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# Supporting Information

## Ru-Ag and Ru-Au Dicarbene Complexes from an Abnormal Carbene Ruthenium System

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# Table of Contents

# a) Experimental Procedures and Spectra

## General Considerations

Unless otherwise specified, all reactions were performed under oxygen free, dry conditions in an argon atmosphere using standard Schlenk and glovebox techniques. The solvents used were purified, degassed and dried according to standard purification techniques[1] or obtained from a M. Braun SPS purification system. Hydroxomethyldiphenylphosphine oxide,[2] mesitylimidazole,[3] $Ru(OAc)_2(PPh_3)_2$[4] and Au(tht)Cl[5] were obtained following standard literature procedures. If not noted differently, all further chemicals were purchased from commercial sources and used as received. NMR spectra were acquired on a Bruker Avance Ultrashield 400 MHz and a Bruker DPX 400 MHz spectrometer (Munich), and a Bruker AC 200 spectrometer (Udine). All $^1H$ and $^{13}C$ chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak serving as internal reference.[6] $^{31}P$ NMR spectra are referenced to 85% $H_3PO_4$ as external standard. The following abbreviations are used for the signal multiplicities: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, br – broad. Single crystals were measured in the SC-XRD laboratory of the Catalysis Research Center at Technische Universität München. FAB mass spectrometry was carried out using a Finnigan MAT 90 and ESI mass spectra were acquired on a Thermo Scientific LCG Fleet. Flash chromatography was perfomed with an Agilent 971-FP system using PuriFlash Interchim silica columns. GC analysis was done with an HP 6890 GC system using an Agilent DB-225ms column (24.8 m × 250 µm × 0.25µm). CHN analyses were carried out in the microanalytical laboratory at Technische Universität München. Solvent contents of solvates were determined by integration of the respective signals in the $^1H$ NMR spectra or by single crystal X-ray analysis and are included in the calculated EA values if applicable.

### Synthesis of Bromomethyldiphenylphosphine oxide (S-1)

The compound was prepared following a modified literature procedure.[7] Hydroxomethyldiphenylphosphine oxide (6.0 g, 25.8 mmol, 1.0 equiv.) was dissolved in 50 mL of $CH_2Cl_2$ in a round-bottom flask and cooled to 0 °C. To the stirred solution, thionyl bromide (8.1 g, 38.7 mmol, 3.0 mL, 1.5 equiv.) was slowly added. After the addition was finished, the mixture was warmed to room temperature and stirred for 20 h. The resulting red solution was carefully quenched with 15 mL of ice, followed by neutralization with a saturated aqueous solution of $NaHCO_3$. The mixture was extracted with dichloromethane, and the combined organic phases were dried with $MgSO_4$. The solvent was removed in vacuo and the obtained yellow crude product was purified by flash chromatography using EtOAc as eluent. **S-1** was obtained as a colorless powder in 30 % yield (2.2 g, 7.7 mmol).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ [ppm] = 7.82 – 7.77 (m, 4H, $PPh_2$), 7.61 – 7.48 (m, 6H, $PPh_2$), 3.80 (d, $^2J_{HP}$ = 5.6 Hz, $CH_2P$).

$^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$): $\delta$ [ppm] = 132.7 (d, $^4J_{CP}$ = 2.7 Hz, *p*-CH), 131.6 (d, $^2J_{CP}$ = 9.4 Hz, *o*-CH), 130.1 (d, $^1J_{CP}$ = 105.0 Hz, *ipso*-C), 128.9 (d, $^3J_{CP}$ = 12.2 Hz, *m*-CH), 23.7 (d, $^1J_{CP}$ = 69.6 Hz, $CH_2P$).

$^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ [ppm] = 27.1 (s, $O{=}PPh_2$).

### Synthesis of 1-(Methyldiphenylphosphinoxide)-3-(mesityl) imidazolium bromide (S-2)

The compound was prepared following a literature procedure for a related ligand precursor.[8] **S-1** (2.1 g, 7.2 mmol, 1.0 equiv.) and mesitylimidazole (2.1 g, 10.8 mmol, 1.5 equiv.) were mixed in a sealed pressure tube (ACE GLASS Inc., 38 mL, back-seal with FETFE-sealing) and heated to 140 °C for 3 days. After cooling, the light brown solid was dissolved in 10 mL of dichloromethane and the crude product was precipitated with diethyl ether. The obtained off-white solid was triturated with diethyl ether for 2 h until the product appeared as a colorless powder. The ether was decanted off and the product dried in vacuo. Yield: 94% (3.3 g, 6.8 mmol).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ [ppm] = 10.16 (s, 1H, NC*H*N), 8.26 – 8.21 (m, 4H, Ar-H), 8.11(*pseudo*-t, $^3J_{HH} = {}^4J_{HH}$ = 1.7 Hz, 1H, NC*H*CHN), 7.56 – 7.53 (m, 6H, Ar-H), 6.97 (*pseudo*-t, $^3J_{HH} = {}^4J_{HH}$ = 1.8 Hz, 1H, NCHC*H*N), 6.92 (s, 2H, Mes-H), 6.17 (d, $^2J_{HP}$ = 6.9 Hz, 2H, $CH_2P$), 2.31 (s, 3H, $CH_3$), 1.70 (s, 6H, $CH_3$).

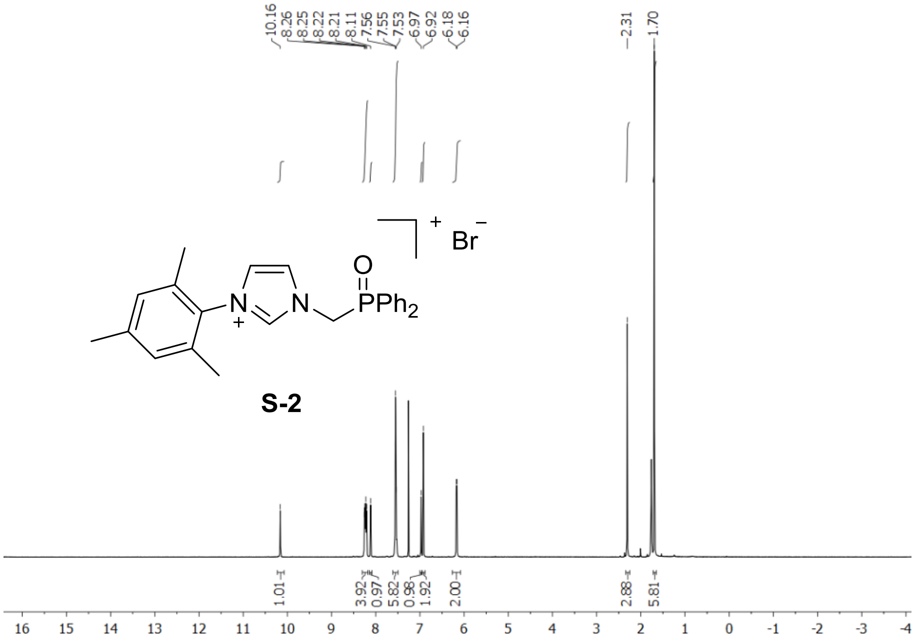


**Figure S-1:** $^1$H NMR spectrum of 1-(Methyldiphenylphosphinoxide)-3-(mesityl) imidazolium bromide (**S-2**).

$^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 141.7, 137.8, 134.1, 133.2 (d, $^4J_{CP}$ = 2.7 Hz, *p*-CH), 131.6 (d, $^2J_{CP}$ = 10.2 Hz, *o*-CH), 130.3, 129.9, 129.4 (d, $^3J_{CP}$ = 12.6 Hz, *m*-CH), 127.8 (d, $^1J_{CP}$ = 103.3 Hz, *ipso*-C), 124.3, 122.7, 49.5 (d, $^1J_{CP}$ = 65.4 Hz, CH$_2$P), 21.2, 17.2 (s, CH$_3$ groups).

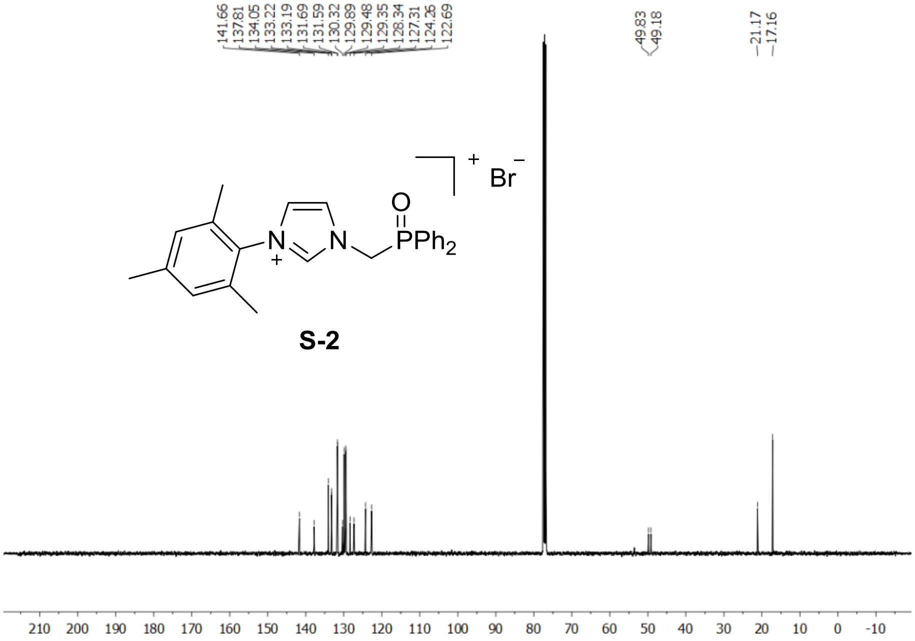


**Figure S-2:** $^{13}$C **{$^1$H}** NMR spectrum of 1-(Methyldiphenylphosphinoxide)-3-(mesityl) imidazolium bromide (**S-2**).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ [ppm] = 27.6 (s, O=$PPh_2$).

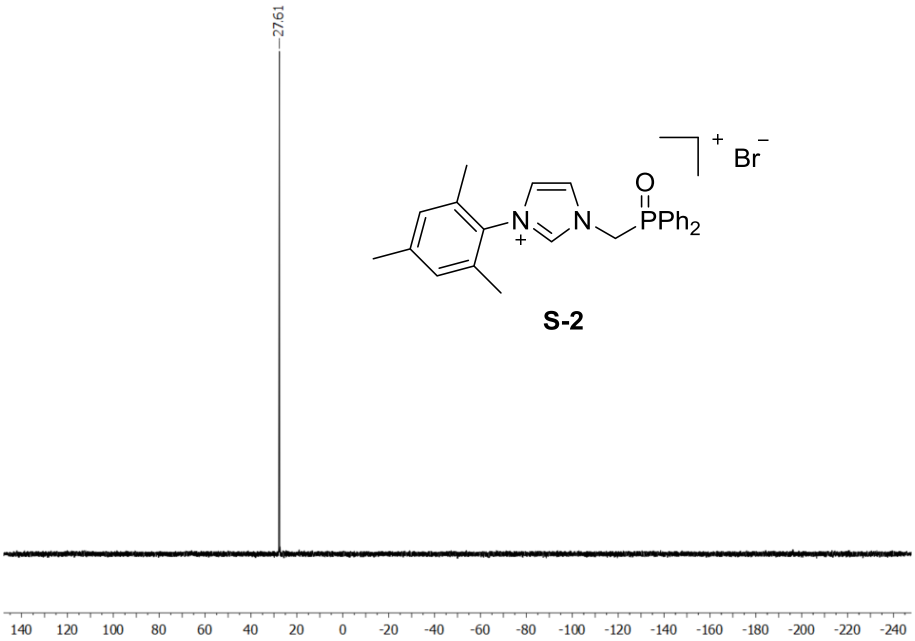


**Figure S-3:** $^{31}P\{^1H\}$ NMR spectrum of 1-(Methyldiphenylphosphinoxide)-3-(mesityl) imidazolium bromide (**S-2**).

MS (ESI): *m/z* (%) = 401.35 (100) [$M^+$-Br], 282.2 (10) [$M^+$-Br-Mes].

Elemental analysis calcd (%) for $C_{25}H_{26}BrN_2OP$: C, 62.38; H, 5.44; N, 5.82. Found: C, 62.04; H, 5.50; N, 5.84.

### Synthesis of 1-(Methyldiphenylphosphine)-3-(mesityl) imidazolium bromide (P-NHC × HBr)

The compound was prepared following a literature procedure for a related ligand precursor.[8] **S-2** (3.3 g, 6.8 mmol, 1.0 equiv.), chlorobenzene (50.0 mL) and trichlorosilane (5.5 g, 40.6 mmol, 4.1 mL, 6.0 equiv.) were mixed in a sealed thick wall glass reactor (500 mL Schott screw cap bottle with J-Young adapter and round bottom) and heated to 120 °C. The solution was stirred for 2 h, cooled and 40 mL of degassed dichloromethane were added. The mixture was then carefully treated with 70 mL of a degassed aqueous solution of sodium hydroxide (10%), and the organic phase was extracted with dichloromethane under argon. The combined organic phases were dried with $MgSO_4$ and filtered. Upon solvent removal in vacuo, the product precipitated as colorless solid. The crude product was washed with diethyl ether (3 × 50 mL) and further purified by precipitation from dichloromethane with diethyl ether. P-NHC × HBr × 0.5 $CH_2Cl_2$ was obtained as colorless, air-sensitive powder in 78% yield (2.7 g, 5.8 mmol).

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 10.33 (s, 1H, NC*H*N), 7.73 – 7.69 (m, 4H, Ar-H), 7.47 (*pseudo*-t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 1.6 Hz, 1H, NC*H*CHN), 7.42 – 7.36 (m, 6H, Ar-H), 6.97 (*pseudo*-t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 1.7 Hz, 1H, NCHC*H*N), 6.91 (s, 2H, Mes-H), 5.69 (d, $^{2}J_{HP}$ = 6.6 Hz, 2H, CH$_2$P), 2.29 (s, 3H, CH$_3$), 1.82 (s, 6H, CH$_3$).

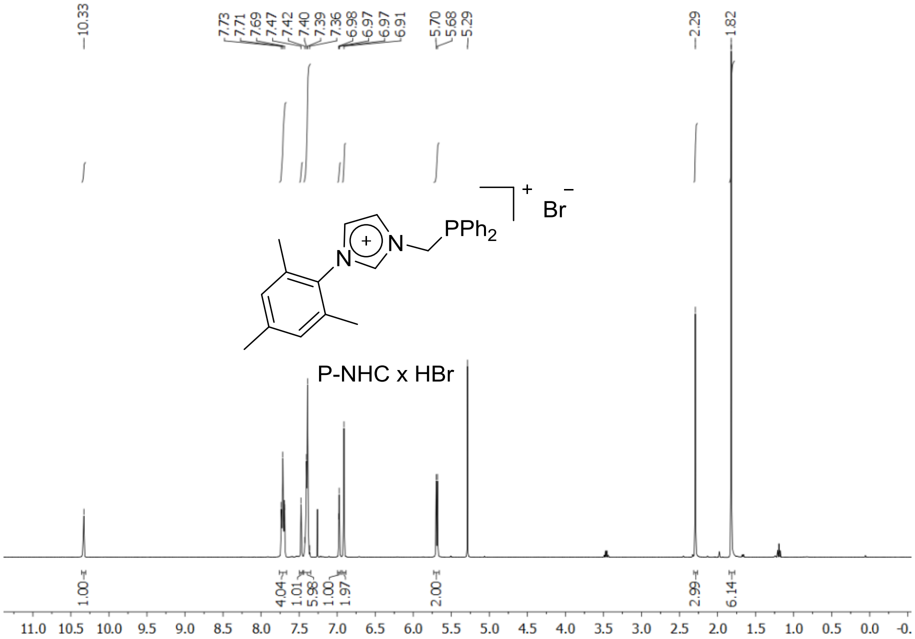


**Figure S-4:** $^{1}$H NMR spectrum of 1-(Methyldiphenylphosphine)-3-(mesityl) imidazolium bromide (P-NHC × HBr).

$^{13}$C {$^{1}$H} NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 141.3 (s, N*C*HN), 138.7, 134.2, 133.6 (d, $^{2}J_{CP}$ = 20.4 Hz, PPh$_2$), 132.6 (d, $^{1}J_{CP}$ = 11.8 Hz, PPh$_2$), 130.5, 130.3, 129.7, 129.2 (d, $^{3}J_{CP}$ = 7.6 Hz, PPh$_2$), 122.6, 122.4 (d, $^{4}J_{CP}$ = 4.8 Hz, PPh$_2$), 48.8 (d, $^{1}J_{CP}$ = 19.4 Hz, CH$_2$P), 21.1, 17.4 (s, CH$_3$ groups).

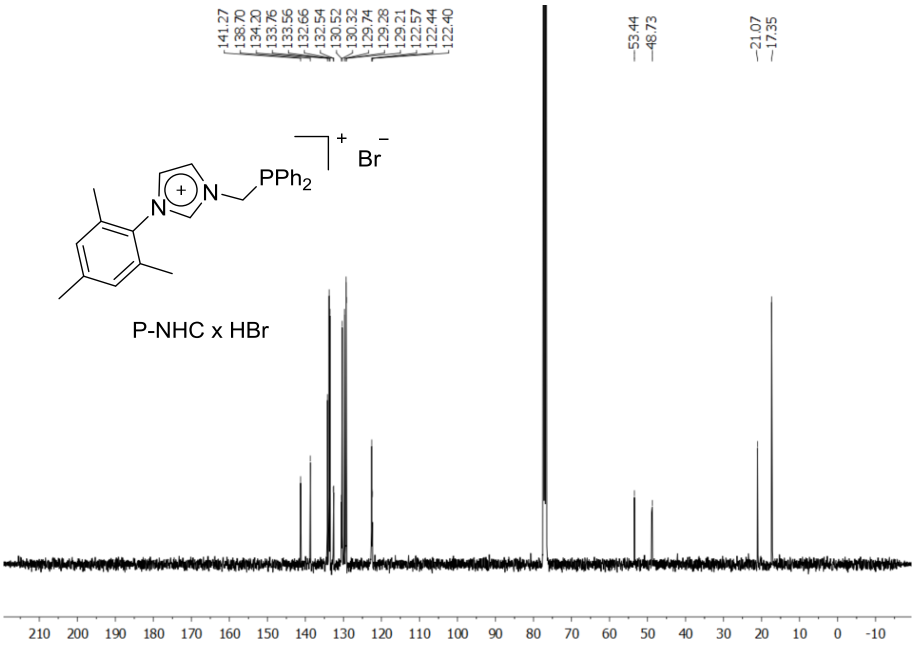


**Figure S-5:** $^{13}C\ \{^1H\}$ NMR spectrum of 1-(Methyldiphenylphosphine)-3-(mesityl) imidazolium bromide (P-NHC × HBr).

$^{31}P\ \{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ [ppm] = –11.1 (s, $PPh_2$).

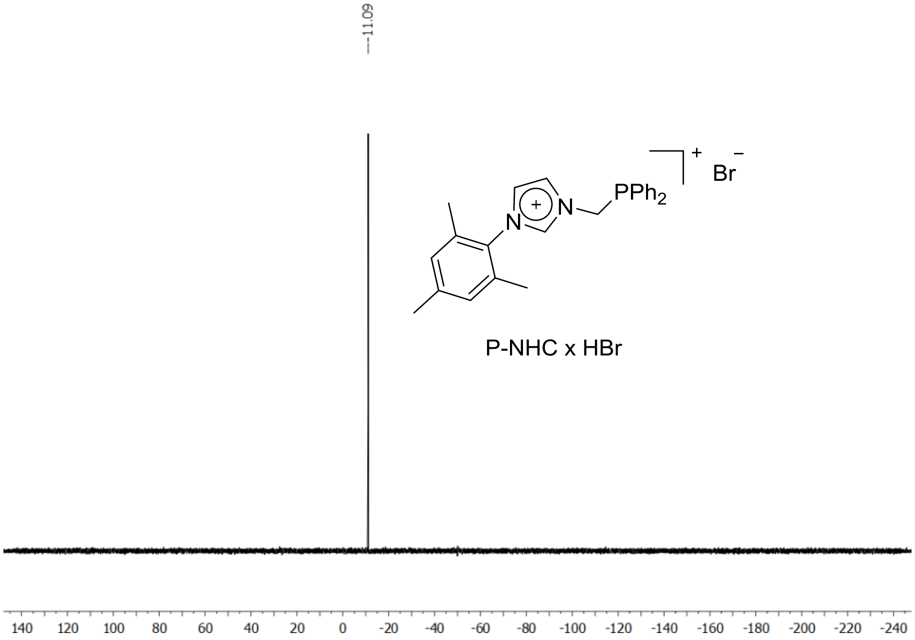


**Figure S-6:** $^{31}P\ \{^1H\}$ NMR spectrum of 1-(Methyldiphenylphosphine)-3-(mesityl) imidazolium bromide (P-NHC × HBr).

MS (ESI): *m/z* (%) = 384.7 (100) [$M^+$-Br].

Elemental analysis calcd (%) for $C_{25}H_{26}BrN_2P$ × 0.5 $CH_2Cl_2$: C, 60.31; H, 5.36; N, 5.52; Cl+Br 22.71. Found: C, 60.41; H, 5.36; N, 5.52; Cl+Br 21.70.

### Synthesis of RuBr(OAc)($PPh_3$)(P-NHC) (1)

Ru(OAc)$_2$($PPh_3$)$_2$ (196 mg, 0.26 mmol, 1.0 equiv.), P-NHC × HBr (129 mg, 0.28 mmol, 1.05 equiv.) and anhydrous sodium acetate (43 mg, 0.53 mmol, 2.0 equiv.) were suspended in 8 mL of *tert*-butanol and heated to 80 °C for 3 h. The resulting precipitate was filtered off, washed with methanol (3 × 4 mL) and subsequently dried in vacuo. **1** was obtained as red powder in 85% yield (196 mg, 0.22 mmol).

$^1$H NMR (400 MHz, $CD_2Cl_2$, major species): $\delta$ [ppm] = 7.49 – 7.46 (m, 2H, $PPh_2$), 7.40 – 7.17(m, 8H, $PPh_2$), 7.04 – 6.93 (m, 15H, $PPh_3$), 6.85 – 6.83 (m, 3H, Mes-H and NC*H*CHN), 6.74 (s, 1H, NCHC*H*N), 5.31 (m, 1H, C*H*H), 4.34 (*pseudo*-t, $^2J_{HH} = {}^2J_{HP}$ = 11.7 Hz, CH*H*), 2.37 (s, 3H, $CH_3$), 2.28 (s, 3H, $CH_3$), 1.98 (s, 3H, $CH_3$), 0.14 (s, 3H, $CH_3$).

$^1$H NMR (400 MHz, $CD_2Cl_2$, minor species): $\delta$ [ppm] = 7.49 – 7.46 (m, 2H, $PPh_2$), 7.40 – 7.17(m, 8H, $PPh_2$), 7.04 – 6.93 (m, 15H, $PPh_3$), 6.85 – 6.83 (m, 3H, Mes-H and NC*H*CHN), 6.74 (s, 1H, NCHC*H*N), 5.26 (m, 1H, C*H*H), 4.27 (*pseudo*-t, $^2J_{HH} = {}^2J_{HP}$ = 12.4 Hz, CH*H*), 2.34 (s, 3H, $CH_3$), 2.28 (s, 3H, $CH_3$), 1.97 (s, 3H, $CH_3$), 0.15 (s, 3H, $CH_3$).

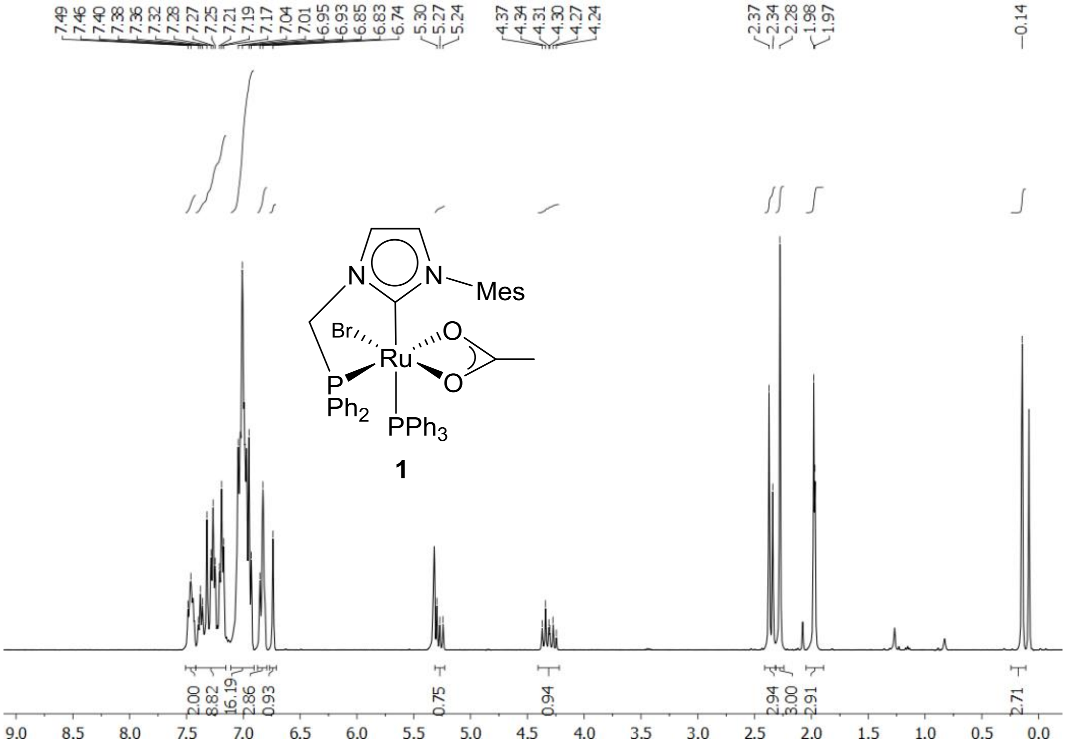


**Figure S-7:** $^1$H NMR spectrum of RuBr(OAc)($PPh_3$)(P-NHC) (**1**).

$^{13}$C {$^{1}$H} NMR (101 MHz, $CD_2Cl_2$, major species): $\delta$ [ppm] = 190.3 (dd, $^{2}J_{CPcis}$ = 11.6 Hz, $^{2}J_{CPtrans}$ = 109.6 Hz, N*C*N), 186.4 (s, OAc), 139.0, 138.6, 138.5, 138.2, 137.2, 135.5, 134.8 – 134.6, 134.5, 134.3, 133.0, 130.3, 129.9, 129.2 – 129.1, 128.5, 128.1, 127.6, 124.7, 121.2 (aromatic carbon signals), 55.6 (d, $^{1}J_{CP}$ = 36.8 Hz, N*C*$H_2$P), 22.9, 21.2, 19.5, 17.6 (s, $CH_3$ groups).

$^{13}$C {$^{1}$H} NMR (101 MHz, $CD_2Cl_2$, minor species): $\delta$ [ppm] = 190.5 (dd, $^{2}J_{CPcis}$ = 12.6 Hz, $^{2}J_{CPtrans}$ = 110.4 Hz, N*C*N), 186.2 (s, OAc), 139.0, 138.6, 138.5, 138.2, 137.2, 135.4, 134.8 – 134.6, 134.5, 134.3, 133.0, 130.3, 129.7, 129.2 – 129.1, 128.5, 128.1, 127.6, 124.5, 121.2 (aromatic carbon signals), 54.5 (N*C*$H_2$P), 22.6, 21.2, 19.1, 17.6 (s, $CH_3$ groups).

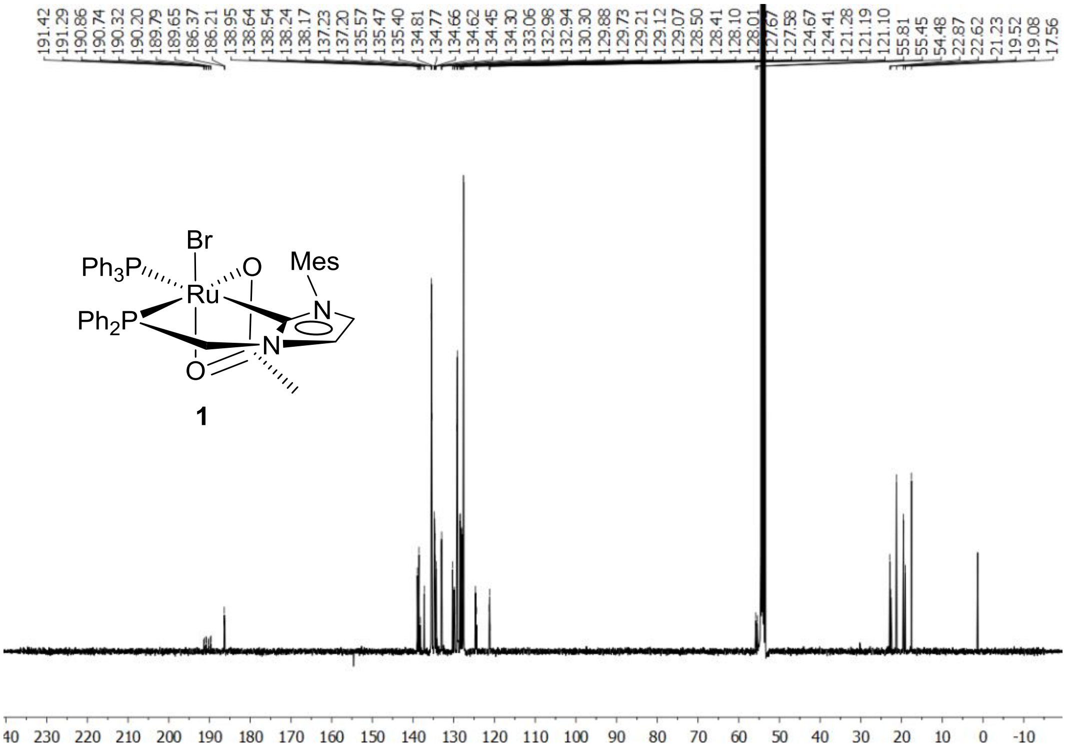


**Figure S-8:** $^{13}$C {$^{1}$H} NMR of RuBr(OAc)($PPh_3$)(P-NHC) (**1**).

$^{31}$P {$^{1}$H} NMR (162 MHz, $CD_2Cl_2$, major species): $\delta$ [ppm] = 72.6 (d, $^{2}J_{PP}$ = 23.5 Hz), 35.1 (d, $^{2}J_{PP}$ = 23.6 Hz).

$^{31}$P {$^{1}$H} NMR (162 MHz, $CD_2Cl_2$, minor species): $\delta$ [ppm] = 72.5 (d, $^{2}J_{PP}$ = 22.5 Hz), 34.9 (d, $^{2}J_{PP}$ = 23.4 Hz).

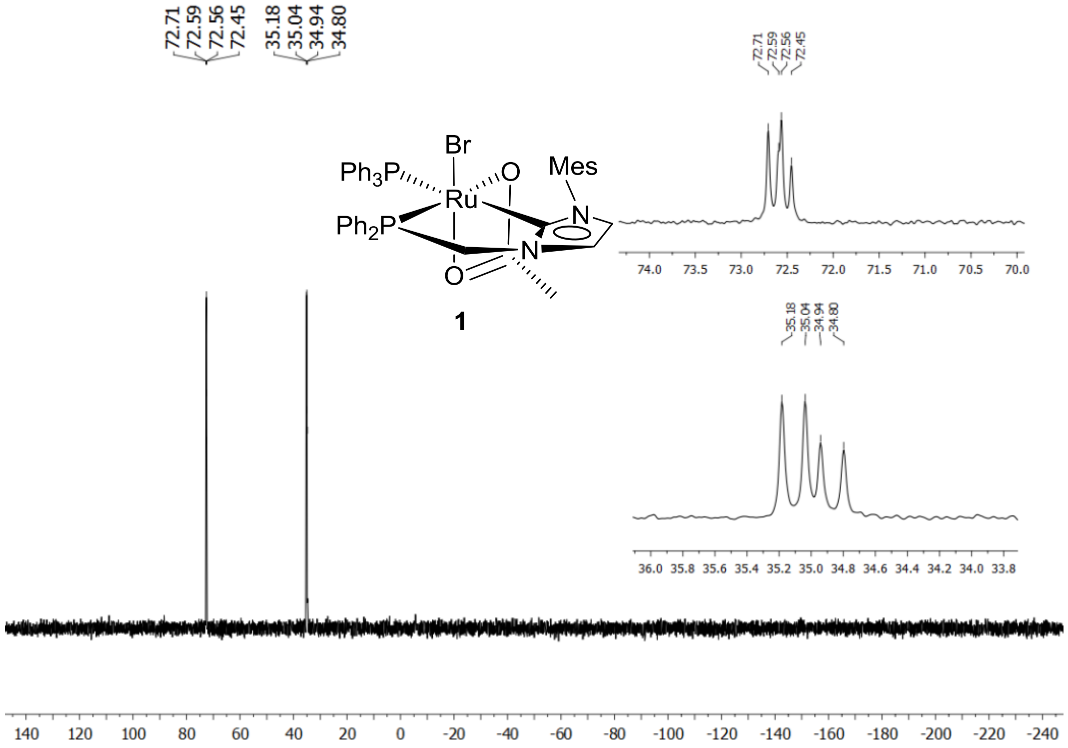


**Figure S-9:** $^{31}$P {$^{1}$H} NMR of RuBr(OAc)(PPh$_3$)(P-NHC) (**1**).

MS (FAB): *m/z* (%) = 885.4 (10) [$M^+$], 826.6 (19) [$M^+$-OAc], 806.6 (29) [$M^+$-Br], 746.7(11) [$M^+$-Br-OAc], 625.9 (100) [$M^+$-PPh$_3$], 485.1 (49) [$M^+$-Br-PPh$_3$-OAc].

Elemental analysis calcd (%) for $C_{45}H_{43}BrN_2O_2P_2Ru$: C, 60.95; H, 4.89; N, 3.16. Found: C, 61.25; H, 5.10; N, 3.15.

### Synthesis of [Ru(OAc)(P-aNHC)(P-NHC)]Br (2)

*I) Method from complex* **1***:*

Complex **1** (32 mg, 0.04 mmol, 1.0 equiv.), P-NHC × HBr (17 mg, 0.04 mmol, 1.0 equiv.) and anhydrous sodium acetate (6 mg, 0.07 mmol, 2.0 equiv.) were suspended in 2.5 mL of tetrahydrofuran and heated to 80 °C for 3 h. After cooling, the resulting yellow precipitate was filtered off with a filter cannula and washed with tetrahydrofuran (3 × 1 mL). The solid was dried in vacuo, then redissolved in 1.5 mL of dichloromethane and filtered to remove inorganic salts. The solvent was distilled off, and the residue was washed with *n*-pentane (2 mL). After drying in vacuo, **2** was obtained as bright yellow powder in 80% yield (29 mg, 0.03 mmol).

*II) Method from Ru(OAc)$_2$(PPh$_3$)$_2$:*

Ru(OAc)$_2$(PPh$_3$)$_2$ (650 mg, 0.87 mmol, 1.0 equiv.), P-NHC × HBr (834 mg, 1.79 mmol, 2.05 equiv.) and anhydrous sodium acetate (143 mg, 1.75 mmol, 2.0 equiv.) were suspended in 25 mL of tetrahydrofuran and heated to 80 °C for 3 h. After cooling, the resulting yellow precipitate was filtered off with a filter cannula and washed with tetrahydrofuran (3 × 10 mL). The solid was dried in vacuo, then redissolved in 10 mL of dichloromethane and filtered to remove inorganic salts. The solvent was distilled off, and the residue was washed with *n*-pentane (10 mL). After drying in vacuo, **2** was obtained as bright yellow powder in 88% yield (776 mg, 0.77 mmol).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 9.75 (s, 1H, NC*H*N), 7.88 – 7.83 (m, 2H, Ar-H), 7.54 – 7.29 (m, 8H, Ar-H), 7.22 – 7.16 (m, 5H, Ar-H), 7.07 (s, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 6.94 – 6.89 (m, 6H, Ar-H), 6.76 (s, br, 1H, NC*H*CHN), 6.23 – 6.19 (m, 2H, Ar-H), 5.92 (d, $^4J_{HH}$ = 1.1 Hz, 1H, NCC*H*N), 5.20 (dd, $^2J$ = 14.2 Hz, $^2J$ = 9.5 Hz, 1H, C*H*HP), 4.66 (*pseudo*-d, $^2J$ = $^2J$ = 13.0 Hz, 1H, CH*H*P), 4.23 (dd, $^2J$ = 12.7 Hz, $^2J$ = 10.9 Hz, 1H, C*H*HP), 2.47 (dd, $^2J$ = 14.5 Hz, $^2J$ = 2.6 Hz, 1H, CH*H*P), 2.36 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$), 2.23 (s, 3H, CH$_3$), 2.14 (s, 3H, CH$_3$), 2.02 (s, 3H, CH$_3$), 1.99 (s, 3H, CH$_3$), 0.57 (s, 3H, CH$_3$).

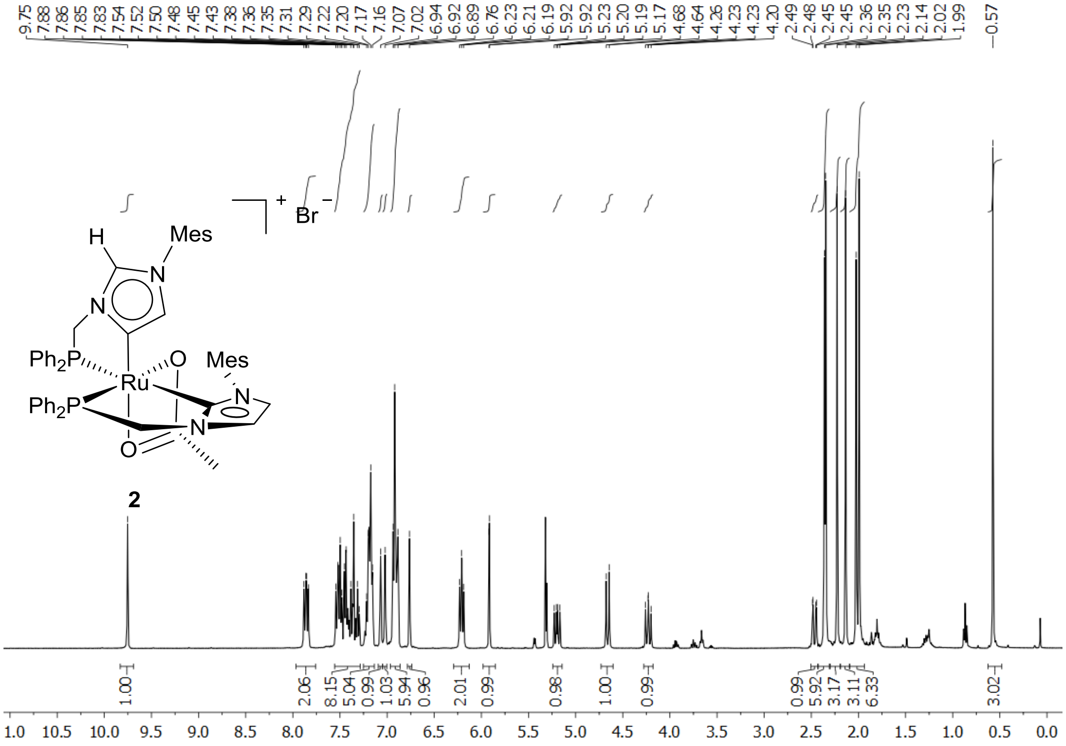


**Figure S-10:** $^1$H NMR of [Ru(OAc)(P-aNHC)(P-NHC)]Br (**2**).

$^{13}$C {$^{1}$H} NMR (101 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 191.6 (dd, $^{2}J_{\mathrm{CP}cis}$ = 11.4 Hz, $^{2}J_{\mathrm{CP}trans}$ = 102.5 Hz, N*C*N), 185.3 (s, OAc), 163.0 (dd, $^{2}J_{\mathrm{CP}cis}$ = 8.5 Hz, $^{2}J_{\mathrm{CP}cis}$ = 18.4 Hz, N*C*CHN), 140.8, 139.1, 137.1, 136.3, 136.1, 135.7, 135.5, 135.3, 134.8, 134.7, 134.2, 133.7, 133.4, 133.3, 132.9, 131.4, 131.0, 130.6, 130.2, 129.8, 129.5, 129.1 – 128.6, 125.1, 124.8, 121.1 (aromatic carbon signals), 53.0, 48.2 (d, $^{1}J_{\mathrm{CP}}$ = 36 Hz, N*C*H$_2$P carbon signals), 23.5, 21.4, 21.1, 19.3, 18.3, 17.7, 17.5 ($CH_3$ groups).

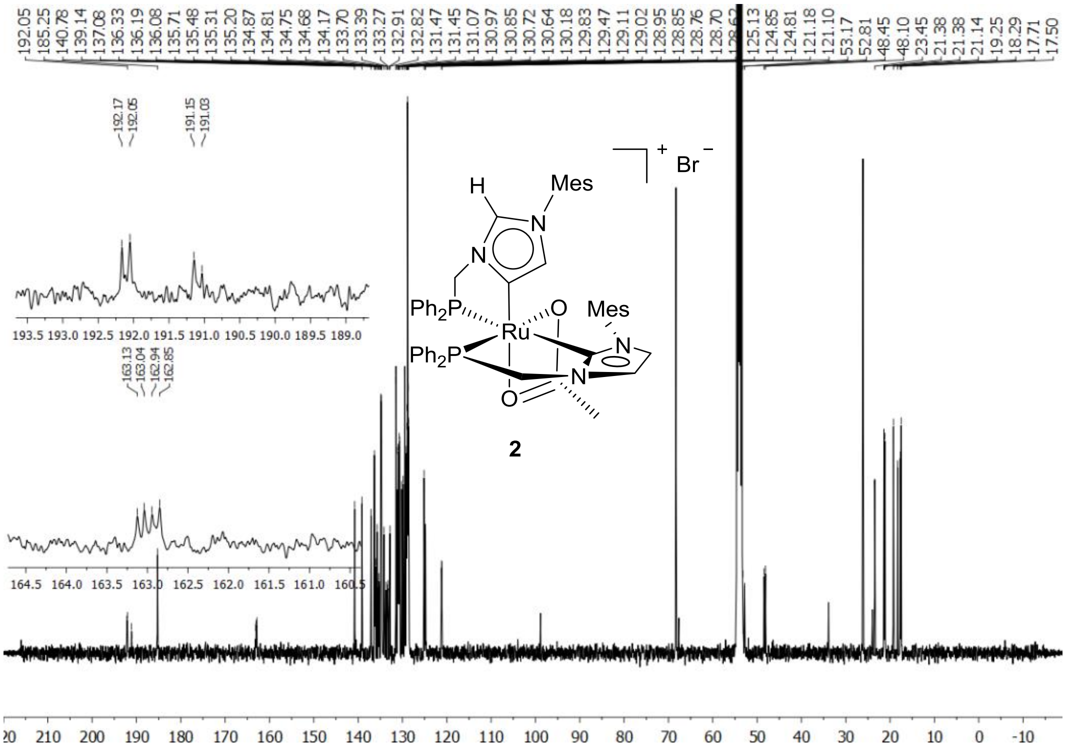


**Figure S-11:** $^{13}$C {$^{1}$H} NMR of [Ru(OAc)(P-aNHC)(P-NHC)]Br (**2**).

$^{31}$P {$^{1}$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 79.5 (d, $^{2}J_{\mathrm{PP}}$ = 24.1 Hz), 62.9 (d, $^{2}J_{\mathrm{PP}}$ = 23.6 Hz).

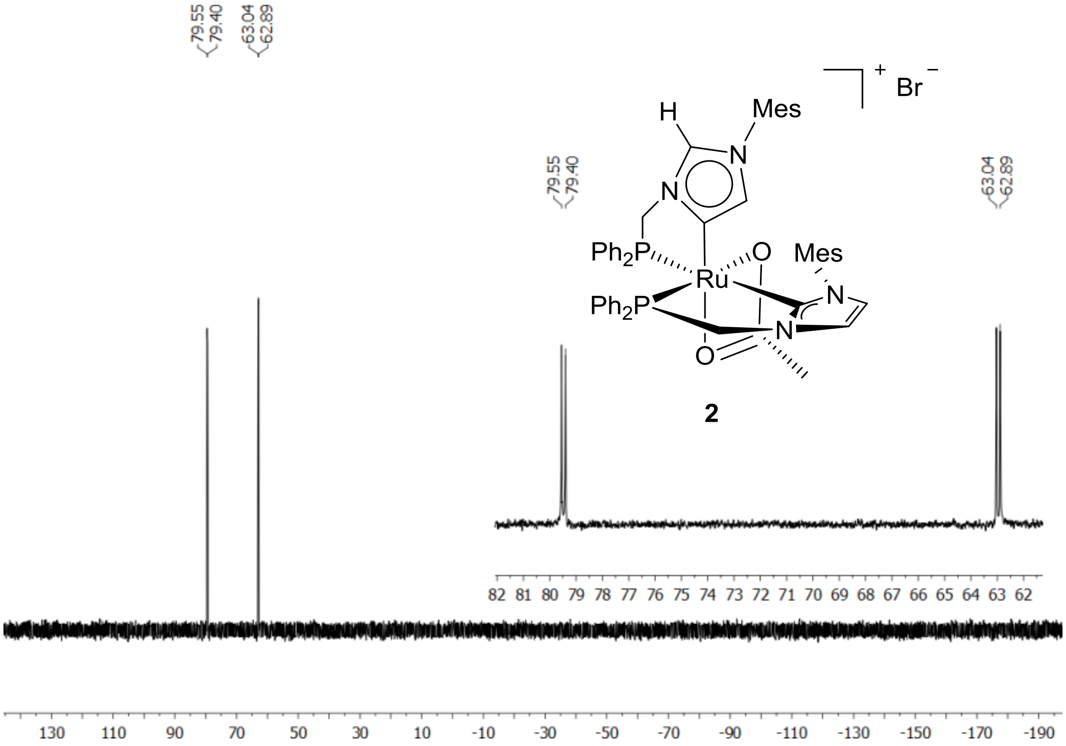


**Figure S-12:** $^{31}P\{^1H\}$ NMR of [Ru(OAc)(P-aNHC)(P-NHC)]Br (**2**).

MS (FAB): *m/z* (%) = 928.5 (100) [$M^+$-Br-H].

Elemental analysis calcd (%) for $C_{52}H_{53}BrN_4O_2P_2Ru$: C, 61.90; H, 5.30 N, 5.55. Found: C, 61.88; H, 5.73; N, 5.11.

## Synthesis of {Ag[Ru(OAc)(P-aNHC)(P-NHC)]$_2$}[AgBr$_2$] (3)

Complex **2** (300 mg, 0.30 mmol, 1.0 equiv.) and $Ag_2O$ (69 mg, 0.30 mmol, 1.0 equiv.) were suspended in 15 mL of dichloromethane and stirred at room temperature for 7 days under protection from light. The mixture was then filtrated through a filter cannula and a pad of Celite®, and the solvent removed under reduced pressure. The residue was washed with *n*-pentane (3 × 4 mL) and subsequently dried in vacuo to yield **3** as yellow powder in 92% yield (305 mg, 0.14 mmol). Single crystals were obtained by layering a dichloromethane solution of **3** with diethyl ether, resulting in crystallization of **3** × $CH_2Cl_2$ or **3** × $Et_2O$ as yellow crystals.

$^{1}$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 7.89 (t, $^{3}J_{HH}$ = 8.7 Hz, 4H, Ar-H), 7.55 – 7.35 (m, 12H, Ar-H), 7.30 – 7.18 (m, 14H, Ar-H), 7.04 (s, 2H, Ar-H), 7.00 (s, 2H, Ar-H), 6.92 – 6.87 (m, 12H, Ar-H), 6.71 (s, 2H, Ar-H), 6.29 (t, $^{3}J_{HH}$ = 8.7 Hz, 4H, Ar-H), 5.72 (s, 2H, Ar-H), 4.75 – 4.69 (m, 4H, $CH_2P$), 4.13 (*pseudo*-t, $^{2}J$ = 11.6 Hz, 2H, C*H*HP), 2.49 (dd, $^{2}J$ = 13.7 Hz, $^{2}J$ = 1.6 Hz, 2H, CH*H*P), 2.36 (s, 6H, $CH_3$), 2.35 (s, 6H, $CH_3$), 2.23 (s, 6H, $CH_3$), 2.15 (s, 6H, $CH_3$), 1.99 (s, 6H, $CH_3$), 1.97 (s, 6H, $CH_3$), 0.58 (s, 6H, $CH_3$).

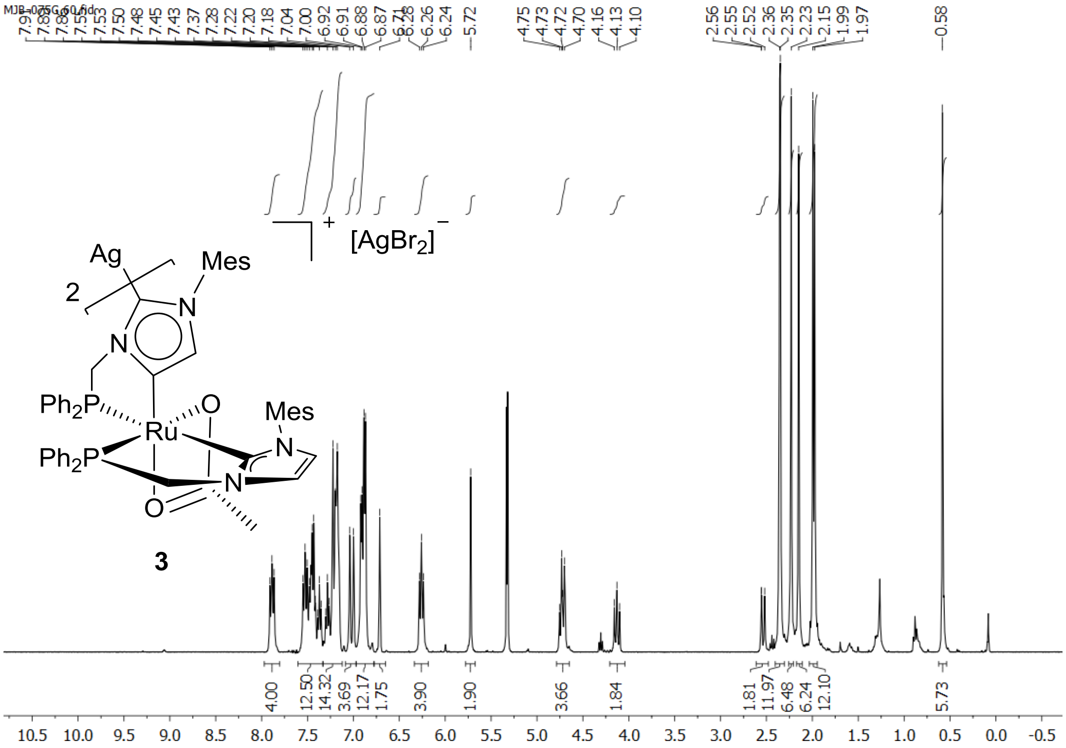


**Figure S-13:** $^{1}$H NMR of {Ag[Ru(OAc)(P-aNHC)(P-NHC)]$_2$}[$AgBr_2$] (**3**).

$^{13}$C {$^{1}$H} NMR (101 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 193.2 (dd, $^{2}J_{CPcis}$ = 11.2 Hz, $^{2}J_{CPtrans}$ = 101.7 Hz, N*C*N), 184.4 (s, OAc), 154.7 (dd, $^{2}J_{CPcis}$ = 9.2 Hz, $^{2}J_{CPcis}$ = 18.9 Hz, N*C*CHN), 138.9, 138.0, 137.4, 137.2, 136.6, 136.5, 136.4, 136.0, 135.0 – 134.7, 134.3, 134.0, 133.5, 131.3, 131.0, 130.8, 130.4, 129.7, 129.3, 128.9, 128.8 – 128.4, 125.1, 124.2, 120.6, (aromatic carbon signals), 53.2, 51.7 (d, $^{1}J_{CP}$ = 37 Hz, N$CH_2$P carbon signals), 23.4, 21.4, 21.1, 19.3, 18.6, 17.8, 17.5 ($CH_3$ groups).

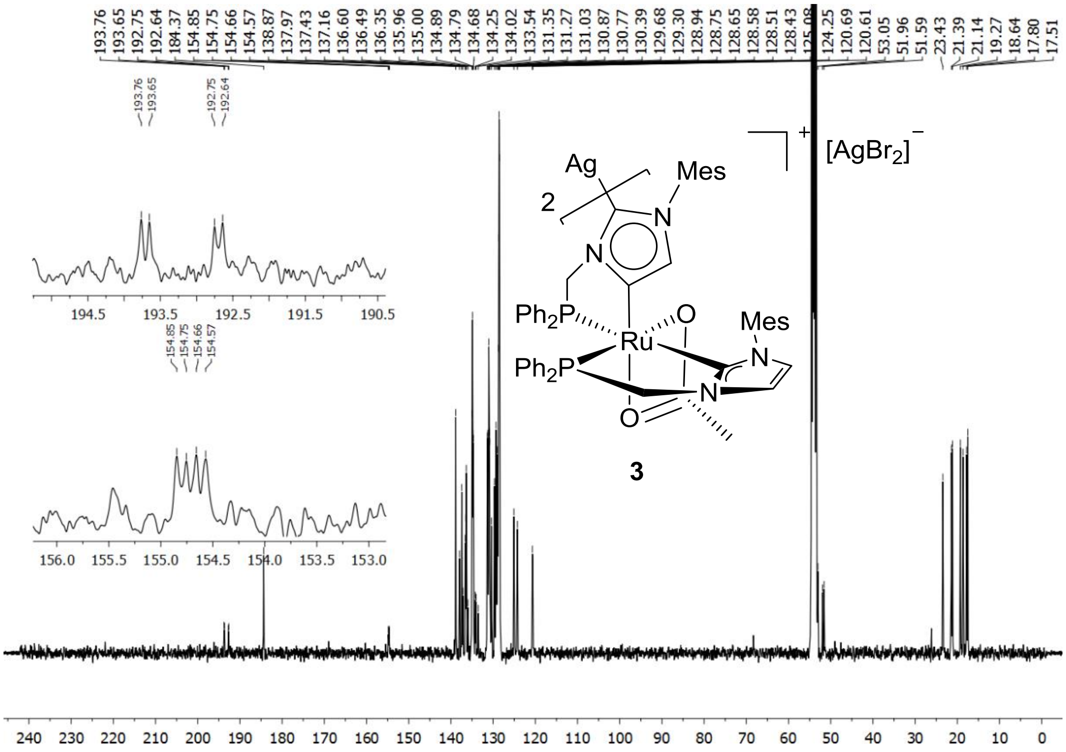


**Figure S-14:** $^{13}C$ {$^{1}H$} NMR of {Ag[Ru(OAc)(P-aNHC)(P-NHC)]$_2$}[AgBr$_2$] (**3**).

$^{31}P$ {$^{1}H$} NMR (162 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 81.0 (d, $^{2}J_{PP}$ = 24.6 Hz), 56.3 (d, $^{2}J_{PP}$ = 24.2 Hz).

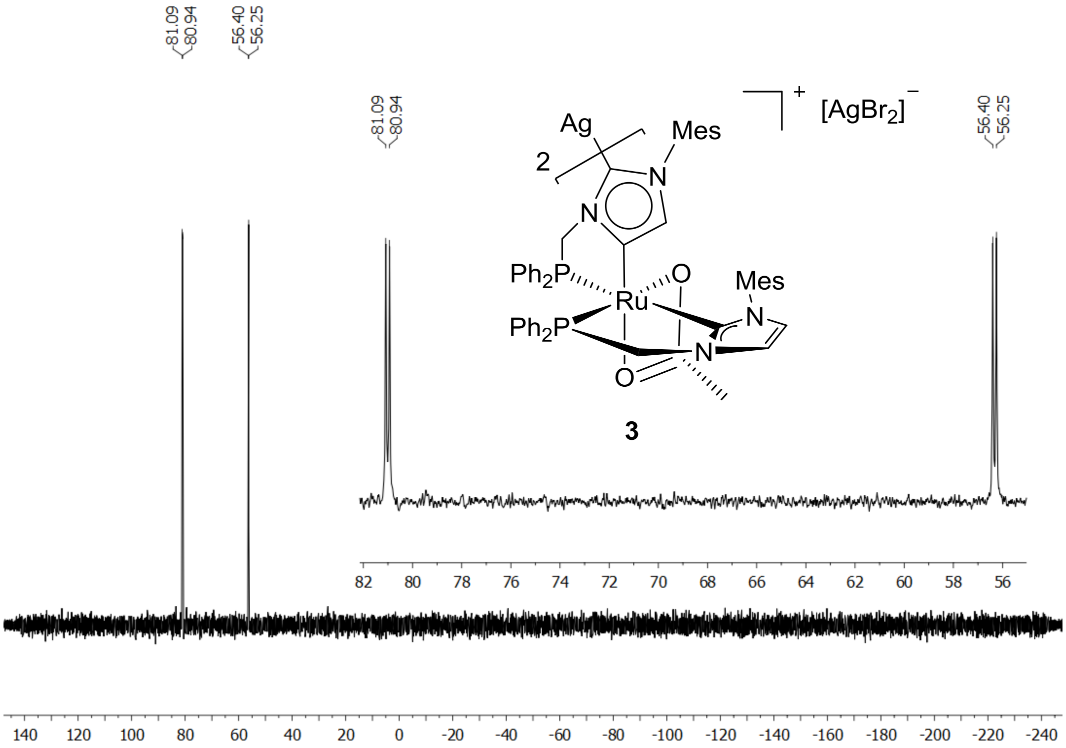


**Figure S-15:** $^{31}P$ {$^{1}H$} NMR of {Ag[Ru(OAc)(P-aNHC)(P-NHC)]$_2$}[AgBr$_2$] (**3**).

Elemental analysis calcd (%) for $C_{104}H_{104}Br_2N_8O_4P_4Ag_2Ru_2$ × $Et_2O$: C, 56.26; H, 4.98 N, 4.86. Found: C, 56.57; H, 5.10; N, 4.88.

Elemental analysis calcd (%) for $C_{104}H_{104}Br_2N_8O_4P_4Ag_2Ru_2$ × $CH_2Cl_2$: C, 54.44; H, 4.61 N, 4.84. Found: C, 54.33; H, 4.75; N, 4.70.

### Synthesis of AuCl[Ru(OAc)(P-aNHC)(P-NHC)] (4)

Complex **3** (200 mg, 0.09 mmol, 1.0 equiv.) and Au(tht)Cl (59 mg, 0.18 mmol, 2.05 equiv.) were dissolved in 8 mL of dichloromethane, and the formation of silver halide was immediately observed. The solution was stirred at room temperature for 48 h under protection from light and subsequently filtered through a filter cannula. The solvent was removed under reduced pressure and the obtained residue was washed with *n*-pentane (3 × 2 mL) to yield **4** as yellow-green powder in 93% (200 mg, 0.17 mmol). Single crystals were obtained by layering a dichloromethane solution of **4** with diethyl ether, resulting in crystallization of **4** × $Et_2O$ as yellow crystals.

$^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 7.91 – 7.87 (m, 2H, Ar-H), 7.56 – 7.29 (m, 7H, Ar-H), 7.23 – 7.16 (m, 6H, Ar-H), 7.05 (s, 1H, Ar-H), 7.01 (s, 1H, Ar-H), 6.92 – 6.88 (m, 6H, Ar-H), 6.72 (s, 1H, Ar-H), 6.27 (t, $^3J_{HH}$ = 8.7 Hz, 2H, Ar-H), 5.69 (s, 1H, Ar-H), 4.88 (dd, $^2J$ = 14.0 Hz, $^2J$ = 10.3 Hz, 1H, C*H*HP), 4.72 (*pseudo*-d, $^2J$ = $^2J$ = 12.5 Hz, 1H, CH*H*P), 4.14 (*pseudo*-t, $^2J$ = 11.4 Hz, 1H, C*H*HP), 2.44 (dd, $^2J$ = 14.3 Hz, $^2J$ = 1.8 Hz, 1H, CH*H*P), 2.38 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$), 2.23 (s, 3H, $CH_3$), 2.15 (s, 3H, $CH_3$), 2.00 (s, 6H, $CH_3$), 0.59 (s, 3H, $CH_3$).

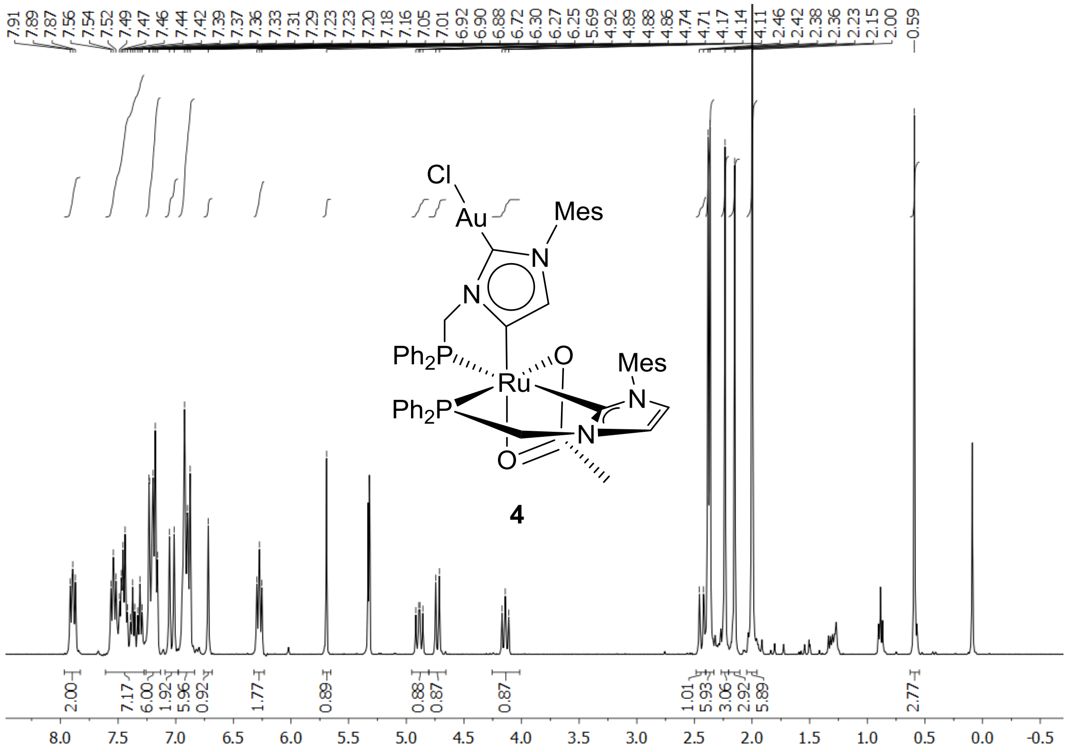


**Figure S-16:** $^1H$ NMR of AuCl[Ru(OAc)(P-aNHC)(P-NHC)] (**4**).

$^{13}$C {$^{1}$H} NMR (101 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 192.9 (dd, $^{2}J_{CP\mathit{cis}}$ = 11.6 Hz, $^{2}J_{CP\mathit{trans}}$ = 101.5 Hz, N*C*N), 184.5 (s, OAc), 167.3 (d, $^{3}J_{CP}$ = 12.7 Hz, N*C*'N), 155.2 (dd, $^{2}J_{CP\mathit{cis}}$ = 9.6 Hz, $^{2}J_{CP\mathit{cis}}$ = 19.4 Hz, N*C*CHN), 139.1, 138.9, 137.4, 137.2, 136.9, 136.5, 136.3, 136.2, 135.8, 134.9, 134.5, 134.1, 133.8, 133.3, 131.3 – 131.1, 130.8, 130.7, 130.4, 129.7, 129.3, 129.0, 128.8 – 128.5, 124.7, 124.3, 120.7 (aromatic carbon signals), 53.2, 51.9 (d, $^{1}J_{CP}$ = 37 Hz, N*C*$H_2$P carbon signals), 23.5, 21.4, 21.1, 19.3, 18.7, 17.9, 17.5 ($CH_3$ groups).

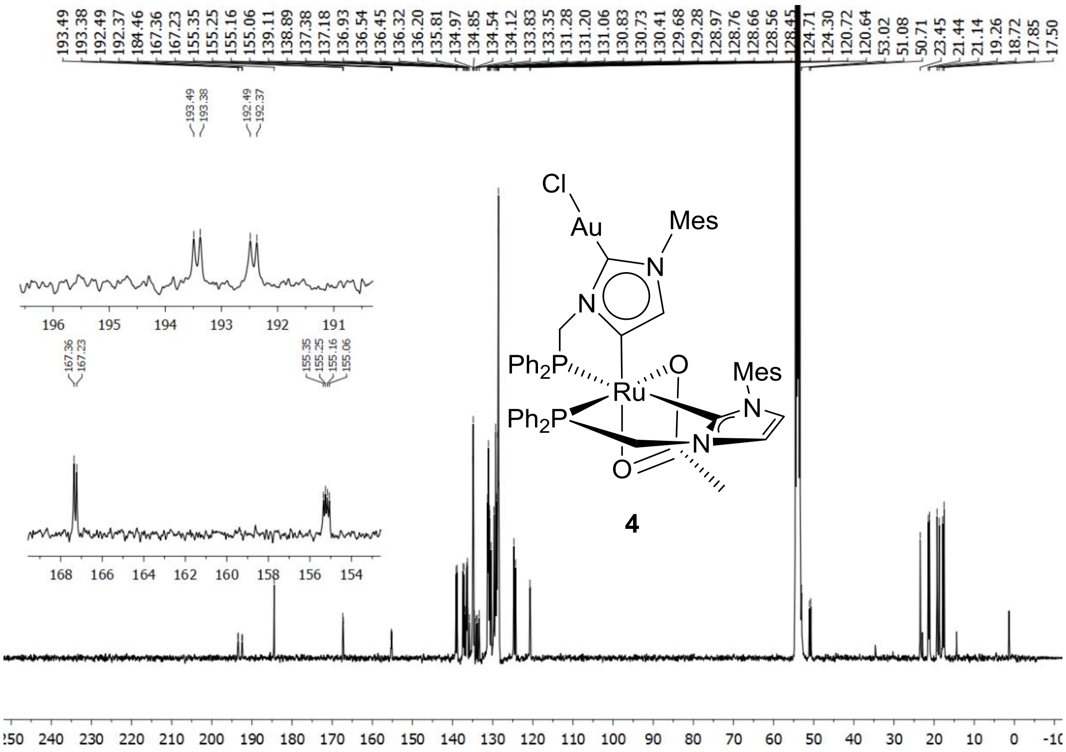


**Figure S-17:** $^{13}$C {$^{1}$H} NMR of AuCl[Ru(OAc)(P-aNHC)(P-NHC)] (**4**).

$^{31}P$ {$^1H$} NMR (162 MHz, $CD_2Cl_2$): $\delta$ [ppm] = 80.7 (d, $^2J_{PP}$ = 24.2 Hz), 56.7 (d, $^2J_{PP}$ = 24.1 Hz).

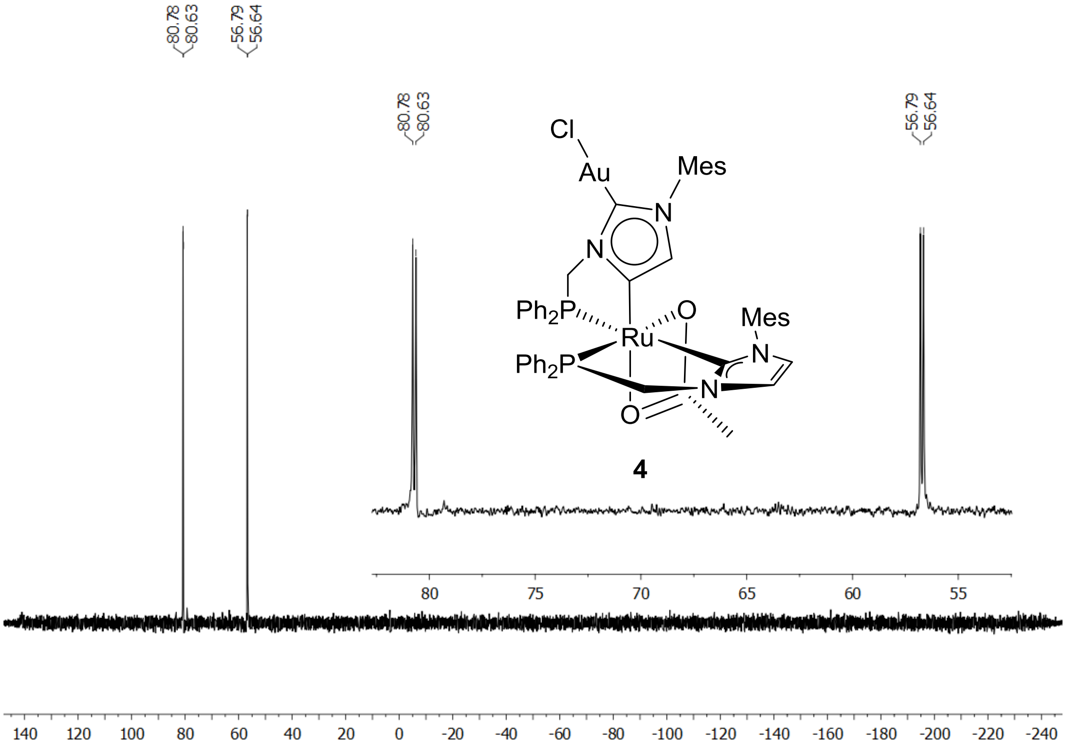


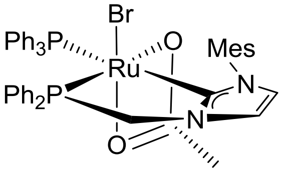
**Figure S-18:** $^{31}P$ {$^1H$} NMR of AuCl[Ru(OAc)(P-aNHC)(P-NHC)] (**4**).

MS (FAB): *m/z* (%) = 1158.1 (100) [$M^+$-2H], 484.8 (45) [$M^+$-AuCl-(P-NHC)-OAc)], 199.4 (55) [$H_2C$-$PPh_3$]$^+$.

Elemental analysis calcd (%) for $C_{52}H_{52}AuClN_4O_2P_2Ru$ × $Et_2O$: C, 54.48; H, 5.07 N, 4.54. Found: C, 54.15; H 4.76; N, 4.74.

## b) Detailed NMR characterization of the obtained complexes

### RuBr(OAc)(PPh$_3$)(P-NHC) (1)



**1**

**Figure S-19:** Molecular structure of **1**.

The $^{31}$P NMR spectrum of **1** shows the presence of two closely related species in about 3 : 2 molar ratio, also confirmed by $^{1}$H and $^{13}$C NMR measurements, consistent with the presence of two conformers involving the P-NHC five-membered ring. Each isomer gives rise to a signal set comprising of two doublets at 72.6 ppm and 35.1 ppm or 72.5 ppm and 34.9 ppm, respectively. A *cis* RuP$_2$ arrangement has been assigned on the basis of the small $^{2}J_{PP}$ = 23.6 Hz (major isomer). The $^{13}$C NMR carbene of the major isomer shows signals at $\delta$ = 190.3 ppm, as a doublet of doublets with $^{2}J_{CP}$ = 109.6 and 11.6 Hz, for *trans* and *cis* P atoms, respectively, very close to those of the minor isomer ($\delta$ = 190.5 ppm), thus establishing the geometry of **1**. The rotation about the N–C$_{Mes}$ bond is hindered as there are separate signals for each methyl group present in the $^{1}$H- and $^{13}$C NMR (Figure S-20).

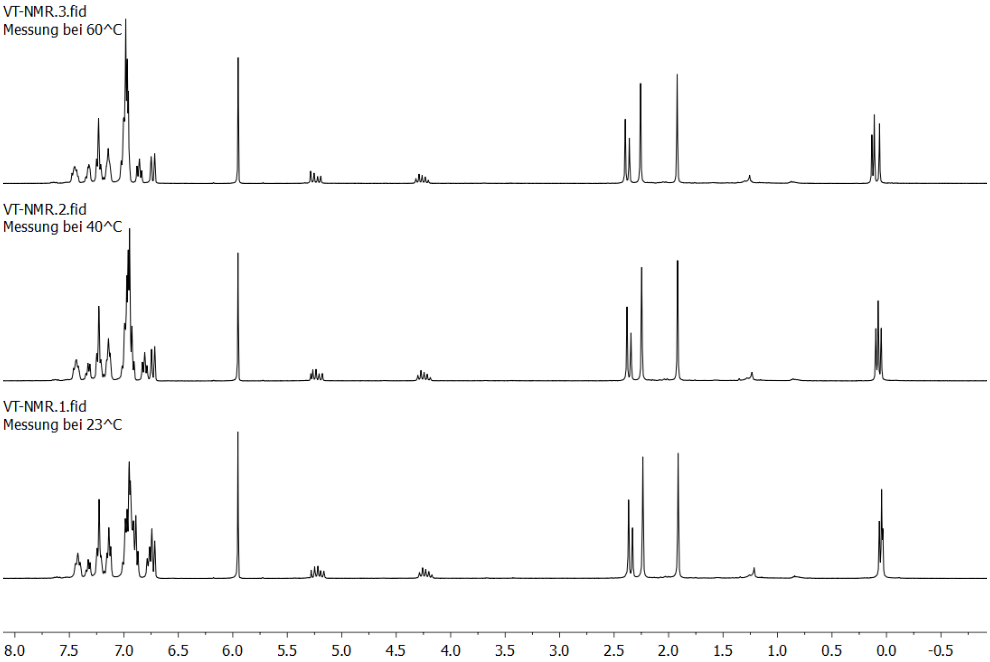


**Figure S-20:** $^{1}$H VT NMR of RuBr(OAc)(PPh$_3$)(P-NHC) showing hindered rotation of Mes group at 60 °C.

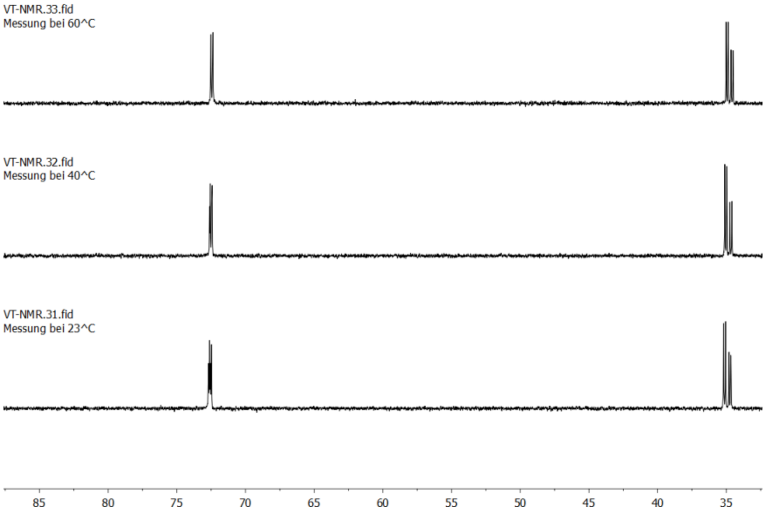
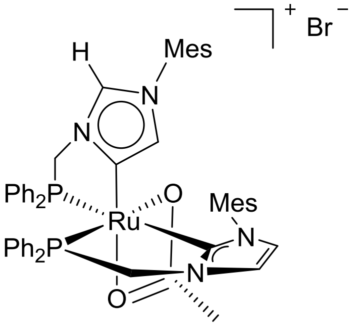


**Figure S-21:** $^{31}P$ {$^{1}H$} VT NMR of RuBr(OAc)(PPh$_3$)(P-NHC) showing the temperature independence of isomer distribution.

## [Ru(OAc)(P-aNHC)(P-NHC)]Br (2)

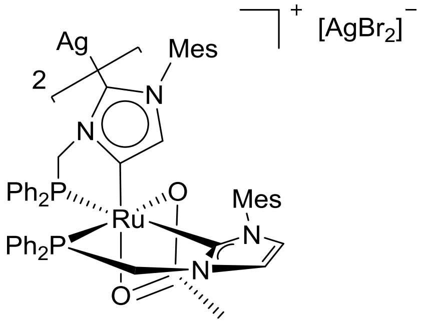


**2**

**Figure S-22:** Molecular structure of **2**.

The coordination of two carbene moieties becomes evident from the respective signals in the $^{13}C$ NMR in $CD_2Cl_2$: The normal carbene is found at 191.6 ppm and split into a doublet of doublets with a $^{13}C$–$^{31}P$ *cis*-coupling of 11.4 Hz and a *trans*-coupling of 102.5 Hz. The abnormal carbene is found at 163.0 ppm and exhibits two $^{13}C$–$^{31}P$ *cis*-couplings of 8.5 and 18.4 Hz. In the $^{31}P$ NMR, two doublets at 79.5 and 62.9 ppm are found, with a $^{31}P$–$^{31}P$ coupling constant of 23.9 Hz. In the $^{1}H$ NMR, the signal of the NCHN proton of the abnormal carbene is exceptionally downfield shifted and can be found at 9.75 ppm, which resembles the chemical shift of this proton in the ligand precursor P-NHC × HBr (10.33 ppm). Rotation about the N–$C_{Mes}$ bonds is hindered as seven separate signals are observed in the $^{1}H$ and $^{13}C$ NMR spectra.

### {Ag[Ru(OAc)(P-aNHC)(P-NHC)]$_2$}[AgBr$_2$] (3)

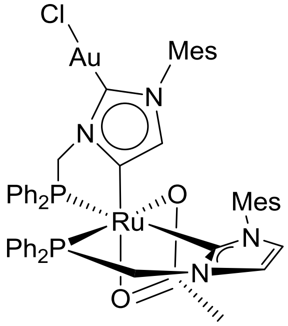


**3**

**Figure S-23:** Molecular structure of **3**.

The formation of the compound is evidenced by two doublets in the $^{31}$P NMR at 81.0 ppm and 56.3 ppm with a $^{31}$P–$^{31}$P coupling constant of 24 Hz. In the $^{13}$C NMR, the signal of the normally coordinated carbene atom at 193.2 ppm exhibits a similar chemical shift as in **2**, while the signal of the C4 carbon atom of the anionic dicarbene moiety is found at 154.7 ppm (compared to 163.0 ppm in for the related carbon atom in **2**) upon coordination of the silver atom in C2-position. The signal of the C2 carbene remains absent in the room temperature $^{13}$C NMR spectrum of **3**, most probably due to a dynamic process involving the [AgBr$_2$]$^-$ counter ion, a phenomenon which is reported for other silver carbene complexes bearing silver halide anions.[9, 10]

### AuCl[Ru(OAc)(P-aNHC)(P-NHC)] (4)



**4**

**Figure S-24:** Molecular structure of **4**.

In the $^{13}$C NMR spectrum, the normal carbene appears as a doublet of doublets at 192.9 ppm, and the C4 carbon atom of the anionic dicarbene can be found as a doublet of doublets at 155.2 ppm. The C2 carbon atom signal at 167.3 ppm appears as a doublet with a $^{13}$C–$^{31}$P coupling constant of 12.7 Hz due to $^3J_{\mathrm{CP}}$ coupling across the bridging methylene unit. In the $^{31}$P NMR spectrum; two doublets are found at 80.7 ppm and 56.7 ppm (compared to 81.0 ppm and 56.3 ppm for **3**) with a $^{31}$P–$^{31}$P coupling constant of 24 Hz.

# c) Catalysis

## General Procedure for Transfer Hydrogenation Catalysis

Catalytic transfer hydrogenation reactions were carried out under an argon atmosphere in Schlenk tubes. In a typical experiment, the reactor was charged with 2-propanol (9.8 ml), the ketone (1 mmol), and the respective amount of catalyst (0.05 – 0.1 mol%). The mixture was heated to reflux for 1 min and a 0.1M solution of NaOiPr in 2-propanol (200 µl, 0.05 mmol, 5 mol%) was added to the stirred mixture. 0.5 mL aliquots of the reaction mixture were taken at the required reaction times and immediately quenched with 1 mL of diethyl ether in a GC vial. The mixture was filtrated over a short pad of silica and analyzed by gas chromatography.

**Table S-1:** Catalytic transfer hydrogenation of ketones using **2.**

| Substrate | Cat [mol%] | Conversion [%]$^{a,b}$ | Time [min] | TOF [1/h]$^{c}$ |
|---|---|---|---|---|
| Acetophenone | 0.1 | 97 | 20 | 13000 |
| Benzophenone | 0.1 | 90 | 80 | 2750 |
| Cyclohexanone | 0.1 | 99 | 5 | 49000 |
| Cyclohexanone | 0.05 | 98 | 5 | 55000 |

Reaction conditions: Ketone (1 mmol), NaO*i*Pr (0.05 mmol, 5 mol%), *i*PrOH (10 mL), 82 °C. $^{a}$Conversions determined via GC analysis as average over two catalytic runs. $^{b}$As already reported in literature,[11] product formation was also observed without catalyst (Acetophenone: 2%, Benzophenone: 5%, Cyclohexanone: 1%). $^{c}$Turnover frequency (TOF) given at 50% conversion (TOF$_{50}$).

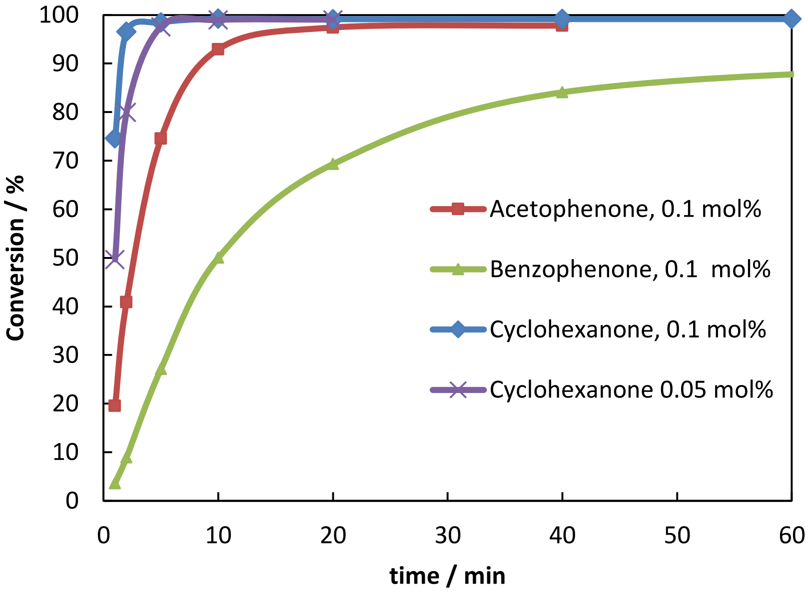


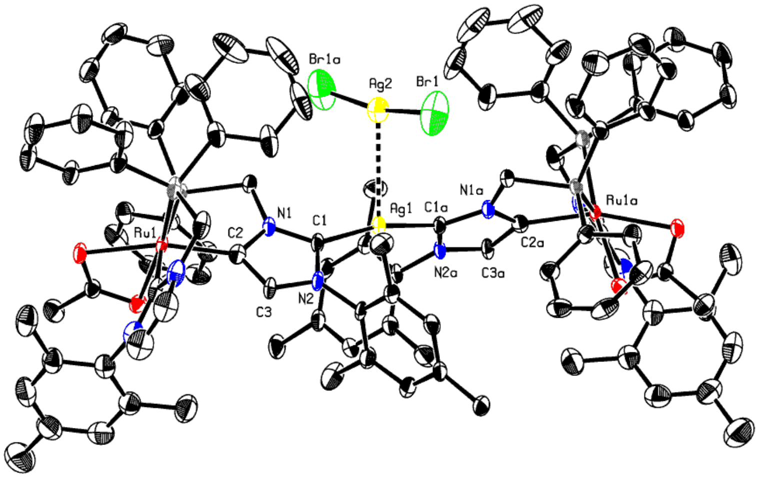
**Figure S-25:** Catalytic performance of **2** in the transfer hydrogenation of ketones.

# d) Crystallographic Data

### *General*

Data were collected on a single crystal X-ray diffractometer equipped with a CCD detector (APEX II, $\kappa$-CCD), a fine-focus sealed tube with $\mathrm{MoK}_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a graphite monochromator (compound **4**), or a rotating anode FR591 equipped with a Montel mirror optic (compound **3**) by using the SMART software package.[12] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[13] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[13] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps,[14] and were refined against all data using the APEX 2 software[12] in conjunction with SHELXL-97 or SHELXL-2014[15] and SHELXLE.[16] Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{\mathrm{iso(H)}} = 1.5 \cdot U_{\mathrm{eq(C)}}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{\mathrm{iso(H)}} = 1.2 \cdot U_{\mathrm{eq(C)}}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97[15] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[17] Images of the crystal structures were generated with Mercury (Version 3.3).[18]

### *Compound 3 (CCDC 1036993)*



Diffractometer operator C. Jandl
scanspeed 5s per frame
dx 70 mm
7257 frames measured in 20 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

*Crystal data*

**$C_{104}H_{104}Ag_2Br_2N_8O_4P_4Ru_2$**

$M_r$ = 2235.17

$D_x$ = 1.396 Mg m$^{-3}$

Monoclinic, *I*2/*a*

Melting point: ? K

Hall symbol: -I 2ya

Mo *K*α radiation, λ = 0.71073 Å

*a* = 17.5519 (5) Å

Cell parameters from 9606 reflections

*b* = 28.3440 (7) Å

θ = 2.2–28.3°

*c* = 21.9816 (9) Å

μ = 1.51 mm$^{-1}$

β = 103.863 (2)°

*T* = 123 K

*V* = 10617.1 (6) Å$^3$

Fragment, yellow-orange

*Z* = 4

0.30 × 0.27 × 0.23 mm

*F*(000) = 4512

*Data collection*

Bruker APEX-II CCD diffractometer

Radiation source: rotating anode FR591

MONTEL optic monochromator

Detector resolution: 16 pixels mm$^{-1}$

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS*, Bruker, 2008b

$T_{\min} = 0.667$, $T_{\max} = 0.746$

166767 measured reflections

9736 independent reflections

8899 reflections with $i > 2\sigma(i)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 25.4°$, $\theta_{\min} = 1.9°$

$h = -21$   $21$

$k = -34$   $34$

$l = -26$   $26$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.181$

$S = 1.04$

9736 reflections

576 parameters

0 restraints

? constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.1087P)^2 + 116.4003P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.75$ e Å$^{-3}$

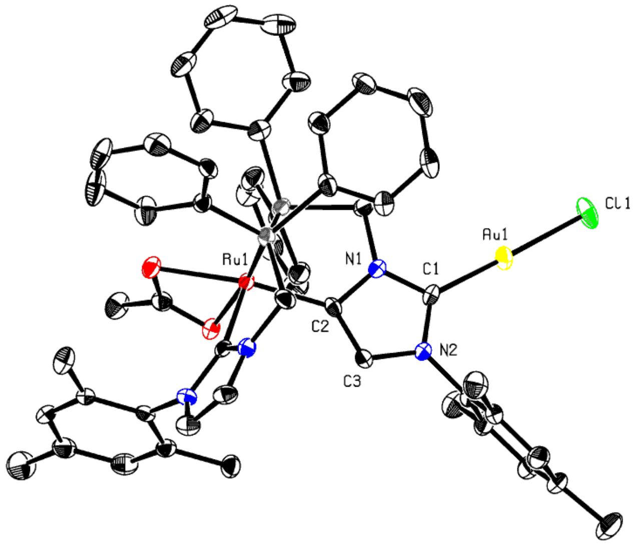
$\Delta\rho_{\min} = -3.44$ e Å$^{-3}$

Extinction correction: none

Extinction coefficient: ?

Refinement on $F^2$ for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The observed criterion of $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

## *Compound 4 (CCDC 1036994)*



Diffractometer operator C Jandl
scanspeed 30 s per frame
dx 50 mm
3297 frames measured in 6 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

*Crystal data*

**$C_{52}H_{52}AuClN_4O_2P_2Ru$**

$M_r$ = 1160.45

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a$ = 16.5689 (8) Å

$b$ = 16.4932 (9) Å

$c$ = 19.4827 (10) Å

$D_x$ = 1.540 Mg m$^{-3}$

Melting point: ? K

Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å

Cell parameters from 9583 reflections

$\theta$ = 2.3–25.6°

$\mu$ = 3.39 mm$^{-1}$

$\beta$ = 109.963 (3)°

$V$ = 5004.2 (5) Å$^3$

$Z$ = 4

$F(000)$ = 2312

$T$ = 123 K

Fragment, yellow

0.30 × 0.24 × 0.19 mm

*Data collection*

Bruker APEX-II CCD diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16 pixels mm$^{-1}$

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS*, Bruker, 2008b

$T_{\min}$ = 0.671, $T_{\max}$ = 0.745

79515 measured reflections

10030 independent reflections

7673 reflections with $i > 2\sigma(i)$

$R_{\text{int}}$ = 0.066

$\theta_{\max}$ = 26.4°, $\theta_{\min}$ = 2.2°

$h$ = −20 20

$k$ = −20 20

$l$ = −24 24

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.033

$wR(F^2)$ = 0.078

$S$ = 1.05

10030 reflections

575 parameters

0 restraints

? constraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.0372P)^2]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.002

$\Delta\rho_{\max}$ = 1.04 e Å$^{-3}$

$\Delta\rho_{\min}$ = −1.25 e Å$^{-3}$

Extinction correction: none

Extinction coefficient: ?

Primary atom site location: structure-invariant direct methods

Refinement on $F^2$ for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

# e) References

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