Supplementary material

Antitumor activity of new hydridotris(pyrazolyl)borate ruthenium(II) complexes containing the water-soluble phosphanes 1,3,5-triaza-7-phosphaadamantane (PTA) and 1-methyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane (1-CH_3-PTA)

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Experimental

Synthesis of complexes [RuCl{κ^3(N,N,N)-Tp}(L)(PTA)] (L = PMe_2Ph (1c), PMe_3 (1d), $P(OMe)_3$ (1e), $P(OPh)_3$ (1f)).

To a solution of [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] complex (100 mg, 0.13 mmol) in toluene (10 mL), an excess of the corresponding phosphane or phosphite was added and the mixture was heated at reflux temperature. Once the reaction was completed, the solvent was removed under reduced pressure and the solid residue was dissolved in dichloromethane (0.5 mL). Addition of hexane (60 mL) afforded the desired product as a pale yellow (**1c**) or white (**1d-f**) precipitate. In the synthesis of [RuCl{κ^3(*N,N,N*)-Tp}(PMe_3)(PTA)] complex (**1d**), the reaction mixture was heated at 125º C using a pressure tube. **1c** (56 mg, 67%): Stoichiometry 1:1.5. Reaction time: 6 h. $S_{20ºC}$ (H_2O) = 3.0 mg/mL. IR(KBr): ν_{max}/cm^{-1} 2462 (BH). ^{1}H-NMR δ_H(400.1 MHz, CD_2Cl_2, 20º C) 8.02 (d, 1H, H^{3,5} (pz)), 7.80 (d, 1H, H^{3,5} (pz)), 7.69 (d, 1H, H^{3,5} (pz)), 7.65 (d, 1H, H^{3,5} (pz)), 7.58 (d, 1H, H^{3,5} (pz)), 7.45 - 7.35 (m, 5H, Ph), 7.13 (d, 1H, H^{3,5} (pz)), 6.25 (t, 1H, H^4 (pz)), 6.19 (t, 1H, H^4 (pz)), 6.05 (t, 1H, H^4 (pz)), 4.44 (AB spin system, 3H, J_{AB} = 13 Hz, NCH_2N), 4.28 (AB spin system, 3H, J_{AB} = 13 Hz, NCH_2N), 3.95 (AB spin system, 3H, J_{AB} = 15 Hz, NCH_2P), 3.71 (AB spin system, 3H, J_{AB} = 15 Hz, NCH_2P), 1.89 (d, 3H, $^2J_{HP}$ = 9 Hz, P(CH_3)$_2$Ph), 1.55 (d, 3H, $^2J_{HP}$ = 9 Hz, P(CH_3)$_2$Ph). ^{13}C- NMR δ_C(100.6 MHz, CD_2Cl_2, 20º C) 147.1 (C-3 (pz)), 143.5 (C-3(pz)), 143.0 (C-3 (pz)), 142.3 (d, J_{CP} = 37 Hz, C-1 Ph), 136.3 (C-5 (pz)), 135.5 (C-5 (pz)), 129.9 (d, 2C, $^2J_{CP}$ = 8 Hz, C-2,6 Ph), 128.9 (C-4 Ph), 128.4 (d, 2C, $^3J_{CP}$ = 8 Hz, C-3,5 Ph), 105.7 (C-4 (pz)), 105.1 (C-4 (pz)), 104.9 (C-4 (pz)), 73.2 (d, 3C, $^3J_{CP}$ = 5 Hz, NCH_2N), 52.2 (d, 3C, J_{CP} = 14 Hz, NCH_2P), 17.1 (d, J_{CP} = 29 Hz, P(CH_3)$_2$Ph), 15.2 (d, J_{CP} = 29 Hz, P(CH_3)$_2$Ph). ^{31}P-NMR δ_P(161.9 MHz, CD_2Cl_2, 20º C) 21.1 (d, $^2J_{PP}$ = 36 Hz, PMe_2Ph), -26.6 (d, $^2J_{PP}$ = 36 Hz, PTA). Found: C, 42.68; H, 4.75; N,19.52. Calc. for $C_{23}H_{33}BClN_9P_2Ru$: C, 42.84; H, 5.16; N, 19.55. **1d** (34 mg, 45 %): Stoichiometry 1:5. Reaction time: 4 h. $S_{20ºC}$ (H_2O) = 3.8 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2468 (BH)). ^{1}H-NMR δ_H(400.1 MHz, CD_2Cl_2, 20º C) 7.98 (d, 1H, H^{3,5} (pz)), 7.85(d, 1H, H^{3,5} (pz)), 7.78 (d, 1H, H^{3,5} (pz)), 7.71 (d, 2H, H^{3,5} (pz)), 7.29 (d, 1H, H^{3,5} (pz)), 6.24 – 6.21 (m, 3H, H^4 (pz)), 4.57 (AB spin system, 3H, J_{AB} = 13 Hz, NCH_2N), 4.48 (AB spin system, 3H, J_{AB} = 13 Hz, NCH_2N), 4.26 (AB spin system, 3H, J_{AB} = 15 Hz, NCH_2P), 4.17 (AB spin system, 3H, J_{AB} = 15 Hz, NCH_2P), 1.37 (d, 9H, $^2J_{HP}$ = 8 Hz, P(CH_3)$_3$). ^{13}C- NMR δ_C(100.6 MHz, CD_2Cl_2, 20º C) 146.6 (C-3 (pz)), 143.8 (C-3 (pz)), 142.7 (C-3 (pz)), 136.4 (C-5 (pz)), 135.1 (C-5 (pz)), 134.8 (C-5 (pz)), 105.8 (C-4 (pz)), 105.1 (C-4 (pz)), 105.0 (C-4 (pz)), 73.4 (d, 3C, $^3J_{CP}$ = 6 Hz, NCH_2N), 53.3 (d, 3C, J_{CP} = 14 Hz, NCH_2P), 18.1 (d, 3C, J_{CP} = 29 Hz, P(CH_3)$_3$). ^{31}P-NMR δ_P(161.9 MHz, CD_2Cl_2, 20º C) 13.9 (d, J_{PP} = 39 Hz,

$P(CH_3)_3$), -30.0 (d, J_{PP} = 39 Hz, PTA). Found: C, 35.29; H, 5.55; N, 20.00. Calc. for $C_{18}H_{31}BClN_9P_2Ru\cdot 1/2CH_2Cl_2$: C, 35.54; H, 5.16; N, 20.16. **1e** (40 mg, 49%): Stoichiometry 1:10. Reaction time: 5 h. $S_{20ºC}$ (H_2O) = 3.0 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2478 (BH). ^{1}H-NMR δ_H(400.1 MHz, CD_2Cl_2, 20º C) 8.00 (d, 1H, $H^{3,5}$ (pz)), 7.84 (d, 1H, $H^{3,5}$ (pz)), 7.74 (d, 2H, $H^{3,5}$ (pz)), 7.69 (d, 1H, $H^{3,5}$ (pz)), 7.62 (d, 1H, $H^{3,5}$ (pz)), 6.28 (t, 1H, H^4 (pz)), 6.23 (t, 1H, H^4 (pz)), 6.15 (t, 1H, H^4 (pz)), 4.54 (AB spin system, 3H, J_{AB} = 13 Hz, NCH_2N), 4.45 (AB spin system, 3H, J_{AB} = 13 Hz, NCH_2N), 4.29 – 4.14 (m, 6H, NCH_2P), 3.35 (d, 9H, $^3J_{HP}$ = 10 Hz, $P(OCH_3)_3$). ^{13}C- NMR δ_C(100.6 MHz, CD_2Cl_2, 20º C) 147.4 (C-3 (pz)), 143.7 (C-3 (pz)), 143.5 (C-3 (pz)), 136.4 (C-5 (pz)), 135.0 (C-5 (pz)), 134.4 (C-5 (pz)), 105.5 (2C, C-4 (pz)), 105.0 (C-4 (pz)), 73.3 (d, 3C, $^3J_{CP}$ = 6 Hz, NCH_2N), 52.9 (d, 3C, J_{CP} = 15 Hz, NCH_2P), 51.3 (d, 3C, $^2J_{CP}$ = 6 Hz, $P(OCH_3)_3$). ^{31}P-NMR δ_P(161.9 MHz, CD_2Cl_2, 20º C) 151.5 (d, J_{PP} = 64 Hz, $P(OCH_3)_3$), -32.3 (d, J_{PP} = 64 Hz, PTA). Found: C, 34.34, H, 4.98; N, 19.78 (M^+, 632). Calc. for $C_{18}H_{31}BClN_9O_3P_2Ru$: C, 34.27; H, 4.95; N, 19.98. **1f** (59 mg, 56 %): Stoichiometry 1:10. Reaction time: 6 h. $S_{20ºC}$ (H_2O) = 4.0 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2480 (BH). cm^{-1}. ^{1}H-NMR δ_H(400.1 MHz, acetonitrile-d_3, 20º C) 8.10 (d, 1H, $H^{3,5}$ (pz)), 8.01 (d, 1H, $H^{3,5}$ (pz)), 7.90 (d, 1H, $H^{3,5}$ (pz)), 7.77 (d, 1H, $H^{3,5}$ (pz)), 7.56 (d, 1H, $H^{3,5}$ (pz)), 7.42 (d, 1H, $H^{3,5}$ (pz)), 7.11 – 7.07 (m, 6H, Ph), 7.01 – 6.98 (m, 3H, Ph), 6.81 – 6.79 (m, 6H, Ph), 6.31 (br, 2H, H^4 (pz)), 5.67 (t, 1H, H^4 (pz)), 4.50 (s, 6H, NCH_2N), 4.30 (s, 6H, NCH_2P). ^{13}C- NMR δ_C(100.6 MHz, acetonitrile-d_3, 20º C) 152.4 (d, 3C, $^2J_{CP}$ = 13 Hz, C-1 Ph), 147.6 (C-3 (pz)), 144.1 (C-3 (pz)), 143.5 (C-3 (pz)), 137.0 (C-5 (pz)), 135.3 (C-5 (pz)), 134.3 (C-5 (pz)), 129.1 (6C, C-2,6 Ph), 123.8 (3C, C-4 Ph), 120.1 (d, 6C, $^4J_{CP}$ = 4 Hz, C-3,5 Ph), 106.4 (C-4 (pz)), 105.5 (C-4 (pz)), 105.1 (C-4 (pz)), 72.7 (d, 3C, $^3J_{CP}$ = 6 Hz, NCH_2N), 52.3 (d, 3C, J_{CP} = 16 Hz, NCH_2P). ^{31}P-NMR δ_P(161.9 MHz, acetonitrile-d_3, 20º C) 128.7 (d, J_{PP} = 64 Hz, $P(OPh)_3$), -34.9 (d, J_{PP} = 64 Hz, PTA). Found: C, 48.43; H, 4.50; N 15.35 (M^+, 818). Calc. for $C_{33}H_{37}BClN_9O_3P_2Ru$: C, 48.51; H, 4.56; N, 15.43.

Synthesis of complexes [RuCl{κ^3(N,N,N)-Tp}(L)(1-CH_3-PTA)][CF_3SO_3] (L = PMe_2Ph (2c), PMe_3 (2d), $P(OMe)_3$ (2e), $P(OPh)_3$ (2f)).

Methyl triflate (16 µL, 0.13 mmol) was added to a solution of corresponding complex [RuCl(Tp)(L)(PTA)] (L = PMe_2Ph (**1c**), PMe_3 (**1d**), $P(OMe)_3$ (**1e**), $P(OPh)_3$ (**1f**)) (0.13 mmol) in dichloromethane (2 mL) at -30º C. The reaction mixture was stirred at -30º C for 40 minutes. Addition of hexane (30 mL) afforded a precipitate. The solvents were decanted and the solid was washed with hexane (3 x 5 mL) and dried under reduced pressure. **2c** (66 mg, 63 %): Conductivity (acetonitrile, 20º C): Λ = 128 $S\cdot cm^2\cdot mol^{-1}$. $S_{20ºC}$ (H_2O) = 1.9 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2481 (BH), 1258, 1163, 1031 (CF_3SO_3). ^{1}H-NMR δ_H(400.1 MHz, acetonitrile-d_3, 20º C) 8.04 (d, 1H, $H^{3,5}$ (pz)), 7.90 (d, 1H, $H^{3,5}$ (pz)), 7.78 (d, 1H, $H^{3,5}$ (pz)), 7.72 (d, 1H, $H^{3,5}$ (pz)), 7.56 (d, 1H, $H^{3,5}$ (pz)), 7.43 – 7.34 (m, 6H, Ph and $H^{3,5}$ (pz)), 6.29 (br, 2H, H^4 (pz)), 6.06 (t, 1H, H^4 (pz)), 4.75 – 4.65 (m, 4H, 1-CH_3-PTA), 4.31 – 3.65 (m, 6H, 1-CH_3-PTA), 3.55 (AB spin system, 1H, J_{AB} = 15 Hz, 1-CH_3-PTA), 3.34 (AB spin system, 1H, J_{AB} = 15 Hz, 1-CH_3-PTA), 2.62 (s, 3H, CH_3N), 1.83 (d, 3H, $^2J_{HP}$ = 9 H, $P(CH_3)_2Ph$), 1.49 (d, 3H, $^2J_{HP}$ = 9 Hz, $P(CH_3)_2Ph$). ^{13}C- NMR δ_C(100.6 MHz, acetonitrile-d_3, 20º C) 147.9 (C-3 (pz)), 143.9 (C-3 (pz)), 143.2 (C-3 (pz)), 141.7 (d, J_{CP} = 43 Hz, C-1 Ph), 136.9 (C-5 (pz)), 135.7 (C-5 (pz)), 135.4 (C-5 (pz)), 129.9 (d, 2C, $^2J_{CP}$ = 9 Hz, C-2,6 Ph), 129.4 (C-4 Ph), 128.8 (d, 2C, $^2J_{CP}$ = 9 Hz, C-3,5 Ph), 121.2 (q, J_{CF} = 254 Hz, CF_3SO_3), 106.7 (C-4 (pz)), 105.7 (C-4 (pz)), 105.2 (C-4 (pz)), 80.4 (d, 2C, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 69.0 (d, $^3J_{CP}$ = 5 Hz, NCH_2N), 57.7 (d, J_{CP} = 6 Hz, CH_3NCH_2P), 49.0 (CH_3N), 48.3 (d, J_{CP} = 15 Hz, NCH_2P), 47.9 (d, J_{CP} = 15 Hz, NCH_2P), 16.3 (d, J_{CP} = 30 Hz, $P(CH_3)_2Ph$), 14.2 (d, J_{CP} = 30 Hz, $P(CH_3)_2Ph$). ^{31}P-NMR δ_P(161.9 MHz, acetonitrile-d_3, 20º C) 18.8 (d, J_{PP} = 35 Hz, PMe_2Ph), -8.2 (d, J_{PP} = 35 Hz, 1-CH_3-PTA). Found: C, 36.30; H, 5.52; N, 15.08; S, 3.86 (M^+, 660). Calc. for $C_{25}H_{36}BClF_3N_9O_3P_2RuS\cdot 1/4CH_2Cl_2$: C, 36.53; H, 5.43; N, 15.18; S, 3.86. **2d** (58 mg, 60 %): Conductivity (acetonitrile, 20º C): Λ = 130 $S\cdot cm^2\cdot mol^{-1}$. $S_{20ºC}$ (H_2O) = 2.8 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2481 (BH), 1259, 1162, 1031 (CF_3SO_3). ^{1}H-NMR δ_H(400.1 MHz, acetonitrile-d_3, 20º C) 7.98 (d, 1H, $H^{3,5}$ (pz)), 7.86 (d, 2H, $H^{3,5}$ (pz)), 7.78 (d, 2H, $H^{3,5}$ (pz)), 7.41 (d, 1H, $H^{3,5}$ (pz)), 6.27 (br, 2H, H^4 (pz)), 6.25 (t, 1H, H^4 (pz)), 4.88 – 4.82 (m, 4H, 1-CH_3-PTA), 4.44 – 4.37 (m, 4H, 1-CH_3-PTA), 4.21 – 4.16 (m, 2H, 1-CH_3-PTA), 3.93 (br, 2H, 1-CH_3-PTA), 2.73 (s, 3H, CH_3N), 1.32 (d, 9H, $^2J_{HP}$ = 9 Hz, $P(CH_3)_3$). ^{13}C-NMR δ_C(100.6 MHz, acetonitrile-d_3, 20º C) 147.3 (C-3 (pz)), 144.0 (C-3 (pz)), 143.0 (C-3 (pz)), 136.9 (C-5 (pz)), 135.7 (C-5 (pz)), 135.3 (C-5 (pz)), 121.1 (q, J_{CF} = 263 Hz, CF_3SO_3), 106.6 (C-4 (pz)), 105.5 (C-4 (pz)), 105.4 (C-4 (pz)), 80.6 (d, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 80.5 (d, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 69.1 (d, $^3J_{CP}$ = 5 Hz, NCH_2N), 58.4 (d, J_{CP} = 6 Hz, CH_3NCH_2P), 49.5 (d, J_{CP} = 16 Hz, NCH_2P), 49.0 (d, J_{CP} = 16 Hz, NCH_2P), 48.9 (CH_3N), 17.3 (d, 3C, J_{CP} = 30 Hz, $P(CH_3)_3$). ^{31}P-NMR δ_P(161.9 MHz, acetonitrile-d_3, 20º C) 11.6 (d, J_{PP} = 38 Hz, PMe_3), -6.7 (d, J_{PP} = 38 Hz, 1-CH_3-PTA). Found: C, 32.11; H, 4.56; N, 16.79; S, 3.86. Calc. for $C_{20}H_{34}BClF_3N_9O_3P_2RuS$: C, 32.16 H, 4.59; N, 16.88; S, 4.29. **2e** (67 mg, 65%): Conductivity (acetonitrile, 20º C): Λ = 116 $S\cdot cm^2\cdot mol^{-1}$. $S_{20ºC}$ (H_2O) = 3.0 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2485 (BH), 1260, 1163, 1031 (CF_3SO_3). ^{1}H-NMR δ_H(400.1 MHz, acetonitrile-d_3, 20º C) 7.98 (d, 1H, $H^{3,5}$ (pz)), 7.84 (br, 4H, $H^{3,5}$ (pz)), 7.79 (d, 1H, $H^{3,5}$ (pz)), 6.33 (t, 1H, H^4 (pz)), 6.28 (t, 1H, H^4 (pz)), 6.25 (t, 1H, H^4 (pz)), 4.85 – 4.83 (m, 4H, 1-CH_3-PTA), 4.43 – 4.40 (m, 4H, 1-CH_3-PTA), 4.17 (br, 2H, 1-CH_3-PTA), 4.06 – 4.00 (m, 2H, 1-CH_3-PTA), 3.37 (d, 9H, $^3J_{HP}$ = 11 Hz, $P(OCH_3)_3$), 2.76 (s, 3H, CH_3N). ^{13}C- NMR δ_C(100.6 MHz, acetonitrile-d_3, 20º C) 147.8 (C-3 (pz)), 143.9 (C-3 (pz)), 143.7 (C-3 (pz)), 137.1 (C-5 (pz)), 135.7 (C-5 (pz)), 135.0 (C-5 (pz)), 121.1 (q, J_{CF} = 320 Hz, CF_3SO_3), 106.2 (C-4 (pz)), 105.8 (C-4 (pz)), 105.6 (C-4 (pz)), 80.8 (d, $^3J_{CP}$ = 4 Hz, CH_3NCH_2N), 80.7

(d, $^{3}J_{CP}$ = 3 Hz, CH_3NCH_2N), 69.2 (d, $^{3}J_{CP}$ = 5 Hz, NCH_2N), 58.1 (d, J_{CP} = 9 Hz, CH_3NCH_2P), 51.7 (d, 3C, $^{2}J_{CP}$ = 7 Hz, $P(OCH_3)_3$), 49.2 (d, J_{CP} = 18 Hz, NCH_2P), 49.0 (CH_3N), 48.8 (d, J_{CP} = 16 Hz, NCH_2P). ^{31}P-NMR δ_P(161.9 MHz, acetonitrile-d_3, 20º C) 148.1 (d, J_{PP} = 65 Hz, $P(OMe)_3$), -8.2 (d, J_{PP} = 65 Hz, 1-CH_3-PTA). Found: C, 30.44; H, 4.43; N, 15.96; S, 3.86 (M^+, 646). Calc. for $C_{20}H_{34}BClF_3N_9O_6P_2RuS$: C, 30.22; H, 4.31; N, 15.86; S, 4.03. **2f** (83 mg, 65%): Conductivity (acetonitrile, 20º C): Λ = 141 $S{\cdot}cm^2{\cdot}mol^{-1}$. $S_{20ºC}$ (H_2O) = 1.5 mg/mL. IR (KBr): ν_{max}/cm^{-1} 2485 (BH), 1259, 1163, 1031 (CF_3SO_3). ^{1}H-NMR δ_H(400.1 MHz, acetonitrile-d_3, 20º C) 8.10 (d, 1H, $H^{3,5}$ (pz)), 8.04 (d, 1H, $H^{3,5}$ (pz)), 7.96 (d, 1H, $H^{3,5}$ (pz)), 7.82 (d, 1H, $H^{3,5}$ (pz)), 7.57 (d, 1H, $H^{3,5}$ (pz)), 7.44 (d, 1H, $H^{3,5}$ (pz)), 7.13 – 7.03 (m, 10H, Ph), 6.77 – 6.75 (m, 5H, Ph), 6.39 (t, 1H, H^4 (pz)), 6.35 (t, 1H, H^4 (pz)), 5.69 (t, 1H, H^4 (pz)), 4.99 – 4.87 (m, 3H, 1-CH_3-PTA), 4.55 – 4.37 (m, 7H, 1-CH_3-PTA), 4.06 (s, 2H, 1-CH_3-PTA), 2.79 (s, 3H, CH_3N). ^{13}C- NMR δ_C(100.6 MHz, acetonitrile-d_3, 20º C) 152.0 (d, 3C, $^{2}J_{CP}$ = 13 Hz, C-1 Ph), 147.7 (C-3 (pz)), 144.2 (C-3 (pz)), 143.6 (C-3 (pz)), 137.5 (C-5 (pz)), 135.8 (C-5 (pz)), 134.7 (C-5 (pz)), 129.3 (s, 6C, C-2,4 Ph), 124.2 (s, 3C, C-4 Ph), 124.1 (q, J_{CF} = 239 Hz, CF_3SO_3), 120.1 (d, 6C, $^{4}J_{CP}$ = 4 Hz, C-3,5 Ph), 107.0 (C-4 (pz)), 106.0 (C-4 (pz)), 105.4 (C-4 (pz)), 80.8 (d, $^{3}J_{CP}$ = 3 Hz, CH_3NCH_2N), 80.7 (d, $^{3}J_{CP}$ = 3 Hz, CH_3NCH_2N), 69.1 (d, $^{3}J_{CP}$ = 5 Hz, NCH_2N), 57.8 (d, J_{CP} = 10 Hz, CH_3NCH_2P), 49.3 (d, J_{CP} = 13 Hz, NCH_2P), 49.0 (s, CH_3N), 48.3 (d, J_{CP} = 16 Hz, NCH_2P). ^{31}P-NMR δ_P(161.9 MHz, acetonitrile-d_3, 20º C) 127.1 (d, J_{PP} = 65 Hz, $P(OPh)_3$), -10.0 (d, J_{PP} = 65 Hz, 1-CH_3-PTA). Found: C, 41.11; H, 4.43; N, 11.84; S, 3.40 (M^+, 832). Calc. for $C_{35}H_{40}BClF_3N_9O_6P_2RuS{\cdot}1/2CH_2Cl_2$: C, 41.66; H, 4.04; N, 12.32; S, 3.13.