

## A Square-Planar Osmium(II) Complex

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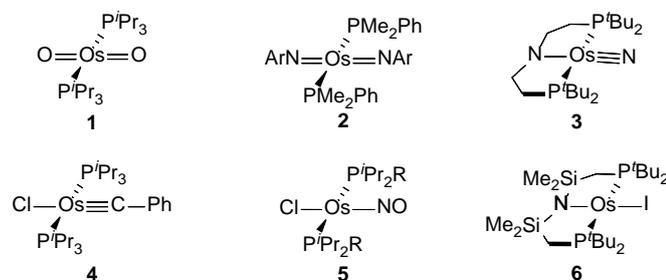
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Reduction of the pincer complex [Os<sup>III</sup>Cl<sub>2</sub>(PNP)] (PNP = N(CHCHPtBu<sub>2</sub>)<sub>2</sub>) affords the isolation and full characterization of an osmium(II) complex with square-planar coordination geometry, i.e. [Os<sup>II</sup>Cl(PNP)]. Spectroscopic, structural and magnetic data in combination with multireference computations indicate strong temperature independent paramagnetism, which arises from an energetically well separated ground state that mixes with excited states through spin-orbit coupling.

The recent advances in bifunctional catalysis also revived interest in osmium complexes with functional ligands that stabilize reactive states.<sup>1</sup> The coordination chemistry of osmium is strongly dominated by six-coordinate Os<sup>VI</sup>. Low coordination numbers are known for high-valent osmium with strong  $\pi$ -donating ligands, such as tetrahedral OsO<sub>4</sub>. Square-planar coordination is particularly rare. It is known for Os<sup>IV</sup> with oxo, imido, nitrido or carbyne ligands (**1-4**, Scheme 1),<sup>2a-d</sup> and for (formal) Os<sup>0</sup> with the strong  $\pi$ -acceptor NO (**5**).<sup>2e</sup> The sole exception is defined by [Os<sup>III</sup>(L<sup>Si</sup>)] (**6**).<sup>2f</sup> Based on <sup>1</sup>H NMR data and DFT computations, a square-planar geometry and a triplet (S=1) electronic ground state were proposed for **6**. This assignment is unparalleled in osmium chemistry, yet resembles that for the analogous Ru<sup>II</sup> complex [RuCl(L<sup>Si</sup>)] (**7**).<sup>3</sup>

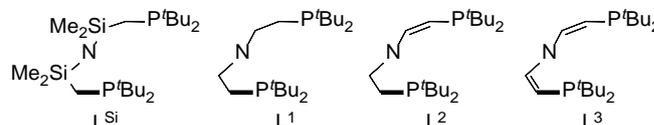


**Scheme 1** Square planar osmium complexes reported in the literature (R = *i*Pr, Ph, Ar = 2,6-*i*Pr-C<sub>6</sub>H<sub>3</sub>).

Over the last years we examined the reactivity of coordinatively unsaturated metal complexes with unusual electronic structures. The use of related diphosphineamido ligands (Scheme 2) enabled the isolation and characterization of square-planar d<sup>6</sup>-complexes like [Co<sup>III</sup>Cl(L<sup>3</sup>)]<sup>+</sup>,<sup>4a</sup> [Ir<sup>III</sup>Cl(L<sup>3</sup>)]<sup>+</sup>,<sup>4b</sup> and the ruthenium(II) series [RuCl(L)] (**8**: L = L<sup>1</sup>, **9**: L = L<sup>2</sup>, **10**: L =

L<sup>3</sup>).<sup>4c,4d,5</sup> A singlet ground-state was assigned for dialkylamide **8**, contrasting with intermediate spin (S = 1) for the vinyl- and divinylamides **9** and **10**, respectively. However, the latter also exhibit large magnetic anisotropy as a consequence of mixing with excited states through spin-orbit coupling (SOC). These findings sparked our interest in analogous 3<sup>rd</sup> row metal complexes, like **6**, and the appropriate description of their electronic structure. We here describe the isolation and full spectroscopic, magnetic and computational characterization of a square-planar osmium(II) complex.

We previously described the synthesis of Os<sup>IV</sup> pincer complex



**Scheme 2** PNP ligands used by Caulton and our group.

[OsCl<sub>2</sub>H(L<sup>1</sup>)] (**11**).<sup>2c</sup> All efforts to access four-coordinate [OsCl(L<sup>1</sup>)] from **11** by HCl elimination resulted in unselective decomposition, even at low temperatures. Therefore, the more robust divinylamide ligand L<sup>3</sup> was employed upon application of our previously reported template ligand dehydrogenation strategy.<sup>4a</sup> Reaction of **11** with excess tris-*tert*-butyl phenoxy radical (TBP) at 50°C in chlorobenzene affords five-coordinate osmium(III) complex [OsCl<sub>2</sub>(L<sup>3</sup>)] (**12**) in almost quantitative isolated yield (Scheme 3). Single-crystal X-ray analysis of **12** (Figure 1) confirms ligand dehydrogenation (C1=C2: 1.323(9) Å). The coordination geometry is best described as square-pyramidal with Cl1 in apical position ( $\tau = 0.02$ ).<sup>7</sup> In contrast to the solid state, C<sub>2v</sub> symmetry on the NMR timescale in solution is indicated by three strongly paramagnetically shifted and broadened <sup>1</sup>H NMR signals. The magnetic moment of **12** derived by Evans' method at room temperature ( $\mu_{\text{eff}} = 1.65 \mu_B$ ) is close to the spin-only value for an S = 1/2 ground-state. Furthermore, the broad, rhombic EPR powder spectrum with large *g*-anisotropy ( $g_x = 1.215$ ,  $g_y = 2.000$ ,  $g_z = 2.220$ ) is in agreement with a metal centered radical. (Super-)Hyperfine coupling was not resolved.

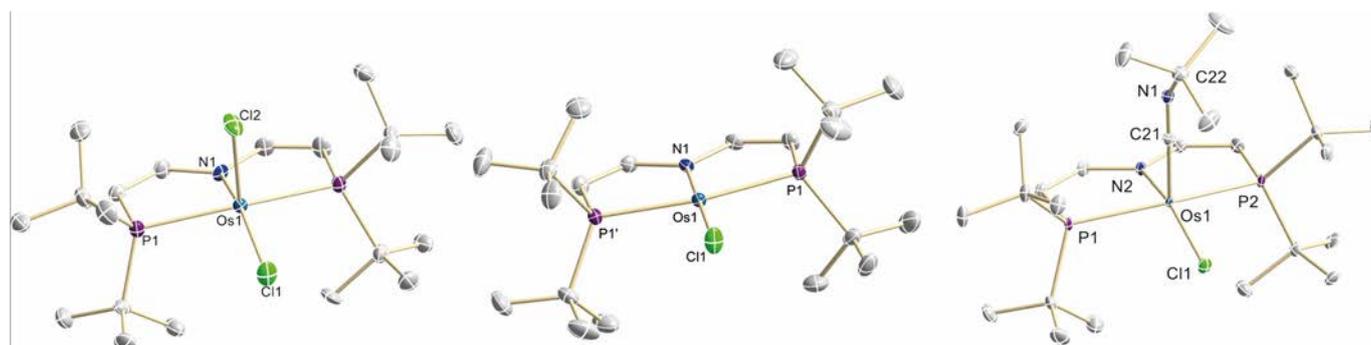
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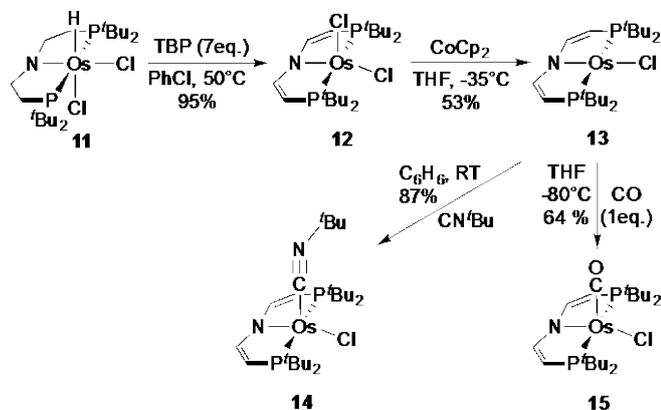
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**Figure 1** Molecular structure of complex **12**, **13** and **14** from single-crystal X-ray diffraction (thermal ellipsoids drawn at the 50% probability level); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **12** (Os1-N1 1.966(6), Os1-Cl1 2.380(3), Os1-Cl2 2.319(2), N1-C1 1.409(6), C1-C2 1.323(9), N1-Os1-Cl1 160.16(19), N1-Os1-Cl2 106.82(19), Cl1-Os1-Cl2 93.02(10)), **13** (Os1-N1 1.980(2), Os1-Cl1 2.3542(7), N1-C1 1.403(2), C1-C2 1.333(3) and **14** (Os1-N2 2.050(3), Os1-C21 1.827(4), Os1-Cl1 2.4046(9), C21-N1 1.197(5), C21-N2-C22 144.4(4).

The redox chemistry of **12** was examined by cyclic voltammetry. Quasi-reversible oxidation was found at  $E_{1/2} = -0.04$  V (vs.  $\text{Fc}^{0/+}$ ) besides two reduction waves at  $E = -1.28$  V and  $-2.05$ , respectively, that remained irreversible at scan rates up to 1000 mV/s, suggesting chloride elimination upon reduction. Accordingly, chemical reduction of **12** with  $\text{CoCp}_2$ , extraction with pentanes at  $-30^\circ\text{C}$  and crystallization over night at  $-35^\circ\text{C}$  allows for the isolation of dark purple, crystalline  $[\text{OsCl}(\text{L}^3)]$  (**13**) in isolated yields over 50%. Complex **13** is not stable at room temperature. In solution, complete, unselective decay is observed over the course of 24 h. NMR spectroscopic detection of isobutene points towards intramolecular decomposition pathways (see ESI), which also prevented reliable characterization by elemental analysis. However, crystallographic, spectroscopic, and mass spectrometric data confirm the proposed structure.

behavior, i.e. a linear ( $\delta \propto T$ ) and very small ( $\Delta\delta < 0.4$  ppm) temperature dependence (see ESI). These observations suggest temperature independent paramagnetism (TIP) indicating an energetically well separated ( $\gg k_B T$ ) ground state.<sup>8</sup> This interpretation is further supported by SQUID magnetometry of a powdered sample. In the range of 2–295 K constant susceptibility  $\chi_M(\text{TIP}) = 1030 \cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  is observed (see ESI). Hence, the magnetic properties are in line with the exclusive thermal population of a ground state, which experiences only second order paramagnetism through mixing with excited states. In comparison, the ruthenium analogue **10** exhibits strongly temperature dependent NMR spectra and magnetic susceptibility in these temperature ranges as a consequence of smaller separations of the lowest spin-orbit states.<sup>4d</sup> This reflects the higher spin-orbit coupling (SOC) constant of osmium ( $\xi_{\text{Os}} \approx 3000 \text{ cm}^{-1}$ ) vs. that of ruthenium ( $\xi_{\text{Ru}} \approx 1000 \text{ cm}^{-1}$ ).<sup>9</sup> Large TIP is typically found for octahedrally coordinated, heavy  $d^4$  ions, like osmium(IV) or rhenium(III), which in fact share an isolobal relationship with square-planar osmium(II) complex **13**.<sup>10</sup>

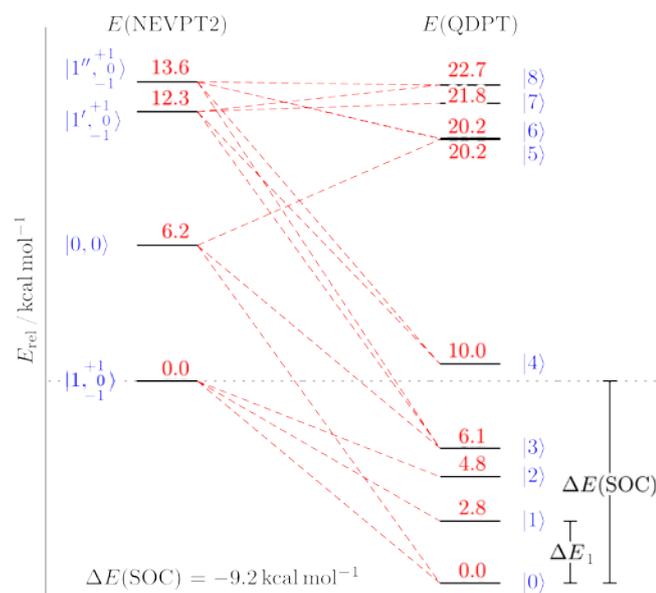


**Scheme 3** Synthesis of **12** by five-fold H atom abstraction via TBP and reduction towards **13** followed by coordination of  $\text{CNtBu}$  (**14**) and CO (**15**).

In the solid state (Figure 1), the osmium ion exhibits square-planar coordination with some distortion due to the pincer bite angle. The bond lengths around Os are close to parent **12**. There are no indications for intermolecular interactions in the solid state. While no  $^{31}\text{P}\{^1\text{H}\}$  NMR signal was found for Caulton's complex **6**, the  $^{31}\text{P}\{^1\text{H}\}$  spectrum of **13** features a signal with an unprecedented chemical shift for a trialkylphosphine ligand ( $\delta_{\text{P}} = -978.2$  ppm). In addition, three strongly shifted ( $\delta_{\text{Bu}} = -4.2$  ppm;  $\delta_{\text{CH}} = +18.4$  and  $-35.3$  ppm), yet sharp signals with resolved  $^1\text{H}$  and  $^{31}\text{P}$   $J$ -coupling are observed in the  $^1\text{H}$  NMR spectrum. Between  $-55^\circ\text{C}$  to  $-15^\circ\text{C}$  the chemical shifts exhibit non-Curie

Further information is obtained from computational analysis of **13**. Correlated single reference *ab initio* calculations, ONIOM(CCSD(T)-F12:PBE0D), predict a triplet ground state separated from the lowest singlet by merely 1.5 kcal mol<sup>-1</sup>. Additional multireference computations were performed to get insights into state mixing through SOC. A state-averaged NEVPT2/CAS(16,10) approach (Figure 2) also indicates a triplet ground state with  $(d_z)^1(d_{xz})^1$  configuration (94% weight). The first excited state lies 6.2 kcal mol<sup>-1</sup> above the triplet and corresponds to the lowest singlet state with  $(d_z)^2(d_{xz})^0$  configuration (86% weight). Hence, these results qualitatively reflect the single reference ONIOM calculations. However, after QDPT/SOC treatment on the NEVPT2/CASSCF energies the ground-state triplet root is stabilized by  $\Delta E(\text{SOC}) = -9.2$  kcal mol<sup>-1</sup> (Figure 2). Furthermore, it splits into three sublevels, where the lowest eigenstate  $|0\rangle$  derives from a triplet contribution with significant admixture (16%) of the lowest singlet state. The two eigenstates  $|1\rangle$  and  $|2\rangle$  are separated from  $|0\rangle$  by 2.8 kcal mol<sup>-1</sup> ( $= \Delta E_1$ ) and 4.8 kcal mol<sup>-1</sup>, respectively, and originate directly from the lowest triplet state. This state-energy diagram supports the rationalization of the

magnetic susceptibility measurements with an energetically isolated ground-state.<sup>11</sup>



**Figure 2** State-energy diagram for **13** based on NEVPT2/SA-CASSCF(16,10) computations. Non-relativistic energies of the lowest four states are shown with their corresponding  $|S, M_S\rangle$  label (left). The lowest nine spin-orbit states (right) are complemented with selected contributions (weights > 10%) of the corresponding spin-free states (dashed red lines).

The osmium(II) pincer platform was further characterized by the coordination of spectroscopic probes. As was reported for Caulton's complex **6**,<sup>2f</sup> the coordinatively unsaturated, low-valent complex **13** undergoes facile coordination of additional  $\pi$ -acceptor ligands. Addition of one equivalent of CNtBu to *in situ* prepared **13**, results in an immediate color change to dark blue and isolation of  $[\text{OsCl}(\text{L}^3)(\text{CNtBu})]$  (**14**) in high yield after column chromatography (Scheme 3). The band at  $\tilde{\nu} = 1931 \text{ cm}^{-1}$  in the IR-spectrum assignable to the  $\text{C}\equiv\text{N}$  stretching vibration indicates strong back bonding. This is confirmed by single crystal X-Ray diffraction (Figure 1). The isonitrile ligand of **14** is situated in the apical position of the square-pyramidal structure and features strong bending ( $\text{C21-N2-C22}$ :  $144.4(4)^\circ$ ), to an extent which is rarely observed.<sup>12</sup> Furthermore, the Os–N bond is slightly elongated with respect to parent **13** ( $\Delta d = 0.07 \text{ \AA}$ ) indicating reduced  $\pi$ -donation by the pincer ligand. In analogy, exposure of *in situ* prepared **13** to 1 equiv. CO gives the pink compound  $[\text{OsCl}(\text{L}^3)(\text{CO})]$  (**15**; Scheme 1). Excess CO results in the formation of several side products like the dicarbonyl complex. As in case of complex **14**, the  $^1\text{H-NMR}$  spectrum is in agreement with  $C_s$  symmetry on the NMR timescale. Complex **15** was fully characterized including single-crystal X-ray diffraction (see ESI). The CO ligand exhibits a rather unusual high-field shift in the  $^{13}\text{C}$  NMR spectrum ( $\delta = 168.3 \text{ ppm}$ ). The CO stretching vibration is observed at  $\tilde{\nu} = 1893 \text{ cm}^{-1}$  in the IR spectrum, almost identical with Caulton's  $[\text{Os}(\text{L}^5)(\text{CO})]$  (**16**;  $1892 \text{ cm}^{-1}$ ).<sup>2f</sup> These values confirm the electron rich nature of the  $\{\text{OsX}(\text{PNP})\}$  platform and increased backbonding in comparison with the Ru<sup>II</sup> analogue  $[\text{RuCl}(\text{L}^3)(\text{CO})]$  ( $1916 \text{ cm}^{-1}$ ).<sup>4d</sup> Importantly, the NMR data of complexes **14** and **15** indicate the

removal of the TIP experienced by parent **13** upon coordination of a fifth ligand.

In summary, we presented the isolation and full characterization of a square-planar osmium(II) complex. Spectroscopic, crystallographic and magnetic characterization of **13** indicates an energetically separated ground state, which is subject to large TIP. A correlated single-reference ab initio formalism on the basis of CCSD(T) expansions predicts a triplet ground state energetically close to an excited singlet state. Multi-reference computations corroborate the experimental picture and assign an electronic triplet ground state, which is strongly stabilized by mixing with excited states through SOC.

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