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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\(^6\), Ru\(^4\), and Ru\(^2\) oxidation states. The octahedral [(PP\(_3\))Ru\(^0\)(Cl)]\(_2\) (2), distorted trigonal bipyramidal [(PP\(_3\))Ru\(^0\)(Cl)]\(_3\) (3), and trigonal bipyramidal [(PP\(_3\))Ru\(^0\)(N\(_3\))]\(_4\) (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\(^1\) and Ru\(^0\) 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.[1] Ru\(^1\) metalloradical complexes are particularly rare[4] 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\(_N\)(SiP\(_4\))\(_3\)] complex supported by an anionic tripodal tetradeinate (SiP\(_4\))\(^{-}\) ligand (SiP\(_4\))\(^{-}\) = (2,6-Pr\(_2\)PC\(_6\)H\(_4\))\(_3\)S. Besides Ru\(^1\), this platform also stabilizes complexes in oxidation states ranging from Ru\(^3\) to Ru\(^II\).[5] Interestingly, the Ru\(^1\) complex was shown to catalyze coupling of aryl azides to azoarenes.[6] Recently, the group of Grützmacher reported the remarkable 4-coordinate 15-electron complex [Ru\(_3\)(tropPPPh\(_2\))\(_3\)]BF\(_4\), featuring two bidentate tropPPPh\(_2\) ligands (trop = 5H-dibenz(o,d)cyclohepten-5-yl)]. Besides Ru\(^1\), this ligand scaffold stabilizes ruthenium complexes in oxidation states ranging from Ru\(^3\) to Ru\(^1\).[3] No further reactivity with this complex has been reported to date.

Inspired by these intriguing examples, we wondered whether stable metalloradical Ru\(^1\) complexes could be accessed in a rigid tripodal PP\(_3\) ligand environment for subsequent reactivity evaluation. The above-mentioned Ru\(^1\) complexes feature either a strongly \(\sigma\)-donating anionic tripodal (SiP\(_4\))\(^{-}\) ligand or two neutral \(\pi\)-accepting bidentate (tropPPPh\(_2\)) ligands. Hence, we surmised that the use of a tripodal tetradeinate ligand featuring both \(\sigma\)-donor and \(\pi\)-accepting phosphorus groups could allow for isolation and reactivity studies of well-defined Ru\(^1\) metalloradicals. We turned our attention to the tripodal, tetradeinate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl)phosphane ligand (1)[6-7] (Figure 1), which we previously used to stabilize the metalloradical rhodium complex [Rh\(^I\)(1Cl)]PF\(_6\).[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\(^3\) 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)]\(_2\) (2) was readily prepared by reacting stoichiometric amounts of 1 and [Ru(Cl)(C\(_6\)H\(_4\))]\(_2\) 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, \(J_{PH} = 26.4, 25.5\) Hz), an apparent triplet (\(\Delta = 77.8\) ppm, \(J_{PH} = 26.5\) Hz), and a triplet of doublets (\(\Delta = 48.5\) ppm, \(J_{PH} = 27.9, 26.9\) 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 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 $\angle P1$–Ru1–P2 of 160.04(3)$^{[8]}$ (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 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 ($E_{\text{red}} = -2.5$ 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 complexes [$1$.24 V (RuII/RuI) and $-2.14$ V (RuI/Ru0) for the SiP$i$Pr3 system in THF; $+0.4$ V (RuII/RuI) and $-0.3$ V (RuI/Ru0) 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-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 tetradentate phosphine RuI complexes.$^{[2c,e, 3]}

Scheme 1. Synthesis of [Ru(1)Cl2] (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 dσ values measured in frozen solution (Aiso=143 MHz; 3 equivalent P atoms), Wiso=25 MHz.

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

anisotropic A-tensor components stemming from the PPh₃ donors measured in frozen solution (Aiso=(|A|x|+|A|y|+|A|z|)/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 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 KC₃ to a THF suspension of 2 under N₂ atmos-
sphere led to formation of the Ru\(^{II}\) dinitrogen complex [Ru\(^{II}\)(N\(_2\))\(_2\)] (4). IR spectroscopy reveals the presence of an absorption at \(\nu_{\text{N-N}} = 2125 \text{ cm}^{-1}\), 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 \(J_{\text{P-P}}\) 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 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.

dinitrogen complex and \(\text{N}_2\) was observed after 20 h. This was expected to result in weaker binding of \(\text{N}_2\) to Ru–P2 angle, which is observed in going from 2 to 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\(^{II}\) 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\(^{II}\) carbene complexes with upon addition of \(\alpha,\alpha\)-dihalide and trihalide compounds to Ru\(^{II}\) 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 dichlorid ruthenium carbene. However, Ru\(^{II}\) 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 metalcarbenes and metalloacarbenes,\(^{[16,10]}\) we decided to investigate the reaction of the low-valent Ru\(^{II}\) and Ru\(^{II}\) 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 metalcarbene intermediate seemed unlikely. We hypothesized that the formation of 2 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\(^{II}\) 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 \(^{31}\)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\(^{II}\) complex 4.

In conclusion, although the formation of Ru\(^{II}\) and Ru\(^{II}\) compounds is rare, we found that the tripodal tetraphosphine scaffold 1 can accommodate ruthenium metal center in the oxidation states Ru\(^{II}\), Ru\(^{III}\), and Ru\(^{IV}\). These complexes are sufficiently stable to be isolated and analyzed by X-ray analysis. Initial reactivity studies show that both open-shell Ru\(^{II}\) and closed-shell Ru\(^{II}\) complexes can undergo facile (net) abstraction of a Cl-atom from dichloromethane, resulting in the formation of the corresponding Ru\(^{II}\) and Ru\(^{II}\) 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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