Metalloradical Reactivity of Ru\textsuperscript{I} 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\textsuperscript{[a]}

Abstract: The tripodal, tetradentate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphane \(\text{PP}\), ligand 1 stabilizes Ru in the Ru\textsuperscript{II}, Ru\textsuperscript{III}, and Ru\textsuperscript{0} oxidation states. The octahedral \([(\text{PP})\text{Ru}(\text{Cl})]\) \(2\), distorted trigonal bipyramidal \([(\text{PP})\text{Ru}(\text{Cl})]\) \(3\), and trigonal bipyramidal \([(\text{PP})\text{Ru}(\text{N})]\) \(4\) 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 C\(_2\) atom from dichloromethane, resulting in formation of the corresponding Ru\textsuperscript{II} and Ru\textsuperscript{0} complexes 2 and 3, respectively.

First, we aimed at the synthesis of the Ru\textsuperscript{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 \([\text{Ru}(1)(\text{Cl})]\) \(2\) was readily prepared by reacting stoichiometric amounts of 1 and \([\text{Ru}(\text{Cl})_2(\text{C}_2\text{H}_4)]\) \(2\) in refluxing THF in good yield (Scheme 1).

The \(^{31}\text{P}\) 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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[a] Dr. F. F. van de Watering, Dr. Ir. J. I. van der Vlugt, Dr. W. I. Dzik, Prof. Dr. B. de Bruin, Prof. Dr. J. N. H. Reek
Homogeneous, Supramolecular and Bio-Inspired Catalysis
Van’t Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904
1098 XH Amsterdam (The Netherlands)
E-mail: wdzik@wpi.nl
B.debruijn@uu.nl

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are equivalent (δ = 77.8 ppm), whereas the third side-arm donor P3 (δ = 101.0 ppm) experiences a different coordination environment. The pivotal, axial phosphine P4 is assigned to the signal at δ = 48.5 ppm. RuII 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, 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 Σ3P1–Ru1–P2 of 160.04(3)° (See the Supporting Information, Table S1) for the two mutually trans aminophosphines in the equatorial plane. The 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).[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 voltammogram of 2 in dichloromethane did not show any reduction wave within the solvent window (E1/2 = –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 [Ru1(1)Cl] (3) requires a stronger reducing agent than the previously reported RuII complexes [–1.24 V (RuII/RuI) and –2.14 V (RuII/RuI) for the SiP(iPr)3 system in THF; +0.4 V (RuII/RuI) and –0.3 V (RuII/RuI) for the tropPPh2 complex]. Therefore, we used KC8 to access the desired RuI and Ru0 species chemically (Scheme 2).

The addition of one molar equivalent of KC8 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 RuI species formed by one-electron reduction. X-band EPR spectroscopy confirmed the presence of the metal-loradicals species [Ru1(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 RuII complexes.[2c,e, 3]

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

Scheme 2. Reactivity of 2 with 1 or 2 equiv KC8 to form 3 or 4, respectively.

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.

Figure 3. Experimental (black) and simulated (red) X-band EPR spectrum of 3 measured in frozen THF ([Bu4N][PF6] 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.

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 d₅ 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 dₓz-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 gₓₓ value of 2.047 and HFIs with three equivalent P atoms (Aₓₓ = 143 MHz). The measured gₓₓ value is close to the average value of the anisotropic g-tensor components (gₓₓ = (gₓₓ + gᵧᵧ + gzz)/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 Aₓₓ 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 (Aₓₓ = Aₓₓ + Aᵧᵧ + Azz)/3 = 143 MHz (3 equivalent P atoms), Wₓₓ = 25 MHz.

Layering of a THF solution of 3 with pentane resulted in the selective formation of the stable Ru' complex 3, which was isolated as 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 the Ru–P bonds (Ru–P₁ = 2.2940(12); Ru–P₂ = 2.2930(12) Å) and decrease of the 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 KC₈ to a THF suspension of 2 under N₂ atmos-

![Figure 4. Singly occupied molecular orbital (SOMO; left) and spin density plot (right) of 3 (top view).](image1)

![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 gₓₓ = 2.0465, Aₓₓ = 143 MHz (3 equivalent P atoms), Wₓₓ = 25 MHz.](image2)

![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.](image3)
Dinitrogen complex \( \text{Ru}^2 \) dinitrogen complex \([\text{Ru}(\text{dinitrogen})(\text{N}_2)_2]\) (4). IR spectroscopy reveals the presence of an absorption at \( \nu_{\text{NH}} = 2125 \text{ cm}^{-1} \), which indicates the formation of a coordinated dinitrogen ligand that is weakly activated.\(^{[12]}\) The \( ^{31}\text{P} \) NMR spectrum shows a doublet and a quartet in a 3:1 ratio, both with a coupling constant \( J_{\text{PP}} \) of 39 Hz. This coupling is indicative of a \( C_4 \)-symmetric complex with three equivalent peripheral phosphine atoms that couple with the central \( \text{P} \) 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 involving 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\(^2\) via Ru\(^{1+}\) to Ru\(^{3+}\) 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\(^{3+}\)) to a distorted trigonal bipyramidal (Ru\(^{1+}\)) and a trigonal bipyramidal (Ru\(^{3+}\)) 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 \( \pi \) arrangement in complex 2. Binding to separate metal orbitals becomes possible upon decreasing the \( \chi \),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 amminophosphines 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\(^2\) carbenes upon addition of \( \alpha,\alpha\)-dihalide and trihalide compounds to Ru\(^2\) complexes, where both the chloride and the carbene ligands originate from the organohalide.\(^{[13]}\) 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 dichloridomethane 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-carbene complexes,\(^{[16-19]}\) we decided to investigate the reaction of the low-valent Ru\(^2\) and Ru\(^3\) complexes with dichloromethane.

Dissolving 4 in dichloromethane resulted in the formation of 2 as evidenced by in situ \( ^{31}\text{P} \) NMR spectroscopy (see the Supporting Information). As no other complexes were detected in the \( ^{31}\text{P} \) 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\(^2\) complex 3 should be an intermediate.

To test this hypothesis, we added two drops of CH\(_2\)Cl\(_2\) to a solution of 3 in \( [d_8] \)THF. This brown solution turned into a light-brown-colored suspension within 3 days and \( ^{31}\text{P} \) 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\(^3\) complex 4.

In conclusion, although the formation of Ru\(^2\) and Ru\(^3\) compounds is rare, we found that the tripodal tetraphosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru\(^3\), Ru\(^2\), and Ru\(^1\). 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\(^3\) complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru\(^2\) and Ru\(^3\) complexes 2 and 3. These results show that indole-based tetraphosphorus ligands provide

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**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.
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.

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