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Metalloradical Reactivity of Ru$^1$ and Ru$^0$ Stabilized by an Indole-Based Tripodal Tetraphosphine Ligand

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Abstract: The tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphane PP$_3$-ligand 1 stabilizes Ru in the Ru$^0$, Ru$^1$, and Ru$^2$ oxidation states. The octahedral [(PP$_3$)Ru$_3$(Cl)$_2$] (2), distorted trigonal bipyramidal [(PP$_3$)Ru$_4$(Cl)$_3$] (3), and trigonal bipyramidal [(PP$_3$)Ru$_5$(N$_3$)$_2$] (4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, IR, and ESI-MS. Both open-shell metalloradical Ru$^1$ complex 3 and the closed-shell Ru$^0$ complex 4 undergo facile (net) abstraction of a C atom from dichloromethane, resulting in formation of the corresponding Ru$^0$ and Ru$^1$ complexes 2 and 3, respectively.

Metals of the 4d and 5d row of the periodic table, particularly late transition metals in low oxidation states, strongly prefer closed-shell 16 or 18 valence electron configurations. As a result, open-shell complexes of these metals are rare, and have a strong tendency to convert into closed-shell products.[1] Ru$^1$ metalloradical complexes are particularly rare[2] and only two types of Ru$^1$ complexes have been successfully isolated thus far. Peters and co-workers reported a five-coordinate 17-electron [Ru$_4$N$_2$(SiP$_3$)$_4$] complex supported by an anionic tripodal tetradentate (SiP$_3$)$_3^{-}$ ligand (SiP$_3$)$_3^{-} = (2\text{-}iPr$_2$PC$_6$H$_4$)$_3$Si). Besides Ru$^1$, this platform also stabilizes complexes in oxidation states ranging from Ru$^0$ to Ru$^{II}$.[3] Interestingly, the Ru$^1$ complex was shown to catalyze coupling of aryl azides to azoarenes.[4] Recently, the group of Grützmann reported the remarkable 4-coordinate 15-electron complex [Ru(tropPP$_3$)$_2$]BF$_4$ featuring two bidentate tropPP$_3$ ligands (trop = 5H-dibenzocyclohepten-5-yl)]. Besides Ru$^1$, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru$^0$ to Ru$^{III}$.[5] No further reactivity with this complex has been reported to date.

Inspired by these intriguing examples, we wondered whether the corresponding ruthenium(0) complex could also be accessible and if these low-valent species would display interesting reactivity.

First, we aimed at the synthesis of the Ru$^0$ complex with ligand 1, as this species could allow entry to the desired low-valent ruthenium species by subsequent selective reduction. The desired complex [Ru(1)(Cl)$_2$] (2) was readily prepared by reacting stoichiometric amounts of 1 and [Ru(Cl)$_2$(C$_6$H$_5$)$_2$]$_2$ in refluxing THF in good yield (Scheme 1).

The $^{31}$P NMR spectrum of complex 2 displays a triplet of doublets ($\delta = 101.0$ ppm, $J_{PP} = 26.4, 25.5$ Hz), an apparent triplet ($\delta = 77.8$ ppm, $J_{PP} = 26.5$ Hz), and a triplet of doublets ($\delta = 48.5$ ppm, $J_{PP} = 27.9, 26.9$ Hz) with the integral ratio 1:2:1. The presence of three different phosphorus NMR signals points to a geometry in which two equatorial aminophosphine donors...
are equivalent \((\delta = 77.8 \text{ ppm})\), whereas the third side-arm donor P3 \((\delta = 101.0 \text{ ppm})\) experiences a different coordination environment. The pivotal, axial phosphine P4 is assigned to the signal at \(\delta = 48.5 \text{ ppm}\).

Ru\(II\) complexes with tripodal tetraphosphine ligands often display five-coordination with either square pyramidal or trigonal bipyramidal geometries around the metal center,\(^8\) however in case of complex 2, an octahedral geometry could not be excluded. Single crystals of 2, suitable for single crystal X-ray diffraction, were obtained by layering a dichloromethane solution with pentane. The molecular structure (Figure 2) reveals a distorted octahedral geometry, with \(\angle \text{P1–Ru1–P2} = 160.04(3)\)° (See the Supporting Information, Table S1) for the two mutually trans aminophosphines in the equatorial plane. The P donors oriented trans to the chlorido ligands have shorter Ru–P distances (Ru1–P3 = 2.2671(9) Å; Ru1–P4 = 2.1932(9) Å) compared to the mutually trans P donors (Ru1–P1 = 2.3727(9) Å; Ru1–P2 = 2.3189(9) Å).\(^9\)

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru\(II/III\) and Ru\(II/0\) reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window \((E_{\text{red}} = -2.5 \text{ vs. } \text{Fc/Fc}^+)\), and the poor solubility of 2 in THF, DMF, acetonitrile, or toluene prevented determination of the reduction potentials of 2 below \(-2.5 \text{ V. Thus, reduction of complex 2 to the desired complex [Ru(1)Cl] (3) requires a stronger reducing agent than the previously reported Ru\(III\) complexes [\(-1.24 \text{ V (Ru\(II/III\)) and } -2.14 \text{ V (Ru\(III/Ru\)) for the SiP}\_3\text{Pr}_3 \text{ system in THF; } +0.4 \text{ V (Ru\(II/Ru\)) and } -0.3 \text{ V (Ru\(II/Ru\)) for the tropPPh}_2 \text{ complex. Therefore, we used KC\(8\) to access the desired Ru\(I\) and Ru\(0\) species chemically (Scheme 2).}

The addition of one molar equivalent of KC\(8\) to a yellow suspension of 2 in THF resulted in a brown solution. The product formed proved to be NMR silent, suggestive of formation of a paramagnetic Ru\(I\) species formed by one-electron reduction. X-band EPR spectroscopy confirmed the presence of the metal-loradical species [Ru(1)Cl] (3). The EPR spectrum reveals a rhombic (albeit almost axial) \(g\)-tensor, characteristic of an \(S = 1/2\) system (Figure 3). Hyperfine coupling interactions (HFIs) with two P atoms are resolved, in line with previous observations for tripodal tetradentate phosphine Ru\(I\) complexes.\(^{2c,e, 3}\)

![Figure 2](image1.png)

**Figure 2.** X-ray crystal structure of 2 (CCDC 1555408). Thermal ellipsoids are set at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.

![Scheme 1](image2.png)

**Scheme 1.** Synthesis of [Ru(1)(Cl)]\((2)\).

![Scheme 2](image3.png)

**Scheme 2.** Reactivity of 2 with 1 or 2 equiv KC\(8\) to form 3 or 4, respectively.

![Figure 3](image4.png)

**Figure 3.** Experimental (black) and simulated (red) X-band EPR spectrum of 3 measured in frozen THF ([(Bu\(_4\)N][PF\(_6\)]) was added to obtain an improved glass). Experimental conditions: Temperature 20 K, microwave power 0.063 mW, field modulation amplitude 4 G, microwave frequency 9.3646 GHz. The simulated spectrum was obtained with the parameters shown in Table S2.

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These results are in agreement with a geometry that is distorted from a trigonal bipyramidal toward a (distorted) square pyramidal Ru’ coordination geometry. Preference for such a Jahn–Teller distorted trigonal bipyramidal geometry has also been observed for other d⁶ transition metal complexes.²³

Simulation of the experimental EPR spectrum revealed the parameters shown in Table S2 (see also the captions of Figures 3 and 5). The geometry of 3 was optimized with DFT (TurboMole, BP86, def2-TZVP), and the EPR parameters were computed with Orca and ADF. The DFT-computed EPR parameters (Table S2) are in qualitative agreement with the experimental data. The computations reveal a mainly metal-centered spin density distribution, as evident from the singly occupied molecular orbital (SOMO) and spin density plots of 3 (Figure 4).

The SOMO of the metalloradical complex (spin population at Ru = 62%) is essentially the Ru dₓ⁻ᵧ orbital pointing in the direction of the apical P donor (P3) of the distorted trigonal bipyramid (Figure 4, left). As a result, the spin population of the axial P donor (P3) is significant (ca. 12%; Figure 4, right), thus explaining the observed large HFIs with this donor atom. The two P donors in the distorted equatorial plane bind rather asymmetrically, leading to a larger spin population at one (8%, P2) compared to the other (5%, P1) P donor. The spin population at the connecting P donor trans to the chlorido ligand is small and negative (−0.8%, P4). The resolved HFIs in the experimental X-band EPR spectrum are thus well-explained by the electronic structure of 3. The g-anisotropy of complex 3 is quite small for a metalloradical complex, but this is fully understandable considering the large energy separation (TurboMole, BP86, def2-TZVP) between the dₓ⁻ᵧ-dominated SOMO and the filled dₓz and dᵧz-dominated MOs (1.4 eV and 1.6 eV, respectively).²⁴

The small g-anisotropy of 3 allows for recording the isotropic EPR spectrum in THF solution at room temperature (Figure 5). Simulation reveals a gₓᵧ value of 2.047 and HFIs with three equivalent P atoms (Aₓᵧ=gₓᵧ+gᵧz+gₓz=143 MHz). The measured gₓᵧ value is close to the average value of the anisotropic g-tensor components (gₓᵧ=(gₓᵧ+gᵧz+gₓz)/3=2.043). Detection of HFIs with three equivalent P atoms in solution points to rapid positional exchange of the axial and equatorial PPh₃ donors on the EPR timescale. In line with this, the measured Aₓᵧ values measured in solution are close to the averaged values of the resolved anisotropic A-tensor components stemming from the PPh₃ donors measured in frozen solution (Aₓᵧ=gₓᵧ+gᵧz+gₓz=143 MHz (3 equivalent P atoms), Wₓᵧ=25 MHz).

Layering of a THF solution of 3 with pentane resulted in the formation of brown needles suitable for single-crystal X-ray diffraction analysis. The molecular structure (Figure 6) is in good agreement with the EPR data and the DFT-optimized structure. The τ-value of 0.70 confirms a geometry in-between a trigonal bipyramid and a square pyramid.²⁵ The one-electron reduction of 2 to 3 is accompanied by the loss of one chlorido ligand and shortening of most of the Ru–P bonds (Ru–P1 = 2.2940(12); Ru–P2 = 2.2930(12) Å) and decrease of the x₁P1–Ru–P2 angle to 134.84(5)° (See the Supporting Information, Table S1).

As one-electron chemical reduction of complex 2 led to the selective formation of the stable Ru’ complex 3, we also explored two-electron reduction of complex 2. Addition of two equivalents of KC₈ to a THF suspension of 2 under N₂ atmos-
The X-ray crystal structure of an isomeric complex of 39 Hz. This coupling was observed after 20 h. This formation of complex 4 with dinitrogen coordinated to the ruthenium (Figure 7). Complex 4 has a trigonal bipyramidal geometry.

Figure 7. X-ray crystal structure of 4 (CCDC 1555410). Thermal ellipsoids are set at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.

try (r = 0.93) with equal Ru–P<sub>equatorial</sub> bond lengths (Ru–P<sub>1</sub> = Ru1 P1 2.2747(12); Ru–P<sub>2</sub> = 2.2752(11); Ru–P<sub>3</sub> = 2.2774(11)), and <sub>P</sub>–Ru–<sub>P</sub> angles that are close to 120°. Additionally, the P4–Ru bond (2.2133(11) Å) from dichloromethane, resulting in the formation of dichlorido Ru<sup>II</sup> complexes, where both the chloride and the carbene ligands originate from the organohalide. The reaction was proposed to proceed through oxidative addition of the CI–C bond, followed by α-chlorine elimination of the CI–R species yielding the dichlorido ruthenium carbene. However, Ru<sup>II</sup> complexes are known to undergo halide atom transfer reactions with organohalides (e.g. catalyzing the Kharash reaction) and thus a radical reaction between complex 3 or 4 and organohalides could not be excluded. Given our interest in the chemistry of metal–halides and metalcarbines, we decided to investigate the reaction of the low-valent Ru<sup>II</sup> and Ru<sup>III</sup> complexes with dichloromethane.

Dissolving 4 in dichloromethane resulted in the formation of 2 as evidenced by in situ <sup>31</sup>P NMR spectroscopy (see the Supporting Information). As no other complexes were detected in the <sup>31</sup>P NMR spectrum, the formation of a metalcarbene intermediate seemed unlikely. We hypothesized that the formation of 2 from 4 could proceed via a radical mechanism in which two chlorine atoms are stepwise abstracted from dichloromethane by the ruthenium complex, leading to two sequential one-electron oxidations of the metal center. This would imply that the Ru<sup>II</sup> complex 3 should be an intermediate. To test this hypothesis, we added two drops of CH<sub>2</sub>Cl<sub>2</sub> to a solution of 3 in [d<sub>8</sub>]THF. This brown solution turned into a light-brown-colored suspension within 3 days and <sup>31</sup>P NMR spectroscopy indicated clean formation of 2. No signals corresponding to residual 3 were observed by EPR spectroscopy, which indeed shows that 3 can undergo one-electron oxidation through chlorine atom transfer from dichloromethane. Complex 2 is stable in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. Having established that 2 can be formed by chlorine atom transfer to 3, we investigated whether complex 3 can be formed from 4 by the same type of transformation. When 1 molar equivalent of CH<sub>2</sub>Cl<sub>2</sub> was added to an in situ-generated solution of 4 in THF a strong EPR signal characteristic for formation of 3 was observed after 20 h. This observation indeed points to radical-type reactivity of the closed-shell Ru<sup>II</sup> complex 4.

In conclusion, although the formation of Ru<sup>II</sup> and Ru<sup>III</sup> compounds is rare, we found that the tripod tetrathosphine scaffold can accommodate ruthenium metal center in the oxidation states Ru<sup>II</sup>, Ru<sup>III</sup>, and Ru<sup>IV</sup>. These complexes are sufficiently stable to be isolated and analyzed by X-ray analysis. Initial reactivity studies show that both open-shell Ru<sup>II</sup> and closed-shell Ru<sup>III</sup> complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru<sup>II</sup> and Ru<sup>III</sup> complexes 2 and 3. These results show that indole-based tetrathosphine ligands provide...
a useful scaffold to explore the chemistry of low-valent ruthenium species. Future studies should aim at application of these systems in catalytic atom transfer reactions.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** chloride atom abstraction · dinitrogen complexes · metalloradicals · ruthenium · tripodal ligands


[16] CCDC 1555408 (2), 1555409 (3), and 1555410 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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