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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)phosphate \(\text{PP}_{3}\)-ligand 1 stabilizes Ru in the Ru\(^5\), Ru\(^4\), and Ru\(^3\) oxidation states. The octahedral \([\text{PP}]_{3}\text{Ru}^{0}(\text{Cl})\) \(\text{(2)}\), distorted trigonal bipyramidal \([\text{PP}]_{3}\text{Ru}^{0}(\text{Cl})\) \(\text{(3)}\), and trigonal bipyramidal \([\text{PP}]_{3}\text{Ru}^{0}(\text{N}_{3})\) \(\text{(4)}\) 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 Cl atom from dichloromethane, resulting in formation of the corresponding Ru\(^{1}\) and Ru\(^{0}\) 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.\(^{[1]}\) 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 \([\text{Ru}^{1}_{2}\text{N}_{3}(\text{SiP})_{3}]\) complex supported by an anionic tripodal tetratadentate \((\text{SiP})_{3}\)\(^{-}\) ligand \((\text{SiP})_{3}^{0} = (2\text{-iprP})_{3}\text{PC}_{6}\text{H}_{5}S_{3}\)). Besides Ru\(^{1}\), this platform also stabilizes complexes in oxidation states ranging from Ru\(^{2}\) to Ru\(^{4}\).\(^{[3]}\) Interestingly, the Ru\(^{1}\) complex was shown to catalyze coupling of aryl azides to azoarenes.\(^{[4]}\) Recently, the group of Grützmacher reported the remarkable 14-electron complex \([\text{Ru}(\text{tropPPPh})_{3}]\)\text{BF}_{4}\) featuring two bidentate tropPPPh\(_{2}\) ligands (trop = 5H-dibenz[a,d]cyclohepten-5-yl)). Besides Ru\(^{1}\), this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\(^{2}\) to Ru\(^{4}\).\(^{[5]}\) No further reactivity with this complex has been reported to date.

Inspired by these intriguing examples, we wondered whether stable metalloradical Ru\(^{1}\) complexes could be accessed in a rigid tripodal \(\text{PP}_{3}\) ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\(^{1}\) complexes feature either a strongly \(\sigma\)-donating anionic tripodal \((\text{SiP})_{3}\)\(^{-}\) ligand or two neutral \(\pi\)-accepting bidentate (tropPPPh\(_{2}\)) ligands. Hence, we surmised that the use of a tripodal tetradentate ligand featuring both \(\sigma\)-donor and \(\pi\)-accepting phosphorus groups could allow for isolation and reactivity studies of well-defined Ru\(^{1}\) metalloradicals. We turned our attention to the tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphate ligand \((\text{SiP})_{3}\)\(^{-}\) \(\text{(1)}\) (Figure 1), which we previously used to stabilize the metalloradical rhodium complex \([\text{Rh}^{1}(\text{Cl})_{4}]\)\(_{2}\).\(^{[6]}\)\(^{[7]}\) \(\text{(1)}\) 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\(^{2}\) complex with ligand 1, as this species could allow entry to the desired low-valent ruthenium species by subsequent selective reduction. The desired complex \([\text{Ru}(1)(\text{Cl})_{4}]\) \(\text{(2)}\) was readily prepared by reacting stoichiometric amounts of \(1\) and \([\text{Ru}(\text{Cl})_{4}(\text{C}_{6}\text{H}_{5})_{2}]\) in refluxing THF in good yield (Scheme 1).

The \(^{31}\text{P}\) NMR spectrum of complex 2 displays a triplet of doublets (\(\delta = 101.0\) ppm, \(J_{\text{PP}} = 26.4, 25.5\) Hz), an apparent triplet (\(\delta = 77.8\) ppm, \(J_{\text{PP}} = 26.5\) Hz), and a triplet of doublets (\(\delta = 48.5\) ppm, \(J_{\text{PP}} = 27.9, 26.9\) 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. 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 $\angle P1$–Ru1–P2 of 160.04(3)\cite{7} (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).\cite{9}

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. Fe/Fe$^+$), 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 RuII complexes [$-1.24$ V (RuII/RuI) and $-2.14$ V (RuII/Ru0)] for the SiP$_3$I$_3$ system in THF; $+0.4$ V (RuI/Ru0) for the tropPPh$_2$ complex. 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 Ru 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 $S = \frac{1}{2}$ system (Figure 3). Hyperfine coupling interactions (HFIs) with two P atoms are resolved, in line with previous observations for tripodal tetradentate phosphine RuI complexes.\cite{2c,e,3}

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

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

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 d⁶ 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 (Turbo mole, 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 dₓz 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 (Turbo mole, BP86, def2-TZVP) between the dₓz-dominated SOMO and the filled dₓz and dₓz-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 gₓxy value of 2.047 and HFIs with three equivalent P atoms (Aₓxy = 143 MHz). The measured gₓxy value is close to the average value of the anisotropic g-tensor components (gₓxy = (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 PPh₃ donors on the EPR timescale. In line with this, the measured Aₓxy 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 (Aₓxy = Aₓxy + Aᵧgy + Azgz + Aₓxy + Aₓxy + Aₓxy)/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 x₁,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 KC₃ to a THF suspension of 2 under N₂ atmos-
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 \(\nu_{NH} = 2125\) cm\(^{-1}\), which indicates the formation of a coordinated dinitrogen ligand that is weakly activated.\(^{[22]}\) The \(^{31}\)P NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant \(J_{PP} \approx 39\) 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. 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.](image)

metal orbitals becomes possible upon decreasing the \(\angle\)P1–Ru–P2 angle, which is observed in going from 2 (160.04(3)\(^\circ\)) to 4 (122.85(4)\(^\circ\)), thus explaining the shortening of the Ru–P1 and Ru–P2 bonds. Moreover, the \(\pi\)-acidic character of the amino-phosphines P1, P2, and P3 can become dominant over their \(\sigma\)-donating capacities in the electron-rich Ru\(^{II}\) 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\(^{II}\) carbene upon addition of \(\alpha,\alpha,\alpha\)-trihalide and trihalide compounds to Ru\(^{II}\) 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, Ru\(^{II}\) 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-rodinals and metallocarbenes\(^{[16, 10]}\), we decided to investigate the reaction of the low-valent Ru\(^{II}\) and Ru\(^{II}\) 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 metalloocene 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\(^{II}\) complex 3 should be an intermediate.

To test this hypothesis, we added two drops of CH\(_2\)Cl\(_2\) 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 CH\(_2\)Cl\(_2\) or CHCl\(_3\). 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\(_2\)Cl\(_2\) 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\(^{II}\) complex 4.

In conclusion, although the formation of Ru\(^{II}\) and Ru\(^{II}\) compounds is rare, we found that the tripod tetrathosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru\(^{II}\), Ru\(^{II}\), and Ru\(^{II}\). 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\(^{II}\) complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru\(^{II}\) and Ru\(^{II}\) complexes 2 and 3. These results show that indole-based tetrathosphorus ligands provide
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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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