Metalloradical Reactivity of Ru$^1$ and Ru$^0$ Stabilized by an Indole-Based Tripodal Tetraphosphine Ligand

Fenna F. van de Watering, Jarl Ivar van der Vlugt, Wojciech I. Dzik,* Bas de Bruin,* and Joost N. H. Reek*[a]

Abstract: The tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphate PP$_3$-ligand 1 stabilizes Ru in the Ru$^0$, Ru$^1$, and Ru$^2$ oxidation states. The octahedral ([PP$_3$]Ru$^1$(Cl)$_2$) (2), distorted trigonal bipyramidal ([PP$_3$]Ru$^1$(Cl)) (3), and trigonal bipyramidal ([PP$_3$]Ru$^2$(N$_3$)) (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. Ru$^1$ and Ru$^2$ metalloradical complexes are particularly rare and only two types of Ru$^0$ complexes have been successfully isolated thus far. Peters and co-workers reported a five-coordinate 17-electron [Ru$_N$(SiP$_3$)$_3$] complex supported by an anionic tripodal tetradentate (SiP$_3$)$_2$ ligand (SiP$_3$)$_2$ = (2-iPr$_2$PC$_6$H$_4$)$_2$Si). Besides Ru$^0$, this platform also stabilizes complexes in oxidation states ranging from Ru$^0$ to Ru$^1$. Interestingly, the Ru$^0$ complex was shown to catalyze coupling of aryl azides to azoarenes. Recently, the group of Grützmacher reported the remarkable 4-coordinate 15-electron complex [Ru(tropPP$_3$)$_2$]BF$_4$ featuring two bidentate tropPP$_3$ ligands (trop = 5H-dibenz[a,d]cyclohepten-5-yl)). Besides Ru$^0$, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru$^0$ to Ru$^1$. 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(2)(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 ($\delta = 101.0$ 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. RuII complexes with tripodal tetraphosphine ligandso ften display five-coordination with either square pyramidal or trigonal bipyramidalg eometries around the metal center,\cite{8} however in case of complex 2, a noctahe-dral 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 $\delta$ P1–Ru1–P2 of 160.04(3)$^\circ$ (See the Supporting Informa-tion, Table S1) for the two mutually trans aminophosphines in the equatorial plane. The Pd onors oriented trans to the chlori-do ligandsh ave shorter Ru@Pd istances (Ru1–P3 (2.2671(9)/C138;Ru1–P4 (2.1932(9)/C138) 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 voltammo-gram 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, acetoni-trile, 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 RuI complexes $[-1.24$ V (RuII/RuI) and $-2.14$ V (RuII/RuI)$^2$ for the SiP$i$Pr$_3$ system in THF; $+0.4$ V (RuII/RuI)$^3$ and $-0.3$ V (RuII/RuI)$^4$ 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 sus-pension of 2 in THF resulted in a brown solution. The product formed proved to be NMR silent, suggestive of formation of a paramagnetic RuI 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 $S = \frac{1}{2}$ system (Figure 3). Hyperfine coupling interactions (HFIs) with two P atoms are resolved, in line with previous observa-tions for tripodal tetradentate phosphine RuI complexes.\cite{2c,e, 3}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure2.png}
\caption{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.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3.png}
\caption{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.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme2.png}
\caption{Reactivity of 2 with 1 or 2 equiv KC$_8$ to form 3 or 4, respectively.}
\end{figure}
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 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).\(^{11}\)

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_{iso} value of 2.047 and HFIs with three equivalent P atoms (A_{iso} = 143 MHz). The measured g_{iso} value is close to the average value of the anisotropic g-tensor components (g_{iso} = (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 PPh₃ donors on the EPR timescale. In line with this, the measured A_{iso} 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 (A_{iso} = (A_x + A_y + A_z)/3 = 143 MHz (3 equivalent P atoms), W_{iso} = 25 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 KC₃₈ to a THF suspension of 2 under N₂ atmos-
dinitrogen complex [Ru(N\(\text{II}\))\(\text{II}\)](2) (4). IR spectroscopy reveals the presence of an absorption at \(v_{\text{N}} = 2125 \text{ cm}^{-1}\), which indicates the formation of a coordinated dinitrogen ligand that is weakly activated.\(^{[12]}\) The \(^{31}\)P NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant \(J_{\text{PRu}}\) of 39 Hz. This coupling is in agreement with a C\(\text{v}\)-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.
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.

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