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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-(diphenylphosphophany1)-3-methyl-1H-indol-2-yl)phosphane PP\textsubscript{3}-ligand 1 stabilizes Ru in the Ru\textsuperscript{3}, Ru\textsuperscript{II}, and Ru\textsuperscript{0} oxidation states. The octahedral [(PP\textsubscript{3})Ru\textsuperscript{II}(Cl)]\textsubscript{2} (2), distorted trigonal bipyramidal [(PP\textsubscript{3})Ru\textsuperscript{II}(Cl)] (3), and trigonal bipyramidal [(PP\textsubscript{3})Ru\textsuperscript{II}(N\textsubscript{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{II} complex 3 and the closed-shell Ru\textsuperscript{0} 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{[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\textsubscript{4}N\textsubscript{2}(SiP\textsubscript{6}Pr\textsubscript{3})\textsuperscript{0}] complex supported by an anionic tripodal tetradentate (SiP\textsubscript{6}Pr\textsubscript{3})\textsuperscript{−} ligand (SiP\textsubscript{6}Pr\textsubscript{3} = (2-iPr\textsubscript{3}PC\textsubscript{6}H\textsubscript{4})\textsubscript{3}Si). Besides Ru\textsuperscript{II}, this platform also stabilizes complexes in oxidation states ranging from Ru\textsuperscript{3} to Ru\textsuperscript{0}.\textsuperscript{[3]} Interestingly, the Ru\textsuperscript{0} 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\textsubscript{2}(tropPP\textsubscript{3})\textsubscript{2}]BF\textsubscript{4} featuring two bidentate tropPP\textsubscript{3} ligands (trop = 5H-dibenz[a,d]cyclo-
hepten-5-yl)). Besides Ru\textsuperscript{II}, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\textsuperscript{3} to Ru\textsuperscript{0}.\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} ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\textsuperscript{II} complexes feature either a strongly \(\pi\)-donating anionic tripodal (SiP\textsubscript{6}Pr\textsubscript{3})\textsuperscript{−} ligand or two neutral \(\pi\)-accepting bidentate (tropPP\textsubscript{3}) ligands. Hence, we surmised that the use of a tripodal tetradentate ligand featuring both \(\sigma\)-donor and \(\pi\)-accepting phosphorous 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-(diphenylphosphophany1)-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][PF\textsubscript{6}].\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 species.

First, we aimed at the synthesis of the Ru\textsuperscript{3} 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\textsubscript{2}(1)Cl\textsubscript{2}] (2) was readily prepared by reacting stoichiometric amounts of 1 and [Ru(Cl\textsubscript{2})(C\textsubscript{6}H\textsubscript{6})\textsubscript{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, \(J_{\text{p-p}} = 26.4, 25.5\) Hz), an apparent triplet (\(\delta = 77.8\) ppm, \(J_{\text{p-p}} = 26.5\) Hz), and a triplet of doublets (\(\delta = 48.5\) ppm, \(J_{\text{p-p}} = 27.9, 26.9\) 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$^{	ext{II}}$ 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 $\angle$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 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).\(^9\))

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^{	ext{II}}$/Ru$^{	ext{I}}$ and Ru$^{	ext{I}}$/Ru$^{	ext{0}}$ 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$^{	ext{I}}$ complexes [$-1.24$ V (Ru$^{	ext{II}}$/Ru$^{	ext{I}}$) and $-2.14$ V (Ru$^{	ext{I}}$/Ru$^{	ext{0}}$) for the SiP$_3$ system in THF; $+0.4$ V (Ru$^{	ext{II}}$/Ru$^{	ext{I}}$) and $-0.3$ V (Ru$^{	ext{I}}$/Ru$^{	ext{0}}$) for the tropPPh$_2$ complex]. Therefore, we used KC$_8$ to access the desired Ru$^{	ext{I}}$ and Ru$^{	ext{0}}$ 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$^{	ext{I}}$ species formed by one-electron reduction. X-band EPR spectroscopy confirmed the presence of the metal–lroradicals 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 tetradeutate phosphine Ru$^{	ext{I}}$ complexes.\(^{[2c,e, 3]}\)

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.

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 d⁷ 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 d₉z 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 d₉z-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_aver value of 2.047 and HFIs with three equivalent P atoms (Δg₉z=143 MHz). The measured g_aver value is close to the average value of the anisotropic g-tensor components (g_aver=(gₓ+gᵧ+g₉z)/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 Δg₉z 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 (A₉z=(Δgₓ+Δgᵧ+Δg₉z+Δgₓ'+Δgᵧ'+Δg₉z')/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 θ(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-

![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 g_aver=2.0465, Δg₉z=143 MHz (3 equivalent P atoms), W_η6=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.
Dinitrogen complex bond lengths (Ru–P1 complexes are is elongated relative to trans and thus are adiabatic to Ru2P12.2747(12); Ru–P2 = 2.2752(11); Ru–P3 = 2.2774(11)), and x,P–Ru–P angles that are close to 120°. Additionally, the P4–Ru bond (2.2133(11) Å) 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 Ru4 via Ru1 to Ru3 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 binding 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 (Ru1) to a distorted trigonal bipyramidal (Ru2) and a trigonal bipyramidal (Ru3) 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 x,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 Ru4 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 Ru3 carbene upon addition of α,α,α-dihalide and trihalide compounds to Ru4 complexes, where both the chloride and the carbene ligands originate from the organohalide.11] The reaction was proposed to proceed through oxidative addition of the Cl–C bond, followed by α-chloride elimination of the Cl–R species yielding the dichlorido ruthenium carbene. However, Ru4 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–halides and metalacarbenes16–19] we decided to investigate the reaction of the low-valent Ru3 and Ru4 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 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 Ru4 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 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 Ru3 complex 4.

In conclusion, although the formation of Ru3 and Ru4 compounds is rare, we found that the triiodal tetraphosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru4, Ru3, and Ru2. These complexes are sufficiently stable to be isolated and analyzed by X-ray analysis. Initial reactivity studies show that both open-shell Ru4 and closed-shell Ru3 complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru4 and Ru3 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.