Unique Orbital Symmetry-Driven Cisoid Tilting of the Axial Ligands in Dialkylruthenium(IV) Porphyrins[†]

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DFT calculations aimed at investigating the diamagnetism of dialkyl/diaryl ruthenium-(IV) porphyrins revealed a unique cisoid tilting of the axial alkyl/aryl groups, which maximizes σ-bonding interactions between the metal and the alkyl/aryl ligands via two specific orbital interactions. Only one such stabilizing orbital interaction is possible for upright and transoid orientations of the axial alkyl/aryl groups.

Introduction

Over the past decade, the availability of density functional theory (DFT) based quantum chemical technology has led to the emergence of a fairly comprehensive electronic−structural overview of the major classes of first-row transition-metal porphyrins.[1] As part of a program aimed at achieving a similar overview of second- and third-row transition-metal porphyrin complexes, we chose to examine the diamagnetism of dialkyl and diarylruthenium(IV) porphyrins,[2−7] which is somewhat unexpected for octahedral low-spin d^4 complexes. Thus, $M(P)X_2$ complexes, where $M = Ru$, Os, P is a porphyrin dianion, and $X = Cl$,[7] Br,[7] hydroxy/alkoxy,[8,9] exhibit the expected triplet ground states. What then accounts for the diamagnetism of $M(P)R_2$ derivatives, where R is an alkyl or aryl group? We will see that the specific metal−ligand orbital interactions that account for the diamagnetism also have a profound structural effect, namely a dramatic cisoid tilting of the axial ligands.

A survey of the literature offered a few clues. Thus, a crystallographic analysis of diamagnetic $Os(TTP)(CH_2-Si(CH_3)_3)_2$ revealed a strong cisoid tilting of the OsC vectors relative to the porphyrin normal, which corresponded to a C−Os−C angle of only about 140°.[10] Similarly, we found a literature citation to the following unpublished result: "The structure of $Ru(OEP)Ph_2$ with a bent C−Ru−C unit has been determined: James, B. R. Private communication".[11] In addition, a DFT study of $Os(P)(CH_3)_2$ revealed an $S = 0$ ground state, for which the optimized geometry exhibited a peculiar cisoid tilting of the methyl groups.[11] The authors[11] attributed this to the strong trans effect of the methyl groups but did not offer any detailed molecular orbital (MO) explanations. Thus, no explanation is at present available as to why the methyl groups should tilt in a cisoid rather than a transoid manner. In this study, we have arrived at a much more explicit explanation of the cisoid tilting—which we also observe for $Ru(P)R_2$ derivatives ($R = CH_3$, CF_3, Ph)—in terms of specific metal−ligand orbital interactions.

Results

DFT(PW91/TZP)[11] calculations (carried out with the ADF program system) with geometry optimizations and different symmetry constraints were carried out for the singlet and triplet states of four molecules—$Ru(P)Cl_2$, $Ru(P)(CH_3)_2$, $Ru(P)(CF_3)_2$, and $Ru(P)Ph_2$—and the main results are as follows.

For $Ru(P)Cl_2$, a D_{4h} $S = 1$ state with a $d_{xy}^2 d_{xz}^1 d_{yz}^1$ electronic configuration (the porphyrin normal being identified with the z direction throughout this study), was clearly the ground state, the lowest singlet state being several tenths of an electronvolt higher in energy. Some key optimized geometry parameters and Mulliken atomic spin populations are shown in Figure 1. In general, these do not warrant detailed comment but may be regarded as providing a basic electronic−structural description of a prototype $S = 1$ six-coordinate Ru(IV) porphyrin derivative.

For the $S = 0$ state of $Ru(P)(CH_3)_2$, a geometry optimization with a C_{2v} symmetry constraint appears to yield the global minimum, which features strongly cisoid-tilted methyl ligands; in contrast, a C_{2h} symmetry constraint, which in principle could lead to a transoid-tilted geometry, leads to a high-energy structure (not a stationary point on the singlet potential energy surface)

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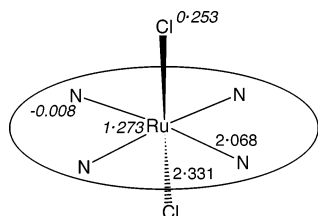
Figure 1. Selected PW91/TZP optimized distances (Å) and Mulliken atomic spin populations (in italics) for Ru(P)Cl$_2$. It should be noted that the porphyrin ligand also carries a small amount of spin, the relevant spin populations being as follows: C$_\alpha$, 0.016; C$_\beta$, 0.022; C$_{meso}$, −0.009.
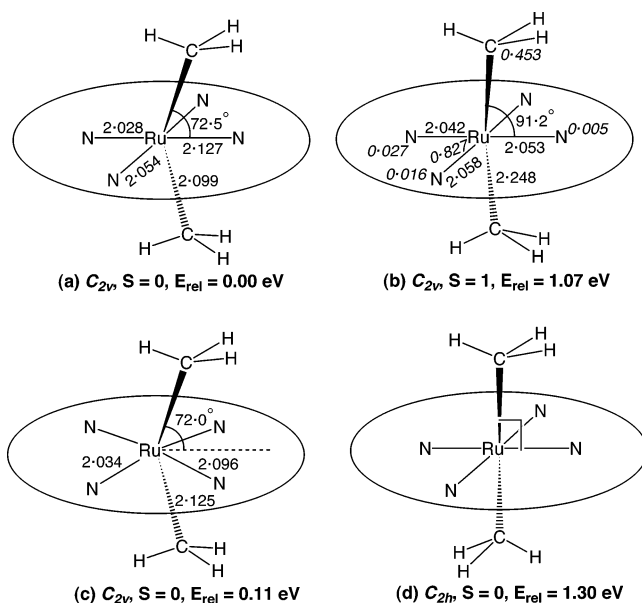

Figure 2. Selected PW91/TZP geometry parameters (Å, deg), Mulliken atomic spin populations (in italics), and relative energies (E_{rel}) for different optimized structures of Ru(P)(CH$_3$)$_2$.

with upright methyl groups. For the $S = 1$ state, essentially upright methyl groups are favored for both C_{2v} and C_{2h} symmetry constraints, but the molecular energies are much higher (>1 eV) than that of the C_{2v} singlet ground state. Figure 2 depicts some key calculated results for Ru(P)(CH$_3$)$_2$. By and large, these do not merit detailed comment, except for a couple points. First, the cisoid tilting of the methyl groups engenders a significant asymmetry in the equatorial Ru–N distances. Second, although the cisoid tilting itself is strongly favored energetically, there is little directional preference associated with the tilting in relation to the macrocycle. Thus, the two singlet C_{2v} conformations shown in Figure 2a,c are essentially equienergetic.

The calculated energetics and structural results for Ru(P)(CF$_3$)$_2$ and Ru(P)Ph$_2$ are qualitatively similar to those obtained for Ru(P)(CH$_3$)$_2$, and some highlights are shown in Figures 3 and 4. One point worth noting is that, in these cases, the triplet states also feature somewhat tilted axial ligands, although the degree of tilting is significantly less than in the singlet ground states.

Discussion

The key point emerging from the results described above as well as from Figures 2−4 is that for Ru(P)-(CH$_3$)$_2$, Ru(P)(CF$_3$)$_2$, and Ru(P)Ph$_2$, the cisoid structures
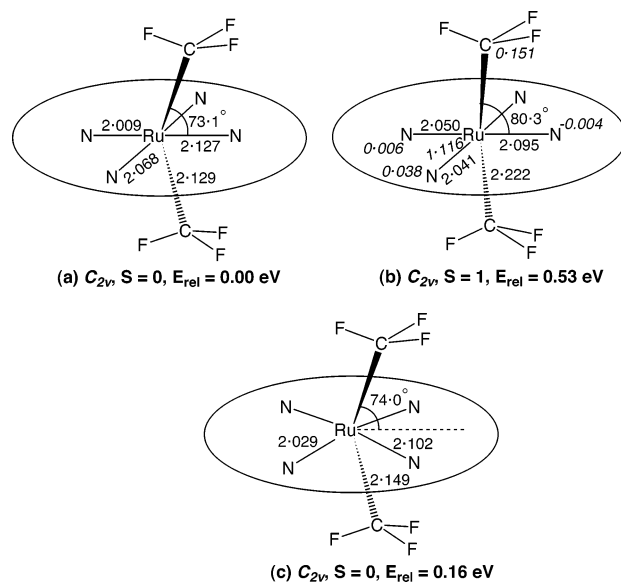

Figure 3. Selected PW91/TZP geometry parameters (Å, deg), Mulliken atomic spin populations (in italics), and relative energies (E_{rel}) for three optimized structures of Ru-(P)(CF$_3$)$_2$.
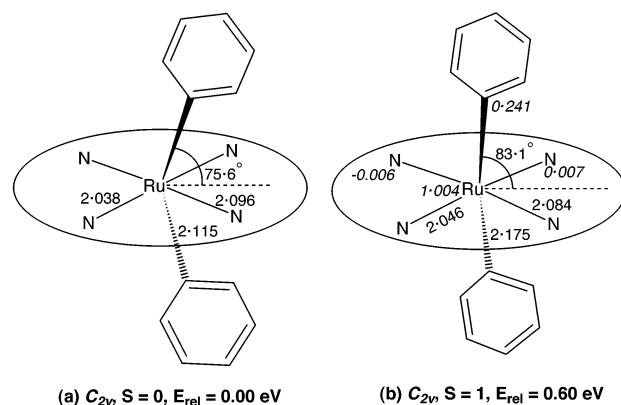

Figure 4. Selected PW91/TZP geometry parameters (Å, deg), Mulliken atomic spin populations (in italics), and relative energies (E_{rel}) for two optimized structures of Ru-(P)Ph$_2$.

are overwhelmingly favored in energy terms. We argued that such an overwhelming preference could not possibly result from subtle steric differences between the cisoid and transoid conformations but had to indicate the operation of a more primal force.[12] Some kind of an orbital symmetry effect seemed a likely candidate for such a force.

Our qualitative MO arguments went as follows. Figure 5 depicts the symmetry-adapted ligand group orbitals (LGOs) associated with the methyl groups for both cisoid- and transoid-tilted conformations of Ru(P)-(CH$_3$)$_2$. Figure 6 shows that, for the cisoid conformation, both LGOs are engaged in favorable bonding interactions with Ru 4d orbitals, but for the transoid conformation, one of the LGOs is orthogonal to all the Ru d orbitals, which provides an attractive explanation for the strong energetic preference for the cisoid conformation. Gratifyingly, an examination of the occupied MOs

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(12) Steric repulsions between the trimethylsilyl groups and the ortho protons of the *p*-tolyl groups were suggested as a likely reason for the cisoid tilting of the axial ligands in Os(TTP)(CH$_2$Si(CH$_3$)$_3$)$_2$.[10]
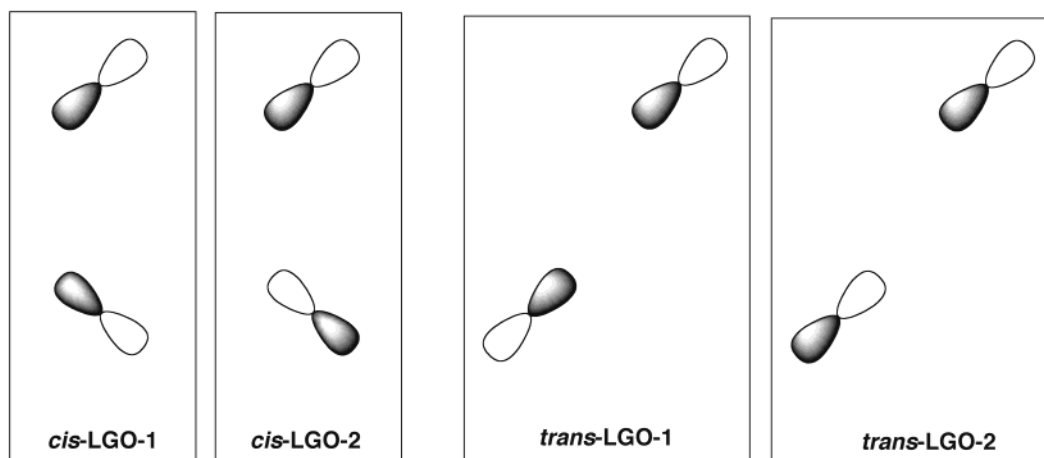
Figure 5. Symmetry-adapted methyl ligand group orbitals (LGOs) for the cisoid- and transoid-tilted conformations of $Ru(P)(CH_3)_2$.
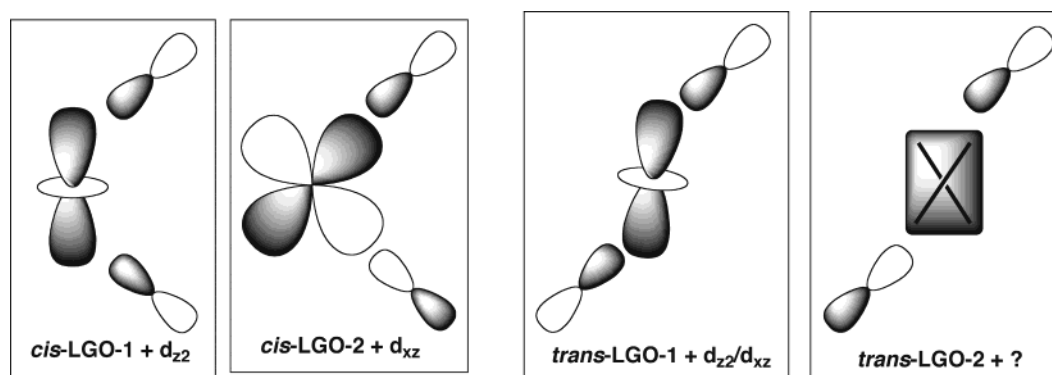

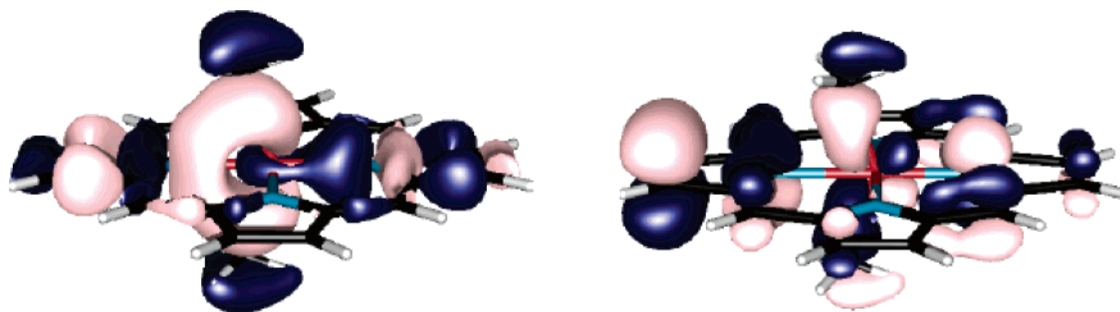**Figure 6.** Schematic representation of bonding interactions with the methyl LGOs and Ru 4d orbitals.

Figure 7. (left) Canonical MO (a_1, HOMO-13 in a spin-restricted calculation) related to the "*cis*-LGO-1 + d_{z^2}" MO of Figure 6. (right) Canonical MO (b_2, HOMO-4 in a spin-restricted calculation) related to the "*cis*-LGO-2 + d_{xz}" MO of Figure 6.

of the ground state of $Ru(P)(CH_3)_2$ confirmed this picture. As shown in Figure 7, two canonical MOs—HOMO-13 (a_1) and HOMO-4 (b_2) from a spin-restricted calculation on the ground state of $Ru(P)(CH_3)_2$—correspond to the MOs denoted as "*cis*-LGO-1 + d_{z^2}" and "*cis*-LGO-2 + d_{xz}" in Figure 6, respectively.

It might be useful to go over the electron bookkeeping even more explicitly. If we view the two methyl electron pairs as occupying "*cis*-LGO-1 + d_{z^2}" and "*cis*-LGO-2 + d_{xz}", the four 4d electrons of the Ru(IV) center then may be regarded as occupying the d_{xy} and d_{yz} orbitals, which do not interact with the methyl lone pairs. In the past, a $d_{xz}^2 d_{yz}^2$ orbital occupancy was proposed to explain the diamagnetism of dialkyl and diaryl Ru/Os(IV) porphyrins,[7] which we found puzzling because we failed to see why these two d orbitals should be preferentially occupied over the d_{xy} orbital. As a result of the findings described above, we no longer need to resort to this somewhat unreasonable picture.

Conclusion

In conclusion, the diamagnetism of dialkyl/diaryl ruthenium(IV) porphyrin derivatives is intimately related to a unique cisoid tilting of the axial ligands. The cisoid tilting maximizes metal–alkyl/aryl σ-bonding, which occurs via two different metal d orbitals, as shown in Figure 6.