Metal-based chirality and spin state change in 16-electron $CpML_2$ systems: a computational study of $CpW(NO)(PH_3)$

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Density functional theory calculations indicate that $CpW(NO)(PH_3)$ possesses a planar triplet ground state, a result with significant implications for the inversion of configuration of 16e, d^6 $CpML_2$ species.

Several highly reactive Cp*W(NO)L intermediates (L = PMe_3,[1] PPh_3,[2] $=CHCMe_3$,[3] HCCPh[4–6]) have previously been shown to be generated by reductive elimination of CMe_4 or $SiMe_4$.† These proposed 16 electron, d^6 Cp*W(NO)L species are not observed as they proceed to activate C–H bonds,[1–4] coordinate weak π-acceptor ligands,[7] or engage in coupling and rearrangement reactions[5,6] with available trapping reagents. Previous theoretical studies[8–10] have demonstrated that the geometries and orbital energies of 16e, d^6 $CpML_2$ species are influenced by the bonding properties of their ligands. For example, π-donor ligands enforce a planar-at-metal conformation (*i.e.* the metal sits on the plane defined by the two ligands L and the Cp center of gravity), while pyramidal geometries are preferred for complexes containing either σ-donor (π-neutral) or π-acceptor ligands. However, these studies were carried out using semiempirical methods and so were confined to the spin singlet energy hypersurface. The computational studies that we report here for the $CpW(NO)(PH_3)$ model system indicate that the spin state can play a previously unsuspected yet critical role in 16e, d^6 $CpML_2$ species.

The optimised geometries and relative energies of the singlet and triplet $CpW(NO)(PH_3)$ complexes are shown in Table 1 and Fig. 1.‡ The singlet is pyramidal at W, as expected for a $CpML_2$ species containing π-acceptor and σ-donor ligands.[9,10] However, triplet $CpW(NO)(PH_3)$ is calculated to possess a planar geometry at W, and to be 3.3 kcal mol^{-1} (1 cal = 4.184 J) more stable than the pyramidal singlet species. No significant variation in W–NO bond distance is observed between the two different spin configurations since the W–NO π-bonding orbitals are fully occupied in both cases.[17] There is, however, the expected[18,19] slight overall extension of all bond lengths in the triplet, as well as an increase in CNT–W–P angle.

Table 1 DFT-B3LYP optimized geometries and energies for $CpW(NO)(PH_3)$

Parameter	Energy minima		Spin-crossover point	
	Singlet	Triplet	Singlet	Triplet
φ (N–W–CNT–P)	125.0	180.0	130.0	130.0
W–CNT	2.018	2.093	2.023	2.107
W–P	2.482	2.522	2.481	2.528
W–N	1.791	1.794	1.792	1.795
N–O	1.251	1.252	1.251	1.253
CNT–W–P	121.38	132.82	122.37	129.37
CNT–W–N	128.55	133.55	128.35	133.48
P–W–N	93.33	93.63	95.36	85.64
W–N–O	175.34	176.71	175.37	176.90
Relative energy/kcal mol	0	−3.3	+0.8	+0.8

While triplet $Cp^*W(NO)(PR_3)$ complexes have yet to be detected spectroscopically, the intermediacy of such a species where R = Ph is consistent with kinetic measurements of the reaction between $Cp^*W(NO)(\eta^2\text{-}PPh_2C_6H_4)H$ and $CNCMe_3$.[7,20] Replacing the Cp and PH_3 ligands of the model complex with bulkier Cp* and PR_3 groups would be expected to enforce a larger CNT–W–P angle and a planar-at-W geometry, thereby further destabilising the singlet state. The steric shielding of the metal centre coupled with the expected reduced reactivity[21] of the high-spin configuration should impart additional stability, making triplet $Cp^*W(NO)(PR_3)$ compounds reasonable synthetic targets.§

In order to explore the role of the triplet spin state in the inversion of pyramidal, diamagnetic $CpML_2$ species, further calculations were performed at various values of ϕ for both spin states (Fig. 1). The highest energy singlet conformation is the planar geometry (ϕ = 180°), leading to an inversion barrier of 7.7 kcal mol^{-1} along the singlet spin surface, which compares well with previous studies on other 16-electron systems.[10] The energy of triplet $CpW(NO)(PH_3)$ increases relatively gradually as the geometry is distorted away from the planar-at-W conformation. As a result, the ϕ angle at which both spin states are equal in energy corresponds to a high degree of pyramidalization ($\phi \approx 130°$), only 0.8 kcal mol^{-1} higher in energy than the singlet ground state.

The one-dimensional energetic situation illustrated in Fig. 1 would suggest a low-energy inversion mechanism for diamagnetic, pyramidal $CpW(NO)(PH_3)$ *via* the spin triplet surface.¶ However, the two geometries at the spin-crossover point are significantly different (Table 1). According to the Franck–Condon principle, both the geometries and the energies must be very similar for the spin flip process to occur. At the crossover

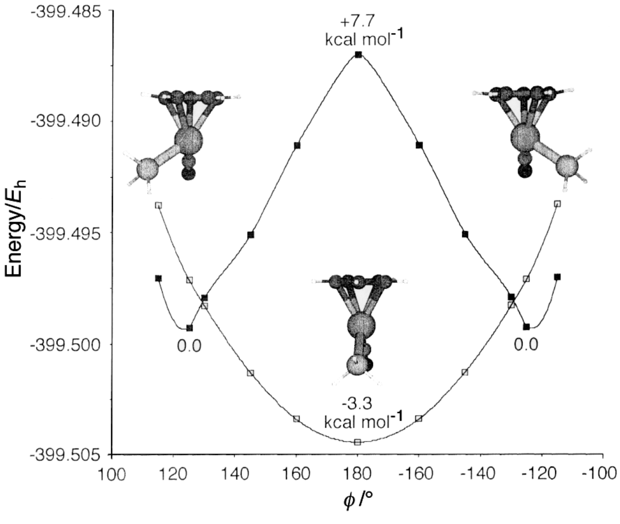

Fig. 1 B3LYP/LANL2DZ energies of optimized singlet (■) and triplet (□) $CpW(NO)(PH_3)$ at various fixed dihedral N–W–CNT–P (ϕ) angles

point (ϕ = 130°), the vertical excitation energies of singlet and triplet geometries (energy of the triplet configuration at the singlet geometry and of the singlet configuration at the triplet geometry) are 6.9 and 8.2 kcal mol^{-1}, respectively. These numbers give an estimate of the upper bound of the spin flip barrier.‖

The energetic proximity of these vertical excitation energies and the inversion barrier along the singlet surface (within *ca.* 1 kcal mol^{-1}) prohibits the definitive identification of the inversion mechanism (two-state *vs.* one-state) for the CpW(NO)(PH_3) species. It is readily apparent, however, that the involvement of the triplet spin state represents a distinct and realistic alternative to a process restricted to the singlet spin surface, the only mechanism which has hitherto been considered for this class of compounds. Further experimental and theoretical work is unquestionably required to explore this possibility for Cp*W(NO)L species, as well as for $CpML_2$ compounds in general.

Several 16e, d^6 Cp*M(PR_3)X species have been invoked in intra- and inter-molecular C–H bond activation reactions (M = Ir, X = CH_3^+;[25] M = Os, X = CH_2SiMe_3;[26] M = Ru, X = CH_2CMe_3;[27] M = Re, X = CO, PMe_3;[28–30] M = W, X = NO[1]). In particular, much recent theoretical, synthetic, and mechanistic work has been focused on the low-temperature alkane C–H bond activation reactions of the Cp*Ir(PMe_3)(CH_3)$^+$ complex,[31–34] but to the best of our knowledge, only one study has addressed the possible involvement of triplet species in this system.[19] The role of the spin state in the reactivity of unsaturated Cp*W(NO)L species is currently under theoretical investigation.[35]

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Notes and References

† Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; CNT = Cp ring centroid.

‡ Calculations were performed using Gaussian 94.[11] The LanL2DZ basis set was employed to perform geometry optimisations with a density functional theory (DFT) approach. The three-parameter form of the Becke, Lee, Yang and Parr functional (B3LYP)[12] was employed. The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H and C[13] and the relativistic electron core potential (ECP) sets of Hay and Wadt for the heavy atoms.[14–16] 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 open shell systems, was considered suitable for the unambiguous identification of the spin state. Ground state energies are based on complete geometry optimisations. The singlet geometry for ϕ = 180° was optimised with an imposed mirror plane. For all other values of ϕ, the C_5 ring of the Cp ligand was fixed as a regular pentagon, the degree of pyramidalisation was set at a specific N–W–CNT–P dihedral angle (ϕ), and the geometry was optimised with no other constrained parameters.

§ For the use of steric bulky ligands in stabilising Cp*Ru(PR_3)X species, see refs. 9, 22 and 23.

¶ For discussion of similar examples of 'two-state reactivity' see ref. 24 and references therein.

‖ For a discussion of the problems inherent in estimating spin-crossover energies, see refs. 18, 21 and 24.

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