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Metalloradical Reactivity of Ru\textsuperscript{1} and Ru\textsuperscript{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 \( \text{PP}_3 \)-ligand 1 stabilizes Ru in the Ru\textsuperscript{II}, Ru\textsuperscript{III}, and Ru\textsuperscript{IV} oxidation states. The octahedral \([\text{PP}_3]\text{Ru}\text{Cl}_3(\text{Cl})\) (2), distorted trigonal bipyramidal \([\text{PP}_3]\text{Ru}([\text{Cl}])\) (3), and trigonal bipyramidal \([\text{PP}_3]\text{Ru}([\text{N}_3])\) (4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, IR, and ESI-MS. Both open-shell metalloradical Ru\textsuperscript{0} complex 3 and the closed-shell Ru\textsuperscript{II} complex 4 undergo facile (net) abstraction of a Cl atom from dichloromethane, resulting in formation of the corresponding Ru\textsuperscript{II} and Ru\textsuperscript{0} 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.\textsuperscript{2} Ru\textsuperscript{II} metalloradical complexes are particularly rare\textsuperscript{2} and only two types of Ru\textsuperscript{II} complexes have been successfully isolated thus far. Peters and co-workers reported a five-coordinate 17-electron \([\text{RuN}_3(\text{SiP}_3)_3]\) complex supported by an anionic tripodal tetradeinate \((\text{SiP}_3)_3^-\) ligand \((\text{SiP}_3)_3 = (2-i\text{Pr}_2\text{PC}_6\text{H}_4)_3\text{Si}\). Besides Ru\textsuperscript{II}, this platform also stabilizes complexes in oxidation states ranging from Ru\textsuperscript{II} to Ru\textsuperscript{II}\textsuperscript{III}.\textsuperscript{3} Interestingly, the Ru\textsuperscript{II} complex was shown to catalyze coupling of aryl azides to azoarenes.\textsuperscript{4} Recently, the group of Grützmacher reported the remarkable 4-coordinate 15-electron complex \([\text{Ru}(\text{tropPPPh})_2]BF_4\) featuring two bidentate tropPPPh\textsubscript{2} ligands \((\text{trop} = \text{5H-dibenzo[alpha,di]cyclohepten-5-yl})\). Besides Ru\textsuperscript{II}, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\textsuperscript{II} to Ru\textsuperscript{II}\textsuperscript{III}.\textsuperscript{5} No further reactivity with this complex has been reported to date.

Inspired by these intriguing examples, we wondered whether stable metalloradical Ru\textsuperscript{1} complexes could be accessed in a rigid tripodal \(\text{PP}_3\) ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\textsuperscript{1} complexes feature either a strongly \(\sigma\)-donating anionic tripodal \((\text{SiP}_3)_3^-\) ligand or two neutral \(\pi\)-accepting bidentate \((\text{tropPPPh})_2\) ligands. Hence, we surmised that the use of a tripodal tetradeinate ligand featuring both \(\sigma\)-donor and \(\pi\)-accepting phosphorus groups could allow for isolation and reactivity studies of well-defined Ru\textsuperscript{1} metalloradicals. We turned our attention to the tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphane ligand \((\text{SiP}_3)_3^-\) (Figure 1), which we previously used to stabilize the metalloradical rhodium complex \([\text{Rh}(1)\text{Cl}](\text{PPPh})_2\).\textsuperscript{6,7} We further wondered whether the corresponding ruthenium(0) complex could also be accessible and if these low-valent species would display interesting reactivity.

![Figure 1](https://example.com/figure1.png)

First, we aimed at the synthesis of the Ru\textsuperscript{II} complex with ligand 1, as this species could allow entry to the desired low-valent ruthenium species by subsequent selective reduction. The desired complex \([\text{Ru}(1)\text{Cl}_2]\) (2) was readily prepared by reacting stoichiometric amounts of 1 and \([\text{Ru}(\text{Cl})_2\text{C}_6\text{H}_4]\) in refluxing THF in good yield (Scheme 1).

The \(^{31}\text{P}\) NMR spectrum of complex 2 displays a triplet of doublets \((\delta = 101.0 \text{ ppm}, J_{\text{PP}} = 26.4, 25.5 \text{ Hz})\), an apparent triplet \((\delta = 77.8 \text{ ppm}, J_{\text{PP}} = 26.5 \text{ Hz})\), and a triplet of doublets \((\delta = 48.5 \text{ ppm}, J_{\text{PP}} = 27.9, 26.9 \text{ Hz})\) 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 ($\delta = 77.8$ ppm), whereas the third side-arm donor P3 ($\delta = 101.0$ ppm) experiences a different coordination environment. The pivotal, axial phosphine P4 is assigned to the signal at $\delta = 48.5$ ppm. RuII complexes with tripodal tetra-phosphine ligands often display five-coordination with either square pyramidal or trigonal bipyramidal geometries around the metal center,\cite{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 $\mu_3$-P1–Ru1–P2 of 160.04(3)$^\circ$ (See the Supporting Information, Table S1) for the two mutually trans aminophosphines in the equatorial plane. The P donors oriented trans to the chloride ligands have shorter Ru–P distances (Ru1–P3 (2.2671(9) \AA; Ru1–P4 (2.1932(9) \AA)) compared to the mutually trans P donors (Ru1–P1 (2.3727(9) \AA; Ru1–P2 (2.3189(9) \AA)).

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the RuII/RuI and RuI/Ru0 reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window ($E_{\text{red}} = -2.5$ vs. Fc/Fc$^+$), and the poor solubility of 2 in THF, DMF, acetonitrile, or toluene prevented determination of the reduction potentials of 2 below $-2.5$ V. Thus, reduction of complex 2 to the desired complex [Ru(1)Cl] (3) requires a stronger reducing agent than the previously reported Ru complexes $\left[-1.24$ V (RuII/RuI) and $-2.14$ V (RuII/RuI) for the SiP$_3$ system in THF; $+0.4$ V (RuII/RuI) and $-0.3$ V (RuII/RuI) for the tropPPh$_2$ complex\right]. Therefore, we used KC$_8$ to access the desired RuI and Ru0 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 RuI species formed by one-electron reduction. X-band EPR spectroscopy confirmed the presence of the metallocradicals 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 phosphate RuI complexes.\cite{2c,e,3}

![Figure 2](attachment.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](attachment.png)

**Scheme 1.** Synthesis of [Ru(1)(Cl)$_2$] (2).

![Scheme 2](attachment.png)

**Scheme 2.** Reactivity of 2 with 1 or 2 equiv KC$_8$ to form 3 or 4, respectively.
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 d⁹ transition metal complexes.⁰

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 d₉ 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 d₉- and d₈-dominated SOMO and the filled d₈ and d₉-dominated MOs (1.4 eV and 1.6 eV, respectively).⁴

The small g-anisotropy of 3 allows for recording the isotropic EPR spectrum in THF solution at room temperature (Figure 5). Simulation reveals a gav value of 2.047 and HFIs with three equivalent P atoms (Aiso = 143 MHz). The measured gav value is close to the average value of the anisotropic g-tensor components (gav = (gₓ + gᵧ + g₂)/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 Aiso 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 (Aiso = (Aₓ + Aᵧ + A₂)/9 = 143 MHz (3 equivalent P atoms), Aₓ = 25 MHz).

Layering of a THF solution of 3 with pentane resulted in 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-

![Figure 4](image-url)

Figure 4. Singly occupied molecular orbital (SOMO; left) and spin density plot (right) of 3 (top view).

![Figure 5](image-url)

Figure 5. Experimental (black) and simulated (red) X-band EPR spectrum of 3 in isotropic solution (THF). Experimental conditions: Temperature 298 K, microwave power 2.0 mW, field modulation amplitude 4 G, microwave frequency 9.3498 GHz. The simulated spectrum was obtained with gav = 2.0465, Aiso = 143 MHz (3 equivalent P atoms), Wiso = 25 MHz.

![Figure 6](image-url)

Figure 6. X-ray crystal structure of 3 (CCDC 1555409). Thermal ellipsoids are set at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.
The 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.

![Diagram of the X-ray crystal structure of 4](image)

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.

The formation led to formation of the Ru<sup>II</sup> dinitrogen complex [Ru(η<sup>2</sup>)(N<sub>2</sub>)]<sub>4</sub> (4). IR spectroscopy reveals the presence of an absorption at <em>v</em><sub>as</sub> = 2125 cm<sup>-1</sup>, which indicates the formation of a coordinated dinitrogen ligand that is weakly activated. The <sup>31</sup>P NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant <em>J</em><sub>PP</sub> of 39 Hz. This coupling is in agreement with a C<sub>3</sub>-symmetric complex with three equivalent peripheral phosphine atoms that couple with the central P atom in the axial position.

Brick-red colored crystals of 4 suitable for X-ray diffraction were grown by diffusion of pentane into a THF solution of the filtered reaction mixture. The molecular structure confirms formation of complex 4 with dinitrogen coordinated to the ruthenium (Figure 7). Complex 4 has a trigonal bipyramidal geometry.

Metal orbitals becomes possible upon decreasing the <em>δ</em>P1–Ru–P2 angle, which is observed in going from 2 (160.04(3)) to 4 (122.85(4)), thus explaining the shortening of the Ru–P1 and Ru–P2 bonds. Moreover, the π-acidic character of the aminophosphines P1, P2, and P3 can become dominant over their σ-donating capacities in the electron-rich Ru<sup>II</sup> complex 4.

With the low oxidation state ruthenium complexes 3 and 4 in hand, we decided to explore their reactivity. Both Roper and Grubbs reported the formation of dichlorido Ru<sup>III</sup> carbene upon addition of α,α-dihalide and trihalide compounds to Ru<sup>III</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 Cl–C bond, followed by α-chlorine elimination of the Cl–R species yielding the dichlorido ruthenium carbene. However, Ru<sup>III</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- and metalcarbenes, 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>III</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 tripodal tetraphosphate scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru<sup>III</sup>, Ru<sup>II</sup>, and Ru<sup>0</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>III</sup> and Ru<sup>II</sup> complexes 2 and 3. These results show that indole-based tetraphosphorus 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.