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# Influence of Chelate Substituents on the Structure and Spin State of Unsaturated $[N(SiMe_2CH_2P^tBu_2)_2]Ru-X$

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Influence of Chelate Substituents on the Structure and Spin State of Unsaturated  $[N(\text{SiMe}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2]\text{Ru}-\text{X}$ 

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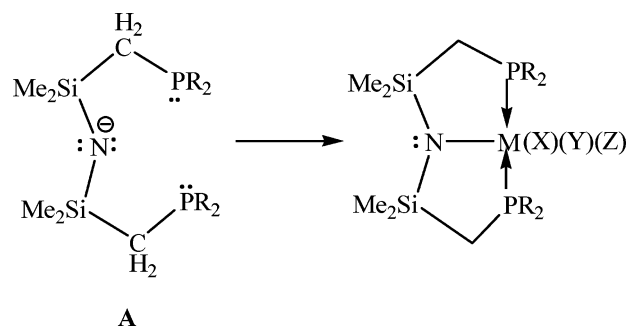
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Density functional theory calculations on the conformational preferences in the two fused five-membered rings of anionic  $N(\text{SiR}_2\text{CH}_2\text{PR}'_2)_2$  chelated to  $\text{RuX}^+$  are compared to several experimental structures ( $\text{X} = \text{halide}$ ). The calculations consider the structures of both singlet and triplet states and reveal that both the four  $t\text{Bu}$  groups and the crowded juncture  $N(\text{SiMe}_2)_2$  of the two rings must be included computationally to understand the observed structures. Computational experiments with different substituents  $\text{R}$  and  $\text{R}'$  show the reality of  $\text{N} \rightarrow \text{Ru} \pi$  donation. The cases where  $\text{X} = \text{H}$  and  $\text{CH}_3$  are also studied.

## Introduction

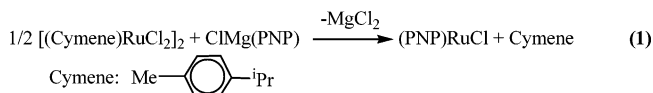
Steric effects involving substituents on pincer ligands<sup>1–7</sup> are of interest for the influence they might have on the metal reactivity in  $(\text{pincer})\text{M}(\text{X})(\text{Y})(\text{Z})$  species. For the pincer ligands developed by the Fryzuk group (**A**, “PNP”),<sup>8,9</sup> the steric effects involve two fused five-membered rings, so conformational preferences in one ring are correlated with and compromised by those in the second ring. Although neither ring will be planar, the conformational preference in one ring will be transmitted to the other by the (planar) amide nitrogen. We will report here on the case of four-coordinate, unsaturated  $(\text{PNP})\text{Ru}-\text{X}$ ,<sup>10</sup> where  $\text{N} \rightarrow \text{Ru} \pi$  donation from the amide lone pair to an available metal d orbital becomes



an electronic factor that can influence the expression of fused-ring conformational preferences. The conformational preferences will therefore be the result of not only steric but also electronic factors and cannot be predicted based solely on molecular mechanics analysis, which cannot model the effect of the metal. Finally, synthesis<sup>10,11</sup> of the unusual four-coordinate  $(\text{PNP})\text{Ru}-\text{Cl}$  seems critically dependent (via cymene displacement, eq 1) on the influence of four bulky  $\text{R}$  groups  $t\text{Bu}$  in **A**, so we will consider only the  $\text{P}^t\text{Bu}_2$  case

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here. Clearly, the conformations of these  $t\text{Bu}$  substituents on the five-membered rings will be influenced by the  $\text{X}$ -group size, but the variable  $\pi$ -donor influence of the  $\text{X}$  group will have its electronic effect on  $\text{Ru}$  and, hence, on

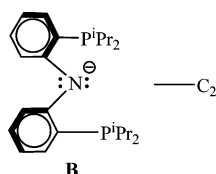
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**Table 1.** DFT-Optimized Structural Features of (PNP)Ru-X,  $bG_c^t$ <sup>a</sup>

X	full model <sup>b</sup>		small model <sup>c</sup>	
	singlet	triplet	singlet	triplet
Cl	178.7P <sub>S</sub> <sup>26.6</sup>	178.2P <sub>S</sub> <sup>22.6</sup>	175.4P <sub>E</sub> <sup>2.1</sup>	179.1P <sub>E</sub> <sup>3.8</sup>
F	154.7N <sub>S</sub> <sup>26.4</sup>	178.5P <sub>S</sub> <sup>22.7</sup>	148.4N <sub>E</sub> <sup>6.0</sup>	176.2P <sub>E</sub> <sup>2.5</sup>
CH <sub>3</sub>	145.0N <sub>S</sub> <sup>43.7</sup>	173.8P <sub>S</sub> <sup>24.6</sup>	134.7N <sub>S</sub> <sup>24.0</sup>	179.2P <sub>E</sub> <sup>3.0</sup>
H	106.7N <sub>S</sub> <sup>27.2</sup>	174.1P <sub>S</sub> <sup>21.8</sup>	113.7N <sub>E</sub> <sup>8.6</sup>	173.2P <sub>E</sub> <sup>3.1</sup>

<sup>a</sup> Key to  $bG_c^t$  notation:  $G$  = Planar or Nonplanar coordination geometry;  $t$  = twist ( $\angle$ P-Ru-N-Si);  $b$  = bend ( $\angle$ N-Ru-X);  $c$  = staggered (S) or eclipsed conformation (E). <sup>b</sup> Full model = (tBu<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>NRu-X. <sup>c</sup> Small model = (Me<sub>2</sub>PCH<sub>2</sub>SiH<sub>2</sub>)<sub>2</sub>NRu-X.

the N-Ru bond. As one consequence, (PNP)RuCl is found to have two unpaired electrons among its six d electrons. Reliable modeling of all these stereoelectronic effects will be attempted using density functional theory (DFT). One of our goals is to understand features of the frontier orbitals that lead to a triplet ground state. It bears mention that the <sup>1</sup>H NMR spectra of these (PNP)Ru-X molecules at 22 °C all show<sup>10,11</sup> dynamically averaged  $C_{2v}$  symmetry, so the barriers for axial-equatorial flexing of the SiMe<sub>2</sub>, CH<sub>2</sub>, and tBu<sub>2</sub> substituents are all small (i.e., in the typical range for conformational energies). This contrasts strongly to the pincer ligands with the more rigid phenylene backbone (**B**),<sup>12-14</sup> which show only  $C_2$  symmetry at 22 °C when attached to a M(X)(Y) moiety.



## Results

**Preferred Ring Conformations.** Our previous calculations used a very simple model of the PNP atoms: [(H<sub>2</sub>-PCH<sub>2</sub>SiH<sub>2</sub>)<sub>2</sub>N]Ru-X. Of special interest were the DFT calculations, which show the triplet state with X = Cl to be of planar (P) NP<sub>2</sub>RuCl geometry but the singlet state to be of nonplanar (N) geometry, mainly via a N-Ru-Cl angle of 150.5°. In contrast (Table 1), new calculations with the full model, [(tBu<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>N]RuCl, show both the singlet and triplet to have a planar coordination geometry, although it still agrees with the experimental result indicating that the triplet is more stable. DFT energies of the analogues with X = F, CH<sub>3</sub>, and H show that the singlet does not have a planar coordination geometry for these anions.<sup>15</sup> For these three X varieties, this nonplanar singlet preferred geometry is also found previously for the very simple model,<sup>10</sup> so the model-dependent geometry discrepancy exists only for X = Cl and the singlet state.

The conformation of the fused five-membered rings (Table 1, full model) is uniformly calculated to be twisted (dihedrals

P-Ru-N-Si of 22.6–43.7°, with most values  $24 \pm 3^\circ$ ) for both nonplanar singlets and planar triplets, putting the two Si atoms alternatively above and below the RuNP<sub>2</sub> plane and their attached methyls in axial and equatorial positions, in turn staggering their four substituents (Figure 1a). A condition accompanying the eclipsing in the small model is that the twist of the NSi<sub>2</sub> plane becomes very small for all X and for both triplets and singlets (Table 1). The dihedral angle P-Ru-N-Si varies from 0.7° to 8.6°.<sup>16</sup> This could be interpreted as SiMe<sub>2</sub>/SiMe<sub>2</sub> being the dominant steric factor in ring conformation. The eclipsed geometry with an essentially planar PRuNSi unit forces the CH<sub>2</sub> carbon to be out of that plane, in an envelope conformation. The geometry refines to two situations (parts b and c of Figure 1), both envelopes with carbons on the same side of the plane and on opposite sides and with negligibly (1.3–3.4 kcal/mol) different energies.

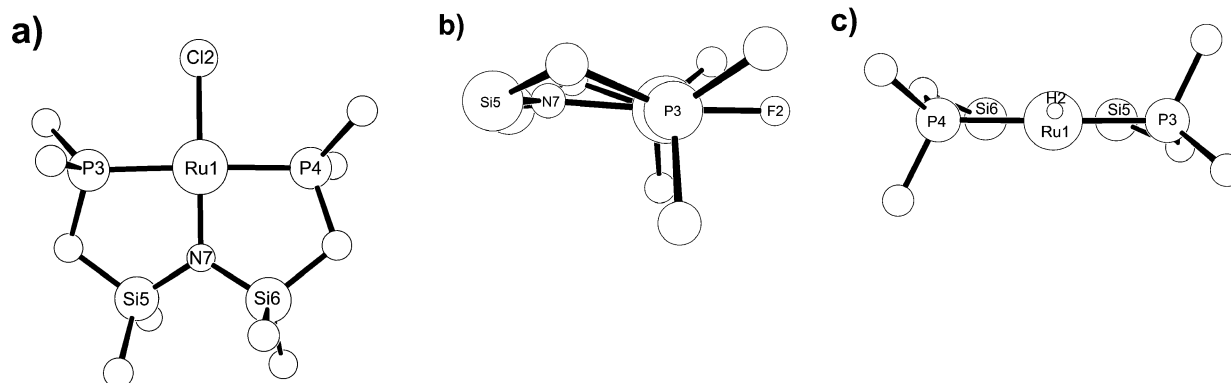
We suspected that the nonbonded repulsions between these SiMe substituents dominated the ring conformational preference, even for the nonplanar coordination geometries. This hypothesis finds apparent support from a computational experiment with a small model: [(Me<sub>2</sub>PCH<sub>2</sub>SiH<sub>2</sub>)<sub>2</sub>N]Ru-X. As shown in Table 1, whereas the more stable coordination geometries are unchanged from the full model, all of the SiR<sub>2</sub>/SiR<sub>2</sub> conformations become eclipsed (S → E); this we attribute to the energetic insignificance of steric conflicts between two SiH substituents in contrast to those between two SiMe substituents.

The relative unimportance of steric conflicts between the tBu substituents and X on Ru is shown by the fact that, even when X = H on Ru, the NSi<sub>2</sub> group is twisted; minimizing Ru-X/tBu substituent interactions by the choice of a small X group does not change the NSi<sub>2</sub> twist.

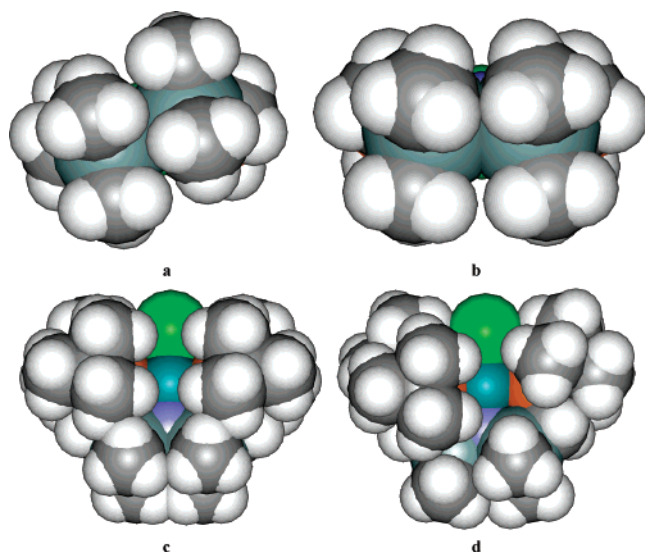
If nonbonded repulsions at the N(SiMe<sub>2</sub>)<sub>2</sub> juncture dominate over phosphine substituent effects, then the model [(H<sub>2</sub>-PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>N]Ru-Cl should give a twisted NSi<sub>2</sub> conformation as the most stable. In fact, both twisted (with staggered) and eclipsed (with no significant twist) structures for this model (triplet state) are essentially degenerate (eclipsed is 0.4 kcal/mol more stable). Space-filling models (parts a and b of Figure 2) show the absence of significant short MeSi/MeSi contacts in both forms. Thus, the preference for the twisted/staggered conformation is only correctly represented with the full set of tBu and Me(Si) substituents. Indeed, with the full model of all atoms, the preference for the twisted/staggered conformation is so strong that the eclipsed (not twisted) structure cannot be located as a minimum; that starting geometry always minimizes to the twisted/staggered conformation. The conclusion that replicating the twisted/staggered conformation is controlled by minimizing contacts between tBu and Me(Si) substituents is supported by parts c and d of Figure 2. Short contacts between tBu and silyl methyls in the eclipsed structure (Figure 2c) disappear in the twisted/staggered conformer (Figure 2d).

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 (15) "Planar" here means a trans N-Ru-X angle of 173.2–179.1°.

- (16) The singlet X = CH<sub>3</sub> case is twisted at 24.0°, but this structure is atypical in that the methyl is agostic.



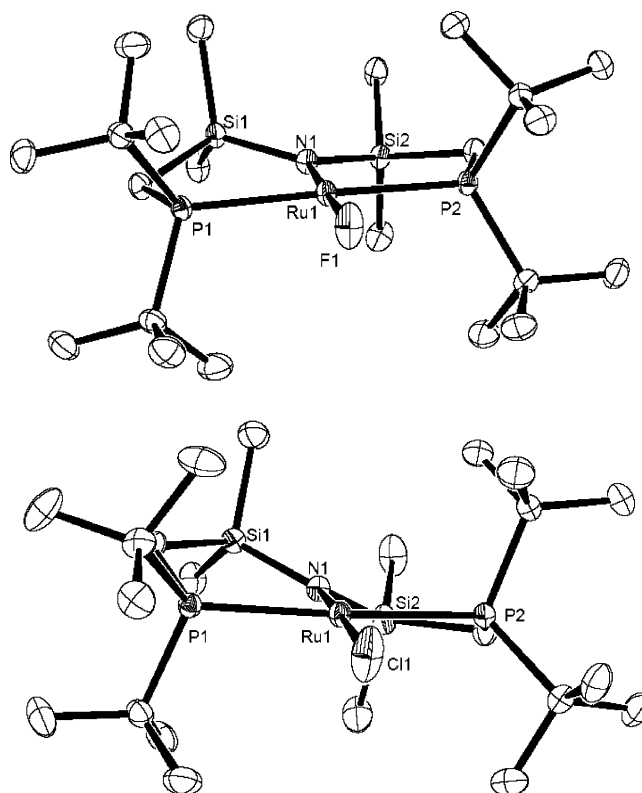
**Figure 1.** DFT-optimized geometries of (pincer)Ru–X for the following: (a) chloride singlet, full model; (b) eclipsed fluoride triplet, small model; (c) staggered hydride triplet, small model.



**Figure 2.** Space-filling drawings of (a) staggered and (b) eclipsed  $[(\text{H}_2\text{PCH}_2\text{Me}_2\text{Si})_2]\text{RuCl}$  viewed down the N–Ru–Cl axis and (c) eclipsed and (d) staggered  $(\text{tBu}_2\text{PCH}_2\text{Me}_2\text{Si})_2\text{NRuCl}$  viewed perpendicular to the  $\text{RuP}_2\text{N}$  plane. Drawing c adds methyls to Si of the eclipsed (untwisted) minimum of  $[(\text{tBu}_2\text{PCH}_2\text{SiH}_2)_2\text{N}]\text{RuCl}$  because the eclipsed structure with the full model is not a minimum.

**Comparison to Experiment.** The X-ray structures of  $(\text{PNP})\text{Ru}-\text{X}$  for  $\text{X} = \text{Cl}$  and  $\text{F}^{17}$  are shown in Figure 3. The two solids crystallize in different space groups, so they are not subject to identical packing forces, yet the conformations of the two fused five-membered rings are very similar. Bond lengths and angles from X-ray diffraction studies show no noteworthy differences from the DFT-optimized values. Both halide complexes show the twist of the  $\text{NSi}_2$  plane (and the staggered silyl methyls) discussed above from the full model DFT results, with the fluoride having a smaller twist angle by about  $12^\circ$ . This is evident in Figure 3.

**Singlet/Triplet Energy Differences and Frontier Orbital Energies.** The singlet/triplet energy differences (e.g., full model, Table 2) fall into a rather narrow range, showing how competitive the two different spin states are after the geometry relaxation of each. Note also (Table 2) the modest influence of model/steric effects on the singlet/triplet gap. A corollary consequence of this is that the model dependence

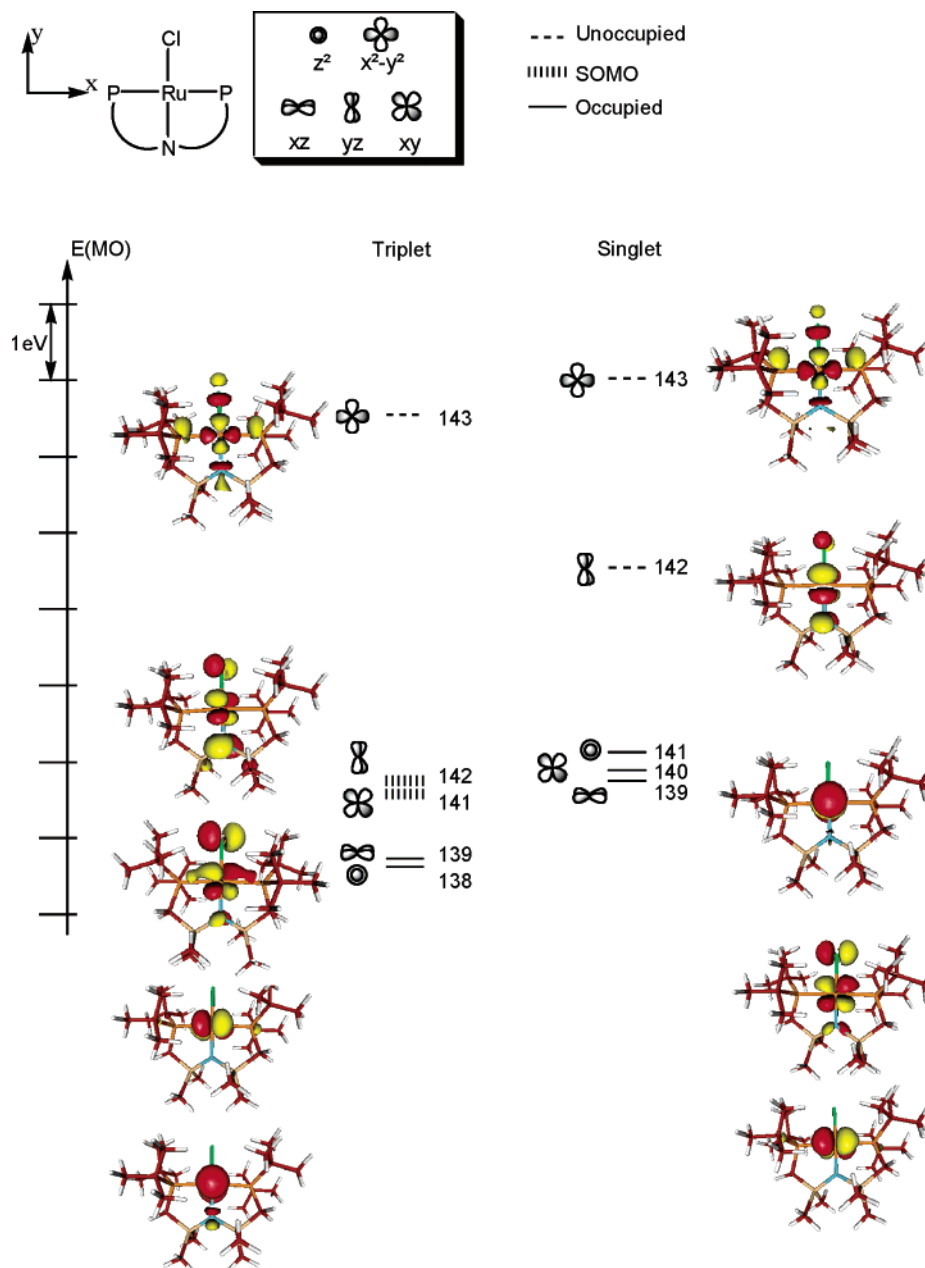


**Figure 3.** ORTEP drawings (50% probability) of the non-hydrogen atoms of  $[\text{N}(\text{SiMe}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2]\text{Ru}-\text{X}$  for  $\text{X} = \text{F}$  (above) and  $\text{Cl}$  (below), showing selected atom labeling. Selected structural parameters for the fluoride: Ru–F, 2.0068(12) Å; Ru–N, 2.0413(16) Å; Ru–P1, 2.3660(5) Å; sum of angles at N =  $359.89^\circ$ ; F–Ru–N,  $178.80(6)^\circ$ ; F–Ru–P1,  $90.87(4)^\circ$ ; F–Ru–P2,  $90.27(4)^\circ$ ; P1–Ru–P2,  $177.630(18)^\circ$ . Dihedral angles of the fluoride: P1–Ru–N–Si1,  $15.62(9)^\circ$ ; P2–Ru–N–Si2,  $9.68(10)^\circ$ . Dihedral angles of the chloride: P1–Ru–N–Si1,  $27.14(8)^\circ$ ; P2–Ru–N–Si2,  $22.99(8)^\circ$ .

of the *coordination* geometry (Table 1) is also only moderate: the angles N–Ru–X vary by  $0.4\text{--}5.4^\circ$  for the triplet states and  $2.8\text{--}10.3^\circ$  for the singlet states with a change of model. The conclusions drawn here seem robust with the various substituents studied. This flexibility of the coordination geometry in turn supports the conclusion that ring substituent conformational effects in the crowded  $\text{N}(\text{SiMe}_2)_2$  juncture can be influential on the observed conformations and thus on the overlap between the amide lone pair and a  $d_\pi$  orbital.

The calculations also permit a discussion of the frontier orbitals of  $(\text{PNP})\text{Ru}-\text{X}$ , with a goal of understanding the

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**Figure 4.** Frontier orbital energies and contours in  $\alpha$  space for the full model of singlet and triplet (PNP)RuCl.

**Table 2.** Singlet/Triplet (S–T) Energy Differences for (PNP)Ru–X with Two Different Models of PNP

	$\Delta E(S-T)$ , kcal/mol			
	PNPRuCl	PNPRuF	PNPRuMe	PNPRuH
full model <sup>a</sup>	10.3	7.6	5.7	–2.3
small model <sup>b</sup>	5.9	2.1	4.0	–2.3

<sup>a</sup> Full model =  $(t\text{Bu}_2\text{PCH}_2\text{SiMe}_2)_2\text{NRu}-\text{X}$ . <sup>b</sup> Small model =  $(\text{Me}_2\text{PCH}_2-\text{SiH}_2)_2\text{NRu}-\text{X}$ .

origin of the triplet ground state. This is most clearly accomplished for the triplet and singlet when  $\text{X} = \text{Cl}$ , since there is no significant geometry difference at their respective energy minima. Figure 4 shows the five d-orbital-derived orbital energies for each spin state. Orbital  $d_{x^2-y^2}$ , being mostly  $\sigma^*$ , lies highest, and  $d_{xz}$ , having little overlap with ligand orbitals, lies relatively low. Orbital  $d_z^2$  lies quite low, due to the absence of ligands along the  $z$  axis. Orbital  $d_{yz}$  is

$\pi^*_{\text{RuN}}$  and is thus raised above orbital  $d_{xz}$ . The calculations show that the SOMOs of the triplet are  $d_{xy}$  and  $d_{yz}$ , with the occupancy of the latter thus diminishing the Ru–N bond strength; these two are nearly degenerate, favoring a triplet ground state. The singlet leaves  $d_{yz}$  empty, hence strengthening the Ru–N bond, and doubly occupies the  $d_z^2$ ,  $d_{xy}$ , and  $d_{xz}$  orbitals, none of which strongly bonds to ligand orbitals. Consistent with this, the Ru–N distance shortens by 0.09 Å from the triplet to the singlet when  $\text{X} = \text{Cl}$  and shortens comparably on spin pairing for  $\text{X} = \text{F}$ ,  $\text{CH}_3$ , and  $\text{H}$ . In contrast, the Ru–P bonds do not shorten on spin pairing. The fact that the N–Si<sub>2</sub> twist angle does not decrease significantly (Table 1) on going from the triplet to the singlet (for better  $\text{N}\pi-\text{d}\pi$  overlap) suggests that these SiMe<sub>2</sub>/SiMe<sub>2</sub> conflicts are energetically more costly than the benefit of  $\text{N} \rightarrow \text{Ru} \pi$  donation. However, the fact that the twist angle



does decrease on going from a given full model to the small model ( $\text{SiH}_2/\text{SiH}_2$ ) suggests that  $\text{N} \rightarrow \text{Ru} \pi$  donation is a stabilizing feature.

## Conclusion

This is a first attempt to do conformational analysis on the fused five-membered rings we have previously neglected in our studies of  $(\text{tBu}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}^-$  in  $(\text{PNP})\text{RuCl}$ . Our previous work has focused mainly on metal reactivity, spin state, and the electronic character of the  $\text{N}-\text{Ru}$  bond. The five-membered ring has more heteroatoms than carbon atoms, with two instances of *gem*-dialkyl substitution in each of the rings, so significant departures from cyclopentane conformational preferences must be anticipated. Nevertheless, the low calculated energy differences conform to the facile ring puckering implied by the NMR equivalence observed at and below 22 °C. The variety of thermally accessible ring conformations is also important in understanding the remarkable observed exchange of deuterons from benzene- $d_6$  into not only the *t*Bu methyls but also the seemingly less accessible  $\text{CH}_2$  and  $\text{SiMe}_2$  hydrogens in  $(\text{PNP})\text{Ru}-\text{X}$  when  $\text{X} = \text{F}$  and  $\text{O}_3\text{SCF}_3$ .<sup>17–19</sup> Correctly modeling steric effects at the  $\text{NSi}_2$  ring juncture is important to correctly representing not only the  $\text{Ru}-\text{N}$  bond but also the interactions with other ligands (e.g., those trans to amide N) and not only those capable of push/pull interaction but also strong trans effect ligands like H and hydrocarbyl and good leaving groups like triflate.

Figure 4 also shows that X groups (and nonplanar geometries) which raise the  $yz$  orbital can lead to production of a singlet ground state.

With the increasing use of pincer (and macrocyclic) ligands,<sup>20</sup> certain tripodal ligands,<sup>21–29</sup> and ligands containing *gem*-dialkyl backbone groups ( $\text{CR}_2$ ),<sup>30,31</sup> stereoelectronic effects analogous to those analyzed here may be increasingly

important to the full understanding of the subtle aspects of molecular structure and bonding.

## Experimental and Computational Section

The synthesis and characterization of  $(\text{PNP})\text{RuF}$  have been described in ref 17. The crystal structure determination is described in the Supporting Information CIF file.

All calculations were carried out using DFT as implemented in the *Jaguar* 5.5 suite<sup>32</sup> of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP<sup>33–36</sup> functional and the 6-31G\*\* basis set. The transition metals were represented using the Los Alamos LACVP\*\* basis<sup>37,38</sup> that includes relativistic effective-core potentials. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple- $\xi$  basis set<sup>39</sup> cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP\*\*, designated as LACV3P\*\*, in which the exponents were decontracted to match the effective-core potential with the triple- $\xi$  basis set.

$\text{Ru}-\text{P}$  distances vary only from 2.36 to 2.45 Å over all species calculated, and angles within a five-membered ring vary only insignificantly. All angles  $\text{P}-\text{Ru}-\text{P}$  are larger than 170.4°. For a given X substituent,  $\text{Ru}-\text{X}$ , and  $\text{Ru}-\text{N}$ , bond lengths differ insignificantly (0.01–0.05 Å) between the small and full models. An inversion of two nearly degenerate orbitals explains the change of one SOMO of triplet  $(\text{PNP})\text{RuCl}$  noted in ref 10 versus that in the present work (Figure 4). In that earlier model, the largest difference is that the absence of bulky substituents on P led to  $\text{Ru}-\text{P}$  distances about 0.05–0.11 Å shorter than the full model employed here, thus changing also the  $\sigma$ -bonding d orbitals. Even for a given model, the rise in the orbital energy of  $yz$  in the singlet (vs triplet) is due in part to the shorter  $\text{Ru}-\text{N}$  distance, strengthening  $\pi$  donation but destabilizing the antibonding component of that interaction. In general, the shorter bond lengths in the singlet state and certainly any geometry change can influence the frontier orbital energies.

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**Supporting Information Available:** CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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