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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-y1)phosphate PP$_3$-ligand 1 stabilizes Ru in the Ru$^0$, Ru$^1$, and Ru$^2$ oxidation states. The octahedral [(PP)$_3$Ru(Cl)$_2$] (2), distorted trigonal bipyramidal [(PP)$_3$Ru(II)(Cl)$_3$] (3), and trigonal bipyramidal [(PP)$_3$Ru$^0$(N$_3$)$_2$] (4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, 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 [RuN$_3$(SIP$_{3}$)$_3$] complex supported by an anionic tripodal tetradeinate (SIP$_{3}$)$_3^-$ ligand (SIP$_{3}$)$_3^-$ = (2-iPr$^1$PC$_6$H$_{14}$)$_3$Si. Besides Ru$^1$, this platform also stabilizes complexes in oxidation states ranging from Ru$^0$ to Ru$^2$.[3] Interestingly, the Ru$^1$ complex was shown to catalyze coupling of aryl azides to azoaromatics.[4] Recently, the group of Grützmacher reported the remarkable 4-coordinate 15-electron complex [Ru(tropPPH$_3$)$_3$]BF$_4$ featuring two bidentate tropPPH$_3$ ligands (trop = 5H-dibenz[a,d]cyclohepten-5-yl)]. Besides Ru$^1$, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru$^0$ to Ru$^3$.[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 PP$_3$ ligand environment for subsequent reactivity evaluation. The above-mentioned Ru$^1$ complexes feature either a strongly $\sigma$-donating anionic tripodal (SIP$_{3}$)$_3^-$ ligand or two neutral $\pi$-accepting bidentate (tropPPH$_3$) ligands. Hence, we surmised that the use of a tripodal tetradeinate 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 (1)[6,7] (Figure 1), which we previously used to stabilize the metalloradical rhodium complex [Rh$^1$(1)Cl]PF$_6$.[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$^1$ species.](image)

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$_5$)$_2$] in refluxing THF in good yield (Scheme 1).

The $^{31}$P NMR spectrum of complex 2 displays a triplet of doublets (δ = 101.0 ppm, $J_{	ext{PP}}$ = 26.4, 25.5 Hz), an apparent triplet (δ = 77.8 ppm, $J_{	ext{PP}}$ = 26.5 Hz), and a triplet of doublets (δ = 48.5 ppm, $J_{	ext{PP}}$ = 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$^2\text{II}$ 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, 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 transaminophosphines 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)).\textsuperscript{[9]}

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^2\text{II}$/Ru$^0$ reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window ($E_{\text{ox}} = -2.5$ 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 [$\Delta E_{\text{Ru}^0/\text{Ru}^2\text{II}} = 1.24$ V (Ru$^2\text{II}$/Ru$^0$) and $-2.14$ V (Ru$^0$/Ru$^2\text{II}$) for the SiP$^3\text{Pr}_3$ system in THF; $\Delta E_{\text{Ru}^0/\text{Ru}^2\text{II}} = 0.4$ V (Ru$^2\text{II}$/Ru$^0$) and $-0.3$ V (Ru$^0$/Ru$^2\text{II}$) for the tropPPh$_2$ complex]. Therefore, we used KC$_8$ to access the desired Ru$^0$ and Ru$^2\text{II}$ 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 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$^0$ complexes.\textsuperscript{[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.](image)

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

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

![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 dₓᵧ 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 dₓᵧ-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 gₐₙₐ value of 2.047 and HFIs with three equivalent P atoms (Aᵧₐₐ = 143 MHz). The measured gₐₙₐ value is close to the average value of the anisotropic g-tensor components (gₐₙₐ = (gₓ + gᵧ + gₕ)/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 Aᵧₐₐ 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 (Aᵧₐₐ = (Aₓₒ + Aᵧₒ + Aₕₒ + Aₓₜₒ + Aᵧₜₒ + Aₕₜₒ)/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 χ₁,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 KC₂ to a THF suspension of 2 under N₂ atmos-

![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 gₐₙₐ = 2.0465, Aᵧₐₐ = 143 MHz (3 equivalent P atoms), Wₘ₀ = 25 MHz.](image)

![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.](image)
The dinitrogen complex [Ru(N)(H)(N)] (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. 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 geometrical structure. The general shortening of all Ru–P bonds on progressing from Ru$^{II}$ via Ru$^{II}$ to Ru$^{II}$ 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 $\sigma$-donor ligands. The stronger metal–phosphorus interactions observed instead are likely the result of several contributing effects. Going from an octahedral six-coordinate species (Ru$^{II}$) to a distorted trigonal bipyramidal (Ru$^{II}$) and a trigonal bipyramidal (Ru$^{II}$) 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 $\angle$P1–Ru–P2 angle, which is observed in going from 2 (160.04(3)$^\circ$) to 4 (127.85(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$^{II}$ carbenes upon addition of chlorido-dihalo- and trihalide compounds to Ru$^{II}$ complexes, where both the chlorine and the carbene ligands originate from the organohalide. The reaction was proposed to proceed through oxidative addition of the Cl–C bond, followed by $\alpha$-chloride elimination of the Cl–C 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) 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 metalcarbenes, 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 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 Ru$^{III}$ 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 tetraphosphine 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 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.

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