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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($\text{Cl}_2$)] (2), distorted trigonal bipyramidal [(PP$_3$)Ru($\text{Cl}_3$)] (3), and trigonal bipyramidal [(PP$_3$)Ru($\text{N}_3$)] (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.[$^1$] Ru$^1$ metalloradicals 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 tetratendate (SiP$_3$)$_3^-$ ligand (SiP$_3$)$_3^- = (2$-$i$-Pr$_2$PC$_6$H$_4$)$_3$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 azoarenes.[$^4$] Recently, the group of Grützmacher reported the remarkable 4-coordinate 15-electron complex [Ru(tropPPh$_3$)$_2$]BF$_4$ featuring two bidentate tropPPh$_3$ ligands (trop = 5H-dibenz[α,d]cyclohepten-5-yl)]. Besides Ru$^1$, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru$^0$ to Ru$^2$.[$^5$]

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.

Figure 1. Ligand systems capable of stabilizing isolable Ru$^1$ species.

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$_{PP} =$ 26.4, 25.5 Hz), an apparent triplet (δ = 77.8 ppm, J$_{PP} =$ 26.5 Hz), and a triplet of doublets (δ = 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 tripod 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, 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 $x$-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 chloride 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)).

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 ($E_{\text{red}} = -2.5$ 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$^\text{III}$ complexes ($-1.24$ V (Ru$^\text{II}$/Ru$^\text{III}$) and $-2.14$ V (Ru$^\text{III}$/Ru$^\text{II}$)) for the SiP$_3$iPr$_3$ system in THF; $+0.4$ V (Ru$^\text{II}$/Ru$^\text{I}$) and $-0.3$ V (Ru$^\text{I}$/Ru$^\text{0}$) for the tropPPPh$_2$ 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 tripod tetradeutate phosphine Ru$^\text{I}$ complexes.$^\text{[2c,e, 3]}$

![Figure 2](image2.png)

**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.

![Scheme 1](image1.png)

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

![Scheme 2](image3.png)

**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\text{I} coordination geometry. Preference for such a Jahn–Teller distorted trigonal bipyramidal geometry has also been observed for other d\text{III} transition metal complexes.\cite{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](image)

**Figure 4.** Singly occupied molecular orbital (SOMO; left) and spin density plot (right) of 3 (top view).

The SOMO of the metalloradical complex (spin population at Ru = 62%) is essentially the Ru\text{d}_{xz} 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 \text{d}_{x,y,z}\text{-dominated SOMO and the filled \text{d}_{xz} and \text{d}_{yz}\text{-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 \text{g}_{\text{av}} value of 2.047 and HFIs with three equivalent P atoms (\text{A}_{\text{iso}} = 143 MHz). The measured \text{g}_{\text{av}} value is close to the average value of the anisotropic g-tensor components (\text{g}_{\text{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 Ph3 donors on the EPR timescale. In line with this, the measured \text{A}_{\text{iso}} values measured in solution are close to the averaged values of the resolved anisotropic A-tensor components stemming from the Ph3 donors measured in frozen solution (\text{A}_{\text{iso}} = (\text{A}_{\text{P1,iso}} + \text{A}_{\text{P2,iso}} + \text{A}_{\text{P3,iso}} + \text{A}_{\text{P4,iso}})/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 \text{g}_{\text{av}} value of 0.70 confirms a geometry in-between a trigonal bipyramid and a square pyramid.\cite{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 \text{g}_{\text{av}} value of 2.0465 to 1.8344(5) Å (See the Supporting Information, Table S1).

As one-electron chemical reduction of complex 2 led to the selective formation of the stable Ru\text{I} 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-

![Figure 5](image)

**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 \text{g}_{\text{av}} = 2.0465, \text{A}_{\text{iso}} = 143 MHz (3 equivalent P atoms), \text{W}_{\text{iso}} = 25 MHz.

![Figure 6](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.

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pherc led to formation of the Ru$^2$ dinitrogen complex [Ru(μ(N$_2$))$_2$]$^4+$(4). IR spectroscopy reveals the presence of an absorption at $\nu_{N=\cdot N} = 2125$ 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 $J_{P-P}$ 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 geometric arrangement, with dinitrogen coordinated to the ruthenium (Figure 7). The 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.

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.

Metal orbitals becomes possible upon decreasing the $\alpha$-P–Ru–P 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 aminophosphines P1, P2, and P3 can become dominant over their $\sigma$-donating capacities in the electron-rich Ru$^2$ 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$^2$ carbene upon addition of a chloro-dihalide and trihalide compounds to Ru$^2$ complexes, where both the chloride and the carbene ligands originate from the organohalides.$^{[13]}$ 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$^2$ 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 carbides and metallocarbenes$^{[15,16]}$ we decided to investigate the reaction of the low-valent Ru$^2$ and Ru$^2$ 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 metallocarbene 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’ complex 3 should be an intermediate.

To test this hypothesis, we added two drops of CH$_2$Cl$_2$ to a solution of 2 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$^2$ complex 4.

In conclusion, although the formation of Ru’ and Ru$^2$ compounds is rare, we found that the tripod tetrathosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru$^0$, Ru$^2$, and Ru$^2$. These complexes are sufficiently stable to be isolated and analyzed by X-ray analysis. Initial reactivity studies show that both open-shell Ru$^2$ and closed-shell Ru$^2$ complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru$^2$ and Ru$^2$ complexes 2 and 3. These results show that indole-based tetrathosphorus 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 · metallo radicals · 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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