state.

The determination of the conformational stability of 16-e [CpML$_2$] complexes is of potential importance to the design of unsaturated, chiral-at-metal complexes. Previous theoretical studies have demonstrated that if the HOMO and LUMO of such complexes are relatively close in energy, then efficient orbital mixing can occur and the pyramidal conformation is strongly preferred.[39, 40] However, a small HOMO–LUMO gap also raises the possibility of triplet species, which have a planar-at-metal geometry for the [CpW(NO)(L)] complexes we have examined. In order to investigate the barriers to changes of conformation-at-metal for both singlet and triplet spin states, the geometries and energies of [CpW(NO)(L)] compounds were calculated at various fixed degrees of pyramidalization (as measured by the N-W-CNT-L dihedral angle, ϕ, in Figures 10 and 11).

The barrier to interconversion of the pyramidal, diamagnetic conformations of [CpW(NO)(L)] along the singlet spin hypersurface is provided by the difference in energy between the singlet minimum and the planar, C_s-imposed structure. The values of 5.7 and 16.1 kcal mol^{-1} for [CpW(NO)(PH$_3$)] and [CpW(NO)(CO)], respectively, are quite high: Ward, Hofmann, and co-workers calculated barriers of up to 6.7 kcal mol^{-1} for 16-electron [CpML$_2$] compounds containing one π-acceptor and one σ-donor ligand, while the inversion barrier for complexes with two π-acceptor groups ranged between 10 and 15 kcal mol^{-1}.[40] Note, however, that the planar triplet [CpW(NO)(L)] species are lower in energy than the singlet maxima at $\phi = 180°$ by 9.0 kcal mol^{-1} for L = PH$_3$ and by 13.3 kcal mol^{-1} for L = CO. This suggests that a low-energy mechanism for the conformational inversion of pyramidal singlet [CpW(NO)(L)] species might be available via the triplet spin surface.

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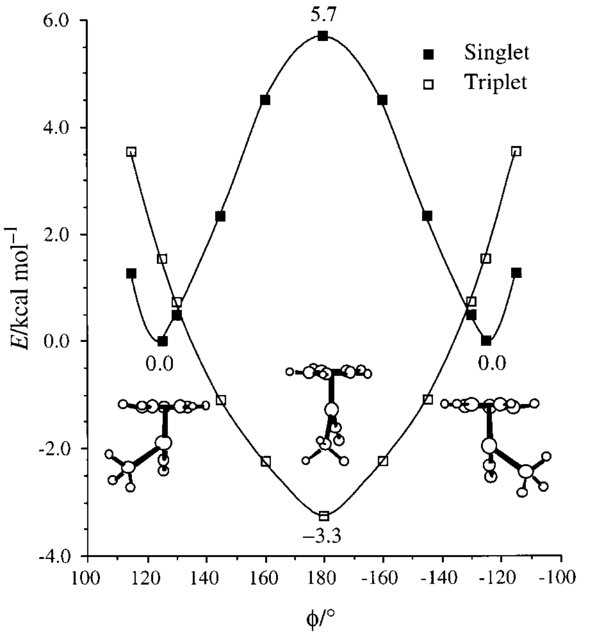

Figure 10. Energies of optimized [CpW(NO)(PH$_3$)] at various fixed dihedral N-W-CNT-P angles.

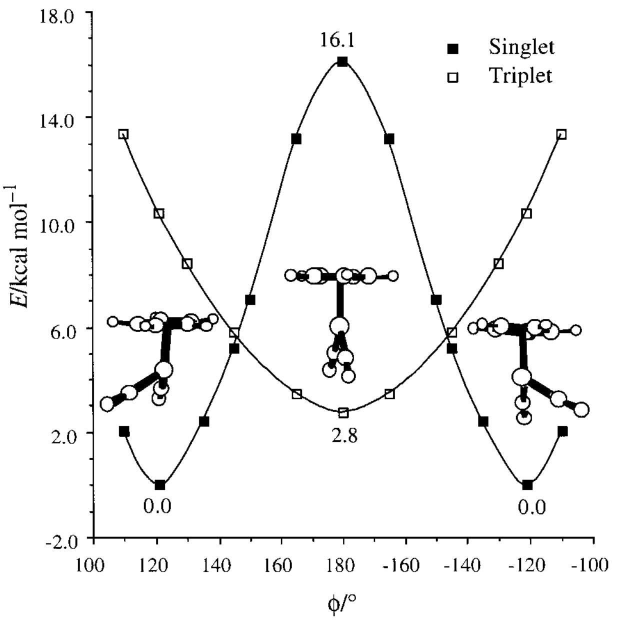

Figure 11. Energies of optimized [CpW(NO)(CO)] at various fixed dihedral N-W-CNT-C angles.

The energy required to change the spin state cannot be directly evaluated by commercial computational programs currently available, because the Franck–Condon principle requires that both states possess similar geometries and energies for the spin-state crossing to occur, and this point is difficult to locate without exploring the complete ($3N-6$)-dimensional conformational space.[41] At the crossover points shown in Figures 10 and 11, the energy and one parameter (the dihedral angle ϕ) are identical, but the other $3N-7$ internal coordinates may be quite different. An upper limit to the spin-flip barrier may be arrived at by calculating the singlet and triplet vertical excitation energies, and adding the smaller of these values to the energy difference between the singlet minimum and the spin-crossover point. The vertical excitation energies are obtained by the use of single-point calculations of both partially optimized geometries at the spin-crossover angle ϕ and imposing the alternative spin state, that is the triplet energy at the geometry of the singlet minimum and the singlet energy at the geometry of the triplet minimum.[4]

The singlet and triplet vertical excitation energies are larger for [CpW(NO)(PH$_3$)] (6.9 and 6.7 kcal mol^{-1} higher than the energy at the spin crossover points, respectively) than for [CpW(NO)(CO)] (4.0 and 5.2 kcal mol^{-1}, respectively). This translates into maximum spin-flip barriers of 7.4 and 7.5 kcal mol^{-1} for PH$_3$ and 9.3 and 8.5 kcal mol^{-1} for L = CO. Since the singlet maximum lies only 5.7 kcal mol^{-1} higher in energy than the singlet minimum for the phosphine complex, that is slightly less than the calculated upper limits of the spin-flip barrier, no conclusion can be reached about whether the inversion will occur along a one-state or a two-state pathway. For [CpW(NO)(CO)], however, the upper limits to the spin-flip barrier are substantially less than the 16.1 kcal mol^{-1} barrier associated with the singlet-only inversion pathway. Thus, conformational inversion of singlet [CpW(NO)(CO)] is expected to proceed along a two-state pathway via the triplet spin hypersurface.

[CpW(NO)(L)] (L = CH$_2$, H$_2$CCH$_2$, HCCH): Ligand rotation: The optimized geometries and relative energies of singlet and triplet [CpW(NO)(L)] (L = CH$_2$, H$_2$CCH$_2$, HCCH) are shown in Figure 12, and the structural parameters for these species are listed in Table 3.[42] As in the 16-e phosphine and carbonyl compounds, the difference in energy

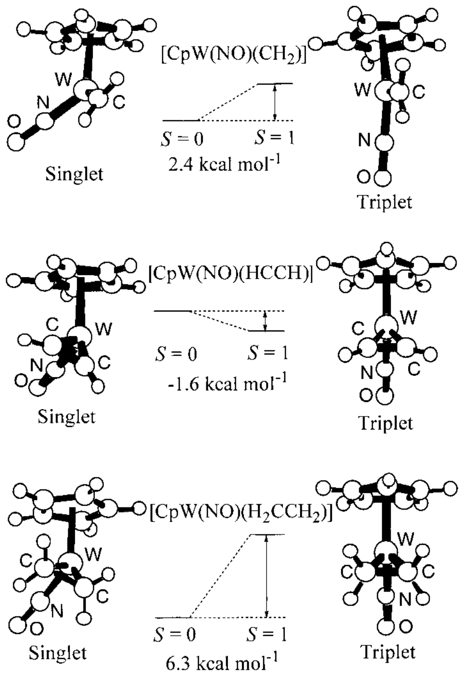

Figure 12. Optimized geometries and relative energies of singlet and triplet [CpW(NO)(L)] (L = CH$_2$, H$_2$CCH$_2$, HCCH).

Table 3. Selected bond lengths [Å] and angles [°] for [CpW(NO)(L)] (L = CH_2, HCCH, H_2CCH_2).

Structural Parameter	L = CH_2 Singlet	L = CH_2 Triplet	L = HCCH Singlet	L = HCCH Triplet	L = H_2CCH_2 Singlet	L = H_2CCH_2 Triplet
CNT–W	2.110	2.113	2.124	2.137	2.111	2.096
W–X[a]	1.949	1.946	1.978	1.934	2.021	2.061
W–NO	1.784	1.820	1.788	1.833	1.778	1.818
N–O	1.248	1.258	1.251	1.251	1.249	1.258
C–C			1.329	1.356	1.497	1.469
CNT-W-X	116.07	114.95	122.44	130.80	123.78	118.13
CNT-W-NO	128.97	144.24	119.03	123.23	126.15	139.08
X-W-NO	96.13	100.80	105.45	105.95	96.94	102.79
W-N-O	176.75	180.00	171.83	177.30	175.34	178.53
N-W-CNT-X	123.3	179.8	135.5	– 179.9	132.0	– 180.0
H-C-W-N	– 164.6	180.0				
C-C-W-N			– 91.3	– 95.1	– 83.5	– 94.2

[a] X = C for L = CH_2 or center of C–C bond for L = HCCH and H_2CCH_2.

between the singlet and the triplet electronic configurations is remarkably small. For [CpW(NO)(HCCH)], the local minimum triplet spin state is 1.6 kcal mol^{-1} more stable than the singlet, while the singlet is more stable than the triplet for [CpW(NO)(CH_2)] and [CpW(NO)(H_2CCH_2)] by 2.4 and 6.3 kcal mol^{-1}, respectively. The optimized triplet geometries are again planar-at-W, while the singlet species are pyramidalized and are structurally similar to the [CpW(NO)(L)] fragments of the [CpW(NO)(PH_3)(L)] compounds (Table 1). The orientation of each L ligand with respect to the W–NO vector is comparable in the structures of the 18-e PH_3 adducts and the 16-e [CpW(NO)(L)] species in both spin states.

All three complexes in Figure 12 exhibit an increase in the W–NO bond length of about 0.04 Å from the singlet to the triplet spin state. The W–L structural parameters also vary with electronic configuration for the alkene and alkyne compounds. The W–alkene interaction is apparently weaker in the triplet state, as indicated by the longer W–X distance and shorter C–C bond for the paramagnetic species, while the W–alkyne interaction appears to be *stronger* in the triplet (shorter W–X distances and longer C–C bond). The Cp–W lengths are relatively invariant of the spin-state for these [CpW(NO)(L)] compounds, and the CNT-W-NO angle increases from the singlet to the triplet spin states by varying amounts in all three cases.

The relationship between the preferred conformation-at-W and the spin state can be rationalized with the aid of the energies, occupancies, and bonding character of the frontier orbitals of [CpW(NO)(L)] (L = CH_2, H_2CCH_2, HCCH; Figure 13). As previously discussed for L = PH_3 and CO (vide supra), the degree of pyramidalization influences the orbital splitting between the HOMO and LUMO. However, while the LUMO is still of σ symmetry with respect to NO and L, the HOMO is no longer perpendicular to the W–NO bond in each case. This orbital is greatly stabilized as a result of the excellent overlap with the π-bonding orbital of the carbene, alkene, or alkyne ligand, and forms the THOMO in each of these cases. As a result, the HOMO is NO π-bonding in character for these singlet [CpW(NO)(L)] compounds. Consequently, one of the NO π-bonding orbitals is only singly occupied in the triplet state. The relative decrease in π-bonding from singlet to triplet is reflected in the lengthened W–NO bond in the triplet.[11]

The slight preference for the singlet spin state in the carbene and alkene complexes can be viewed as a result of the bonding character of the HOMO, SHOMO, and THOMO. Since all three of the t_{2g}-type orbitals are π-bonding in nature, the adoption of a triplet configuration will necessarily lead to diminished π-bonding compared to the singlet state. The enhanced relative stability of the triplet state in [CpW(NO)(HCCH)] can be traced to the additional π-bonding capabilities of the HCCH group. As in the alkene complex, the alkyne ligand in [CpW(NO)(HCCH)] aligns so that it can engage in π backbonding with the orbital perpendicular to the W–NO axis. As observed for [CpW(NO)(HCCH)(PH_3)], this arrangement leaves the filled alkyne $\pi_\perp$ orbital positioned to share a tungsten d orbital with the NO group. For singlet [CpW(NO)(HCCH)], the HOMO is both π-bonding to NO and π-antibonding to HCCH $\pi_\perp$, which results in a 16-e complex with a destabilized HOMO and no net alkyne-to-W π-donation. For triplet [CpW(NO)(HCCH)], this orbital is now singly occupied, which results in the *loss* of W–NO π-bonding and the *gain* of alkyne-to-W π-donation relative to the singlet species. Both of these trends are reflected in the differences in W–NO and W–alkyne structural parameters between singlet and triplet [CpW(NO)(HCCH)] (Table 3). These arguments can also be used to explain why [CpW(NO)(HCCH)] favors the triplet state: unlike [CpW(NO)(CH_2)] or [CpW(NO)(H_2CCH_2)], the loss of an electron from the W–NO π-bonding orbital is mitigated by a partial gain in L-to-W π-donation.

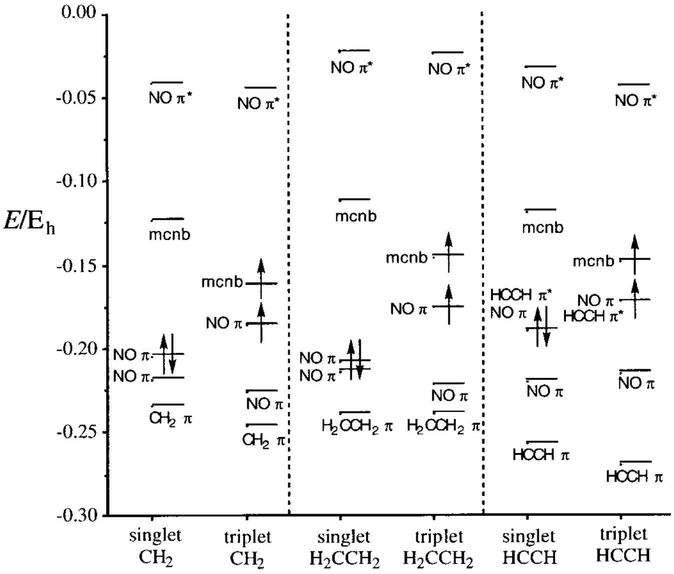

Figure 13. Frontier orbital energies of singlet and triplet [CpW(NO)(L)] (L = CH_2, H_2CCH_2, HCCH).

The barriers to conformational inversion for pyramidal, singlet [CpW(NO)(CH$_2$)] were evaluated by the method described for the carbonyl and phosphine derivatives (vide supra). Calculations at fixed N-W-CNT-C dihedral angles for both singlet and triplet carbene compounds indicated a spin-crossover geometry with $\phi = 145°$ (Figure 14). For all calculated intermediates the carbene ligand remained roughly aligned with the W–NO axis, as judged by the H-C-W-N dihedral angles of $-170 \pm 15°$. Calculation of the vertical excitation energies at the spin-crossover point ($\phi = 145°$) gave upper limits to the spin-flip barriers of 9.3 and 8.6 kcal mol^{-1} relative to the ground-state singlet energy. Since the barrier to conformational inversion of [CpW(NO)(CH$_2$)] along the singlet spin hypersurface is 10.0 kcal mol^{-1}, the two-state pathway offers a lower energy alternative for the interconversion of the two pyramidal-at-W geometries of the singlet carbene complex.

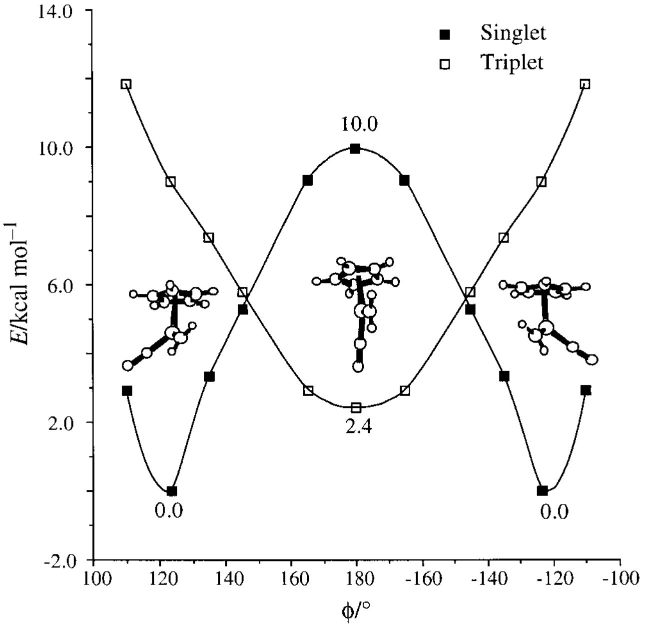

Figure 14. Energies of optimized [CpW(NO)(CH$_2$)] at various fixed dihedral N-W-CNT-C angles.

Unlike that in [CpW(NO)(PH$_3$)] or [CpW(NO)(CO)], rotation about the W–L bond is expected to be difficult for [CpW(NO)(CH$_2$)] as a result of the attendant disruption of the W–CH$_2$ π-bonding interaction.[28, 29] Carbene rotation was examined in both spin states by fixing the H-C-W-N dihedral angle at a specific value between 85° and – 165° and permitting the other structural parameters to optimize freely (Figure 15). Along the singlet spin surface, the energy rises steeply as the carbene rotates away from the electronically preferred alignment with the nitrosyl ligand, and results in a barrier of 17.8 kcal mol^{-1}. The singlet [CpW(NO)(CH$_2$)] species also steadily becomes less pyramidal-at-W as the carbene rotates, until the complex is essentially planar ($\phi = 179°$) when the WCH$_2$ plane is perpendicular to the W–NO axis. Note that although this species is planar-at-W, it lies 7.8 kcal mol^{-1} above the planar singlet carbene species discussed previously, which indicates that this carbene rotation mechanism does *not* provide a lower energy pathway for conformational inversion of singlet, pyramidal [CpW(NO)(CH$_2$)] (vide supra).

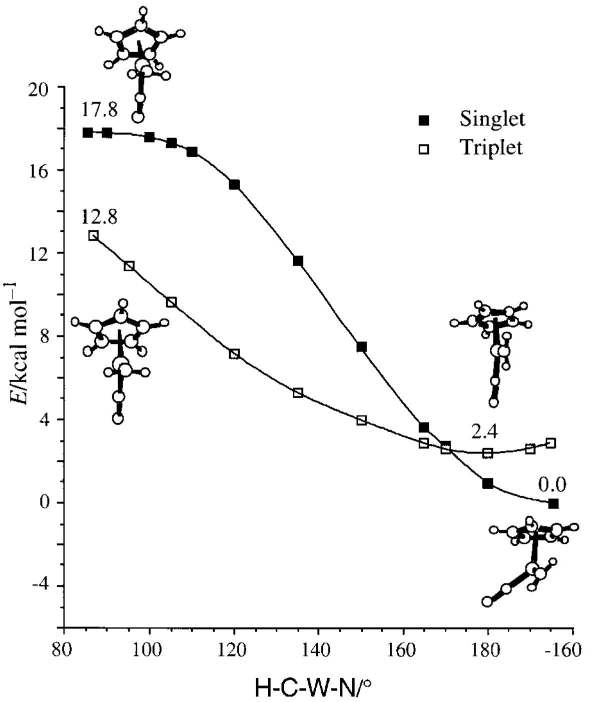

Figure 15. Energies of optimized [CpW(NO)(CH$_2$)] at various fixed dihedral H-C-W-N angles.

Triplet [CpW(NO)(CH$_2$)] retains an approximately planar-at-W conformation throughout the carbene rotation process ($\phi > 171°$). The triplet compound is less sensitive to rotation about the W–CH$_2$ bond, and so the triplet maximum lies only 12.8 kcal mol^{-1} over the singlet minimum, and the spin-crossover geometry (H-C-W-N = 170°) is close to the optimal H$_2$C-W-NO orientation. Although the energy of both spin states is very close at this degree of ligand rotation, the overall geometries are still quite different because of the varying amounts of pyramidalization-at-W, to result in relatively large vertical excitation energies between the two spin states. However, the calculated maximum spin-flip barriers of 13.4 and 15.8 kcal mol^{-1} (relative to the singlet minimum energy) on changing from the triplet to the singlet state and vice versa, respectively, are still lower than the 17.8 kcal mol^{-1} barrier associated with carbene rotation solely along the singlet surface. Thus, rotation of the W–CH$_2$ bond in singlet [CpW(NO)(CH$_2$)] is predicted to occur via a triplet intermediate.

In contrast to the case for the other [CpW(NO)(L)] complexes, the triplet state does not appear to play a significant role for the alkene compound. Singlet [CpW(NO)(H$_2$CCH$_2$)] is 6.3 kcal mol^{-1} more stable than the triplet state, the largest absolute difference between the diamagnetic and paramagnetic ground states calculated for any of the [CpW(NO)(L)] species. Even more significant is the relative energy of the planar-at-W singlet geometry: the C_s-imposed diamagnetic geometry with the alkene oriented perpendicularly to the mirror plane lies only 5.8 kcal mol^{-1} above the singlet ground state. This places the energy maximum for the geometry-inversion process via the singlet spin hypersurface slightly *lower* in energy than the triplet *ground state*. Thus, the interconversion of the two chiral-at-metal, pyramidal, singlet conformers of $[CpW(NO)(H_2CCH_2)]$ is not expected to involve the triplet electronic configuration. Similarly, the triplet state does not appear to play an appreciable role in the process of rotation about the tungsten–alkene bond.[43]

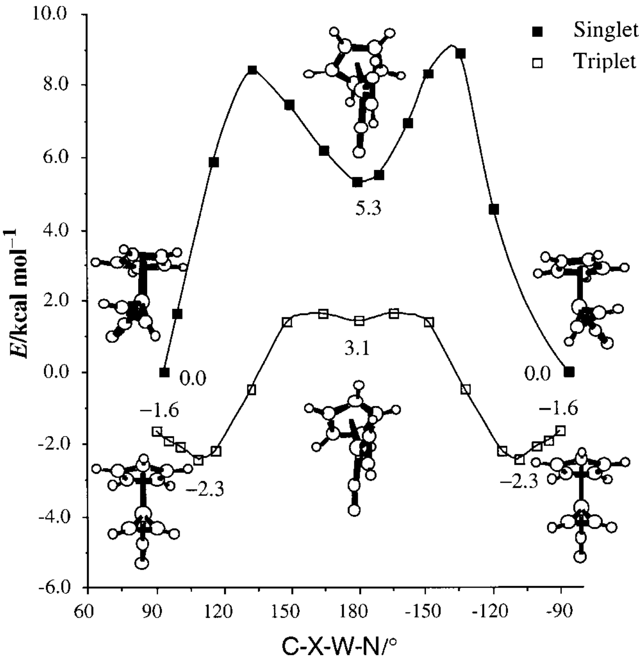

Figure 16. Energies of optimized [CpW(NO)(HCCH)] at various fixed dihedral C-X-W-N angles.

The connection between conformation-at-W and W–L bond rotation is even more marked for [CpW(NO)(HCCH)] than for the carbene compound (Figure 16). For the singlet species, the energy rises sharply and the degree of pyramidalization decreases as the alkyne is turned from its preferred orientation, as observed for the singlet carbene species. As the alkyne is rotated further, however, the energy decreases again from a maximum of ≈ 9 kcal mol^{-1} above the singlet ground state to a structure that has a mirror plane containing the tungsten, the nitrosyl, the alkyne, and the Cp centroid. Since this species is much lower in energy than the planar-at-W singlet complex with a perpendicular alkyne conformation, this suggests that the lowest energy pathway for the inversion of conformation of pyramidal [CpW(NO)(HCCH)] along the singlet hypersurface may involve the concurrent rotation of the tungsten–alkyne bond.

The triplet [CpW(NO)(HCCH)] complex also possesses a local minimum at the C-X-W-N dihedral angle of 180°, although the energy well surrounding this geometry is not nearly as deep or as wide as that calculated for the singlet compound and lies only 3.1 kcal mol^{-1} above the perpendicular alkyne conformation. The energy of the triplet alkyne complex *decreases* slightly as the orientation is changed from the local minimum with the HCCH ligand perpendicular to the W–NO axis, to yield a global minimum at a C-X-W-N dihedral angle of 108.5° (Figure 17). This geometry possesses a slightly pyramidal-at-W conformation ($\phi = 168.2$), and an energy 0.7 kcal mol^{-1} lower than the local minimum shown in Figures 11 and 12. The triplet geometries are essentially planar-at-W ($\phi > 166°$) throughout the ligand rotation process, and are *lower* in energy than the corresponding singlet species *for all values* of the C-X-W-N dihedral angle.

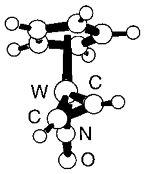

Figure 17. Optimized geometry of triplet [CpW(NO)(HCCH)] (global energy minimum).

Orbital energies, isolobal relationships, and periodic trends: Closer examination of the energy profile of the alkyne ligand rotation serves to illuminate several key points for the [CpW(NO)(L)] system in general. Since the two frontier orbitals not engaged in bonding to the nitrosyl ligand in [CpW(NO)(L)] species *lie on the same plane* perpendicular to the W–NO axis, (e.g. the HOMO and LUMO of singlet $[CpW(NO)(PH_3)]$, Figure 9) the two *orthogonal* $\pi_\perp$ and $\pi^*_\parallel$ alkyne orbitals[38] cannot interact with both of these W orbitals simultaneously. Instead, the orientation of the alkyne ligand with respect to the W–NO vector determines whether it will act as a 4-electron (π-donor) or a 2-electron (π-acceptor) ligand. This type of phenomenon was first recognized three decades ago for another series of W^0 alkyne complexes, namely $[W(RCCR)_3(L)]$,[44] and has since been extended to other π-loaded metal centers with three $1\sigma,2\pi$ ligands.[45] The singlet and triplet [CpW(NO)(HCCH)] complexes both prefer the conformation with the alkyne lying in the plane perpendicular to the W–NO axis (2-electron, π-acceptor), resulting in a 16-electron count for the complex. Such an orientation is in contrast to the isolobal, 18-electron [Cp*Re(CO)(MeCCMe)] complex, which contains a 4-electron donor alkyne ligand aligned with the Re–CO bond.[46]

It has been noted previously by Bursten and co-workers that the HOMO of 18-e $[CpML_2]$ complexes increases in energy upon going from a late transition-metal CO complex to a more electropositive metal containing NO groups (e.g. from $[CpCo(CO)_2]$ to $[CpMn(NO)_2]$), and that this high-energy HOMO can result in the complex with an earlier transition metal being relatively less stable.[47] Although alignment of the alkyne ligand with the W–NO bond would result in an 18-electron, singlet [CpW(NO)(HCCH)] complex similar to the [Cp*Re(CO)(MeCCMe)] compound, the high energy of the resultant metal-centered, nonbonding HOMO (Figure 18) apparently destabilizes this complex with respect to the alternative alkyne conformation depicted in Figure 12. Thus, the M–alkyne conformational variation can be ascribed to the higher energy orbitals of the tungsten(0) nitrosyl complex compared to the isolobal rhenium(I) carbonyl species. Related arguments

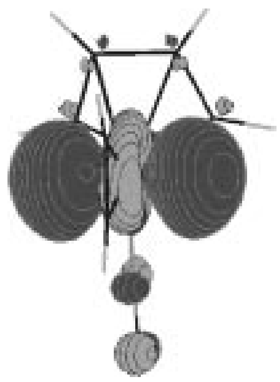

Figure 18. HOMO of singlet [CpW(NO)(HCCH)] with vertical alkyne orientation (local energy minimum).

based on periodic trends and orbital energies have been utilized by Eisenstein and co-workers to account for conformational and reactivity differences between ruthenium(0) and rhodium(I) [ML$_4$] d^8 complexes.[48–50]

Similar considerations help to explain why the [CpW(NO)(L)] compounds possess such a remarkably accessible triplet spin state. Generally, π-acceptor ligands, such as NO, increase the energy gap between HOMO and LUMO, which decreases the relative stability of high-spin electronic configurations.[51] Compared to isolobal complexes containing later transition metals, however, the filled orbitals of the more electropositive, lower valent W^0 center are higher in energy, thereby leading to a smaller HOMO–LUMO gap, and increasing the relative stability of the triplet spin state. For example, at the MP2 and B3LYP DFT levels of theory, singlet [CpRe(CO)$_2$] was calculated to be 5.6 kcal mol^{-1} more stable than the triplet,[7] compared to the 2.8 kcal mol^{-1} gap calculated in the present work for the isoelectronic [CpW(NO)(CO)] complex. These arguments are of potential importance for the design of configurationally stable, unsaturated, chiral-at-metal [CpML$_2$] species. Although energetically proximate HOMO and LUMO orbitals are desirable for the resulting Jahn–Teller distortion which helps enforce the requisite pyramidal-at-metal geometry,[39, 40] a small gap also increases the relative stability of achiral, planar triplet species.

The comparatively high energy of the filled W^0 orbitals is also likely to be responsible for the strong π-bonding interactions found in the [CpW(NO)(PH$_3$)(L)] and [CpW(NO)(L)] species. The filled orbital perpendicular to the W–NO axis, which is very high in energy for complexes such as [CpW(NO)(PH$_3$)$_2$] that lack additional π-acceptor ligands, exhibits excellent overlap with ligands, such as H$_2$CCH$_2$, (Figure 5) which results in bonding combinations even lower in energy than that of the two W–NO π-bonding orbitals. Experimentally, this is reflected by the ability of the [Cp*W(NO)(PPh$_3$)] fragment to bind even poor π-acceptor ligands, such as esters, in an η^2 fashion.[18] From the energies of triplet [CpW(NO)(PH$_3$)], the [CpW(NO)(PH$_3$)(L)] compounds, and the free energies of the various L ligands, it is possible to estimate the tungsten–L bond strengths in the 18-electron phosphine adducts. The strength of the W–L interaction increases in the order PH$_3$ (32.7) < H$_2$CCH$_2$ (48.2) < HCCH (54.6) < CO (70.8 kcal mol^{-1}), with the carbene complex giving unrealistically large W–CH$_2$ bond dissociation energies (> 110 kcal mol^{-1}) as a consequence of the comparative instability of free CH$_2$. While care must be exercised in the interpretation of bond strengths, particularly in complexes with multiple π-bonding interactions,[52] W-to-L π-donation probably contributes, at least partially, to the very large energies for the dissociation of the alkene, alkyne, and CO ligands. The value obtained for the W–CO bond is particularly high, in agreement with recent theoretical and experimental work and suggests that the standard homoleptic carbonyl benchmarks for metal–CO dissociation energies may be misleadingly low.[53]

Conclusions

Several important features of the [CpW(NO)(L)] complexes can be attributed to the relatively high occupied orbital energies in these formally W^0 species. The orbital not involved in W–NO π-bonding forms strong π interactions in [CpW(NO)(PH$_3$)(L)] compounds as a result of excellent energy matching and overlap. The overall high energy of the occupied orbitals in unsaturated [CpW(NO)(L)] complexes leads to highly pyramidalized, Jahn–Teller distorted geometries for the spin singlet species because of good mixing between the HOMO and the LUMO. However, the energetic proximity of these two orbitals also enhances the relative stability of the planar-at-W triplet [CpW(NO)(L)] compounds. The conformation at W, the orientation of the L group, and the π-bonding capabilities of L all influence the relative energies of the singlet and triplet spin states. Both inversion of conformation-at-W and W–L rotation have the possibility of proceeding by a two-state pathway, crossing over from the singlet to the triplet state and back again.

Theoretical studies are currently underway to use the [CpW(NO)(L)] complexes reported here to model the intermolecular alkane C–H bond activation reactions performed by the [Cp*W(NO)(L)] species.

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