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van de Watering, F.F.; van der Vlugt, J.I.; Dzik, W.I.; de Bruin, B.; Reek, J.N.H.

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Metalloradical Reactivity of Ru\textsuperscript{1} and Ru\textsuperscript{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)phosphane PP\textsubscript{3}-ligand 1 stabilizes Ru in the Ru\textsuperscript{3+}, Ru\textsuperscript{4+}, and Ru\textsuperscript{0} oxidation states. The octahedral [(PP\textsubscript{3})Ru\textsubscript{3}(Cl)\textsubscript{2}] (2), distorted trigonal bipyramidal [(PP\textsubscript{3})Ru(Cl)\textsubscript{3}] (3), and trigonal bipyramidal [(PP\textsubscript{3})Ru(N\textsubscript{3})\textsubscript{2}] (4) complexes were isolated and characterized by single-crystal X-ray diffraction, NMR, EPR, IR, and ESI-MS. Both open-shell metalloradical Ru\textsuperscript{3+} complex 3 and the closed-shell Ru\textsuperscript{0} complex 4 undergo facile (net) abstraction of a halogen atom from dichloromethane, resulting in formation of the corresponding Ru\textsuperscript{3+} 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{3+} metalloradical complexes are particularly rare\textsuperscript{(2)} and only two types of Ru\textsuperscript{3+} complexes have been successfully isolated thus far. Peters and co-workers reported a five-coordinate 17-electron [Ru\textsubscript{2}N\textsubscript{2}(SiP\textsubscript{3})\textsubscript{3}] complex supported by an anionic tripodal tetradentate (SiP\textsubscript{3})\textsubscript{3}− ligand (SiP\textsubscript{3})\textsubscript{3}−(2-\textit{i}Pr\textsubscript{3}PC\textsubscript{6}H\textsubscript{4}S)\textsubscript{3}. Besides Ru\textsuperscript{3+}, this platform also stabilizes complexes in oxidation states ranging from Ru\textsuperscript{3+} to Ru\textsuperscript{0}.\textsuperscript{(3)} Interestingly, the Ru\textsuperscript{3+} complex was shown to catalyze coupling of aryl azides to azoarenes.\textsuperscript{(4)} Recently, the group of Grützmacher reported the remarkable 15-electron complex [Ru(tropPPH\textsubscript{3})\textsubscript{2}]BF\textsubscript{4} featuring two bidentate tropPPH\textsubscript{3} ligands (trop = 5H-dibenz[a,d]cyclohepten-5-yl)). Besides Ru\textsuperscript{3+}, this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\textsuperscript{3+} to Ru\textsuperscript{0}.\textsuperscript{(5)}

Inspired by these intriguing examples, we wondered whether stable metalloradical Ru\textsuperscript{1} complexes could be accessed in a rigid tripodal PP\textsubscript{3} ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\textsuperscript{3+} complexes feature either a strongly σ-donating anionic tripodal (SiP\textsubscript{3})− ligand or two neutral π-accepting bidentate (tropPPH\textsubscript{3}) ligands. Hence, we surmised that the use of a tripodal tetradentate ligand featuring both σ-donor and π-accepting phosphorus groups could allow for isolation and reactivity studies of well-defined Ru\textsuperscript{1} metalloradicals. We turned our attention to the tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphane ligand (1)\textsuperscript{(6,7)} (Figure 1), which we previously used to stabilize the metalloradical rhodium complex [Rh\textsuperscript{1}Cl(CPF\textsubscript{6})\textsubscript{3}].\textsuperscript{(8)} 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{3+} 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)\textsubscript{2}] (2) was readily prepared by reacting stoichiometric amounts of 1 and [Ru(Cl)\textsubscript{2}C\textsubscript{6}H\textsubscript{5}] in refluxing THF in good yield (Scheme 1).

The \textsuperscript{31}P NMR spectrum of complex 2 displays a triplet of doublets (\(\delta = 101.0 \text{ ppm}, J_{\text{PP}} = 26.4, 25.5 \text{ Hz}\)), an apparent triplet (\(\delta = 77.8 \text{ ppm}, J_{\text{PP}} = 26.5 \text{ Hz}\)), and a triplet of doublets (\(\delta = 48.5 \text{ ppm}, J_{\text{PP}} = 27.9, 26.9 \text{ Hz}\)) 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$^\II$ 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 nidoctahedral 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).$^{[9]}$

To explore the capability of 1 to stabilize low oxidation states of ruthenium, we attempted to determine the Ru$^{II}$/Ru$^I$ and 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 [$\sim -1.24$ V (Ru$^{II}$/Ru$^I$) and $-2.14$ V (Ru$^I$/Ru$^0$)] for the SiP$_3$ system in THF; $+0.4$ V (Ru$^{II}$/Ru$^I$) and $-0.3$ V (Ru$^I$/Ru$^0$) for the tropPP$_2$ 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-ladoradical 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$^I$ complexes.$[2c,e, 3]$

![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_url)

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

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

![Figure 3. 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.](image_url)
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 d^4 transition metal complexes.\textsuperscript{11}\textsuperscript{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).\textsuperscript{11}\textsuperscript{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_{ax} value of 2.047 and HFIs with three equivalent P atoms (\(A_{\text{iso}}^{\text{av}} = 143\) MHz). The measured g_{ax} value is close to the average value of the anisotropic g-tensor components (\(g_{ax} = (g_x + g_y + g_z)/3 = 2.043\)). Detection of HFIs with three equivalent P atoms in solution points to rapid positional exchange of the axial and equatorial PPh\textsubscript{3} donors on the EPR timescale. In line with this, the measured \(A_{\text{iso}}^{\text{av}}\) values measured in solution are close to the averaged values of the resolved anisotropic A-tensor components stemming from the PPh\textsubscript{3} donors measured in frozen solution (\(A_{\text{iso}}^{\text{av}} = 2.0465, A_{\text{iso}}^{\text{av}} = 143\) MHz (3 equivalent P atoms), \(W_{\text{iso}} = 25\) 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 \(\tau\)-value of 0.70 confirms a geometry in-between a trigonal bipyramid and a square pyramid.\textsuperscript{11}\textsuperscript{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 \(\chi\)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\textsubscript{3} to a THF suspension of 2 under N\textsubscript{2} atmos-

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

**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 \(g_{ax} = 2.0465, A_{\text{iso}}^{\text{av}} = 143\) MHz (3 equivalent P atoms), \(W_{\text{iso}} = 25\) MHz.

**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.
phere 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 \(\nu_{\text{as}} = 2125 \text{ cm}^{-1}\), 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 \(J_{P-P}\) of 39 Hz. This coupling is in agreement with a \(C_3\)-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 (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.

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.

try (\(r = 0.93\)) with equal Ru–P\textsubscript{equatorial} bond lengths (Ru–P\textsubscript{1} = Ru\textsubscript{1} P\textsubscript{1} 2.2747(12); Ru–P\textsubscript{2} = 2.2752(11); Ru–P\textsubscript{3} = 2.2774(11)), and \(\xi\), P–Ru–P angles that are close to 120°. Additionally, the P4–Ru bond (2.2133(11) Å)\textsuperscript{trans} to \(\text{N}\textsubscript{2}\) 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{0} to Ru\textsuperscript{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\textsuperscript{II}) to a distorted trigonal bipyramidal (Ru\textsuperscript{0}) and a trigonal bipyramidal (Ru\textsuperscript{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 \(\text{trans}\) arrangement in complex 2. Binding to separate metal orbitals becomes possible upon decreasing the \(\xi\), P1–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 Grubb reported the formation of dichlorido Ru\textsuperscript{II} carbenes upon addition of \(\alpha\)-, \(\alpha\text{-}\text{dihalide and trihalide compounds to Ru}\textsuperscript{II}\) complexes, where both the chloride and the carbene ligands originate from the organohalides.\textsuperscript{[13]–[15]} 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 dichloridoro ruthenium carbene. However, Ru\textsuperscript{II} complexes are known to undergo halide atom transfer reactions with organohalides (e.g. catalyzing the Kharash reaction)\textsuperscript{[16]–[18]} and thus a radical reaction between complex 3 or 4 and organohalides could not be excluded. Given our interest in the chemistry of metalcarbene and metalcarbenes\textsuperscript{[19]–[20]} we decided to investigate the reaction of the low-valent Ru\textsuperscript{II} and Ru\textsuperscript{II} 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 [\(\text{d}_8\)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{II} compounds is rare, we found that the tripodal tetraphosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru\textsuperscript{II}, Ru\textsuperscript{II}, and Ru\textsuperscript{II}. 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{II} 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{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.

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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