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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$I$(Cl)$_2$) (2), distorted trigonal bipyramidal ([PP$_3$]Ru$I$(Cl)$_3$) (3), and trigonal bipyramidal ([PP$_3$]Ru$^2$(N$_3$)$_2$) (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$^2$ 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$^1$N$_3$(SiP$_3$)$_3$] complex supported by an anionic tripodal tetratadentate (SiP$_3$)$_3$$^-$$^1$ ligand (SiP$_3$)$_2$(2-Pr$_2$PC$_6$H$_4$)$_2$Si). Besides Ru$^0$, this platform also stabilizes complexes in oxidation states ranging from Ru$^2$ to Ru$^II$$^{[3]}$. Interestingly, the Ru$^1$ complex was shown to catalyze coupling of aryl azides to azaarenes.$^{[4]}$ Recently, the group of Grüttmacher reported the remarkable 4-coordinate 15-electron complex [Ru$^0$(tropPPh$_3$)$_2$]BF$_4$, featuring two bidentate tropPPh$_3$ ligands (trop = 5H-dibenz[a,d]cyclohepten-5-yl$^-$). Besides Ru$^0$, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru$^0$ to Ru$^II$$^{[5]}$.

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$_5$)$_2$] 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

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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$^I$ complexes with tripodal tetraphosphine ligands often display five-coordination with either square pyramidal or trigonal bipyramid 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).\cite{11}

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^I$/Ru$^0$ reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window ($E_{\text{red}} = -2.5$ 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$^I$ complexes [$-1.24$ V (Ru$^I$/Ru$^0$) and $-2.14$ V (Ru$^I$/Ru$^0$) for the SiP$_3$iPr$_3$ system in THF; $+0.4$ V (Ru$^I$/Ru$^0$) and $-0.3$ V (Ru$^I$/Ru$^0$) for the tropPh$_2$ complex]. Therefore, we used KC$_8$ to access the desired Ru$^I$ and Ru$^0$ 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$^I$ 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 $S = 1/2$ system (Figure 3). Hyperfine coupling interactions (HFIs) with two P atoms are resolved, in line with previous observations for tripodal tetradeinate phosphine Ru$^I$ 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′ geometry. Preference for such a Jahn–Teller distorted trigonal bipyramidal geometry has also been observed for other d⁶ 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).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 gₓz value of 2.047 and HFIs with three equivalent P atoms (Aₓz = 143 MHz). The measured gₓz value is close to the average value of the anisotropic g-tensor components \( g_{xyz} = (g_x + g_y + g_z)/3 \approx 2.043 \). 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 Aₓz 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 (Aₓz = (Aₓ₁z + Aₓ₂z + Aₓ₃z + Aₓ₄z + Aₓ₅z + Aₓ₆z)/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 x₂P2–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 KC₈ to a THF suspension of 2 under N₂ atmos-
The coordination of the dinitrogen complex [Ru(122.85(4))2N2]2− to Ru4 complexes can accommodate ruthenium metal center in the oxidation state 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 RuI and closed-shell RuII 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 tetraphosphorus ligands provide a suitable platform for the preparation of functionalized ruthenium complexes.

In conclusion, although the formation of RuII and RuI 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 RuII 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 suitable platform for the preparation of functionalized ruthenium complexes.

Figure 7. X-ray crystal structure of 4 (CCDC 1555410). Thermal ellipsoids are set at 50% probability.
Keywords: chloride atom abstraction · dinitrogen complexes · metalloradicals · ruthenium · tripod al ligands

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Conflict of interest

The authors declare no conflict of interest.


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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