Metalloradical Reactivity of RuI and Ru0 Stabilized by an Indole-Based Tripodal Tetraphosphine Ligand

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Published in:
CHEMISTRY-A EUROPEAN JOURNAL

DOI:
10.1002/chem.201702727

Citation for published version (APA):
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\(^{IV}\), Ru\(^{III}\), and Ru\(^{II}\) oxidation states. The octahedral [(PP\(_3\))RuCl\(_2\)] (2), distorted trigonal bipyramidal (PP\(_3\))RuCl\(_2\)] (3), and trigonal bipyramidal (PP\(_3\))RuCl\(_2\) (4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, IR, and ESI-MS. Both open-shell metalloradical Ru\(^{II}\) complex 3 and the closed-shell Ru\(^{IV}\) complex 4 undergo facile (net) abstraction of a Cl atom from dichloromethane, resulting in formation of the corresponding Ru\(^{III}\) and Ru\(^{IV}\) 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\(^{II}\) metalloradical complexes are particularly rare\(^{[2]}\) and only two types of Ru\(^{II}\) complexes have been successfully isolated thus far. Peters and co-workers reported a five-coordinate 17-electron [Ru\(_2\)N\(_2\) (SiP\(_3\))\(_3\)] complex supported by an anionic tripodal tetradentate (SiP\(_3\))\(_2\) ligand (SiP\(_3\) = (2-iPr\(_2\)PC\(_6\)H\(_4\))S). Besides Ru\(^{II}\), this platform also stabilizes complexes in oxidation states ranging from Ru\(^{0}\) to Ru\(^{IV}\).\(^{[3]}\) Interestingly, the Ru\(^{II}\) complex was shown to catalyze coupling of aryl azides to azoarenes.\(^{[4]}\) Recently, the group of Grützmaecher reported the remarkable 4-coordinate 15-electron complex [Ru(tropPP\(_3\))BF\(_4\)] featuring two bidentate tropPP\(_3\) ligands (trop = 5H-dibenz[a,d]cyclohept-5-enyl). Besides Ru\(^{II}\), this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\(^{0}\) to Ru\(^{IV}\).\(^{[5]}\) No further reactivity with this complex has been reported to date.

Inspired by these intriguing examples, we wondered whether stable metalloradical Ru\(^{II}\) complexes could be accessed in a rigid tripodal PP\(_3\) ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\(^{II}\) complexes feature either a strongly σ-donating anionic tripodal (SiP\(_3\))\(_2\) ligand or two neutral π-accepting bidentate (tropPP\(_3\)) ligands. Hence, we surmised that the use of a tripodal tetradentate ligand featuring both σ-donor and π-accepting phosphorus groups could allow for isolation and reactivity studies of well-defined Ru\(^{II}\) metalloradicals. We turned our attention to the tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)-phosphane ligand (1) (Figure 1), which we previously used to stabilize the metalloradical rhodium complex [Rh\(^{II}\)Cl\(_2\)PF\(_6\)].\(^{[6]}\) We further 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\(_5\))] 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 ($\delta = 77.8$ 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$^{II}$ 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 $\angle$P1–Ru1–P2 of 160.04(3)$^\circ$ (See the Supporting Information, Table S1) for the two mutually trans amiphosphines in the equatorial plane. The P donors oriented trans to the chloride 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$^{II}$/Ru$^0$ and Ru$^0$/Ru$^0$ 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$^0$ complexes [$\Delta -1.24$ V (Ru$^{II}$/Ru$^0$) and $-2.14$ V (Ru$^{II}$/Ru$^0$) for the SiP$_3$ system in THF; $+0.4$ V (Ru$^{II}$/Ru$^0$) and $-0.3$ V (Ru$^{II}$/Ru$^0$) for the tropPPh$_2$ complex]. Therefore, we used KC$_8$ to access the desired Ru$^0$ 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$^0$ species formed by one-electron reduction. X-band EPR spectroscopy confirmed the presence of the metalloradicals species [Ru(1)Cl] (3). The EPR spectrum reveals a rhombic (albeit almost axial) $g$-tensor, characteristic of an $S = \frac{1}{2}$ system (Figure 3). Hyperfine coupling interactions (HFIs) with two P atoms are resolved, in line with previous observations for tripodal tetradentate phosphine Ru$^0$ complexes.\cite{2c,e,3}

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

Scheme 2. Reactivity of 2 with 1 or 2 equiv KC$_8$ to form 3 or 4, respectively.

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.

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.
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 d⁸ 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 d₃z-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 gₐav value of 2.047 and HFIs with three equivalent P atoms (Aₓav = 143 MHz). The measured gₐav value is close to the average value of the anisotropic g-tensor components (gₐav= (gₓ + gᵧ + gz)/3 = 2.043). Detection of HFIs with three equivalent P atoms in solution points to rapid positional exchange of the axial and equatorial PPh₂ donors on the EPR timescale. In line with this, the measured Aₓav values measured in solution are close to the averaged values of the resolved anisotropic A-tensor components stemming from the PPh₂ donors measured in frozen solution (Aₓav = (AₓP1 + AₓP2 + AₓP3 + AₓP4 + AₓP5 + AₓP6)/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 x,Ru–P1–Ru–P2 angle to 134.84(5)⁰ (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-

![Figure 4](image-url) - Singly occupied molecular orbital (SOMO; left) and spin density plot (right) of 3 (top view).

![Figure 5](image-url) - 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 gₐav = 2.0465, Aₓav = 143 MHz (3 equivalent P atoms), Wₓav = 25 MHz.

![Figure 6](image-url) - 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.
phere led to formation of the Ru\(^ {II} \) dinitrogen complex [Ru\(^ {II} \)(N\(_2 \))\(_2 \)] (4). IR spectroscopy reveals the presence of an absorption at \( v_{N_2} = 2125 \text{ cm}^{-1} \), which indicates the formation of a coordinated dinitrogen ligand that is weakly activated.\(^{[2]} \) The \(^{31} \)P NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant \( J_{P-P} \) of 39 Hz. This coupling is in agreement with a \( C_2 \) 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.

![Figure 7](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.

Table 1. Selected geometric parameters for complexes 2–4

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru–P1–Ru2</th>
<th>Ru–P2–Ru3</th>
<th>Ru–P3–Ru4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>57.0(1)</td>
<td>57.0(1)</td>
<td>57.0(1)</td>
</tr>
<tr>
<td>3</td>
<td>57.0(1)</td>
<td>57.0(1)</td>
<td>57.0(1)</td>
</tr>
<tr>
<td>4</td>
<td>57.0(1)</td>
<td>57.0(1)</td>
<td>57.0(1)</td>
</tr>
</tbody>
</table>

As there are neither intramolecular backdonation nor trans influence, the 10-membered metallacycle formation is not considered. Instead, the metal–phosphorus distances in 4 are in the range of the corresponding Ru complexes 2 and 3. The smaller bite angle of 4 with respect to 2 and 3 is supported by the shorter P–Ru bond lengths in 4 (2.2133(11) \( \AA \)) compared to 2 (2.2774(11) \( \AA \)).

In conclusion, although the formation of Ru\(^ {II} \) and Ru\(^ {IV} \) compounds is rare, we found that the tripod tetrathiaporphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru\(^ {II} \), Ru\(^ {III} \), and Ru\(^ {IV} \). These complexes are sufficiently stable to be isolated and analyzed by X-ray analysis. Initial reactivity studies show that both open-shell Ru\(^ {II} \) and closed-shell Ru\(^ {IV} \) complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru\(^ {II} \) and Ru\(^ {IV} \) complexes 2 and 3. These results show that indole-based tetrathiaporphine 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.

**Acknowledgements**

We thank the National Research School Combination Catalysis (NRSC-C) and the Netherlands Organization for Scientific Research (NWO-CW, VENI grant 722.013.002 for W.I.D.) and the University of Amsterdam (RPA Sustainable Chemistry) for funding. We thank Jan Meine Ernsting for assistance with NMR spectroscopy, Ed Zuidinga for mass spectrometry and Monalisa Goswami for assistance with EPR spectroscopy measurements.

**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.

Manuscript received: June 13, 2017
Revised manuscript received: July 28, 2017
Accepted manuscript online: August 16, 2017
Version of record online: August 30, 2017