Square-Planar Ru^{II}

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A Square-Planar Ruthenium(II) Complex with a Low-Spin Configuration[**]

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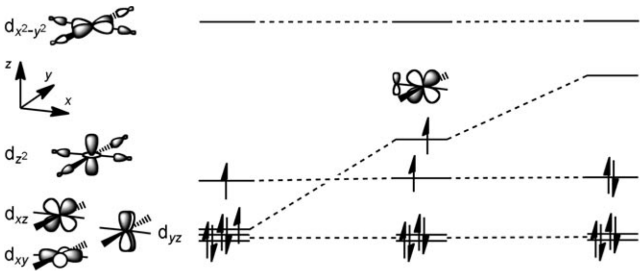
Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

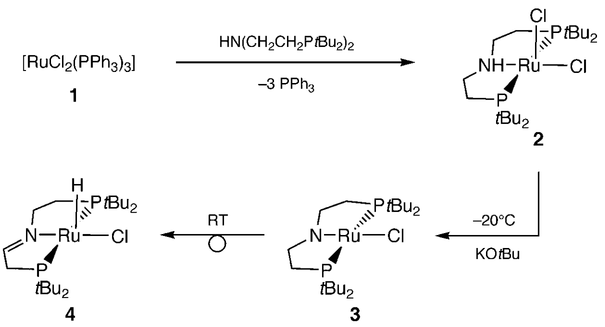
The coordination chemistry of d^6 ions of Group 8 is dominated by octahedral complexes. Four coordination is mainly observed in case of tetrahedral iron complexes, which exhibit an electronic high-spin configuration ($S = 2$, HS). With macrocyclic, chelating, and few monodentate ligands, square-planar, intermediate-spin ($S = 1$, IS) iron(II) complexes are known (Scheme 1, left).[1–3] On the contrary, four-coordinate ruthenium(II) compounds are typically found to exhibit a butterfly-shaped molecular geometry with an electronic low-spin configuration ($S = 0$, LS). However, owing to the energetically low-lying LUMO, such complexes exhibit C–H agostic interactions with the metal at the vacant coordination sites.[4] Only recently, true four-coordination was described for this geometry for the first time.[5] However, according to density functional theory (DFT) calculations, the PCP pincer complex [RuCl{HC(CH$_2$NHP*t*Bu$_2$)$_2$}] (**A**) was postulated to be an unstable intermediate with square-planar coordination geometry and a triplet ground state (IS).[6] Therefore, the related PNP pincer complexes [RuX{N(SiMe$_2$CH$_2$P*t*Bu$_2$)$_2$}] (X = F (**B^{F}**), Cl (**B^{Cl}**), OTf (**B^{OTf}**)) remain the only square-planar ruthenium(II) compounds that are experimentally accessible and have an IS ground-state configuration.[7] DFT calculations showed that the highest singly occupied molecular orbital (SOMO) of **B^{Cl}** exhibits strong d$_{xz}$-orbital character owing to the π interaction with the disilylamido π donor (Scheme 1, middle). However, this interaction is not sufficient to effect spin pairing. Accordingly, square-planar d^6 14-electron complexes with an electronic low-spin configuration are not known, to date.[8,9]



Scheme 1. Qualitative d-orbital splitting of square-planar d^6 complexes with pure σ-donor ligands (left), with one weak π-donor ligand (middle), and one strong π-donor ligand (right).

Starting from the chelating amino ligand HN(CH$_2$CH$_2$P*i*Pr$_2$)$_2$ (*H*PNP^{iPr}), we recently reported the synthesis of octahedral ruthenium(II) amino complexes and the corresponding five-coordinate amides.[10] In this context, the comparison of **A** und **B^{Cl}** (see above) raises the question whether the expected even stronger π donation of the dialkylamido PNP ligand,[11] as compared with the disilylamido ligand in **B^{Cl}**, enables the stabilization of an unprecedented square-planar d^6 complex with a low-spin ground state (Scheme 1, right).

The reaction of [RuCl$_2$(PPh$_3$)$_3$] (**1**) with *H*PNP^{tBu} in THF gives amine complex [RuCl$_2$(*H*PNP^{tBu})] (**2**) in quantitative yield (Scheme 2).[12] The two sets of broadened signals in the ^{31}P and ^{1}H NMR spectra and the exchange signals in the ^{1}H NOESY NMR spectrum (CD$_2$Cl$_2$) of **2** at room temperature, respectively, are in agreement with two C_s symmetric, square-pyramidally coordinated diastereomers, which undergo exchange on the NMR time scale. Accordingly, below 0 °C



Scheme 2. Synthesis of amido complex **3** and β-hydrogen elimination to give compound **4** (RT = room temperature).

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sharp peaks are observed in the ^{1}H NMR spectrum which allow assignment of the signals by ^{1}H COSY and ^{1}H-^{13}C HMQC NMR spectroscopy. Further cooling to −80 °C leads to broadening and splitting of the ^{1}H NMR signal of one *tert*-butyl group per diastereomer (Supporting Information). This observation suggests C−H agostic interactions with the metal center at the vacant coordination site. The molecular structure of one diastereomer with square-pyramidal coordination geometry was derived by single-crystal X-ray diffraction (Figure 1).[12,13] The short $\text{Ru-H}^{t\text{Bu}}$ (2.39 Å) distances at the vacant coordination site confirm stablilization of the coordinatively unsaturated metal center by C−H agostic interactions in the solid state.

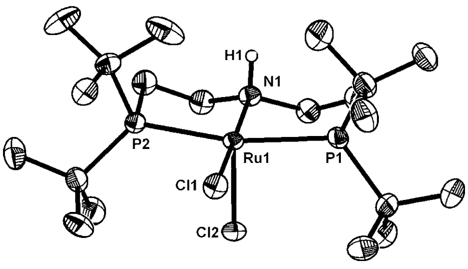

Figure 1. DIAMOND plot of the crystal structure of complex **2** (one of two crystallographically independent molecules; thermal ellipsoids set at 50 % probability). Hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths [Å] and angles [°] (values for the second independent molecule in parentheses): Ru1−Cl1 2.4506(6) (2.4478(6)), Ru1−Cl2 2.3438(6) (2.3579(8)), Ru1−N1 2.130(2) (2.131(2)), Ru1−P1 2.3854(6) (2.3888(7)), Ru1−P2 2.3405(6) (2.3397(7)); N1-Ru1-Cl1 175.79(5) (176.47(6)), N1-Ru1-Cl2 90.52(5) (91.19(6)), P1-Ru1-P2 164.08(2) (163.81(2)).

Deprotonation of **2** with KO*t*Bu at −78 °C and isolation at −20 °C gives amido complex [RuCl(PNP$^{t\text{Bu}}$)] (**3**) in over 80 % yield (Scheme 2). Complex **3** is thermally unstable at room temperature and, over the course of 2 days in solution, undergoes β-hydrogen elimination to give [RuHCl{N(CHCH$_2$P*t*Bu$_2$)(CH$_2$CH$_2$P*t*Bu$_2$)}] (**4**) quantitatively. However, **3** can be stored for several days without decomposition at temperatures below −30 °C in solution or at room temperature in the solid state, allowing for full characterization. Integration and the chemical shift of the ^{1}H NMR hydride signal of **4** confirm the absence of further H$_2$ ligands at the vacant coordination site. Furthermore, monitoring the β-hydrogen elimination of **3** to **4** by ^{1}H NMR spectroscopy in a sealed tube at room temperature in [D$_8$]THF provides no indication for further free or coordinated H$_2$.

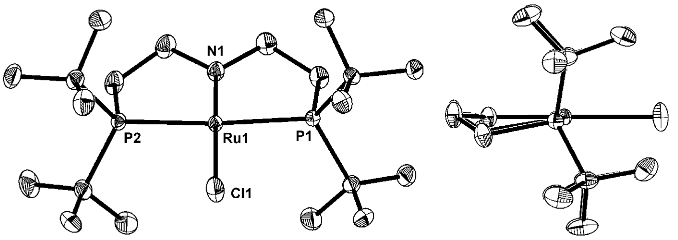

Figure 2. DIAMOND plot of the crystal structure of complex **3** (left: front view; right: side view; thermal ellipsoids set at 50 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1−N1 1.890(2), Ru1−Cl1 2.3805(6), Ru1−P1 2.3316(5), Ru1−P2 2.3240(6); N1-Ru1-Cl1 179.63(6), P1-Ru1-P2 168.13(2).

In the crystal structure, the metal center of **3** exhibits a planar, slightly distorted coordination geometry with a typical PNP bite angle P1-Ru1-P2 of 168.13(2)° and an almost linear N1-Ru1-Cl1 arrangement (179.63(6)°; Figure 2).[12,13] Planar coordination of the nitrogen atom ($\Sigma_{\text{angles}} = 360.0°$) and the particularly short Ru-N1 distance (1.890(2) Å), as compared with, for example, square-planar **B**$^{\text{Cl}}$ (2.050(1) Å) or the five-coordinate ruthenium(II) alkylamides [RuHPMe$_3$(PNP$^{i\text{Pr}}$)] (2.023(1) Å) and [RuH(HNCMe$_2$CMe$_2$NH$_2$)(PPh$_3$)$_2$] (1.967(1) Å), indicates a strong N→Ru π-bonding contribution.[7a,10d,14] Likewise, a relatively short Ru1-Cl1 distance (2.3805(6) Å) is found, for example, as compared with the basal Ru-Cl bond in **2** (2.4506(6), 2.4478(6) Å).

Neither the IR nor the ^{1}H NMR spectrum (180–280 K) of **3** provides evidence for the presence of hydride ligands. Therefore, the reactivity (see above) and the spectroscopic characterization exclude the assignment of a hydride complex, such as [Ru(H)$_2$Cl(PNP$^{t\text{Bu}}$)]. The ^{31}P, ^{1}H, and ^{13}C NMR spectra suggest C_{2v} symmetry on the NMR time scale in solution. However, particularly the ^{31}P signal (C$_6$D$_6$: $\delta = -22.58$ ppm; $\Delta\nu_{1/2} = 8$ Hz) and the NCH$_2$ ^{1}H signal (C$_6$D$_6$: $\delta = 14.41$ ppm; $\Delta\nu_{1/2} = 12$ Hz) are slightly broadened and exhibit unusual chemical shifts with a strong temperature dependence.[12,15] For example, the NCH$_2$ ^{1}H NMR signal is shifted by 3.64 ppm upfield upon cooling from 280 K to 180 K in [D$_8$]THF. These NMR spectroscopic properties of **3** can be rationalized with the presence of a LS ground state and an energetically low-lying IS excited state. The ^{13}C NMR signals, which are not significantly paramagnetically shifted,[11,16] therefore indicate hyperconjugation as the predominant transfer mechanism of spin density.[17] However, in the solid state (SQUID measurement) no magnetic moment could be detected ($\mu_{\text{eff}} < 0.01\ \mu_{\text{B}}$) in the temperature range of 2–300 K. Therefore, the thermodynamic parameters of the singlet–triplet transition were estimated in solution by modeling the chemical shifts as a function of temperature with the equation: $\delta = \delta^{\text{dia}} + C/(Te^{(\Delta H + T\Delta S)})$.[12,18] The relatively small experimentally accessible temperature range does not permit a very precise assessment ([D$_8$]toluene: $\Delta H^0 = (10.6 \pm 0.3)\ \text{kJ mol}^{-1}$; $\Delta S^0 = (4.2 \pm 0.8)\ \text{J mol}^{-1}\text{K}$). However, the result is in agreement with the observation that the population of the triplet state is not sufficient to be detected by magnetometry.[19] Interestingly, for the related complex [IrCl{=C(CH$_2$CH$_2$P*t*Bu$_2$)$_2$}] unusual chemical shifts were found for the Ir=C−CH$_2$ protons by ^{1}H NMR spectroscopy, as well ($\delta = -2.77$ ppm).[20] However, this observation was not closely examined.

The experimental results were reassessed by DFT calculations. Geometry optimizations of a full model of **3** in the singlet state (6-31 + G**) with different functionals (B3LYP and BP86) were in excellent agreement with the experimentally derived molecular structure by X-ray diffraction.[12] However, simplified models with PMe$_2$ instead of P*t*Bu$_2$

substituents resulted in minimum structures with butterfly conformations (N-Ru-Cl < 160°), as typically found for four-coordinate ruthenium(II) compounds (see above). This result suggests that the square-planar molecular geometry is mainly stabilized by the large steric pressure of the bulky chelating ligand.[21] A comparison of the electronic structures in the singlet and triplet states confirms the simplified bonding model (Scheme 1). The strong metal d_{z^2} character of the HOMO in the singlet state explains the absence of C–H agostic interactions at the vacant axial coordination sites of **3** (Figure 3), reminiscent of square-planar d^8 complexes.[22]

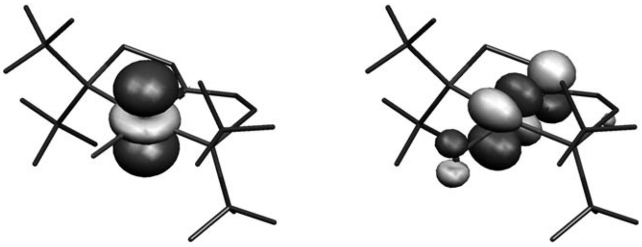

Figure 3. Kohn–Sham HOMO (left) and LUMO (right) plots of complex **3** in the singlet state (B3LYP/6-31+G**).

Furthermore, in the singlet state the antibonding combination of the Ru–N and Ru–Cl π bonds is not occupied (LUMO). Hence, strong Ru–N π bonding results, which accounts for the short Ru–N distance, as compared with the triplet state ($\Delta d_{S-T} = -0.1$ Å; BP86) which exhibits strong Ru–N π* character for the highest occupied SOMO. Accordingly, in the singlet state, less-negative NPA charges at the N ($\Delta q_{S-T} = +0.14\,e$; B3LYP) and Cl ($\Delta q_{S-T} = +0.08\,e$; B3LYP) atoms, a more negative charge at the metal ($\Delta q_{S-T} = -0.29\,e$; B3LYP) and larger Wiberg bond indices (WBI) for the Ru–N ($\Delta WBI_{S-T} = +0.43$; B3LYP) and Ru–Cl ($\Delta WBI_{S-T} = +0.15$; B3LYP) bonds are found. The calculated small energy gap between the singlet and triplet states ($\Delta E_{S-T} = -2.0$ kcal mol^{-1} (BP86); $+2.3$ kcal mol^{-1} (B3LYP)) does not permit a reliable assignment of the electronic ground state on the applied level of theory.[23] However, within the error of the method, this result is in agreement with the experimentally derived singlet ground state and an energetically low-lying excited triplet state.[24]

The experimental and quantum-chemical results for **3** demonstrate that the unprecedented electronic LS configuration in this coordination geometry can be attributed to a combination of the steric bulk and the strong π donation caused by the chelating amido ligand.[25,26] Therefore, the simple variation of the M–N π interaction by replacing a disilyl amido with a dialkyl amido ligand in the related compounds $\mathbf{B^{Cl}}$ (IS) and **3** (LS) allows for control of the electronic ground state, consequently offering an interesting approach for the design of novel spin-crossover materials. The high thermal stability of the 14-electron complex $\mathbf{B^{Cl}}$ and concomitant absence of C–H agostic stabilization was attributed by Caulton et al. to the triplet character of the compound.[7a] However, the singlet state can also be efficiently stabilized, if possible decomposition pathways, such as β-hydrogen elimination or C–H oxidative addition, can be effectively suppressed by the chelate effect and the high charge density at the vacant coordination sites.

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[13] **2**: turquoise columns, $C_{20}H_{45}Cl_2NP_2Ru$, $M_r = 533.48$; monoclinic, space group $P2_1/c$ (Nr. 14), $a = 19.389(1)$, $b = 13.420(1)$, $c = 22.854(2)$ Å, $\beta = 91.103(4)°$, $V = 5945.5(7)$ Å^3, $Z = 8$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.820$ mm^{-1}, $\rho_{\mathrm{calcd}} = 1.192$ g cm^{-3}, $T = 153(1)$ K, $F(000) = 2240$, crystal dimensions $0.08 \times 0.13 \times 0.61$ mm. $R1 = 0.0291$ (observed reflexes), $wR2 = 0.0719$ (all reflexes), $GOF = 1.041$, 493 parameters, $\Delta\rho_{\mathrm{max/min}} = 0.65/-0.56$ e Å^{-3}. **3**: brown needles, $C_{20}H_{44}ClNP_2Ru$, $M_r = 497.02$; monoclinic, space group $P2_1/c$ (Nr. 14), $a = 12.0574(6)$, $b = 16.0573(7)$, $c = 13.0190(6)$ Å, $\beta = 104.438(2)°$, $V = 2441.0(2)$ Å^3, $Z = 4$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.887$ mm^{-1}, $\rho_{\mathrm{calcd}} = 1.352$ g cm^{-3}, $T = 123(1)$ K, $F(000) = 1048$, crystal dimensions $0.02 \times 0.02 \times 0.15$ mm. $R1 = 0.0239$ (observed reflexes), $wR2 = 0.0587$ (all reflexes), $GOF = 1.074$, 402 parameters, $\Delta\rho_{\mathrm{max/min}} = 0.59/-0.31$ e Å^{-3}. CCDC 771336 (**2**) and CCDC 771337 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of

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