Metalloradical Reactivity of RuI and Ru0 Stabilized by an Indole-Based Tripodal Tetraphosphine Ligand

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

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Fenna F. van de Watering, Jarl Ivar van der Vlugt, Wojciech I. Dzik,* Bas de Bruin,* and Joost N. H. Reek*[a]

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Supporting Information for:

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*Fenna F. van de Watering, Jarl Ivar van der Vlugt, Wojciech I. Dzik, Bas de Bruin, and Joost N.H. Reek*
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1. General methods

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in the glovebox. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et₂O were distilled from sodium benzophenone ketyl, CH₂Cl₂ was distilled from CaH₂ under nitrogen. NMR spectra (¹H, ³¹P, and ¹³C{¹H, ³¹P}) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer. IR spectra (ATR mode) were recorded with a Bruker Alpha-p FT-IR spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP mass spectrometer using cold electron-spray ionization (CSI) at -40 °C. Ligand 1 was prepared in two steps from 3-methylindole.[¹] KC₈ was prepared by the method of Rabinovitz[²] which yielded a finely dispersed brown powder.

2. Synthesis of new compounds

Ru(1)Cl₂ (2): 1 (348.5 mg, 0.36 mmol) and [RuCl₂(C₆H₆)]₂ (89.6 mg, 0.18 mmol) were suspended in THF (6 mL) and stirred at 60 °C overnight. After cooling the yellow precipitated complex was filtered off, washed with THF (3 x 2 mL) and pentane (3 x 3 mL) and dried overnight in the vacuum oven at 40 °C. Recrystallization of the complex by layering a DCM solution with pentane at 5 °C gave crystals suitable for X-ray diffraction analysis. Yield: 0.3968 g of a yellow solid (97%).

³¹P-NMR (162 MHz, CDCl₃): δ 104.80 (dt, J = 28.0, 27.1 Hz, 1P), 81.63 (t, J = 26.3 Hz, 2P), 52.36 (dt, J = 28.0, 27.1 Hz, 1P) ppm.

¹³C{¹H, ³¹P}-NMR (75 MHz, CDCl₃): δ 139.99, 139.89, 139.44, 139.34, 136.46, 136.38, 135.49, 135.42, 134.80, 134.45, 134.01, 132.99, 132.85, 132.71, 132.61, 131.91, 131.82, 131.43, 131.37, 131.28, 129.65, 129.44, 129.27, 128.16, 128.13, 127.69, 127.61, 126.32, 126.27, 123.98, 123.84, 121.74, 121.59, 120.45, 120.38, 117.27, 117.23, 12.13 (CH₃), 11.92 (CH₃) ppm.


Ru(1)Cl (3): In a nitrogen filled glovebox, complex 2 (103.8 mg, 0.09 mmol), KC₈ (Strem, 15.9 mg, 0.12 mmol) and 10 mL THF were placed in a 50 mL Schlenk flask and the mixture was stirred for two days forming a brown solution with residual yellow solid. The solution was filtered off, evaporated to dryness and extracted with 3 x 1 mL of THF. Pentane was added to this THF solution, until all 3 had precipitated. The brown solid was collected and dried. Yield: 14.4 mg (14 %). Alternatively, the THF solution of 3 was layered with pentane, resulting in the formation of crystals suitable for X-ray diffraction. The EPR spectrum was measured in THF, for the frozen measurement [Bu₄N](PF₆) was added. Mass analysis (CSI) [3-Cl⁺]: found: 1075.2038, calc: 1075.2095.

Ru(1)N₂ (4): In a nitrogen filled glovebox, complex 2 (94.0 mg, 0.082 mmol), KC₈ (homemade, 25.6 mg, 0.19 mmol) and 1.7 mL of THF were placed in a 50 mL Schlenk flask and the mixture was stirred for 2 hours. The red solution with black solids was filtered and set for crystallization by diffusion of pentane vapor into a THF solution of 4 yielding single crystals suitable for X-ray diffraction analysis. Yield: 33.7 mg (37 %).
$^1$H-NMR (300 MHz, THF-$d_8$): $\delta$ 7.48 (d, $J = 8.0$ Hz, 3H), 7.03 (t, $J = 7.0$ Hz, 3H), 6.88 (d, $J = 8.3$ Hz, 30H), 6.67 (t, $J = 7.8$ Hz, 3H), 6.40 (d, $J = 8.4$ Hz, 3H), 2.54 (s, 9H) ppm.

$^{31}$P-NMR (122 MHz, THF-$d_8$): $\delta$ 97.93 (d, $J = 39.0$ Hz, 3P), 52.22 (q, $J = 39.2$ Hz, 1P) ppm.

$^{13}$C[$^1$H, $^{31}$P]-NMR (75 MHz, THF): $\delta$ 129.33 (s, CH$_2$-ph), 127.82 (m, CH$_2$-ph), 127.07 (m, CH$_2$-ph), 122.83 (s, CH$_2$-ind), 119.95 (s, CH-ind), 119.67 (s, CH-ind), 115.21 (s, CH-ind), 9.49 (s, CH$_3$) ppm. (quaternary carbon peaks were not resolved)

FTIR: $\nu_{N_2} = 2025$ cm$^{-1}$.


Alternative method for the synthesis of complex 4: In a nitrogen filled glovebox, complex 2 (165.3 mg, 0.145 mmol) and 10% Na/Hg (67.9 mg, 0.30 mmol) and 10 mL THF were placed in a 50 mL flask equipped with a glass stirring bar and the resulting suspension was stirred for 2 days. The red solution with mercury particles was evaporated to dryness, extracted with benzene (2, 1 and 1 mL) and dried in vacuo. Yield: 168.8 mg (83%).

3. Reactivity studies

**Reaction of Ru(1)N$_2$ (4) with dichloromethane to form complex 2**

In a nitrogen filled glovebox, complex 2 (166.3 mg, 0.145 mmol), Na/Hg (33.2 mg, 0.14 mmol) and 10 mL of THF were placed in a 50 mL flask equipped with a glass stirring bar and the mixture was stirred for 4 days. A red-brown solution with residual unreacted yellow solid of 2 formed. The mixture was filtered and 0.35 mL of the resulting solution was transferred to an NMR tube equipped with a J. Young valve. The $^{31}$P-NMR analysis of the filtrate showed the sole presence of 4. In the glovebox, 1 drop of CH$_2$Cl$_2$ was added to this NMR tube and left for 1 day. $^{31}$P-NMR analysis of this lighter brown solution the next day showed full conversion to 2.

**Reaction of Ru(1)N$_2$ (4) with dichloromethane to form complex 3**

In a nitrogen filled glovebox, complex 2 (53.3 mg, 0.047 mmol), Na/Hg (50.5 mg, 0.23 mmol) and 3 mL of THF were placed in a 50 mL flask equipped with a glass stirring bar and the mixture was stirred for 4 days. A red-brown solution with unreacted yellow solid of 2 formed. The mixture was filtered and 0.30 mL of the resulting solution was transferred to an EPR tube equipped with a J. Young valve and the EPR spectrum was measured showing small amounts of residual complex 3. To this mixture, 9.5 µL of 3:97 v/v DCM:THF mixture was added (0.285 µL DCM, 1 equivalent) in the glovebox. After 20 hours EPR spectrum was measured showing 6 fold increase of the integral value.

**Reaction of 3 with dichloromethane**

In an NMR tube equipped with a J. Young valve, complex 3 (4.5 mg, 4.0 µmol) was dissolved in 0.3 mL of THF-$d_8$. After conformation of the absence of 2 in this brown solution by $^{31}$P-NMR spectroscopy, 2 drops of dichloromethane were added. This addition caused a gradual color change (2 days) to light brown and in situ $^{31}$P-NMR analysis showed formation of 2.
4. Single crystal data

**Table S1**: Selected bond distances (Å) and angles (°) of the crystal structures of ruthenium complexes with ligand 1 in the oxidation states +II, +I and 0.

<table>
<thead>
<tr>
<th></th>
<th>[Ru(1)(Cl)2] (2)</th>
<th>[Ru(1)(Cl)] (3)</th>
<th>[Ru(1)(N2)] (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru1–P1</td>
<td>2.3727(9)</td>
<td>2.2930(12)</td>
<td>2.2747(12)</td>
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<tr>
<td>Ru1–P2</td>
<td>2.3189(9)</td>
<td>2.2940(12)</td>
<td>2.2752(11)</td>
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<tr>
<td>Ru1–P3</td>
<td>2.2671(9)</td>
<td>2.2717(13)</td>
<td>2.277(1)</td>
</tr>
<tr>
<td>Ru1–P4</td>
<td>2.1932(9)</td>
<td>2.1956(12)</td>
<td>2.2133(11)</td>
</tr>
<tr>
<td>Ru1–Cl1</td>
<td>2.4869(9)</td>
<td>2.4296(14)</td>
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<tr>
<td>Ru1–Cl2</td>
<td></td>
<td>2.4471(9)</td>
<td></td>
</tr>
<tr>
<td>Ru1–N1</td>
<td>2.011(4)</td>
<td></td>
<td>2.011(4)</td>
</tr>
<tr>
<td>N1–N2</td>
<td>1.085(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1–Ru1–P2</td>
<td>160.04(3)</td>
<td>134.84(5)</td>
<td>122.85(4)</td>
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<tr>
<td>P1–Ru1–P3</td>
<td>94.27(3)</td>
<td>109.91(4)</td>
<td>118.33(4)</td>
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<tr>
<td>P2–Ru1–P3</td>
<td>102.23(3)</td>
<td>112.22(5)</td>
<td>115.80(4)</td>
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<tr>
<td>P1–Ru1–P4</td>
<td>82.67(3)</td>
<td>83.90(4)</td>
<td>83.91(4)</td>
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<td>P2–Ru1–P4</td>
<td>87.06(3)</td>
<td>84.57(4)</td>
<td>84.14(4)</td>
</tr>
</tbody>
</table>

**Table S2**: Crystallographic data for [Ru(1)(Cl)2], [Ru(1)(Cl)] and [Ru(1)(N2)].

<table>
<thead>
<tr>
<th></th>
<th>[Ru(1)(Cl)2] (2)</th>
<th>[Ru(1)(Cl)] (3)</th>
<th>[Ru(1)(N2)] (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C63H51Cl2N3P4Ru, 3(CH2Cl2) + solvent</td>
<td>C63H51ClN3P4Ru, CuH8O</td>
<td>C63H51N3P4Ru, CuH8O</td>
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<td>fw</td>
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<td>1182.58</td>
<td>1175.15</td>
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<tr>
<td>temperature [K]</td>
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<td>150</td>
<td>150</td>
</tr>
<tr>
<td>radiation</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>wavelength [Å]</td>
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<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>cryst syst</td>
<td>Triclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a [Å]</td>
<td>12.8184(5)</td>
<td>11.6983(6)</td>
<td>11.8899(7)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>16.5363(6)</td>
<td>15.1903(8)</td>
<td>14.9630(9)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>17.1910(7)</td>
<td>16.9434(9)</td>
<td>17.0562(10)</td>
</tr>
<tr>
<td>α [deg]</td>
<td>83.529(2)</td>
<td>84.059(3)</td>
<td>84.089(4)</td>
</tr>
<tr>
<td>β [deg]</td>
<td>79.551(2)</td>
<td>85.957(3)</td>
<td>86.582(4)</td>
</tr>
<tr>
<td>γ [deg]</td>
<td>67.905(2)</td>
<td>71.186(3)</td>
<td>70.619(4)</td>
</tr>
<tr>
<td>volume [Å3]</td>
<td>3316.4(2)</td>
<td>2832.5(3)</td>
<td>2846.2(3)</td>
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<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>color</td>
<td>yellow</td>
<td>black</td>
<td>dark red</td>
</tr>
<tr>
<td>θ-max</td>
<td>25.652</td>
<td>25.217</td>
<td>25.242</td>
</tr>
<tr>
<td>density [Mg m−3]</td>
<td>1.403a</td>
<td>1.387</td>
<td>1.371</td>
</tr>
<tr>
<td>absorb coeff [mm−1]</td>
<td>0.697a</td>
<td>0.484</td>
<td>0.437</td>
</tr>
<tr>
<td>F(000)</td>
<td>1428.0a</td>
<td>1222.0</td>
<td>1216.0</td>
</tr>
<tr>
<td>R1/wR2/S</td>
<td>0.0488/0.1584/1.108</td>
<td>0.0551/0.1283/1.017</td>
<td>0.0474/0.1414/0.892</td>
</tr>
</tbody>
</table>

*Excluding the disordered solvent contribution.*
Crystallographic data was obtained using a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator. The intensities were integrated with the SAINT software package. Multiscan absorption correction and scaling was performed with SADABS. The structure was solved with Intrinsic Phasing Methods using SHELXT. Least-squares refinement was performed with SHELXL 2013 against $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. The structure of RuCl$_2$L$_1^H$ has solvent accessible voids filled with disordered solvent. Their contribution to the structure factors in the refinement was taken into account with the PLATON/SQUEEZE approach.

CCDC 1555408, 1555409 and 1555410 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.
5. EPR Spectroscopy

Table S3. Experimental and DFT calculated EPR parameters of complex 3.

<table>
<thead>
<tr>
<th></th>
<th>Exp. (a)</th>
<th>DFT (b) Orca x-ray geometry</th>
<th>DFT (c) ADF x-ray geometry</th>
<th>DFT (b) Orca DFT x-ray optimized geometry (d)</th>
<th>DFT (b) ADF DFT-D3 Optimized Geometry (e)</th>
<th>DFT (c) ADF DFT-D3 Optimized Geometry (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g_x</td>
<td>2.002</td>
<td>2.009</td>
<td>1.995</td>
<td>2.010</td>
<td>2.007</td>
<td>1.996</td>
</tr>
<tr>
<td>g_y</td>
<td>2.056</td>
<td>2.060</td>
<td>2.057</td>
<td>2.060</td>
<td>2.050</td>
<td>2.054</td>
</tr>
<tr>
<td>g_z</td>
<td>2.072</td>
<td>2.093</td>
<td>2.083</td>
<td>2.090</td>
<td>2.074</td>
<td>2.077</td>
</tr>
</tbody>
</table>

| W_x | 12      | -                           | -                         | -                                             | -                                        | -                                        |
| W_y | 14      | -                           | -                         | -                                             | -                                        | -                                        |
| W_z | 13      | -                           | -                         | -                                             | -                                        | -                                        |

A_P1^x | 450 | 350 | 416 | 368 | 359 | 430 | 420 |
A_P1^y | 370 | 356 | 347 | 373 | 446 | 367 | 352 |
A_P1^z | 370 | 442 | 340 | 454 | 354 | 360 | 346 |

A_P2^x | 30 (NR) | 57 | 50 | 32 | 23 | 24 | 16 |
A_P2^y | 85 | 99 | 88 | 71 | 61 | 60 | 51 |
A_P2^z | 105 | 64 | 55 | 39 | 30 | 30 | 21 |

A_P3^x | NR | -16 | -24 | 1 (7) | 1 (7) | -6 | 1 |
A_P3^y | NR | 18 | 6 | 35 (41) | 35 (41) | 24 | 7 |
A_P3^z | NR | -7 | -24 | 8 (14) | 8 (14) | -1 | 3 |

A_P4^x | NR | -23 | -25 | -24 | -25 | -29 | -29 |
A_P4^y | NR | -25 | -26 | -26 | -22 | -27 | -26 |

(a) Parameters from spectral simulations (least square ‘best fit’).
(b) DFT calculated EPR parameters (Orca, b3-lyp, def2-TZVP).
(c) DFT calculated EPR parameters (ADF, B3LYP, TZ2P).
(d) Optimized with Turbomole (BP86, def2-TZVP).
(e) Optimized with Turbomole (DFT-D3 (disp3), BP86, def2-TZVP).
Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). The spectra were simulated by iteration of the anisotropic g-values, (super)hyperfine coupling constants and line widths using the W95EPR program (available upon request from Prof. Frank Neese, University of Bonn).

6. DFT and EPR property calculations

The geometry of the full atom model of complex 3 was fully optimized with the Turbomole program\textsuperscript{[8a]} coupled to the PQS Baker optimizer\textsuperscript{[9]} at the BP86 level\textsuperscript{[10]} using the def2-TZVP basis,\textsuperscript{[8c,f]} with and without Grimme’s version 3 dispersion corrections (DFT-D3, disp3, zero damping\textsuperscript{[11]}). EPR parameters\textsuperscript{[12]} were subsequently calculated with both the ADF\textsuperscript{[13]} and Orca\textsuperscript{[14]} program systems, using the coordinates from the structure optimized in Turbomole as input. In the ADF calculations we used the (Gaussian-defined) B3LYP functional with the ZORA/TZ2P basis set supplied with the program (all electron, core double zeta, valence triple zeta polarized basis set on all atoms), and the unrestricted SPINORBIT COLLINEAR approach (for the g-values we used the restricted SPINORBIT approach). In the Orca calculations we used the Ahlrich’s def2-TZVP basis set and the (Turbomole-defined) b3-lyp functional.\textsuperscript{[15]}
7. NMR spectra of complexes 2, 3 and 4

NMR spectra of Ru(1)Cl₂ (2):
FF269/13
FF269-13(CDCl3)(DRX300ppm)+H COSY
NMR spectra of Ru(1)N₂(4):
pentane
anti-solvent

THF
crystallization
solvent

D (0)
6.93
R (0)
7.08
A (0)
7.52
F (0)
6.71
G (s)
6.43

-1800
-1700
-1600
-1500
-1400
-1300
-1200
-1100
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800

15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5

S13
8. References


[5] Sheldrick, G. M. *SHELXT - Universit"{a}t G"{o}ttingen, Germany*; 2012.


[9] (a) PQS version 2.4, 2001, Parallel Quantum Solutions, Fayetteville, Arkansas, USA (the Baker optimizer is available separately from PQS upon request); (b) J. Baker *J. Comput. Chem.* 1986, **7**, 385.


[14] Neese, F. ORCA – An ab initio, Density Functional and Semiempirical program package, version 3.0.3, University of Bonn, **2009**.