Spin State and Ligand Dissociation in [$CpCoL_2$] Complexes ($L = PH_3, H_2C{=}CH_2$): A Computational Study

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Keywords: Cobalt / Density functional calculations / Electronic structure / Ligand effects / Spin state

The relative energies of [CpCoL] compounds ($L = PH_3, H_2C{=}CH_2$) were calculated at the DFT/B3LYP level of theory. The triplet spin state was found to be favored over the singlet by between 33.0 and 21.0 kcal mol^{-1} for both fixed and optimized geometries. The basis set size was found to be important for the energy calculations, particularly when the energetics of ligand dissociation was examined. The role of the triplet spin state in facilitating the ligand dissociation process is discussed.

Introduction

The role of spin-state changes in the reactivity of [$CpCoL_2$] species remains under dispute. Several kinetic, spectroscopic, and theoretical studies have investigated this issue. Bergman et. al. examined the mechanism of phosphane substitution in [$CpCo(PPh_3)_2$] in order to determine whether interconversion between singlet and triplet species resulted in an activation barrier for the dissociative pathway. The first step in the ligand-replacement reaction was found to be the rapid, reversible formation of [$CpCo(PPh_3)$].[1] Extended Hückel molecular orbital theory calculations by Hofmann and Padmanabhan suggested that, although linear d^8 [CpML] compounds are symmetry-required to have a triplet ground spin state, a "bent" geometry for [$CpCo(PPh_3)$] (i.e. Cp−Co−P angle < 180°) might allow the substitution reaction to proceed via the singlet spin surface, thereby accounting for the observed lack of a "spin-flip barrier".[2] Later studies by Bergman, Moore, and co-workers demonstrated that photogenerated [CpCo(CO)] and [Cp*Co(CO)] did not form adducts with alkanes or noble gases, although these unsaturated species did react very rapidly with CO.[3] Using a variety of computational techniques including density functional theory (DFT), Siegbahn calculated that [CpCo(CO)] possesses a triplet ground spin state, and attributed the difference in reactivity of the 16-electron species with alkanes and CO to the varying ability of the incoming ligand to induce triplet-to-singlet spin crossover.[4] In contrast, Brookhart et. al. have recently reported C−H activation reactions of [Cp*Co(η^2-$H_2C{=}CHSiMe_3)_2$] that proceed by oxidative addition of benzene or aldehydes to unsaturated [Cp*Co(η^2-$H_2C{=}CHSiMe_3$)].[5]

As part of an ongoing investigation of spin state and reactivity,[6] we have recently used DFT techniques to examine how ligands can affect the relative energy of the singlet and triplet states (ΔE_{S-T}) of 16-electron [CpM(NO)]-containing complexes of Cr, Mo, and W.[7] Ultrafast IR studies have implicated triplet [$CpMn(CO)_2$] in the photolysis of [$CpMn(CO)_3$] in Et_3SiH.[8] Spin-state changes have also been proposed to play a critical role in the reactivity of cytochrome P450.[9] The computational study described in this paper was performed to address the following questions: (1) What is the ground spin state of *bent* [CpCoL] species ($L = PH_3, H_2C{=}CH_2$)? (2) Is ΔE_{S-T} substantially altered for [CpCoL] species by variation of L? (3) Can the observed C−H bond-activation reactivity of [Cp*Co(η^2-$H_2C{=}CHSiMe_3$)] be attributed to a difference in ground spin state compared to triplet [CpCo(CO)]?

Results and Discussion

Calculated Geometries and Energies

The saturated [$CpCoL_2$] ($L = PH_3, H_2C{=}CH_2$) complexes were studied with DFT using the three-parameter form of the Becke, Lee, Yang, and Parr functional (B3LYP)[10] and two basis sets, following the methodology recently developed by Siegbahn and co-workers.[11] The geometries were optimized without constraints (C_1 symmetry) with the LanL2DZ basis set;[12] the structural parameters for both complexes are listed in Table 1. Since energy calculations are more sensitive to basis set size than geometry optimizations,[13] the energies of the LanL2DZ structures were also calculated with the larger 6-311+G(2d,2p) basis set.

Table 1. Optimized geometries for [$CpCo(PH_3)_2$] and [$CpCo(C_2H_4)_2$][a]

Parameter[b]	[$CpCo(PH_3)_2$]	[$CpCo(C_2H_4)_2$]
CNT−Co	1.800	1.837
Co−X	2.231	1.950
	2.235	1.939
CNT−Co−X	131.44	130.45
	130.69	130.26
X−Co−X	97.87	99.28

[a] Bond lengths in Å and angles in°. − [b] CNT = center of gravity of the Cp ring, X = P for [$CpCo(PH_3)_2$] or center of C−C bond for [$CpCo(C_2H_4)_2$].

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1434−1948/99/0505−0877 $ 17.50+.50/0

The bond lengths obtained for the optimized [CpCoL$_2$] geometries are marginally longer than those reported for the solid-state molecular structures of [CpCo(PEt$_3$)$_2$][14b] and [Cp*Co(η^2-H$_2$C=CHSiMe$_3$)$_2$].[5c] For instance, the average calculated Co−C(Cp) bond lengths are 0.09 Å longer than those found experimentally, and the theoretical Co−L(average) distances are 0.015 Å and 0.035 Å longer than those found in the corresponding X-ray molecular structures for the phosphane and alkene complexes, respectively. The alkene orientation of [CpCo(η^2-H$_2$C=CH$_2$)$_2$] corresponds to the alignment observed experimentally, namely parallel with the Cp plane.[5] The calculated alkene C−C bond lengths in [CpCo(η^2-H$_2$C=CH$_2$)$_2$] (1.417 and 1.414 Å) are almost identical to those reported for [Cp*Co(η^2-H$_2$C=CHSiMe$_3$)$_2$] (1.414 and 1.404 Å). The slight distortions in C−C bond lengths in the Cp ligand also correspond well with those previously discussed for related [CpCoL$_2$] derivatives.[14]

As noted in the introduction, Hofmann and Padmanabhan have previously suggested that ligand dissociation from d^8 [CpML$_2$] complexes may remain on the singlet spin hypersurface if the unsaturated [CpML] intermediate adopts a bent geometry.[2] To test this hypothesis, the energies of bent [CpCoL] compounds were calculated in both singlet and triplet spin states, using the optimized [CpCoL$_2$] geometries with one L group removed and leaving the other structural parameters unchanged. For both [CpCo(PH$_3$)] and [CpCo(η^2-H$_2$C=CH$_2$)] in this bent conformation (Cp−Co−L < 132°), the triplet state is greatly favored over the singlet. The value of $\Delta E_{\mathrm{S-T}}$ decreases only slightly when the larger basis set is employed, from −31.0 to −28.1 kcal mol^{-1} for the phosphane system and from −25.9 to −23.9 kcal mol^{-1} for the alkene system. Overall, only a minor difference in $\Delta E_{\mathrm{S-T}}$ is observed upon changing the L group in [CpCoL].

Analogous results are obtained when the [CpCoL] geometries are optimized using B3LYP/LanL2DZ. Optimized triplet [CpCo(PH$_3$)] was found to be 33.0 kcal mol^{-1} more stable using the LanL2DZ basis set, and 27.1 kcal mol^{-1} more stable at the B3LYP/6-311+G(2p,2d) level. For the alkene system, triplet [CpCo(η^2-H$_2$C=CH$_2$)] was calculated to be 26.5 kcal mol^{-1} more stable than the singlet at the B3LYP/LanL2DZ level, and 21.0 kcal mol^{-1} more stable using the larger basis set. By comparison, Siegbahn's B3LYP calculation of [CpCo(CO)] gave a $\Delta E_{\mathrm{S-T}}$ value of −27.8 kcal mol^{-1}, which falls between the results obtained here for the phosphane and alkene derivatives.[4] The structural parameters of the B3LYP/LanL2DZ optimized [CpCoL] geometries are listed in Table 2, and the relative energies are illustrated in Figure 1.

Table 2. Optimized geometries for [CpCo(PH$_3$)] and [CpCo(C$_2$H$_4$)][a]

Parameter[b]	[CpCo(PH$_3$)]	[CpCo(C$_2$H$_4$)]
CNT−Co	1.782 (1.881)	1.793 (1.958)
Co−X	2.241 (2.325)	1.851 (1.932)
CNT−Co−X	140.92 (140.43)	148.32 (149.09)

[a] Singlet bond lengths in Å and angles in°, with triplet parameters indicated in parentheses. − [b] CNT = center of gravity of the Cp ring, X = P for [CpCo(PH$_3$)$_2$] or center of C−C bond for [CpCo(C$_2$H$_4$)$_2$].

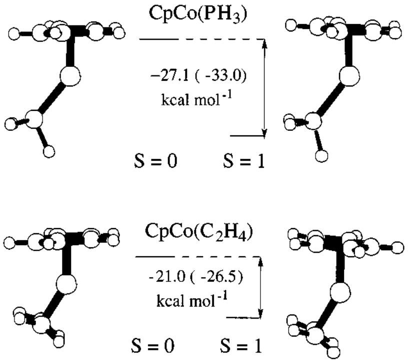

Figure 1. Relative energies of singlet and triplet [CpCo(PH$_3$)] and [CpCo(C$_2$H$_4$)]; $\Delta E_{\mathrm{S-T}}$ calculated at the B3LYP/6-311+G(2d,2p) level of theory, with B3LYP/LanL2DZ values indicated in parentheses

An indication of the energetics of the ligand dissociation process can be attained by comparing the energy of [CpCoL$_2$] complexes with the sum of the energies of optimized [CpCoL] and the free L ligand, as shown in Table 3. For these relative energies, the difference between the values obtained with the two different basis sets is pronounced. In fact, at the B3LYP/LanL2DZ level, [CpCo(PH$_3$)$_2$] is calculated to be 4.3 kcal mol^{-1} less stable than triplet [CpCo(PH$_3$)] and free PH$_3$, contrary to experimental observations. This erroneous result is presumably due to the previously observed correlation between basis set size and bond strength.[4] Thus, while the relative energies calculated with the small basis set are skewed in favor of the dissociated species, employing the larger 6-311+G(2d,2p) basis set results in the saturated complex being 7.3 kcal mol^{-1} more stable, in accord with experimental studies of the [CpCo(PPh$_3$)$_2$] system.[1]

Table 3. Relative energies of [CpCoL$_2$] and [CpCoL] + L[a]

	[CpCo(PH$_3$)]	[CpCo(C$_2$H$_4$)]
Singlet	−34.4 (−28.8)	−24.6 (−25.1)
Triplet	−7.3 (+4.3)	−3.6 (+1.4)

[a] ΔE (in kcal mol^{-1}) calculated at the B3LYP/6-311+G(2d,2p) level of theory, with B3LYP/LanL2DZ values indicated in parentheses.

Implications for Reactivity

It has been previously proposed that the lack of a high activation barrier for ligand exchange reactions in d^8 [CpML$_2$] compounds might be due to the bent geometry of unsaturated [CpML] species, which allows the singlet spin state to be maintained thoughout the dissociative substitution process.[15] Although extended Hückel molecular orbital calculations did not permit the relative energies of the singlet and triplet [CpML] species to be ascertained, Hofmann and co-workers recognized that this possibility was more likely for Rh and Ir than for Co.[2] Our results at the DFT/B3LYP level indicate that even in the bent conformation, the triplet spin state is considerably lower in energy for [CpCo(PH$_3$)] and [CpCo(η^2-H$_2$C=CH$_2$)] than the corresponding singlet electronic configuration.

It should be observed that the crossover from the singlet to the triplet surface upon phosphane dissociation from [CpCo(PPh$_3$)$_2$] will in fact lower the enthalpic barrier to the phosphane exchange process if the crossing point is located below the singlet [CpCo(PPh$_3$)] species. A change in spin state would only translate into an entropic contribution to the activation free energy. Thus, the facile phosphane exchange process observed for [CpCo(PPh$_3$)$_2$] is in fact quite nicely rationalized by the large energetic stabilization of the [CpCo(PPh$_3$)] intermediate upon changing the spin state, accompanied by a low-energy crossing point and lack of a "spin-flip barrier".[16]

Differences in ground spin state between [CpCo(CO)] and the heavier Rh and Ir congeners were utilized by Siegbahn to explain the experimentally observed differences in alkane binding and C−H bond activation reactivity of these species.[4] With this precedent, it seemed conceivable that the H/D exchange reactivity with C$_6$D$_6$ and the aldehyde C−H activation reactions observed by Brookhart and co-workers might be attributable to a low-lying or ground singlet spin state for [Cp*Co(η^2-H$_2$C=CHSiMe$_3$)] intermediates.[5] Although the present study indicates that $\Delta E_{\mathrm{S-T}}$ is *slightly* more favorable for the singlet alkene species than for the analogous phosphane system, the triplet state is still the ground state by over 20 kcal mol^{-1} for [CpCo(η^2-H$_2$C=CH$_2$)]. However, it has previously been shown that photogenerated [CpCo(CO)] *does* form a solvated complex with benzene[17] and forms alkene adducts at diffusion-limited rates.[17][18] Therefore, it is possible that the discrepancy in reactivity between [Cp*Co(CO)] and [Cp*Co(η^2-H$_2$C=CHSiMe$_3$)] is due to substrate effects; i.e. that the aromatic C$_6$D$_6$ solvent or the C=O bond of the aldehyde may help to facilitate the spin state change from triplet to singlet in the 16-electron alkene intermediate, whereas alkanes do not induce this process for [Cp*Co(CO)]. MP2 calculations have indicated that a similar difference in the ability of the incoming ligand to induce spin-crossover was responsible for the experimentally observed variation between the rate of addition of CO and N$_2$ to triplet Cp*MoCl(PMe$_3$)$_2$.[19]

Conclusion

The triplet spin state is calculated to be much more stable than the singlet state for [CpCoL] species, even in "bent" structures derived directly from the saturated [CpCoL$_2$] precursors. Varying the ligand in [CpCoL] exerts only a minor influence on the energy difference between singlet and triplet species: our present results for the PH$_3$ and H$_2$C=CH$_2$ systems lie on either side of the $\Delta E_{\mathrm{S-T}}$ value obtained by Siegbahn for the CO complex. The C−H bond activation reactions reported for [Cp*Co(η^2-H$_2$C=CHSiMe$_3$)] may thus be attributable to substrate effects rather than to a difference in ground spin state of the unsaturated intermediate. The comparatively high energy of the singlet [CpCoL] complexes suggest that the ligand dissociation process from [CpCoL$_2$] may be facilitated by spin crossover to the lower energy triplet species. Although the $\Delta E_{\mathrm{S-T}}$ values are relatively basis-set-independent, the energies of the [CpCoL] species relative to the saturated [CpCoL$_2$] complexes shows a marked dependence on the size of the basis set used.

Experimental Section

General Remarks: All calculations were performed with GAUSSIAN 94[20] using an SGI Origin 200 workstation. The geometries of the [CpCoL$_2$] and [CpCoL] species and the free L ligands were optimized using B3LYP,[10] a DFT type of calculation, employing the LanL2DZ basis set. The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H and C and the core potential sets of Hay and Wadt for the heavy atoms.[12] Electrons outside the core were all those for H and C, the 3s and 3p electrons for P, and the 3s, 3p, 3d, and 4s electrons for Co. All geometries were optimized at the B3LYP/LanL2DZ level without constraints, with the exception of triplet CpCo(PH$_3$), which failed to achieve geometric convergence despite several attempts from various initial geometries. At the suggestion of a reviewer, the complex was optimized with imposed C_s symmetry starting from both possible orientations of the Cp ligand. Convergence was attained in both cases, and the configuration with the unique C−H group opposite to the P was found to be slightly less stable than the other conformation, with an energy difference of less than 0.1 kcal mol^{-1}. The fixed, bent [CpCoL] geometries were obtained from the [CpCoL$_2$] structures by removing one L ligand and keeping all other parameters unchanged. The B3LYP energy calculations were performed separately with both the LanL2DZ basis set and the larger 6-311+G(2d,2p) basis set, which has two sets of polarization functions on all atoms including two f sets on Co, and also diffuse functions.[11]

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 unambiguous identification of the spin state. Spin contamination was carefully monitored and the value of $<S^2>$ for the unrestricted B3LYP (UB3LYP) calculations on the triplet [CpCoL] species using the 6-311+G(2d,2p) basis set (LanL2DZ results shown in parentheses) [L = bent PH$_3$, 2.0261 (2.0228); optimized PH$_3$, 2.0234 (2.0205); bent H$_2$C=CH$_2$, 2.0499 (2.0463); optimized H$_2$C=CH$_2$, 2.0531 (2.0484)] indicated minor spin contamination. The energies shown in the Results and Discussion section correspond to UB3LYP calculations for the triplet [CpCoL] compounds, and to restricted B3LYP calculations for the singlet [CpCoL] and [CpCoL$_2$] complexes.[21]

Acknowledgments

R. P. thanks the Région Bourgogne for supporting this research, and K. M. S. thanks the European Commission for a TMR Marie Curie Postdoctoral Fellowship.

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[21] Note added in proof (March 4, 1999): Recent calculations at the B3LYP/LanL2DZ level indicate that the CpM(Ph$_3$) (M = Rh, Ir) congeners also possess ground triplet spin states, with $\Delta E_{\text{S-T}} = -13.2$ and -16.9 kcal mol^{-1}, respectively: M.-D. Su, S.-Y. Chu, *Chem. Eur. J.* **1999**, *5*, 198−207.

Received December 17, 1998
[I98435]