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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($^0$(Cl)$_2$)] (2), distorted trigonal bipyramidal [(PP$_3$)Ru($^1$(Cl)] (3), and trigonal bipyramidal [(PP$_3$)Ru($^2$(N$_2$)] (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 Cl 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(N$_2$)(SiP$_3$)$_3$] complex supported by an anionic tripodal tetradentate (SiP$_3$)$^-$ ligand (SiP$_3^-$) = (2,6-iPr$_2$PC$_6$H$_4$)$_2$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 Grützmaecher reported the remarkable 4-coordinate 15-electron complex [Ru(tropPPh$_3$)$_2$]BF$_4$ featuring two bidentate tropPPh$_3$ ligands (trop = 5H-dibenzocyclo-

hepten-5-yl)]. Besides Ru$^1$, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru$^0$ to Ru$^{II}$.[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$_6$)$_2$] 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, $\Delta = 26.4, 25.5$ Hz), an apparent triplet ($\delta = 77.8$ ppm, $\Delta = 26.5$ Hz), and a triplet of doublets ($\delta = 48.5$ ppm, $\Delta = 27.9, 26.9$ 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 bipyramid geometries around the metal center,\textsuperscript{[8]} however in case of complex 2, a 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)\textdegree (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) 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).\textsuperscript{[9]}

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^\text{II}$/Ru$^\text{III}$ and Ru$^\text{III}$/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, acetone, 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$^\text{II}$ complexes [–1.24 V (Ru$^\text{II}$/Ru$^\text{III}$) and $-2.14$ V (Ru$^\text{III}$/Ru$^\text{II}$) for the SiP$^3$ system in THF; $+0.4$ V (Ru$^\text{II}$/Ru$^\text{III}$)] and $-0.3$ V (Ru$^\text{III}$/Ru$^\text{II}$) 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.\textsuperscript{[2c,e, 3]}
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.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).

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

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 (Turbomole, BP86, def2-TZVP) between the dₓz-dominated SOMO and the filled dₓz and dₓy-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 gₐ₀ value of 2.047 and HFIs with three equivalent P atoms (Aₑ₀=143 MHz). The measured gₐ₀ value is close to the average value of the anisotropic g-tensor components (gₐ₀=(gₓ+gᵧ+gₚ)/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 Aₑ₀ 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 (Aₑ₀=(Aₓ²+Aᵧ²+Aₚ²+Aₓₚ+Aₓᵧ+Aᵧₚ)/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 %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 atm...
phere led to formation of the RuII dinitrogen complex [RuII(1)(N2)] (4). IR spectroscopy reveals the presence of an absorption at νN2 = 2125 cm⁻¹, which indicates the formation of a coordinated dinitrogen ligand that is weakly activated.[12] The 31P NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant J_{PP} of 39 Hz. This coupling is in agreement with a C3v 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 with a Ru–P1 equatorial bond length of 2.2747(12) Å, Ru–P2 = 2.2752(11) Å, Ru–P3 = 2.2774(11) Å, and P–Ru–P angles that are close to 120°. Additionally, the P4–Ru bond (2.2133(11) Å) is trans to N2, is elongated relative to 2 and 3. This is likely a result of weakening of the π backbonding between Ru and P4 attributable to competition for the same metal orbital with the π-acidic dinitrogen ligand. The general shortening of all Ru–P bonds on progressing from RuII via Ru(I) to Ru0 in complexes 2, 3, and 4 is somewhat unexpected, as a lower oxidation state of the metal center is intuitively expected to result in weaker bonding of σ-donor ligands. The stronger metal–phosphorus interactions observed instead are likely the result of several contributing effects. Going from an octahedral six-coordinate species (RuII) to a distorted trigonal bipyramidal (RuI) and a trigonal bipyramidal (Ru0) 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 χ,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 amino-phosphines P1, P2, and P3 can become dominant over their σ-donating capacities in the electron-rich RuII 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 α,α,α-trihalide and trihalide compounds to RuII 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 α-chloride elimination of the Cl–Ru species yielding the dichloridoro ruthenium carbene. However, RuII 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 complexes,[15,16] we decided to investigate the reaction of the low-valent RuII and Ru0 complexes with dichloromethane.

Dissolving 4 in dichloromethane resulted in the formation of 2 as evidenced by in situ 31P NMR spectroscopy (see the Supporting Information). As no other complexes were detected in the 31P NMR spectrum, the formation of a metalcarbido intermediate seemed unlikely. We hypothesized that the formation of 2 from 4 could proceed via a radical mechanism in which both 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 RuII complex 3 should be an intermediate. To test this hypothesis, we added two drops of CH2Cl2 to a solution of 3 in [d8]THF. This brown solution turned into a light-brown-colored suspension within 3 days and 31P 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 chloride 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 RuII complex 4.

In conclusion, although the formation of RuII and Ru0 compounds is rare, we found that the tripodal tetrathosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states RuII, RuI, and Ru0. 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 Ru0 complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding RuII and RuI complexes 2 and 3. These results show that indole-based tetrathosphorus 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.

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