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Metalloradical Reactivity of Ru\textsuperscript{I} and Ru\textsuperscript{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 PP\textsubscript{3}-ligand 1 stabilizes Ru in the Ru\textsuperscript{II}, Ru\textsuperscript{III}, and Ru\textsuperscript{0} oxidation states. The octahedral $[\text{PP}_3]\text{Ru}(\text{Cl})$ (2), distorted trigonal bipyramidal $[\text{PP}_3]\text{Ru}(\text{Cl})$ (3), and trigonal bipyramidal $[\text{PP}_3]\text{Ru}(\text{N}_5)$ (4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, IR, and ESI-MS. Both open-shell metalloradical Ru\textsuperscript{I} 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{I} metalloradical complexes are particularly rare\textsuperscript{[2]} and only two types of Ru\textsuperscript{I} complexes have been successfully isolated thus far. Peters and co-workers reported a five-coordinate 17-electron $[\text{Ru}_2\text{N}_2(\text{SiP}_3)_3]^+$ complex supported by an anionic tripodal tetradeinate (SiP\textsubscript{3})\textsuperscript{3–} ligand (SiP\textsubscript{3})\textsuperscript{3–} = (2-2\textsubscript{a}Pr\textsubscript{2}PC\textsubscript{6}H\textsubscript{4})Si\textsuperscript{3–}. Besides Ru\textsuperscript{I}, this platform also stabilizes complexes in oxidation states ranging from Ru\textsuperscript{III} to Ru\textsuperscript{0}\textsuperscript{[3]} (Figure 1), which we previously used to stabilize the metalloradical rhodium complex $[\text{Rh}(1\text{C}1\text{C})\text{PF}_6]$.\textsuperscript{[4]} 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\textsuperscript{II} complex with ligand 1, as this species could allow entry to the desired low-valent ruthenium species by subsequent selective reduction. The desired complex $[\text{Ru}(1\text{C})\text{Cl}]$ (2) was readily prepared by reacting stoichiometric amounts of $1$ and $[\text{Ru}(\text{Cl})_2\text{C}_{6}\text{H}_{5}]$ 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$^\text{II}$ complexes with tripodal tetraphosphine ligands often display five-coordination with either square pyramidal or trigonal bipyramidal geometries around the metal center,\[8\] 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)$^\text{o}$ (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)$\text{Å}$; Ru1–P4 (2.1932(9)$\text{Å}$) compared to the mutually trans P donors (Ru1–P1 (2.3727(9)$\text{Å}$; Ru1–P2 (2.3189(9)$\text{Å}$).\[9\]

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^\text{II}$/Ru$^\text{I}$ and Ru$^\text{I}$/Ru$^\text{0}$ reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window ($E_{\text{ox}} = -2.5$ 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$^\text{I}$ complexes ($-1.24$ V (Ru$^\text{II}$/Ru$^\text{I}$) and $-2.14$ V (Ru$^\text{I}$/Ru$^\text{0}$)) for the SiP$i\text{Pr}_3$ system in THF; $+0.4$ V (Ru$^\text{I}$/Ru$^\text{0}$) 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-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 phosphate Ru$^\text{I}$ complexes.\[2c,e, 3\]
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 d⁰ 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 d\(_{xy}\) 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 \(d_{xy}\)-dominated SOMO and the filled \(d_{xy}\) and \(d_{yz}\)-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 \(g_{av}\) value of 2.047 and HFIs with three equivalent P atoms (\(A_{iso}^{\text{vm}}=143\) MHz). The measured \(g_{av}\) value is close to the average value of the anisotropic \(g\)-tensor components (\(g_{av}=(g_x+g_y+g_z)/3=2.043\)). Detection of HFIs with three equivalent P atoms in solution points to rapid positional exchange of the axial and equatorial PPh\(_3\) donors on the EPR timescale. In line with this, the measured \(A_{iso}^{\text{vm}}\) values measured in solution are close to the averaged values of the resolved anisotropic \(A\)-tensor components stemming from the PPh\(_3\) donors measured in frozen solution (\(A_{iso}^{\text{vm}}=(A_{iso}^{P1}+A_{iso}^{P2}+A_{iso}^{P3}+A_{iso}^{P4}+A_{iso}^{P5})/9=157\) 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 \(\tau\)-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 \(\tau\)-value of Ru–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 KC\(_3\) to a THF suspension of 2 under N\(_2\) atmos-
sphere led to formation of the Ru\textsuperscript{II} dinitrogen complex [Ru\textsuperscript{II}(N\textsubscript{2})\textsubscript{2}] (4). IR spectroscopy reveals the presence of an absorption at $\nu_{\text{N}=\text{N}} = 2125$ cm\textsuperscript{-1}, which indicates the formation of a coordinated dinitrogen ligand that is weakly activated.\textsuperscript{[12]} The \textsuperscript{31}P NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant $J_{\text{P}-\text{P}}$ of 39 Hz. This coupling is in agreement with a C\textsubscript{5} 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 three phosphorus cycles of 39 Hz. This coupling is in agreement with a C\textsubscript{5} symmetric complex with three equivalent peripheral phosphine atoms that couple with the central P atom in the axial position.

![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-url)

The $\nu_{\text{N}=\text{N}}$ value for complex 2 was added and the 2,2747(12); Ru–P2 = 2.2752(11); Ru–P3 = 2.2774(11), and 2,2752(11) Å $J_{\text{P}-\text{P}}$ angles that are close to 120°. Additionally, the P4–Ru bond (2.2133(11) Å) $trans$ to N\textsubscript{2} is elongated relative to 2 and 3. This is likely a result of weakening of the $\pi$ backbonding between Ru and P4 attributable to competition for the same metal orbital with the $\pi$-acidic dinitrogen ligand. The general shortening of all Ru–P bonds on progressing from Ru\textsuperscript{II} via Ru\textsuperscript{III} to Ru\textsuperscript{IV} 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\textsuperscript{II}) to a distorted trigonal bipyramidal (Ru\textsuperscript{III}) and a trigonal bipyramidal (Ru\textsuperscript{IV}) 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 $\delta$P–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 $\pi$-acidic character of the amino-phosphines P1, P2, and P3 can become dominant over their $\sigma$-donating capacities in the electron-rich Ru\textsuperscript{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\textsuperscript{III} carbones upon addition of $\alpha$,$\alpha$-dihalide and trihalide compounds to Ru\textsuperscript{II} complexes, where both the chloride and the carbene ligand originate from the organohalide.\textsuperscript{[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\textsuperscript{II} complexes are known to undergo halide atom transfer reactions with organohalides (e.g. catalyzing the Kharash reaction)\textsuperscript{[14]} and thus a radical reaction between complex 3 or 4 and organohalides could not be excluded. Given our interest in the chemistry of metallo-derivatives and metalcarbene\textsuperscript{[15,16]} we decided to investigate the reaction of the low-valent Ru\textsuperscript{II} and Ru\textsuperscript{III} complexes with dichloromethane.

Dissolving 4 in dichloromethane resulted in the formation of 2 as evidenced by in situ \textsuperscript{31}P NMR spectroscopy (see the Supporting Information). As no other complexes were detected in the \textsuperscript{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\textsuperscript{II} complex 3 should be an intermediate. To test this hypothesis, we added two drops of CH\textsubscript{2}Cl\textsubscript{2} to a solution of 3 in [d\textsubscript{8}]THF. This brown solution turned into a light-brown-colored suspension within 3 days and \textsuperscript{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\textsubscript{2}Cl\textsubscript{2} or CHCl\textsubscript{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\textsubscript{2}Cl\textsubscript{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\textsuperscript{II} complex 4.

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