1,2-Migration in the Reactions of Ruthenium Vinyl Carbene with Propargyl Alcohols

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1. Crystallographic details

Crystallographic Analysis: All single crystals were mounted on glass fibers and transferred into a cold stream of nitrogen. Diffraction data for 2 were obtained on a Rigaku R-AXIS SPIDER IP CCD area detector at 173(2) K, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction data for 3, 5, 6 were collected on an Oxford Gemini-S Ultra charge coupled device (CCD) diffractometer at 173(2) K, with monochromated Mo Kα radiation (λ = 0.71073 Å). Semi-empirical or multi-scan absorption corrections (SADABS) were applied.[1] Structures were solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F² using the SHELXTL program package.[2] Non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. For all the complexes, crystals suitable for X-ray diffraction were grown from CH₂Cl₂ solution layered with hexane.


Table 1 Crystal data and structure refinement for 2, 3, 5 and 6.

<table>
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<tr>
<th>complex</th>
<th>2·3CH₂Cl₂</th>
<th>3·4CH₂Cl₂</th>
<th>5·1.5CH₂Cl₂</th>
<th>6·CH₂Cl₂</th>
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<tr>
<td>formula</td>
<td>C₅₉H₄₆BCl₂F₄N₂P₂Ru</td>
<td>C₅₈H₄₆BCl₂F₄N₂P₂Ru</td>
<td>C₅₈H₄₆BCl₂F₄NO₂P₂Ru</td>
<td>C₅₈H₄₆BCl₂F₄NO₂P₂Ru</td>
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<tr>
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<td>1385.34</td>
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<td>1080.51</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
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<tr>
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<td>P-1</td>
<td>P2(1)/c</td>
<td>P2(1)/c</td>
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<tr>
<td>a, Å</td>
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<td>23.3968(8)</td>
<td>13.0587(4)</td>
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<tr>
<td>b, Å</td>
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<td>13.1912(7)</td>
<td>10.7057(4)</td>
<td>25.8151(7)</td>
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<tr>
<td>c, Å</td>
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<td>20.2329(12)</td>
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<tr>
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<td>γ, °</td>
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<td>90</td>
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<td>3089.3(3)</td>
<td>4792.7(3)</td>
<td>4917.3(2)</td>
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<tr>
<td>Z</td>
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<td>2</td>
<td>4</td>
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**Figure S1-1** Molecular structure for complex 3 (ellipsoids at the 50% probability level). The phenyl rings in PPh₃ groups and the counter anion are omitted for clarity. Selected bond distances [Å] and angles [°]: Ru(1)–O(1) 2.111(3), O(1)–C(11) 1.235(6), C(11)–C(10) 1.509(6), C(9)–C(10) 1.537(6), C(1)–C(9) 1.396(6), C(2)–C(1) 1.482(6), C(2)–C(3) 1.343(6), C(3)–C(4) 1.462(7), N(1)–C(4) 1.348(6), Ru(1)–C(1) 2.150(4), Ru(1)–C(9) 2.158(4), Ru(1)–N(1) 2.182(4), O(1)–Ru(1)–C(9) 74.67(14), O(1)–Ru(1)–C(1) 109.24(15), O(1)–C(11)–C(10) 119.0(4), C(11)–C(10)–C(9) 105.9(4), C(10)–C(9)–Ru(1) 110.5(3), C(9)–C(1)–C(2) 131.2(4), C(3)–C(2)–C(1) 128.9(4), C(2)–C(3)–C(4) 129.4(5), N(1)–C(4)–C(3) 120.9(4), O(1)–Ru(1)–N(1) 83.05(13), C(4)–N(1)–Ru(1) 127.4(3), C(1)–Ru(1)–C(9) 37.81(16).
Figure S1-2 Molecular structure for complex 5 (ellipsoids at the 50% probability level). The phenyl rings in PPh₃ groups and the counter anion are omitted for clarity. Selected bond distance [Å] and angles [°]: Ru(1)–O(1) 2.108(2), O(1)–C(11) 1.231(5), C(11)–C(10) 1.483(5), C(9)–C(10) 1.501(5), C(2)–C(1) 1.486(5), C(3)–C(4) 1.334(5), C(9)–N(1) 1.364(4), Ru(1)–C(1) 2.156(3), Ru(1)–C(9) 2.145(3), Ru(1)–N(1) 2.202(3), O(1)–Ru(1)–C(9) 74.63(11), O(1)–Ru(1)–C(1) 109.26(12), O(1)–C(11)–C(10) 118.1(3), C(11)–C(10)–C(9) 107.5(3), C(10)–C(9)–Ru(1) 107.5(2), C(9)–C(1)–C(2) 124.3(3), C(3)–C(2)–C(1) 129.2(3), C(2)–C(3)–C(4) 130.1(3), N(1)–C(4)–C(3) 121.1(3), O(1)–Ru(1)–N(1) 79.72(10), C(4)–N(1)–Ru(1) 128.0(2), C(9)–Ru(1)–C(1) 37.92(12).

2. NMR spectra

Figure S2-1 The ¹H NMR spectrum of complex 2 in CD₂Cl₂ at 400.13 MHz.
Figure S2-2 The $^{31}$P NMR spectrum of complex 2 in CD$_2$Cl$_2$ at 161.96 MHz.

Figure S2-3 The $^{13}$C NMR spectrum of complex 2 in CD$_2$Cl$_2$ at 100.63 MHz.
Figure S2-4 The $^1$H–$^{13}$C HSQC of complex 2 in CD$_2$Cl$_2$ at 100.63 MHz.

Figure S2-5 The $^1$H NMR spectrum of complex 3 in CD$_2$Cl$_2$ at 400.13 MHz.

Additional peaks: 9.47, 6.62, 5.24, 4.40, 3.61, 1.67 ppm (a minor unidentified byproduct).
Figure S2-6 The $^{31}\text{P}$ NMR spectrum of complex 3 in CD$_2$Cl$_2$ at 161.96 MHz.

Figure S2-7 The $^{13}\text{C}$ NMR spectrum of complex 3 in CD$_2$Cl$_2$ at 100.63 MHz.

Additional peaks: 232.52, 156.10, 150.52, 148.76, 116.12, 87.48, 74.56, 66.67, 28.87 ppm (a minor unidentified byproduct).
Figure S2-8 The $^1$H-$^{13}$C HSQC spectrum of complex 3 in CD$_2$Cl$_2$ at 100.63 MHz.

Figure S2-9 The in-situ $^1$H NMR spectrum of complex 4 in CD$_2$Cl$_2$ at 400.13 MHz. Additional peaks: peaks for other byproducts.
Figure S2-10 The in-situ $^{31}$P NMR spectrum of complex 4 in CD$_2$Cl$_2$ at 161.96 MHz.

Figure S2-11 The in-situ $^{13}$C NMR spectrum of complex 4 in CD$_2$Cl$_2$ at 100.63 MHz.
Figure S2-12 The $^1$H NMR spectrum of complex 5 in CD$_2$Cl$_2$:CDCl$_3$ = 3:5 at 400.13 MHz.

Figure S2-13 The $^{31}$P NMR spectrum of complex 5 in CD$_2$Cl$_2$:CDCl$_3$ = 3:5 at 161.96 MHz.
Figure S2-14 The $^{13}$C NMR spectrum of complex 5 in CD$_2$Cl$_2$:CDCl$_3$ = 3:5 at 100.63 MHz.

Figure S2-15 The $^1$H-$^{13}$C HSQC of complex 5 in CD$_2$Cl$_2$:CDCl$_3$ = 3:5 at 100.63 MHz.
Figure S2-16 The $^1$H NMR spectrum of complex 6 in CD$_2$Cl$_2$ at 400.13 MHz.

Figure S2-17 The $^{31}$P NMR spectrum of complex 6 in CD$_2$Cl$_2$ at 161.96 MHz.
Figure S2-18 The $^{13}$C NMR spectrum of complex 6 in CD$_2$Cl$_2$ at 100.63 MHz.

Figure S2-19 The $^1$H-$^{13}$C HSQC spectrum for complex 6 in CD$_2$Cl$_2$ at 100.63 MHz.