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Articles

Geometric Distortions in Four-Legged Piano-Stool Cyclopentadienyl Transition-Metal Complexes

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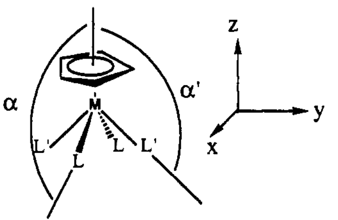
Ab initio calculations with effective core potentials are used to obtain structural parameters of "four-legged piano-stool" (also viewed as pseudo-square-pyramidal) cyclopentadienyl transition-metal complexes, CpML$_{4-n}$L'$_n$ (n = 0–3), where M = Ru, Os, Rh, and Ir, and L, L' = PH$_3$, CO, H, SiH$_3$, Cl, Li, and Be. These four-legged piano-stool complexes distort from an ideal pseudo-square-pyramidal geometry in such a way that the two larger L–M–Ct (Ct = centroid of the Cp ligand) angles correspond to trans ligands, as do the two smaller ones. These distortions are explained in terms of a σ-interaction model that differs considerably from a previous one, which emphasized the M–L π-interactions. A rehybridization between d_{z^2} (one of the two nonbonding d orbitals in a pseudo-C_{4v} CpML$_4$ complex) and $d_{x^2-y^2}$ (σ antiboding with L's) occurs in the process of distortion from pseudo-C_{4v} to C_{2v} symmetry. The result of the rehybridization is a preference for strong covalently σ-bonding ligands to be coordinated to the transition metal with a small L–M–Ct angle.

Introduction

Cyclopentadienyl transition-metal complexes play a major role in modern chemistry. Compounds of the formula CpML$_4$, which have been described as "four-legged piano stools", may also be viewed as pseudo-square-pyramidal[1-3] (see 1). When the four L ligands are not identical, a unique structural feature is the way in which the four legs distort from an ideal pseudo-square-pyramidal geometry (as measured by the angle L–M–Ct or α; Ct = centroid of the Cp ligand). The ligands distort in a pairwise fashion; the two larger α-angles correspond to one pair of trans ligands and the two smaller ones correspond to the other pair. Such distortions were named "angular trans influence" in a recent theoretical paper,[3] which emphasized π interactions between the four leg ligands and the central metal atom. The considerable interest in transition-metal polyhydride complexes[4-6] prompted us to do systematic quantum–mechanical calculations on 18-electron transition-metal polyhydride model complexes with molecular formula of CpMH$_n$L$_{4-n}$ (n = 2–4),[7e] where M = Ru, Rh, Os, and Ir, and L = PH$_3$ or CO. The predicted structures of these "four-legged piano-stool" polyhydrides also show the unique distortion mentioned above. However, the distortion discovered in these polyhydrides cannot be satisfactorily explained by a π-interaction model. Here, we show how these distortions may arise from M–L σ-bonding by examining predicted structures for a large variety of CpML$_{4-n}$L'$_n$ (n = 0–3), where M = Tc, Ru, Os, Rh, and Ir, and L, L' = PH$_3$, CO, H, SiH$_3$, Cl, Li, and Be.



(1)

Theoretical Details

Ab initio effective core potentials[8] were employed in all calculations. All geometries were optimized at the restricted Hartree–Fock (HF) level. In this study, all aryl and alkyl groups were replaced by H atoms, i.e., PR$_3$ was replaced by PH$_3$ and SiR$_3$ by SiH$_3$. The internal geometry of these model ligands was fixed as follows: H–P–H = 103.4°, P–H = 1.44 Å, H–Si–H = 109.47°, and Si–H = 1.48 Å. The C$_5$H$_5$ unit is also fixed as planar with C–C and C–H bond lengths of 1.41 and 1.08 Å, respectively.

In the effective core potentials (ECP's) for the transition metals,[8a] the outermost core orbitals, which correspond to ns^{2}np^6 configuration, were treated explicitly on an equal footing with the nd, (n + 1)s and (n + 1)p valence orbitals. The basis sets of the second and third transition series atoms were described as (541/41/211) and (541/41/111), respectively, which correspond to a double-ζ representation of the (n + 1)s/np electrons and a triple-ζ representation of the nd electrons. For ligand atoms, the ECP's and double-ζ basis sets of Stevens, Basch, and Krauss were used.[8b] [He] and [Ne] configurations were taken as cores

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(8) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985,** *82,* 299. (b) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984,** *81,* 6026.

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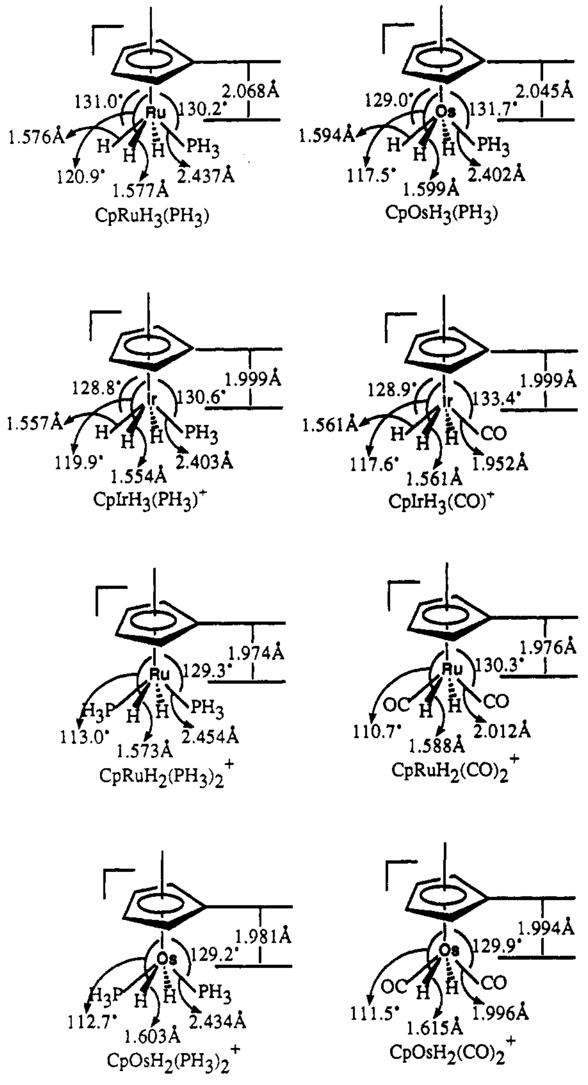
Chart I



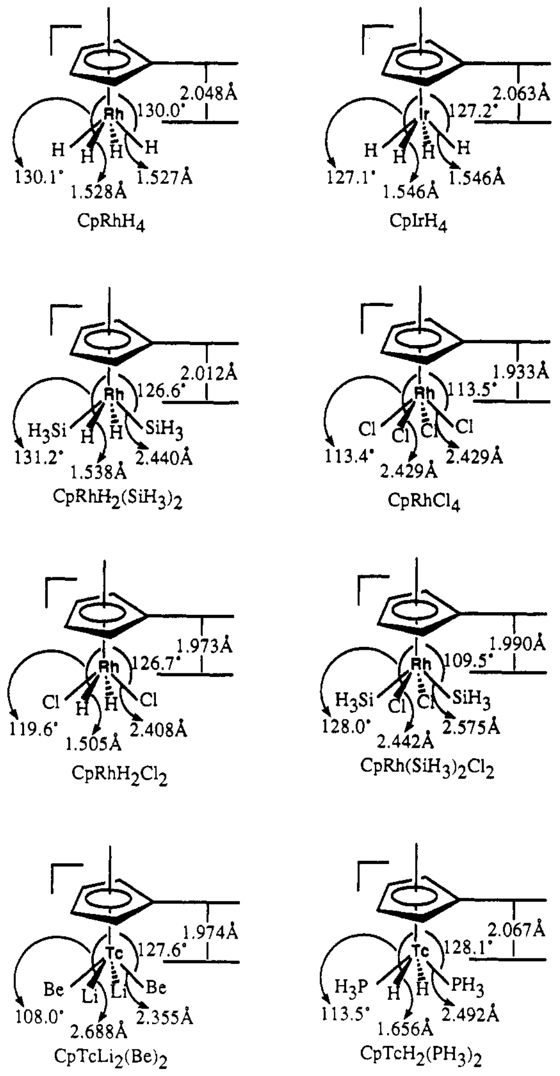
$CpRuH_3(PH_3)$ $CpOsH_3(PH_3)$

$CpIrH_3(PH_3)^+$ $CpIrH_3(CO)^+$

$CpRuH_2(PH_3)_2^+$ $CpRuH_2(CO)_2^+$

$CpOsH_2(PH_3)_2^+$ $CpOsH_2(CO)_2^+$

Chart II



$CpRhH_4$ $CpIrH_4$

$CpRhH_2(SiH_3)_2$ $CpRhCl_4$

$CpRhH_2Cl_2$ $CpRh(SiH_3)_2Cl_2$

$CpTcLi_2(Be)_2$ $CpTcH_2(PH_3)_2$

for the first- and second-row main-group atoms. The Dunning-Huzinaga double-ζ basis set (31) was used for H atom[9] and Huzinaga's (33) basis sets were split to (321) for Li and Be atoms.[10]

All HF calculations were performed with the GAMESS package.[11] All GAMESS calculations were made at the Cornell National Supercomputer Facility (CNSF) on an IBM 3090-600VF, at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116, and at a Chemistry Department on a FPS model 522. The Laplacian of valence electron density was plotted with the use of the program MOPLOT.[12]

Results and Discussion

Structural Feature in the Four-Legged Piano-Stool Geometry. Geometry optimizations at the HF level have been done on the polyhydride model complexes listed in Chart I. All these model complexes conform to the 18-electron rule. Calculated structural parameters of the classical isomers are presented in Chart I for those complexes with formula $CpMH_2L_2$ and $CpMH_3L$ ($L = PH_3$ or CO). In this class of four-legged piano-stool structures, the distortion of the four legs from ideal pseudo-square-pyramidal geometry is clearly seen from Chart I. The two smaller L–M–Ct (α) angles (110–120°) are always associated with the two trans hydrogens, while the two larger ones (126–133°) are associated with the two L ligands or with one L and the hydrogen trans to it. From the structural parameters of those complexes with molecular formula, $CpMH_3L$, we can see that the α-angles for H ligands that are trans to each other are quite different from the α-angle for the H ligand trans to an other ligand. Similar behavior was observed for the CO ligand in a large number of four-legged piano-stool complexes and was referred as "angular trans influence".[3]

To study the origin of this distortion, we also optimized the geometries of some other model complexes; the results are shown in Chart II. The reliability of these calculated structural parameters can be examined by comparing calculated complexes, such as $CpIrH_3(PH_3)^+$ (see Chart I) and $CpRhH_2(SiH_3)_2$ (see Chart II) with the related neutron diffraction structures.[5,6] The calculated metal–hydrogen geometries agree quite well with the experimental one: the metal–hydrogen bond lengths are within 0.045 Å, and the α-angles are within 2°. The metal–silicon,

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[9] (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

[10] *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier: Amsterdam, 1984.

[11] Guest, M. F.; Sherwood, P. Daresbury Laboratory, Warrington, WA4 4AD, U.K.

[12] Interactive MOPLOT: a package for the interactive display and analysis of molecular wave functions incorporating the program MOPLOT (D. Lichtenburger), PLOTDEN (R. F. W. Bader, D. J. Kenworthy, P. M. Beddal, G. R. Runtz, and S. G. Anderson), SCHUSS (R. F. W. Bader, G. R. Runtz, S. G. Anderson, and F. W. Biegler-Koenig), and EXTREM (R. F. W. Bader and F. W. Biegler-Koenig), P. Sherwood and P. J. MacDougall, 1989.

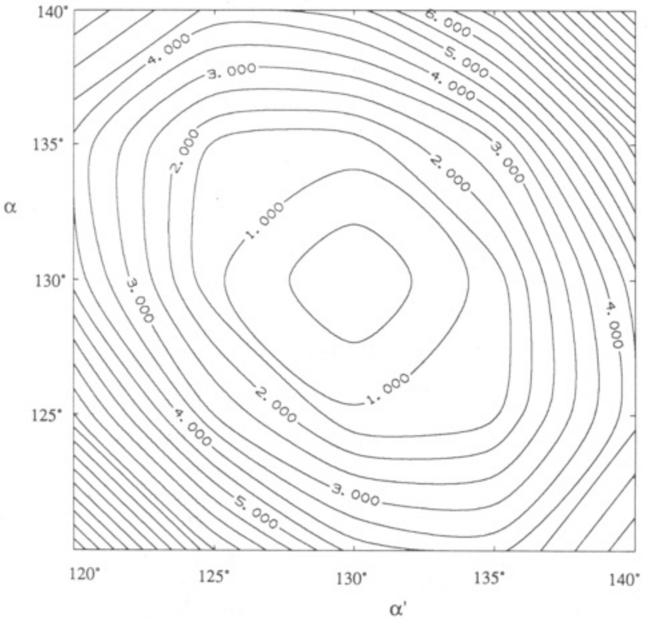


Figure 1. The plot of the potential surface in the vicinity of the optimized $CpRhH_4$ structure against α- and α′-angles (see **1** for the definition of the two angles).

metal–Ct (M–Ct), and metal–phosphine lengths are all slightly longer than the experimental values (0.061 Å for Rh–Si, <0.110 Å for M–Ct, and 0.130 Å for Ir–P), as is generally true in this basis set at the Hartree–Fock level.[13] Overall, the calculated structural parameters are quite reasonable.

The complexes in Chart II do not follow the same pattern as those in Chart I. When the four-legged ligands are identical, the α-angles are almost the same (see $CpRhH_4$, $CpIrH_4$, and $CpRhCl_4$ complexes in Chart II). The α-angles in the $CpRhH_4$ and $CpIrH_4$ complexes are 130° and 127°, respectively, while the α-angles in the $CpRhCl_4$ complex are 113.5°. In $CpRhH_2(SiH_3)_2$, the two distinct angles (α and α′, see **1**) are close to those found in $CpRhH_4$ and $CpIrH_4$ with larger H–Rh–Ct (131.2°) and smaller Si–Rh–Ct (126.6°) angles. Surprisingly, in $CpRhH_2Cl_2$ complex, the Cl–Rh–Ct (126.7°) is much larger than the H–Rh–Ct (119.6°) (see Chart II), a result which is unexpected from the results on $CpRhH_4$ and $CpRhCl_4$ complexes. In $CpRh(SiH_3)_2Cl_2$, the Cl–Rh–Ct (128.0°) is again unexpectedly larger than the Si–Rh–Ct (109.5°). We also did calculations on model complexes, $CpTcLi_2Be_2$ and $CpTcH_2(PH_3)_2$. The result for $CpTcH_2(PH_3)_2$ is similar to those in Chart I with a smaller H–Tc–Ct angle. In $CpTcLi_2Be_2$, the Li–Tc–Ct angle is much smaller than the Be–Tc–Ct angle, a result that is impossible to explain through a π-interaction model.

To examine how the total energy changes with the unique distortion, we plot the potential energy surface in the vicinity of the optimized $CpRhH_4$ structure against α- and α′-angles (see **1** for α- and α′-angles) in Figure 1. The potential surface is flatter along the diagonal line connecting the upper-left to bottom-right in the figure. This feature means that the distortions from a pseudo-C_{4v} to a pseudo-C_{2v} geometry with a pair of larger α-angles and another pair of smaller α-angles are likely to occur through a second-order Jahn–Teller effect,[14] which allows an orbital mixing between occupied and unoccupied molecular orbitals, usually the HOMO and LUMO, when different L ligands are present.

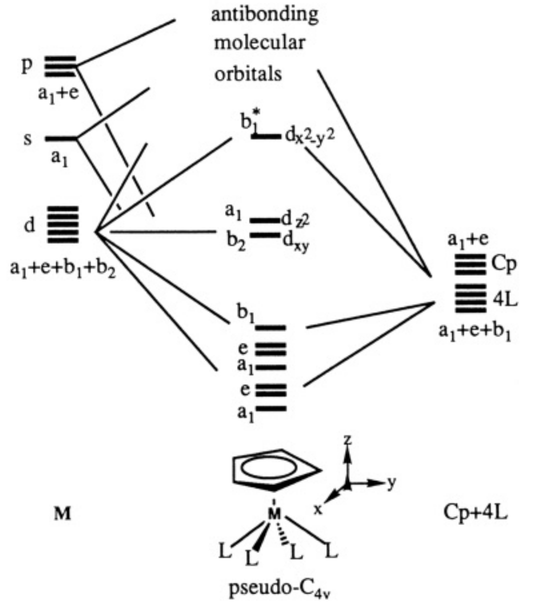
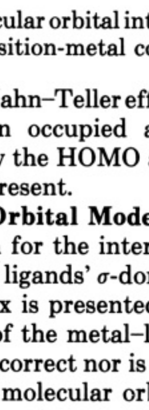
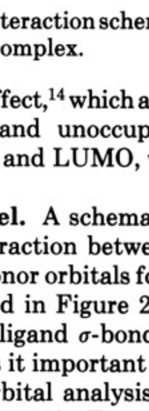


Figure 2. Molecular orbital interaction scheme for a pseudo-C_{4v} $CpML_4$ transition-metal complex.

Molecular Orbital Model. A schematic molecular-orbital diagram for the interaction between the central metal atom and ligands' σ-donor orbitals for a pseudo-C_{4v} $CpML_4$ complex is presented in Figure 2. The energy-level ordering of the metal–ligand σ-bonding orbitals is not necessarily correct nor is it important for our discussion. Detailed molecular orbital analysis can be found elsewhere;[2] the ordering chosen in Figure 1 is for convenience of our discussion. The $d_{x^2-y^2}$ orbital interacts with the four L ligands in a σ-fashion. This σ-interaction results in one bonding orbital (b_1) with more ligand character and one antiboding orbital (b_1*) with more metal $d_{x^2-y^2}$ character. The d_{xz} and d_{yz} orbitals are involved with both the Cp and L ligands. For an 18-electron complex, the two nonbonding orbitals (d_{z^2} (a_1) **2** and d_{xy} (b_2) **3**) are fully occupied with a d^4 configuration. Recently, Poli explained the distortions in the "legs" of existing four-legged piano-stool structures to be largely dependent on the π-bonding ability of the four L ligands with the two metal nonbonding d orbitals.[3] He assumed that the d_{z^2} orbital is a better base than the d_{xy} orbital. Therefore, he concluded that larger α-angles are associated with stronger π-accepting ligands because maximizing the π-interaction between the d_{z^2} and ligands' π-accepting orbitals would stabilize the d_{z^2} more strongly than it destabilized the d_{xy}. Smaller α-angles would be favored by π-donating ligands because minimizing the corresponding repulsive π-inter-



(2)



(3)

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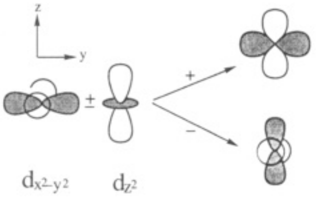
(13) (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (b) Eckart, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324. (c) Haynes, G. R.; Martin, R. L.; Hay, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 28.

(14) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interaction in Chemistry*; John Wiley: New York, 1985.

Scheme I



action dominates the energy. This conclusion can be used to explain the distortions observed for $CpMH_2L_2$ (L = CO and PH_3) complexes (with larger L–M–Ct angles) in Chart I as long as we assume that the phosphine ligands are π-accepting ligands. However, the distortions found in $CpMH_3L$ complexes in Chart I and the complexes in Chart II cannot be explained by the conclusion above. For example, each complex with molecular formula of $CpMH_3L$ (L = PH_3 or CO) has a larger H–M–Ct angle (see Chart I), in which the H atom is trans to L ligand, although H atom is a neutral ligand rather than a π-acceptor. These exceptions imply an incompleteness of this π-only interaction model.

The failure of the π-only interaction model to explain the distortions observed in this paper leads us to examine the importance of the relevant σ-interactions. A distortion from C_{4v} to C_{2v} allows a significant mixing (rehybridization) of d_{z^2} (a_1) and $d_{x^2-y^2}$ (b_1*) orbitals which are both a_1 in C_{2v}. The d_{xy} (b_2) orbital does not change and remains nonbonding because the four L ligands are always located on its nodal planes. The extent of mixing depends on the type of L ligands. The complete mixing of d_{z^2} and $d_{x^2-y^2}$, which results in the formation of two new hybrid orbitals (hy+ and hy−), is illustrated in Scheme I. Since the d_{xy} orbital remains nonbonding in the distortion from C_{4v} to C_{2v} structure and is occupied with two d electrons, the remaining two d electrons will occupy one of the two hybridized orbitals (hy±). When hy+ is occupied with two d electrons, the two L ligands in the *yz* plane would locate themselves in the hy+'s nodal planes with α-angles of 135° to minimize the repulsive interaction, while the other two L ligands in the *xz* plane will occupy in the $\pm x$ directions with α angles of 90° to maximize the σ interaction with the empty hy− orbital. A similar consequence can be seen when the hy− is occupied with two d electrons. The distortion in a four-legged piano-stool structure from the C_{4v} to the C_{2v} geometry with two larger α angles (maximum, 135°) and two smaller α-angles (minimum, 90°) leads to $d_{z^2} \pm d_{x^2-y^2}$ rehybridization. The rehybridization results in the formation of two hybridized orbitals in which the amplitude of each one is maximized in a particular plane, either *xz* or *yz* plane. In other words, the two hybridized orbitals become more localized and, therefore, interact more effectively with different pairs of ligands.

As a consequence of this rehybridization, a strong covalently σ-bonding ligand tends to coordinate to the central metal atom with a smaller α-angle since the small angle maximizes the covalent σ-interaction. Therefore, all complexes with the formula $CpMH_2L_2$ (L = PH_3 or CO) have small H–M–Ct angles and large L–M–Ct ones. Because the $d_{z^2} \pm d_{x^2-y^2}$ rehybridization, which occurs in the distortion from C_{4v} to C_{2v}, produces two pairs of high-symmetry hybridized orbitals (see Scheme I), each trans pair of L ligands in the four legs tend to move symmetrically inward (increasing α-angles) or outward (decreasing α-angles). This pairwise movement explains why the α-angle (H–M–Ct) associated with the H trans to L increases simultaneously with the α-angle (L–M–Ct) associated with the L ligand in $CpMH_3L$ complexes (see Chart I). The two smaller H–M–Ct angles are a result of maximizing the covalent M–H σ-interaction. Therefore, the "angular trans influence" in $CpMH_3L$ complexes can be well explained in terms of this symmetrical $d_{z^2} \pm d_{x^2-y^2}$ rehybridization.

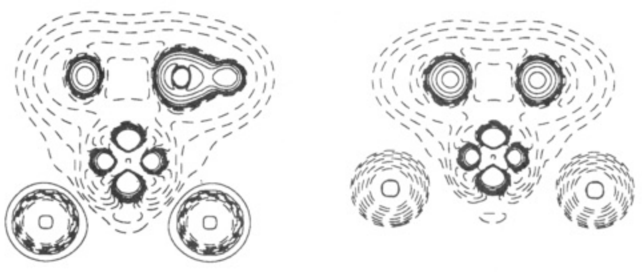

(a) (b)

Figure 3. The plots of the Laplacian of the valence electron density, $-\nabla^2\rho$, in planes of $TcBe_2$ (a) and $TcLi_2$ (b) in $CpTcLi_2Be_2$ model complex.

For complexes in Chart II with four identical L ligands, all L ligands compete equally in the σ-interaction, and the four α-angles are almost equal. In such cases, the π-interaction dominates. When the four L ligands are π-netral ligands (e.g., H, CH_3, SiR_3, etc.), the α-angles are found to be about 127–130°, a value which is close to the ideal α-angle (125.25°), which is found when L ligands are located on the nodal plane of the d_{z^2} nonbonding orbital (i.e., no rehybridization). The H–Rh–Ct (131.2°) and Si–Rh–Ct (126.6°) angles in $CpRhH_2(SiH_3)_2$ complex are close to those α-angles in $CpRhH_4$ and $CpIrH_4$ complexes (see Chart II) because both H and SiH_3 are similar in covalent σ-bonding ability. A slightly smaller Si–Rh–Ct angle indicates a more covalent σ-bond in Rh–Si than that in Rh–H. Because the silyl group is less electronegative it more easily donates its valence electron to the metal–silicon region and forms a more covalent bond (equally shared bonding electrons). When the four L's are π-donating ligands (e.g., halides) the α-angles are all relatively small, e.g., 113.5° in $CpRhCl_4$, a result which tends to minimize the π-antibonding interaction with the d_{z^2} orbital. In $CpRhH_2Cl_2$ and $CpRh(SiH_3)_2Cl_2$ complexes (see Chart II), the σ-interaction dominates, and therefore, large Cl–Rh–Ct angles are found although the chloride ligand is considered as π-donating ligand.

Obviously, the distortions in $CpTcLi_2Be_2$ (and in more realistic analog $CpTcH_2(PH_3)_2$) must be explained in terms of dominating σ-interactions. Here, we would argue that the two Li atoms form covalent σ-bonds with Tc, while the two Be atoms form mainly dative σ-bonds with Tc. The argument above is strongly supported by the Laplacian of the valence electron density, $-\nabla^2\rho$, of model complex $CpTcLi_2Be_2$ (Figure 3). In the contour plots, solid lines denote $-\nabla^2\rho > 0$, where the electron charge is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron charge is locally depleted.[15] As we can from Figure 3, the two Be atoms (see Figure 3a) are bonded to the Tc through the depletions around the central metal atom since the Be ligands are coordinated to metal mainly through a dative bonding interaction. The two Li atoms (Figure 3b) tend to be bonded through the concentrations because Tc and Li interact mainly through covalent bonding.

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[15] (a) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594. (b) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.

Previously, the distortion of the four legs from an ideal pseudo-square-pyramidal geometry in a large number of four-legged piano-stool complexes has been explained through the π-interaction model mentioned above. Most complexes discussed in terms of the π-interaction model either do not have significant differences in the σ-bonding abilities of the four leg ligands or can be explained by both models, e.g., the σ- and π-interaction models are consistent in explaining the distortions observed in several $CpMH_2L_2$ complexes. Those examples, such as $CpRhH_2(SiEt_3)_2$ and $CpMH_3L$ complexes, that seem at odds with the π-interaction model[3] can be explained by the σ-interaction model developed in this paper.

For those complexes that deviate from 18-electron rule, the π-interaction model may be valid. Initial calculation on the model complex *trans*-$(C_6H_6)ZrI_2(PH_3)_2$ (low spin and 16 valence electrons) suggests that occupation of d_{xy} orbital is favored in this d^2 complex. The predicted geometric trends, I–Zr–I = 121.4° and P–Zr–P = 142.6°, agree well with the experimental results on $(C_7H_7SiMe_3)Zr(PMe_3)_2I_2$ complex.[16]

Conclusion

Through an examination of the geometric distortion of four-legged piano-stool complexes, we have discovered the importance of σ-interaction in their characteristic distortions and concluded that the more covalently σ-bonding pair of trans ligands tend to be coordinated to the transition metal with the smaller α- (L–M–Cp) angle. The "angular trans influence" is a result of symmetrical $d_{z^2} \pm d_{x^2-y^2}$ rehybridization arising from the distortion of an ideal pseudo-C_{4v} geometry to a pseudo-C_{2v} one. When the four leg ligands are identical or have similar σ-bonding, they compete equally in the σ-interaction, and therefore, the four α-angles are close to each other and the π-interaction model will dominate the remaining differences.

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[16] Green, L. H. M.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* 1989, 908.