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Metalloradical Reactivity of Ru\textsuperscript{I} 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 PP\textsubscript{3}\textsubscript{t} ligand \textsuperscript{1} stabilizes Ru in the Ru\textsuperscript{II}, Ru\textsuperscript{III}, and Ru\textsuperscript{IV} oxidation states. The octahedral [(PP\textsubscript{3}\textsubscript{t})Ru\textsuperscript{II}(Cl\textsubscript{2})] \textsuperscript{2}(2), distorted trigonal bipyramidal [(PP\textsubscript{3}\textsubscript{t})Ru\textsuperscript{III}(Cl\textsubscript{2})] \textsuperscript{3}(3), and trigonal bipyramidal [(PP\textsubscript{3}\textsubscript{t})Ru\textsuperscript{IV}(N\textsubscript{3})] \textsuperscript{4}(4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, IR, and ESI-MS. Both open-shell metalloradical Ru\textsuperscript{II} complex \textsuperscript{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{III} complexes \textsuperscript{2} and \textsuperscript{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{[1]} 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 [Ru(N\textsubscript{3})(PP\textsubscript{3}\textsubscript{t})\textsuperscript{3}] complex supported by an anionic tripodal tetradentate (SiP\textsubscript{3}\textsuperscript{i})\textsuperscript{2} ligand (SiP\textsubscript{3}\textsubscript{i} = (C\textsubscript{6}H\textsubscript{4}Si)\textsubscript{2}N\textsubscript{3}). Besides Ru\textsuperscript{II}, this platform also stabilizes complexes in oxidation states ranging from Ru\textsuperscript{II} to Ru\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 [Ru\textsuperscript{III}(tropPP\textsubscript{3}\textsubscript{t})\textsubscript{3}]BF\textsubscript{4}, featuring two bidentate tropPP\textsubscript{3}\textsubscript{t} ligands (trop = 5H-dibenz[a,d]cyclohepten-5-yl). Besides Ru\textsuperscript{II}, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\textsuperscript{II} to Ru\textsuperscript{IV}.\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{II} complexes could be accessed in a rigid tripodal PP\textsubscript{3}\textsubscript{t} ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\textsuperscript{II} complexes feature either a strongly o-donating anionic tripodal (SiP\textsubscript{3}\textsuperscript{i})\textsuperscript{2} ligand or two neutral \(\pi\)-accepting bidentate (tropPP\textsubscript{3}\textsubscript{t}) ligands. Hence, we surmised that the use of a tripodal tetradentate ligand featuring both o-donor and \(\pi\)-accepting phosphorus groups could allow for isolation and reactivity studies of well-defined Ru\textsuperscript{II} metalloradicals. We turned our attention to the tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphane ligand (1)\textsuperscript{[6,7]} (Figure 1), which we previously used to stabilize the metalloradical rhodium complex [Rh\textsuperscript{II}(1)Cl\textsubscript{2}]\textsuperscript{8}.

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. Ligand systems capable of stabilizing isolable Ru\textsuperscript{II} species.](image)

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 [Ru(1)(Cl\textsubscript{2})] \textsuperscript{2}(2) was readily prepared by reacting stoichiometric amounts of 1 and [Ru(1)(Cl\textsubscript{2})(C\textsubscript{6}H\textsubscript{4})\textsubscript{2}] in refluxing THF in good yield (Scheme 1).

The \(\textsuperscript{31}P\) NMR spectrum of complex 2 displays a triplet of doublets (\(\delta = 101.0\) ppm, \(J_{PH} = 26.4, 25.5\) Hz), an apparent triplet (\(\delta = 77.8\) ppm, \(J_{PH} = 26.5\) Hz), and a triplet of doublets (\(\delta = 48.5\) ppm, \(J_{PH} = 27.9, 26.9\) 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 ($\delta = 77.8$ 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. Ru$^\text{II}$ complexes with tripodal tetraphosphine ligands often display five-coordination with either square pyramidal or trigonal bipyramidal geometries around the metal center; 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 $\angle \text{P}1-\text{Ru}1-\text{P}2$ 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 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). 

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^\text{II}$/Ru$^\text{I}$ and Ru$^\text{I}$/Ru$^\text{0}$ reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window ($E_{\text{red}} = -2.5$ 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$^\text{I}$ complexes $-1.24$ V (Ru$^\text{II}$/Ru$^\text{I}$) and $-2.14$ V (Ru$^\text{II}$/Ru$^\text{I}$) for the SiPr$_3$ system in THF; $+0.4$ V (Ru$^\text{II}$/Ru$^\text{I}$) and $-0.3$ V (Ru$^\text{II}$/Ru$^\text{I}$) for the tropPPh$_2$ complex. Therefore, we used KC$_8$ to access the desired Ru$^\text{I}$ and Ru$^\text{0}$ 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$^\text{I}$ species formed by one-electron reduction. X-band EPR spectroscopy confirmed the presence of the metal-loradicals 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$^\text{I}$ complexes. 

![Figure 2](image-url)  
**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](image-url)  
**Scheme 1.** Synthesis of [Ru(1)(Cl)$_2$] (2).

![Scheme 2](image-url)  
**Scheme 2.** Reactivity of 2 with 1 or 2 equiv KC$_8$ to form 3 or 4, respectively.

![Figure 3](image-url)  
**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 d⁰ transition metal complexes.[10]

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 d₃z 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 dₓz-dominated SOMO and the filled dₓz and dᵧz-dominated MOs (1.4 eV and 1.6 eV, respectively).[10]

The small g-anisotropy of 3 allows for recording the isotropic EPR spectrum in THF solution at room temperature (Figure 5). Simulation reveals a g_av value of 2.047 and HFIs with three equivalent P atoms (Aₓz = 143 MHz). The measured g_av value is close to the average value of the anisotropic g-tensor components (g_av = (gₓ + gᵧ + g_z)/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 Aₓz 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 (Aₓz = (Aₓz + Aᵧz + A_zz + Aₓz + Aᵧz + A_zz)/9 = 157 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.[11] 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 τ, P₁–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-

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was a distorted trigonal bipyramidal (RuV) and a trigonal bipyramidal (RuVI) five-coordinate species lowers the steric hindrance between the phosphorus atoms and allows for better overlap of Ru and P orbitals, resulting in shortening of the Ru–P bonds. Another factor that can play a role is that the P1 and P2 phosphorus donor atoms compete strongly for the same metal orbital as they are in a trans arrangement in complex 2. Binding to separate metal orbitals becomes possible upon decreasing the \( \chi \)-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 \( \chi \)-acidic character of the amino-phosphines P1, P2, and P3 can become dominant over their \( \sigma \)-donating capacities in the electron-rich RuIV 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 RuIII carbenes upon addition of \( \alpha,\alpha,\alpha \)-dihalide and trihalide compounds to RuIV complexes, where both the chloride and the carbene ligands originate from the organohalide.[13] The reaction was proposed to proceed through oxidative addition of the Cl–C bond, followed by \( \alpha \)-chloride elimination of the Cl–R species yielding the dichlorido ruthenium carbene. However, RuIV complexes are known to undergo halide atom transfer reactions with organohalides (e.g., catalyzing the Kharash reaction)[14] and thus a radical reaction between complex 3 or 4 and organohalides could not be excluded. Given our interest in the chemistry of metal-carbido and metalcarbenes[15,16] we decided to investigate the reaction of the low-valent RuII and RuIV complexes with dichloromethane.

Dissolving 4 in dichloromethane resulted in the formation of 2 as evidenced by in situ \( ^{31} \)P NMR spectroscopy (see the Supporting Information). As no other complexes were detected in the \( ^{31} \)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 RuIV complex 3 should be an intermediate. To test this hypothesis, we added two drops of CH2Cl2 to a solution of 3 in \( [d_8] \)THF. This brown solution turned into a light-brown-colored suspension within 3 days and \( ^{31} \)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 CH2Cl2 or CHCl3. 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 CH2Cl2 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 RuIV complex 4.

In conclusion, although the formation of RuII and RuIV complexes is rare, we found that the tripod tetrathosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states RuIII, RuII, and RuIV. These complexes are sufficiently stable to be isolated and analyzed by X-ray analysis. Initial reactivity studies show that both open-shell RuII and closed-shell RuIV complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding RuIII and RuIV 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 • metallaradicals • 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.