

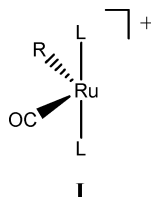
Four-Coordinate, Planar Ru(II). A Triplet State as a Response to a 14-Valence Electron Configuration

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The vast majority of complexes of divalent ruthenium are 6-coordinate and octahedral, while the small class of 5-coordinate Ru(II) complexes (generally prevented from halide-bridged dimerization by bulky phosphines and by the trans influence of a hydride or an alkyl ligand) are often square pyramidal. Four-coordinate examples are essentially unknown;¹ the molecules RuH(CO)-(P^tBu₂Me)₂⁺ and Ru(Ph)(CO)(P^tBu₂Me)₂⁺ both²⁻⁴ have a structure which is adequately described as *cis*-divacant octahedral (**I**). Each



of these is distinguished by having agostic interactions from one ^tBu group on each phosphine L. A four-coordinate candidate case might be Ru(porphyrin), but these avoid monomeric character by forming a dimer via a Ru=Ru bond.⁵⁻⁸

We have reported that the Fryzuk ligand⁹ (R₂PCH₂SiMe₂)₂N⁻ (PNP^R) furnishes a way to install on Ru a stronger π -donor ligand than the chloride in the analogue RuHCl(PⁱPr₃)₂ which is itself a halide-bridged dimer.¹⁰ This has made possible¹¹ the synthesis of (PNHP)RuHCl(H₂) and (PNP^{Cy})RuH(H₂). We report here how this ligand permits access to a Ru(II) species which is not only structurally unprecedented but whose triplet state is also unconventional for Ru(II) chemistry; this spin state can be seen to be a *consequence* of the low coordination number and the lack of agostic interactions.

(PNP^{tBu})RuCl was prepared from the reaction of (PNP^{tBu})MgCl (dioxane), [(cymene)RuCl₂], and 1,4-dioxane in toluene at ambient temperature. Filtering the suspension and reducing and cooling the filtrate resulted in the formation of yellow crystals of (PNP^{tBu})RuCl in 63% isolated yield. A similar reaction using Li(PNP^{tBu}) instead of the magnesium salt did not give the (PNP^{tBu})RuCl product. Using PNP^{Cy}Li and the same synthetic method resulted in the formation of an η^3 -allyl compound by dehydrogenation of the P-Cy hydrogens.¹¹ The crystal structure¹² of [PNP^{tBu}]RuCl, crystallized from toluene, shows (Figure 1) an essentially planar and four-coordinate molecule without any agostic interactions (^tBu H and C are over 3 Å away from Ru). The Ru/N distance, 2.050(1) Å, is short, compared to the distance (2.145(1) Å) in (PNP^{Cy})Ru(H)(PPh₃).¹¹ Strong amide lone pair-to-Ru donation, reflected in this short Ru-N distance, is also evident in the *lengthened* N/Si distances (Figure 1 caption). A short (2.361(1) vs 2.526(1) Å in (PNHP^{tBu})RuH₃Cl) Ru-Cl distance also reflects the highly unsaturated character of this Ru center. N-Ru-Cl and P-Ru-P bond angles of 177.90(4)^o and 175.10(2)^o, respectively demonstrate the essential planarity of this complex. Because of the envelope conformation of the five-membered ring formed by half

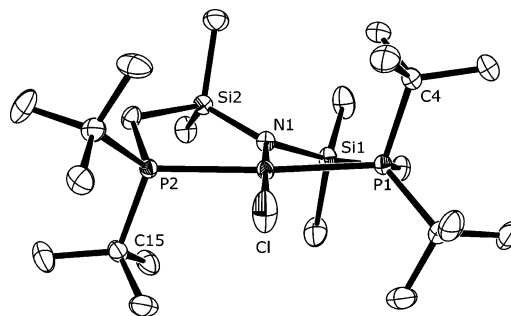


Figure 1. ORTEP drawing (50% probability ellipsoids) of the non-hydrogen atoms of Ru[(^tBu)₂PCH₂SiMe₂)₂N]Cl. Note the axial positioning of the ^tBu groups of C4 and C15 in their respective five-membered rings. Unlabeled atoms are carbon. N1-Si1 = 1.724(1) Å; N1-Si2 = 1.727(2) Å; N1-Ru-P1 = 87.71(4)^o; N1-Ru-P2 = 87.89(4)^o. The sum of angles at N1 is 359.97^o.

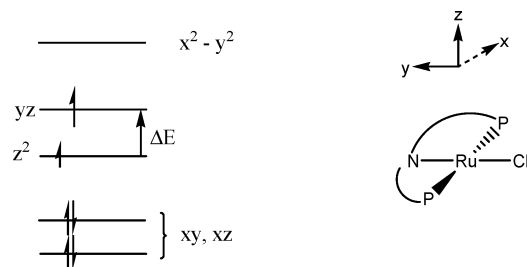
the PNP ligand, the ^tBu ligands on each PR₂ are axial and equatorial such that the axial P ^tBu are trans to each other. That is, one ^tBu lies above and one below the PNP RuCl plane. Such steric protection may help prevent dimerization.

The NMR spectral features of (PNP^{tBu})RuCl in benzene or toluene at 20 °C are unusual. No ³¹P{¹H} NMR signals are detected in a window from + 500 to - 500 ppm. The ¹H NMR spectrum shows signals for all groups in the molecule, but with chemical shifts characteristic of paramagnetism. Resonances due to the Si-CH₃, CMe₃, and P-CH₂-Si are found at 29.21, -11.09, and -41.82 ppm, respectively, in C₆D₆. While fairly sharp, these signals show no evidence of P-H coupling. The number of resonances is in agreement with the near-C_{2v} symmetry found in the solid. Spectra taken in toluene-d₈ from +60 to -68 °C show¹³ temperature-dependent shifts, linear in T⁻¹. These shifts are considerably greater than those observed for *temperature-independent* paramagnets such as ReL₃Cl₃. Undecoupled ¹³C spectra also are in agreement with the C_{2v} symmetry found in the solid state, with all C chemical shifts seen along with the J_{C-H} couplings. The ¹³C chemical shifts are also paramagnetically shifted, and no coupling of the C nuclei to P is evident. The magnetic susceptibility at 298 K is consistent with a $\chi_m T$ of 1.03, which indicates paramagnetism, and near the value predicted for two unpaired electrons, 1.0, when g = 2 is employed. A paramagnetic Ru(II) complex is without precedent.

A simplified d-orbital splitting diagram for near-planar (PNP)-RuCl (Scheme 1), offers the *possibility* of both singlet and triplet ground states, depending on the occupancy of the z² and yz orbitals. For ΔE small compared to spin pairing energy, S = 1 is the ground state; for ΔE large, S = 0 is the ground state.

The diagram clearly reveals that, in the singlet state of this 14 e⁻ complex, two orbitals (yz and x² - y²) are empty. Increased π interaction with the amide nitrogen lone pair orbital raises the energy of the yz orbital above z², but singly *populating* the Ru/N π -antibonding yz orbital (i.e., forming the triplet state from the *filled*

Scheme 1



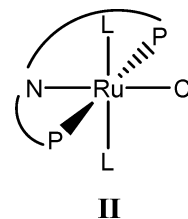
z^2 singlet state) weakens the $N \rightarrow Ru$ π bond. The half-filled orbitals have the effect of prohibiting agostic interactions (the $x^2 - y^2$ orbital being sterically inaccessible), as is observed.

DFT geometry optimization of the model $[(H_2PCH_2SiH_2)_2N]RuCl$ as a triplet, using an unrestricted wave function, results in $(PNP^H)RuCl$ having a planar geometry, with geometric parameters quite similar to those of the experimental solid state determination.¹³ 8.3 kcal/mol higher is a minimum corresponding to the singlet electronic state. This optimized structure has a *nonplanar* geometry, with an $\angle N-Ru-Cl$ of 150.5° . The calculated $Ru-N$ and $Ru-Cl$ distances of this bent structure, 1.976 and 2.324 Å, respectively, are also similar to the experimental (i.e., triplet) values, although somewhat shorter, perhaps due to reduced competition for the same orbital for N and Cl lone-pair π donation. The longer Ru/N distance in the planar triplet results from the potential acceptor orbital for the N lone pair (yz) being already half occupied.

The complexity of the system, the idealization of the model, and the difficulty of reliably calculating an intermediate spin state with DFT make us reluctant to draw conclusions about relative singlet/triplet stability from the 8.3 kcal/mol energy difference; we do however consider that the calculations establish that the unprecedented planar structure is indeed more stable than the cis-divacant octahedron (I). These calculations also guide our understanding of the orbital composition of the HOMO, LUMO, and S(singly)OMO. In the triplet state (unrestricted DFT calculation), the SOMOs are primarily d_{z^2} and d_{yz} , while the LUMO is $d_{x^2-y^2}$.¹³ The two SOMOs correspond with the HOMO and LUMO at the singlet state, which are primarily d_{z^2} and d_{yz} , respectively.

The magnetic susceptibility,¹³ measured between 300 and 6 K, shows a $\chi_M T$ value decreasing from $1.03 \text{ cm}^{-1} \text{ mol}^{-1} \text{ K}$ at 300 K to near zero when $T \rightarrow 0$. $\chi_M T$ was fit^{7,14} to a model of an $S = 1$ state where μ_{eff} drops to zero as $T \rightarrow 0$ K because of zero field splitting which places $M_s = 0$ below $M_s = \pm 1$. The fit gives $g = 2.089$ and $D = 273 \text{ cm}^{-1}$.

We investigated the possibility that the compound synthesized might be $Ru^{III}H(PNP^{tBu})Cl$, since it is especially difficult to prove the presence (or absence) of a hydride in paramagnetic species. The compound under study reacts with PhCN at 23°C within minutes in benzene to give a single product, whose diamagnetism is evident from the appearance of a sharp ${}^{31}\text{P}\{^1\text{H}\}$ NMR singlet, in contrast to the absence of a detectable ${}^{31}\text{P}$ NMR signal for $(PNP^{tBu})RuCl$. The ${}^1\text{H}$ NMR data, including integrations, are consistent with a formula and structure II ($L = \text{PhCN}$) for this product. There is



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no ${}^1\text{H}$ NMR signal for evolved H_2 at 4.5 ppm. These reactivity results are fully consistent with the $(Ru^{II}, \text{nonhydride})$ identity $(PNP^{tBu})RuCl$ for this new molecule.

For Pd(II), Espinet¹⁵ has made the provocative statement: "Although 14 electron species are conceivable as transition states in many reactions...it is unlikely that a detectable concentration of these highly unsaturated species can survive in a condensed state." Those authors cite agostic bonding in such apparent 14-electron species as proof of their general statement. The present structure shows that agostic interactions are not inevitable in a 14-electron species, but that a triplet state, with half-filling of two orbitals, is another way to make the best outcome of an otherwise electron-deficient (14 e) situation.

Acknowledgment. This work was supported by the Department of Energy. L.A.W. thanks the NSF for a graduate fellowship. We thank Dr. Cristina Cañada Vilalta and Prof. B. N. Figgis for central contributions to the magnetic susceptibility study and Aurora Clark for assistance with the computational study.

Supporting Information Available: Synthesis and characterization of $[PNP^{tBu}]RuCl$ as well as crystallographic and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA035166P