Journal of Organometallic Chemistry 695 (2010) 162–169

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Alkyne activation by half-sandwich ruthenium(II) complexes bearing the water-soluble phosphane 1,3,5-triaza-7-phosphaadamantane (PTA)

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ARTICLE INFO

Article history:
Received 16 September 2009
Received in revised form 13 October 2009
Accepted 14 October 2009
Available online 20 October 2009

Keywords:
Water-soluble phosphanes
Hydridotris(pyrazolyl)borate
Alkyne activation
Ruthenium(II)

ABSTRACT

Complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] (κ^3(*N,N,N*)-Tp = hydridotris(pyrazolyl)borate) containing the water-soluble phosphane 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (PTA) reacts with terminal alkynes producing to the corresponding neutral alkynyl complexes [Ru(C≡CR){κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] (R = Ph (**1a**), ^{n}Bu (**1b**), 1-cyclopentenyl (**1c**), *p*-methoxyphenyl (**1d**), 6-methoxynaft-2-yl (**1e**)). When halide is extracted from complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] followed by treatment with propargyl alcohols, the corresponding allenylidene complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(C=C=CPh_2)][X] (X = PF_6 (**2a**), CF_3SO_3 (**2b**)) and [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(C=C=$CC_{12}H_8$)][PF_6] (**3**) result. Electrophilic attack on the complexes thus obtained leads chemoselectively to the alkynyl complexes [Ru(C≡CR){κ^3(*N,N,N*)-Tp}(PPh_3)(1-CH_3-PTA)][CF_3SO_3] (R = Ph (**4a**), ^{n}Bu (**4b**), and 1-cyclopentenyl (**4c**)) and to the dicationic allenylidene complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(1-H-PTA)(C=C=$CC_{12}H_8$)][PF_6]$_2$ (**5**) and [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(1-CH_3-PTA)(C=C=CPh_2)][CF_3SO_3]$_2$ (**6**).

1. Introduction

In recent years, environmental concerns have prompted a new approach to chemical technology in search of sustainable chemical processes. The replacement of organic solvents for water has attracted interest over the last few decades due to a large extent to the aqueous-biphasic technology in catalysis [1,2]. Moreover, the use of transition metal complexes as antitumoral drugs [3,4] has heightened interest in this type of chemistry, since the complexes must be stable at physiological pH.

One of the most common approaches to obtaining water-soluble organometallic compounds is by means of ligands with hydrophilic properties. Among water-soluble phosphanes, particular attention is recently being paid to the cage-like tertiary phosphane 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (PTA) (Fig. 1) [5] whose high solubility in water has been ascribed to the extensive participation of its three nitrogen atoms in hydrogen interactions with water molecules.

Thus, water-soluble ruthenium(II) complexes, particularly those containing the PTA ligand have been used in stoichiometric processes [6], catalysis [7,8] and in biological assays [9–14].

In a previous work, we reported the synthesis, and biological interest of a series of ruthenium(II) complexes containing the phosphane PTA ligand [RuX{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] [15]. Electrophilic attacks on one of the nitrogen atoms of the PTA phosphane as well as unprecedented formal C–H activation processes on the former ligands have been also reported [16].

Continuing with our interest in the chemistry of ruthenium(II) complexes containing PTA ligand, we describe the reactivity of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] towards terminal alkynes yielding the first alkynyl, and allenylidene complexes of ruthenium(II) containing the PTA phosphane as well as their reaction with electrophiles.

2. Experimental

2.1. General procedures

All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried following standard methods and distilled under nitrogen before use. The compound [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] was prepared by a previously reported method [15]. Infrared spectra were recorded on a Perkin–Elmer FT-IR Paragon 1000 spectrometer. The C, H, and N analyses were carried out with a C, N, H, S Perkin–Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker AC-400 instrument at 400.1 MHz (^{1}H), 161.9 (^{31}P) or 100.6 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all the compounds. Coupling constants *J* are given in hertzs.

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doi:10.1016/j.jorganchem.2009.10.017

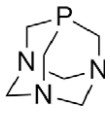
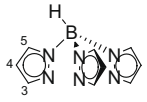


Fig. 1. 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (PTA).

Resonances due to the Tp ligand are reported by chemical shift and multiplicity only, since all $^3J_{HH}$ values for pyrazolyl rings are 2 Hz. Abbreviations used: br, broad signal; s, singlet; d, doublet; dd, doublet of doublets; m, multiplet; q, quartet; quin, quintuplet; sext, sextuplet; t, triplet. The following atom labels have been used for the ^{1}H and ^{13}C{^{1}H} spectroscopic data of the hydridotris(pyrazolyl)borate(Tp) ligand:



*2.2. Synthesis of complexes [Ru(C≡CR){κ^3(N,N,N)-Tp}(PPh$_3$)(PTA)] (R = Ph (**1a**), ^{n}Bu (**1b**), 1-cyclopentenyl (**1c**), p-methoxyphenyl (**1d**), 6-methoxynaft-2-yl (**1e**))*

To a solution of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (0.13 mmol, 100 mg) in methanol (10 mL), triethylamine (1.3 mmol, 227 μL) and the corresponding alkyne (1.3 mmol) were added. The reaction mixture was refluxed for 6 h. After cooling to room temperature, the solvents were decanted and the yellow solid residue was washed with hexane (5 × 5 mL) and dried under reduced pressure.

For complex **1c** chromatographic purification, using methanol as eluent was required.

*2.2.1. Complex **1a***

Yield: 75 mg (69%). IR (KBr): 2487 (BH), 2082 (C≡C). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 8.30 (d, 1H, H^{3,5} (pz)), 7.85–7.60 (m, 9H, H^{3,5} (pz) and Ph), 7.39–7.25 (m, 13H, Ph), 7.10–7.05 (m, 1H, Ph), 6.69 (d, 1H, H^{3,5} (pz)), 6.27–6.25 (m, 2H, H^{3,5} y H^4 (pz)), 5.86 (t, 1H, H^4 (pz)), 5.79 (t, 1H, H^4 (pz)), 4.37 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 4.19 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 3.84 (s, 6H, NCH_2P). ^{13}C{^{1}H} NMR (75.4 MHz, dichloromethane-d_2): 144.5 (s, C-3 (pz)), 144.2 (s, C-3 (pz)), 137.2 (d, J_{CP} = 39 Hz, C-1 PPh$_3$), 135.7 (s, C-5 (pz)), 135.4 (s, C-5 (pz)), 135.0 (s, C-5 (pz)), 134.5 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh$_3$), 130.8 (s, C-4 PPh$_3$),130.7 (s, C-1 Ph), 129.5 (s, C-2 and C-6 Ph), 128.2 (m, C-3,5 PPh$_3$, C-3 and C-5 Ph), 126.7 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 16 Hz, Cα), 123.6 (s, C-4 Ph), 111.2 (s, C$_β$), 105.6 (s, C-4 (pz)),105.4 (s, C-4 (pz)), 104.8 (s, C-4 (pz)), 73.5 (d, $^3J_{CP}$ = 6 Hz, NCH_2N), 52.8 (d, J_{CP} = 14 Hz, NCH_2P). ^{31}P{^{1}H} NMR (121.5 MHz, dichloromethane-d_2): 53.9 (d, $^2J_{PP}$ = 34 Hz, PPh$_3$), −31.5 (d, $^2J_{PP}$ = 34 Hz, PTA). Anal. Calc. for $C_{41}H_{42}BN_9P_2Ru$: C, 59.00; H, 5.07; N, 15.10. Found: C, 58.98; H, 5.21; N, 15.26%.

*2.2.2. Complex **1b***

Yield: 42 mg (40%). IR (KBr): 2486 (BH), 2095 (C≡C). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 8.26 (s, 1H, H^{3,5} (pz)), 7.83–7.77 (m, 5H, PPh$_3$), 7.65–7.63 (m, 2H, H^{3,5} (pz)), 7.59 (d, 1H^{3,5}(pz)), 7.36–7.26 (m, 10H, PPh$_3$), 6.70 (d, 1H, H^{3,5} (pz)), 6.22 (t, 1H, H^4 (pz)), 6.19 (d, 1H, H^{3,5} (pz)), 5.81 (t, 1H, H^4 (pz)), 5.76 (t, 1H, H^4 (pz)), 4.36 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 4.18 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 3.78 (s, 6H, NCH_2P), 2.56 (t, J_{HH} = 7 Hz, 2H, CH_2CH$_2$CH$_2$), 1.69 (quin, J_{HH} = 7 Hz, 2H, CH$_2$CH_2CH$_2$), 1.59 (sext, J_{HH} = 7 Hz, 2H, CH_2CH$_3$), 1.02 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75.4 MHz, dichloromethane-d_2): 144.5 (s, C-3 (pz)), 144.4 (s, C-3 (pz)), 144.3 (s, C-3 (pz)), 137.8 (d, J_{CP} = 38 Hz, C-1 PPh$_3$), 135.5 (s, C-5 (pz)), 135. 1 (s, C-5 (pz)), 134.8 (s, C-5 (pz), 134.4 (d, $^2J_{CP}$ = 10 Hz, C-2,6 PPh$_3$)), 129.3 (s, 3C, C-4 PPh$_3$), 128.0 (d, $^3J_{CP}$= 9 Hz, C-3,5 PPh$_3$), 107.7 (s, C$_β$), 105.3 (s, C-4 (pz)), 105.2 (s, C-4 (pz)), 104.6 (s, C-4 (pz)), 101.6 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 20 Hz, C$_α$), 73.5 (d, $^3J_{CP}$ = 7 Hz, NCH_2N), 52.9 (d, J_{CP} = 15 Hz, NCH_2P), 34.5 (s, CH_2CH$_2$CH$_2$), 23.1 (s, CH$_2$CH_2CH$_2$), 22.7 (s, CH_2CH$_3$), 14.3 (s, CH_3). ^{31}P{^{1}H} NMR (161.9 MHz, dichloromethane-d_2): 54.2 (d, $^2J_{PP}$ = 34 Hz, PPh$_3$), −30.7 (d, $^2J_{PP}$ = 34 Hz, PTA). Anal. Calc. for $C_{39}H_{46}BN_9P_2Ru$: C, 57.50; H, 5.69; N, 15.47. Found: C, 57.47; H, 5.94; N, 15.51%.

*2.2.3. Complex **1c***

Yield: 49 mg (46%). IR (KBr): 2464 (BH), 2066 (C≡C). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 8.22 (d, 1H, H^{3,5} (pz)), 7.76–7.71 (m, 5H, PPh$_3$), 7.66 (d, 1H, H^{3,5} (pz)), 7.62 (d, 1H, H^{3,5} (pz)), 7.58 (d, 1H, H^{3,5} (pz)), 7.35–7.27 (m, 10H, PPh$_3$), 6.62 (d, 1H, H^{3,5} (pz)), 6.22 (m, 2H, H^{3,5} (pz) and C=C*H*), 5.82 (t, 1H, H^4 (pz)), 5.72 (t, 1H, H^4 (pz)), 5.55 (t, 1H, H^4 (pz)), 4.35 (AB spin system, J_{HAHB} = 10 Hz, 3H, NCH_2N), 4.17 (AB spin system, J_{HAHB} = 10 Hz, 3H, NCH_2N), 3.78 (s, 6H, NCH_2P), 2.53–2.45 (m, 4H, CH_2CH$_2$CH_2), 1.93 (quin, 2H, $^3J_{HH}$ = 6 Hz, CH$_2$CH_2CH$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): 144.1 (s, C-3 (pz)), 144.0 (s, C-3 (pz)), 143.8 (s, C-3 (pz)), 137.0 (d, J_{CP} = 41 Hz, C-1 PPh$_3$), 135.2 (s, C-5 (pz)), 134.9 (s, C-5 (pz)), 134.6 (s, C-5 (pz), 134.0 (d, $^2J_{CP}$ = 11 Hz, C-2,6 PPh$_3$)), 130.3 (s, *C*=CH), 129.0 (s, C-4 PPh$_3$), 127.7 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh$_3$), 125.2 (s, C=*C*H), 124.7 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 22 Hz, C$_α$), 107.8 (s, C$_β$), 105.1 (s, C-4 (pz)), 104.9 (s, C-4 (pz)), 104.4 (s, C-4 (pz)), 73.1 (d, $^3J_{CP}$ = 6 Hz, NCH_2N), 52.4 (d, J_{CP} = 15 Hz, NCH_2P), 38.0 (s, CCH_2), 32.5 (s, CH*C*H$_2$), 23.5 (s, CH_2CH_2CH$_2$). ^{31}P{^{1}H} NMR (161.9 MHz, dichloromethane-d_2): 53.3 (d, $^2J_{PP}$ = 34 Hz, PPh$_3$), −32.2 (d, $^2J_{PP}$ = 34 Hz, PTA). Anal. Calc. for $C_{40}H_{44}BN_9P_2Ru{\cdot}0.5CH_2Cl_2$: C, 56.10; H, 5.23; N, 14.54. Found: C, 55.92; H, 5.68; N, 14.54%.

*2.2.4. Complex **1d***

Yield: 74 mg (66%). IR (KBr): 2481 (BH), 2082 (C≡C). ^{1}H NMR (400.1 MHz, dichloromethane-d_2): 8.32 (d, 1H, H^{3,5} (pz)), 7.81–7.77 (m, 5H, PPh$_3$), 7.70–7.63 (m, 3H, H^{3,5} (pz), H-2 and H-6 Ph), 7.34–7.31 (m, 12H, H^{3,5} (pz) and PPh$_3$), 6.85–6.83 (m, 2H, H-3 and H-5 Ph), 6.70 (d, 1H, H^{3,5} (pz)), 6.27 (sa, 2H, H^{3,5} and H^4 (pz)), 5.86 (t, 1H, H^4 (pz)), 5.79 (t, 1H, H^4 (pz)), 4.37 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 4.19 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 3.84 (s, 9H, OCH_3 and NCH_2P). ^{13}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): 156.2 (s, *C*OCH$_3$), 144.1 (s, C-3 (pz)), 144.06 (s, C-3 (pz)), 143.8 (s, C-3 (pz)), 136.9 (d, J_{CP} = 39 Hz, C-1 PPh$_3$), 135.3 (s, C-5 (pz)), 134.6 (s, C-5 (pz)), 134.5 (s, C-5 (pz)), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh$_3$), 131.3 (s, C-2,6 Ph), 129.1 (s, C-4 PPh$_3$), 127.8 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh$_3$), 123.3 (s, C-1 Ph), 121.8 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 19 Hz, C$_α$), 113.5 (s, C-3,5 Ph), 109.8 (s, C$_β$), 105.2 (s, C-4 (pz)),105.0 (s, C-4 (pz)), 104.4 (s, C-4 (pz)), 73.1 (d, $^3J_{CP}$ = 6 Hz, NCH_2N), 55.2 (s, OCH_3), 52.5 (d, J_{CP} = 15 Hz, NCH_2P). ^{31}P{^{1}H} NMR (161.9 MHz, dichloromethane-d_2): 53.5 (d, $^2J_{PP}$ = 34 Hz, PPh$_3$), −31.6 (d, $^2J_{PP}$ = 34 Hz, PTA). Anal. Calc. for $C_{42}H_{44}BN_9OP_2Ru$: C, 58.34; H, 5.13; N, 14.58. Found: C, 57.81; H, 5.41; N, 14.36%.

*2.2.5. Complex **1e***

Yield: 74 mg (62%). IR (KBr): 2491 (BH), 2065 (C≡C). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 8.36 (s, 1H, H^{3,5} (pz)), 7.80–7.64 (m, 14H, PPh$_3$ and 6-methoxynaft-2-yl), 7.50 (s, 1H, H^{3,5} (pz)), 7.35–7.31 (m, 10H, PPh$_3$ and 6-methoxynaft-2-yl), 7.13 (sa, 2H, H^{3,5} (pz)), 6.72 (d, 1H, H^{3,5} (pz)), 6.29 (d, 1H, H^{3,5} (pz)), 6.27 (t, 1H, H^4 (pz)), 5.86 (t, 1H, H^4 (pz)), 5.80 (t, 1H, H^4 (pz)), 4.39

(AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 4.22 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 3.94 (s, 3H, OCH_3), 3.87 (s, 6H, NCH_2P). $^{13}C\{^1H\}$ NMR (100.6 MHz, dichloromethane-d_2): 156.6 (s, *C*–OCH$_3$), 144.2 (s, C-3 (pz)), 144.1 (s, C-3 (pz)), 143.8 (s, C-3 (pz)), 136.8 (d, J_{CP} = 39 Hz, C-1 PPh$_3$), 135.4 (s, C-5 (pz)), 135.0 (s, C-5 (pz)), 134.7 (s, C-5 (pz)), 134.1 (s, C-7a 6-methoxynaft-2-yl), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh$_3$), 131.6 (s, C-3 6-methoxynaft-2-yl), 130.5 (s, C-1 and C-3 6-methoxynaft-2-yl), 129.4 (s, C-3a 6-methoxynaft-2-yl), 129.1 (s, C-4 PPh$_3$), 128.3 (s, C-4 6-methoxynaft-2-yl), 127.8 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh$_3$), 127.6 (s, C-3 6-methoxynaft-2-yl), 126.0 (s, C-8 6-methoxynaft-2-yl), 125.7 (br, C_α), 118.3 (s, C-5 6-methoxynaft-2-yl), 111.1 (s, C_β), 105.8 (s, C-7 6-methoxynaft-2-yl), 105.2 (s, C-4 (pz)), 105.0 (s, C-4 (pz)), 104.5 (s, C-4 (pz)), 73.1 (d, $^3J_{CP}$ = 6 Hz, NCH_2N), 55.2 (s, OCH_3), 52.4 (d, J_{CP} = 14 Hz, NCH_2P). $^{31}P\{^1H\}$ NMR (161.9 MHz, dichloromethane-d_2): 53.5 (d, $^2J_{PP}$ = 34 Hz, PPh$_3$), −32.2 (d, $^2J_{PP}$ = 34 Hz, PTA). Anal. Calc. for $C_{46}H_{46}BN_9OP_2Ru$: C, 60.40; H, 5.07; N, 13.78. Found: C, 59.97; H, 5.13; N, 13.96%.

2.3. Synthesis of complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh$_3$)(PTA)(C=C=CPh$_2$)][X] (X = PF$_6$ (**2a**), CF$_3$SO$_3$ (**2b**))

To a solution of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (0.13 mmol, 100 mg) in methanol (15 mL) the corresponding salt, NaPF$_6$ (0.26 mmol, 44 mg) (**2a**) or NaCF$_3$SO$_3$ (0.26 mmol, 45 mg) (**2b**) and 1,1-diphenyl-2-propyn-1-ol (0.26 mmol, 54 mg) were added. The reaction mixture was refluxed for 6 h. After cooling to room temperature, the solvent was evaporated and the solid residue was extracted with dichloromethane and the resulting solution filtered through kieselguhr and concentrated under vacuum to ca. 1 mL. The addition of hexane rendered a violet-colored precipitate. The solvents were decanted and the solid residue was washed with hexane (3 × 5 mL) and dried under reduced pressure.

2.3.1. Complex **2a**

Yield: 118 mg (85%). Molar conductivity (acetone, 20 °C) Λ_M: 81 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2488 (BH), 1941 (=C=C=C), 840 (PF$_6$). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 7.98 (d, 1H, H^{3,5} (pz)), 7.80–7.77 (m, 7H, 2H^{3,5} (pz) and 5H Ph), 7.61 (d, 1H, H^{3,5} (pz)), 7.48–7.29 (m, 20H, Ph), 6.73 (d, 1H, H^{3,5} (pz)), 6.25 (t, 1H, H^4 (pz)), 6.21 (t, 1H, H^4 (pz)), 6.03 (d, 1H, H^{3,5} (pz)), 5.86 (t, 1H, H^4 (pz)), 4.42 (AB spin system, J_{HAHB} = 16 Hz, 3H, NCH_2N), 4.22 (AB spin system, J_{HAHB} = 16 Hz, 3H, NCH_2N), 3.86–3.71 (m, 6H, NCH_2P). $^{13}C\{^1H\}$ NMR (100.6 MHz, dichloromethane-d_2): 308.9 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 18 Hz, C_α), 202.7 (s, C_β), 163.4 (s, C_γ), 144.8 (s, C-3 (pz)), 144.3 (s, C-3 (pz)), 144.1 (s, C-3 (pz)), 143.7 (s, C-1 Ph), 137.1 (s, C-5 (pz)), 136.9 (s, C-5 (pz)), 136.7 (s, C-5 (pz)), 133.6 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh$_3$), 132.8 (s, C-4 Ph), 132.4 (d, J_{CP} = 45 Hz, C-1 PPh$_3$), 131.3 (s, C-3,5 Ph), 131.0 (s, C-4 PPh$_3$), 129.4 (s, C-3,5 Ph), 128.8 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh$_3$), 128.3 (s, C-2,6 Ph), 127.8 (s, C-4 Ph), 125.8 (s, C-2,6 Ph), 107.4 (s, C-4 (pz)), 106.5 (s, C-4 (pz)), 105.7 (s, C-4 (pz)), 72.7 (d, $^3J_{CP}$ = 5 Hz, NCH_2N), 51.9 (d, J_{CP} =15 Hz, NCH_2P). $^{31}P\{^1H\}$ NMR (161.9 MHz, dichloromethane-d_2): 39.6 (d, $^2J_{PP}$ = 31 Hz, PPh$_3$), −5.1 (d, $^2J_{PP}$ = 31 Hz, PTA), −144.4 (sept, J_{PF} = 709 Hz, PF$_6$). MS (ESI, *m/z*): 924 [M]$^+$. Anal. Calc. for $C_{48}H_{47}BF_6N_9P_3Ru{\cdot}2.5CH_2Cl_2$: C, 47.35; H, 4.09; N, 9.84. Found: C, 47.51; H, 4.67; N, 9.11%.

2.3.2. Complex **2b**

Yield: 84 mg (60%). Molar conductivity (acetone, 20 °C) Λ_M: 80 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2486 (BH), 1940 (=C=C=C), 1278, 1154, 1031 (OTf). ^{1}H NMR (400.1 MHz, dichloromethane-d_2): 7.98 (d, 1H, H^{3,5} (pz)), 7.87–7.75 (m, 6H, Ph), 7.68–7.59 (m, 3H, H^{3,5} (pz)), 7.56–7.25 (m, 19H, Ph), 6.69 (d, 1H, H^{3,5} (pz)), 6.27 (t, 1H, H^4 (pz)), 6.21 (t, 1H, H^4 (pz)), 6.01 (d, 1H, H^{3,5} (pz)), 5.86 (t, 1H, H^4 (pz)), 4.37 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 4.18 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 3.84–3.72 (m, 6H, NCH_2P). $^{13}C\{^1H\}$ NMR (100.6 MHz, dichloromethane-d_2): 309.0 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 17 Hz, C_α), 203.7 (s, C_β), 162.8 (s, C_γ), 145.0 (s, C-1 Ph), 144.7 (s, C-3 (pz)), 144.3 (s, C-1 Ph), 144.1 (s, C-3 (pz)), 143.6 (s, C-3 (pz)), 137.1 (s, C-5 (pz)), 136.9 (s, C-5 (pz)), 136.7 (s, C-5 (pz)), 133.6 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh$_3$), 132.7 (s, C-4 Ph), 132.4 (d, J_{CP} = 45 Hz, C-1 PPh$_3$), 131.2 (s, C-3,5 Ph),131.0 (s, C-4 PPh$_3$), 129.4 (s, C-3,5 Ph), 128.8 (d, $^3J_{CP}$ = 10 Hz, C-3,5 PPh$_3$), 128.2 (s, C-2,6 Ph), 127.7 (s, C-4 Ph), 125.8 (s, C-2,6 Ph), 121.1 (q, J_{CF} = 323 Hz, *C*F$_3$SO$_3$), 107.3 (s, C-4 (pz)), 106.5 (s, C-4 (pz)), 105.6 (s, C-4 (pz)), 72.7 (d, $^3J_{CP}$ = 7 Hz, NCH_2N), 52.2 (d, J_{CP} = 15 Hz, NCH_2P). $^{31}P\{^1H\}$ NMR (161.9 MHz, dichloromethane-d_2): 40.2 (d, $^2J_{PP}$ = 32 Hz, PPh$_3$), −46.5 (d, $^2J_{PP}$ = 32 Hz, PTA). Anal. Calc. for $C_{49}H_{47}BF_3N_9O_3P_2RuS$: C, 54.86; H, 4.42; N, 11.75; S, 2.99. Found: C, 54.77; H, 4.38; N, 11.70; S, 2.95%.

2.4. Synthesis of complex [Ru{κ^3(*N,N,N*)-Tp}(PPh$_3$)(PTA)-(C=C=CC$_{12}$H$_8$)][PF$_6$] (**3**)

To a solution of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (0.13 mmol, 100 mg) in dichloromethane (2 mL) at −30 °C, TlPF$_6$ (0.26 mmol, 93 mg) was added. The reaction mixture was stirred at low temperature for 1 h. After warming to room temperature, a solution of 9-ethynyl-9H-fluoren-9-ol (0.98 mmol, 202 mg) in dichloromethane (5 mL) was added. The reaction mixture was stirred at room temperature for 2.5 days. The solution was then filtered through kieselguhr and concentrated under vacuum to ca. 0.5 mL. The addition of hexane produced a violet-colored precipitate. The solvents were decanted and the solid residue was washed with hexane (4 × 5 mL) and dried under reduced pressure.

Yield: 111 mg (80%). Conductivity (acetone, 20 °C): 81 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2490 (BH), 1941 (=C=C=C), 841 (PF$_6$). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 7.96 (d, 1H, H^{3,5} (pz)), 7.82 (d, 1H, H^{3,5} (pz)), 7.76 (sa, 2H, H^{3,5} (pz)), 7.70–7.10 (m, 23H, Ph), 6.65 (d, 1H, H^{3,5} (pz)), 6.38 (t, 1H, H^4 (pz)), 6.19 (t, 1H, H^4 (pz)), 6.09 (d, 1H, H^{3,5} (pz)), 5.86 (t, 1H, H^4 (pz)), 4.35 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 4.17 (AB spin system, J_{HAHB} = 13 Hz, 3H, NCH_2N), 3.86–3.83 (m, 6H, NCH_2P). $^{13}C\{^1H\}$ NMR (100.6 MHz, dichloromethane-d_2): 309.4 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 20 Hz, C_α), 210.6 (s, C_β), 156.2 (s, C_γ), 146.8 (s, *C* 9H-fluorene), 146.2 (s, C-3 (pz)), 144.6 (s, C-3 (pz)), 144.0 (s, C-3 (pz)), 142.9 (s, *C* 9H-fluorene), 142.5 (s, *C* 9H-fluorene), 139.0 (s, *C* 9H-fluorene), 137.2 (s, C-5 (pz)), 137.1 (s, C-5 (pz)), 136.8 (s, C-5 (pz)), 134.0 (s, *C*H 9H-fluorene), 133.5 (d, $^2J_{CP}$ = 10 Hz, C-2,6 PPh$_3$), 132.2 (d, J_{CP} = 46 Hz, C-1 PPh$_3$), 131.3 (s, C-4 PPh$_3$), 129.9 (s, *C*H 9H-fluorene), 129.8 (s, *C*H 9H-fluorene), 129.1 (d, $^3J_{CP}$ = 10 Hz, C-3,5 PPh$_3$), 128.6 (s, *C*H 9H-fluorene), 124.1 (s, *C*H 9H-fluorene), 124.0 (s, *C*H 9H-fluorene), 121.9 (s, *C*H 9H-fluorene), 120.3 (s, *C*H 9H-fluorene), 107.5 (s, C-4 (pz)), 106.7 (s, C-4 (pz)), 105.8 (s, C-4 (pz)), 72.7 (d, $^3J_{CP}$ = 6 Hz, NCH_2N), 52.0 (d, J_{CP} = 15 Hz, NCH_2P). $^{31}P\{^1H\}$ NMR (161.9 MHz, dichloromethane-d_2): 37.9 (d, $^2J_{PP}$ = 33 Hz, PPh$_3$), −48.3 (d, $^2J_{PP}$ = 33 Hz, PTA), −144.4 (sept, J_{PF} = 709 Hz, PF$_6$). MS (ESI, *m/z*): 922 [M]$^+$. Anal. Calc. for $C_{48}H_{45}BF_6N_9P_3Ru$: C, 54.05; H, 4.25; N, 11.82. Found: C, 53.96; H, 4.20; N, 11.75%.

2.5. Synthesis of complexes [Ru(C≡CR){κ^3(*N,N,N*)-Tp}(PPh$_3$)(1-CH$_3$-PTA)][CF$_3$SO$_3$] (R = Ph (**4a**), ^{n}Bu (**4b**), 1-cyclopentenyl (**4c**))

To a solution of the corresponding complex [Ru{κ^3(*N,N,N*)-Tp}(C≡CR)(PPh$_3$)(PTA)] (0.13 mmol) in dichloromethane (2 mL) at −30 °C, MeOTf (16 μL, 0.13 mmol) was added. The reaction mixture was stirred at −30 °C for 40 min. The addition of hexane (60 mL) produced a pale yellow precipitate. The solvents were decanted and the solid residue was washed with hexane (2 × 5 mL) and dried under reduced pressure.

*2.5.1. Complex **4a***

Yield: 60 mg (46%). Molar conductivity (acetone, 20 °C): 115 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2504 (BH), 2024 (C≡C), 1258, 1161, 1032 (OTf). ^{1}H NMR (400.1 MHz, dichloromethane-d_2): 8.17 (d, 1H, H^{3,5} (pz)), 7.82 (d, 1H, H^{3,5} (pz)),7.71 (br, 2H, H^{3,5} (pz)), 7.52–7.10 (m, 20H, Ph and PPh_3), 6.86 (d, 1H, H^{3,5} (pz)), 6.69 (d, 1H, H^{3,5} (pz)), 6.25 (t, 1H, H^4 (pz)), 6.04 (t, 1H, H^4 (pz)), 5.84 (t, 1H, H^4 (pz)), 5.06 (br, 2H, 1-CH_3-PTA), 4.46–4.32 (m, 3H, 1-CH_3-PTA), 4.05–3.96 (m, 2H, 1-CH_3-PTA), 3.82–3.75 (m, 4H, 1-CH_3-PTA), 3.35 (d, J_{HH} = 14 Hz, 1H, 1-CH_3-PTA), 2.58 (s, 3H, C*H*$_3$N). ^{13}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): 145.3 (s, C-3 (pz)), 144.4 (s, C-3 (pz)), 136.1 (s, C-5 (pz)), 135.9 (s, C-5 (pz)), 135.7 (d, J_{CP} = 40 Hz, C-1 PPh_3), 135.6 (s, C-5 (pz)), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh_3), 130.5 (s, C-2 and C-6 Ph), 129.8 (s, C-4 PPh_3), 129.5 (s, C-1 Ph), 128.3 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh_3), 128.2 (s, C-3 and C-5 Ph), 124.1 (s, C-4 Ph), 123.1 (dd, $^2J_{CP}$ = $^2J_{CP'}$ = 22 Hz, C_α), 120.7 (q, J_{CF} = 320 Hz, *C*F_3SO_3), 110.8 (s, C_β), 106.2 (s, C-4 (pz)), 105.6 (s, C-4 (pz)), 105.1 (s, C-4 (pz)), 81.0 (d, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 80.7 (d, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 69.3 (d, $^3J_{CP}$ = 5 Hz, NCH_2N), 58.3 (d, J_{CP} = 7 Hz, CH_3NCH_2P), 49.9 (d, J_{CP} = 16 Hz, NCH_2P), 49.8 (s, *C*H_3N), 49.3 (d, J_{CP} = 15 Hz, N*C*H_2P). ^{31}P{^{1}H} NMR (161.9 MHz, dichloromethane-d_2): 47.3 (d, $^2J_{PP}$ = 32 Hz, PPh_3), −10.3 (d, $^2J_{PP}$ = 32 Hz, 1-CH_3-PTA). Anal. Calc. for $C_{43}H_{45}BF_3N_9O_3P_2RuS$: C, 51.71; H, 4.54; N, 12.62; S, 3.21. Found: C, 51.99; H, 4.53; N, 12.38; S, 3.13%.

*2.5.2. Complex **4b***

Yield: 59 mg (46%). Molar conductivity (acetone, 20 °C): 111 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2504 (BH), 2035 (C≡C), 1258, 1160, 1030 (OTf). ^{1}H NMR (400.1 MHz, acetonitrile-d_3): 8.17 (d, 1H, H^{3,5} (pz)), 7.80 (d, 1H, H^{3,5} (pz)), 7.72 (d, 2H, H^{3,5} (pz)), 7.53–7.21 (m, 15H, PPh_3), 6.92 (d, 1H, H^{3,5} (pz)), 6.69 (d, 1H, H^{3,5} (pz)), 6.22 (t, 1H, H^4 (pz)), 5.97 (t, 1H, H^4 (pz)), 5.79 (t, 1H, H^4 (pz)), 4.71–4.66 (m, 2H, 1-CH_3-PTA), 4.47–4.44 (m, 2H, 1-CH_3-PTA), 4.25–4.21 (m, 1H, 1-CH_3-PTA), 4.08–4.05 (m, 1H, 1-CH_3-PTA), 3.96 (d, J_{HH} = 14 Hz, 1H, 1-CH_3-PTA), 3.79–3.59 (m, 4H, 1-CH_3-PTA), 3.50–3.46 (m, 1H, 1-CH_3-PTA), 2.58 (s, 3H, C*H*$_3$N), 2.50 (t, $^3J_{HH}$ = 7 H, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.61 (quin, $^3J_{HH}$ = 7 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.54 (sext, $^3J_{HH}$ = 7 Hz, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.00 (t, $^3J_{HH}$ = 7 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, acetonitrile-d_3): 145.8 (s, C-3 (pz)), 145.0 (s, C-3 (pz)), 144.1 (s, C-3 (pz)), 136.4 (d, J_{CP} = 39 Hz, C-1 PPh_3), 135.8 (s, C-5 (pz)), 135.4 (s, C-5 (pz)), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh_3), 129.6 (s, C-4 PPh_3), 128.0 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh_3), 121.1 (q, J_{CF} = 321 Hz, *C*F_3SO_3), 106.0 (s, C_β), 105.7 (s, C-4 (pz)), 105.2 (s, C-4 (pz)), 104.7 (s, C-4 (pz)), 100.0 (dd, $^2J_{CP}$ = 22 Hz, $^2J_{CP'}$ = 17 Hz C_α), 80.5 (d, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 80.4 (d, $^3J_{CP}$ = 3 Hz, CH_3NCH_2N), 68.9 (d, $^3J_{CP}$ = 5 Hz, NCH_2N), 58.2 (d, J_{CP} = 7 Hz, CH_3NCH_2P), 49.3 (s, *C*H_3N), 48.8 (d, J_{CP} = 17 Hz, NCH_2P), 48.7 (d, J_{CP} = 16 Hz, NCH_2P), 33.5 (s, *C*H$_2$CH$_2$CH$_2$), 22.3 (s, CH$_2$CH$_2$CH$_2$), 21.8 (s, CH$_2$CH$_2$CH$_2$), 13.3 (s, CH$_2$CH$_3$). ^{31}P{^{1}H} NMR (161.9 MHz, acetonitrile-d_3): 48.5 (d, $^2J_{PP}$ = 33 Hz, PPh_3), −10.0 (d, $^2J_{PP}$ = 33 Hz, 1-CH_3-PTA). Anal. Calc. for $C_{41}H_{49}BF_3N_9O_3P_2RuS$: C, 50.31; H, 5.05; N, 12.88; S, 3.28. Found: C, 50.23; H, 4.98; N, 12.81; S, 3.22%.

*2.5.3. Complex **4c***

Yield: 59 mg (46%). Molar conductivity (acetone, 20 °C): 109 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2481 (BH), 2008 (C≡C), 1258, 1160, 1031 (OTf). ^{1}H NMR (600.2 MHz, dichloromethane-d_2): 8.05 (d, 1H, H^{3,5} (pz)), 7.80 (d, 1H, H^{3,5} (pz)), 7.69 (br, 2H, H^{3,5} (pz)), 7.39–7.33 (m, 15H, PPh_3), 6.88 (d, 1H, H^{3,5} (pz)), 6.51 (d, 1H, H^{3,5} (pz)), 6.21 (t, 1H, H^4 (pz)), 6.00 (t, 1H, H^4 (pz)), 5.80 (t, 1H, H^4 (pz)), 5.62 (sa, 1H, CC*H*), 5.15–5.11 (m, 2H, 1-CH_3-PTA), 4.45 (AB spin system, J_{HAHB} = 12 Hz, 1H, 1-CH_3-PTA), 4.37 (AB spin system, J_{HAHB} = 12 Hz, 1H, 1-CH_3-PTA), 4.21–4.20 (m, 1H, 1-CH_3-PTA), 4.03–3.96 (m, 3H, 1-CH_3-PTA), 3.85–3.75 (m, 3H, 1-CH_3-PTA), 3.02–3.00 (m, 1H, 1-CH_3-PTA), 2.95 (s, 3H, C*H*$_3$N), 2.54–2.44 (m, 4H, C*H*$_2$CH$_2$C*H*$_2$), 1.98–1.91 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (150.9 MHz, dichloromethane-d_2): 145.3 (s, C-3 (pz)), 144.4 (s, C-3 (pz)), 144.2 (s, C-3 (pz)), 136.2 (s, C-5 (pz)), 136.0 (s, C-5 (pz)), 135.7 (s, C-5 (pz)), 135.6 (d, J_{CP} = 39 Hz, C-1 PPh_3), 134.1 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh_3), 129.9 (s, C-4 PPh_3), 129.5 (s, *C*≡CH), 128.3 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh_3), 125.2 (s, C≡*C*H), 121.9 (dd, $^2J_{CP}$ = 24 Hz, $^2J_{CP'}$ = 18 Hz, C_α), 120.6 (q, J_{CF} = 320 Hz, *C*F_3SO_3), 107.8 (s, C_β), 106.1 (s, C-4 (pz)), 105.5 (s, C-4 (pz)), 105.2 (s, C-4 (pz)), 80.9 (s, CH_3NCH_2N), 80.4 (s, CH_3NCH_2N), 69.1 (s, NCH_2N), 58.1 (d, J_{CP} = 9 Hz, CH_3NCH_2P), 50.0 (s, *C*H$_3$N), 49.9 (d, J_{CP} = 17 Hz, NCH_2P), 49.0 (d, J_{CP} = 12 Hz, NCH_2P), 38.0 (s, C*C*H$_2$), 32.5 (s, CH*C*H$_2$), 23.4 (s, CH$_2$*C*H$_2$CH$_2$). ^{31}P{^{1}H} NMR (242.9 MHz, dichloromethane-d_2): 46.8 (d, $^2J_{PP}$ = 32 Hz, PPh_3), −11.3 (d, $^2J_{PP}$ = 32 Hz, 1-CH_3-PTA). MS (ESI, *m/z*): 840 [M]$^+$. Anal. Calc. for $C_{42}H_{47}BF_3N_9O_3P_2RuS$: C, 51.02; H, 4.79; N, 12.75; S, 3.24. Found: C, 50.85; H, 4.75; N, 12.71; S, 3.18%.

*2.6. Synthesis of complex [Ru{κ^3(N,N,N)-Tp}(PPh$_3$)(1-H-PTA)-(C=C=CPh$_2$)][PF$_6$]$_2$ (**5**)*

To a solution of the complex [Ru{κ^3(*N,N,N*)-Tp}(C=C=CPh$_2$)-(PPh_3)(PTA)][PF_6] (**2a**) (0.05 mmol, 54 mg) in dichloromethane (2 mL) at −30 °C, 1.0 equiv. of HPF_6 (0.05 mmol, 7 μL) was added. The reaction mixture was stirred at −30 °C for 30 min. The addition of hexane (70 mL) resulted in the formation of a violet-colored precipitate. The solvents were decanted and the solid residue was washed with hexane (2 × 5 mL) and dried under reduced pressure.

Yield: 36 mg (60%). Molar conductivity (acetone, 20 °C): 298 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2488 (BH), 1941 (=C=C=C), 839 (PF_6). ^{1}H NMR (300.1 MHz, dichloromethane-d_2): 8.07 (d, 1H, H^{3,5} (pz)), 7.88–7.65 (m, 9H, H^{3,5} (pz) and Ph), 7.60–7.22 (m, 20H, H^{3,5} (pz) and Ph), 6.37 (t, 1H, H^4 (pz)), 6.24 (d, 1H, H^{3,5} (pz)), 6.21 (t, 1H, H^4 (pz)), 5.91 (t, 1H, H^4 (pz)), 4.74 (AB spin system, J_{HAHB} = 9 Hz, 3H, NCH_2N), 4.50 (AB spin system, J_{HAHB} = 9 Hz, 3H, N*C*H$_2$N), 3.88 (CD spin system, J_{HCHD} = 16 Hz, 3H, N*C*H$_2$P), 3.73 (CD spin system, J_{HCHD} = 16 Hz, 3H, N*C*H$_2$P). ^{13}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): 308.0 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 18 Hz, C_α), 194.1 (s, C_β), 168.3 (s, C_γ), 145.9 (s, C-3 (pz)), 144.4 (s, C-3 (pz)), 144.1 (s, C-3 (pz)), 143.8 (s, C-1 Ph), 137.5 (s, C-5 (pz)), 137.2 (s, C-5 (pz)), 133.6 (s, C-3,5 Ph), 133.5 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh_3), 132.3 (d, J_{CP} = 46 Hz, C-1 PPh_3), 132.0 (s, C-4 Ph), 131.3 (s, C-4 PPh_3), 129.4 (s, C-2,6 Ph), 128.9 (d, $^3J_{CP}$ = 10 Hz, C-3,5 PPh_3), 108.3 (s, C-4 (pz)), 107.2 (s, C-4 (pz)), 106.1 (s, C-4 (pz)), 71.8 (s, NCH_2N), 49.1 (s, J_{CP} = 16 Hz, NCH_2P). ^{31}P{^{1}H} NMR (161.9 MHz, dichloromethane-d_2): 36.1 (d, $^2J_{PP}$ = 31 Hz, PPh_3), −29.1 (d, $^2J_{PP}$ = 31 Hz, 1-H-PTA), −144.1 (sept, J_{PF} = 703 Hz, PF_6). Anal. Calc. for $C_{48}H_{48}BF_{12}N_9P_4Ru{\cdot}3CH_2Cl_2$: C, 41.68; H, 3.70; N, 8.58. Found: C, 41.49; H, 4.06; N, 8.28%.

*2.7. Synthesis of complex [Ru{κ^3(N,N,N)-Tp}(PPh$_3$)(1-CH$_3$-PTA)-(C=C=CPh$_2$)][CF$_3$SO$_3$]$_2$ (**6**)*

To a solution of complex [Ru{κ^3(*N,N,N*)-Tp}(C=C=CPh$_2$)(PPh_3)-(PTA)][CF_3SO_3] (**2b**) (0.05 mmol, 54 mg) in dichloromethane (2 mL) at −30 °C, $MeCF_3SO_3$ (6.2 μL, 0.05 mmol) was added. The reaction mixture was stirred at −30 °C for 30 min. The addition of hexane (70 mL) led to the formation of a violet precipitate. The solvents were decanted and the solid residue was washed with hexane (2 × 5 mL) and dried under reduced pressure.

Yield: 52 mg (84%). Molar conductivity (acetone, 20 °C): 217 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2488 (BH), 1948 (=C=C=C), 1257, 1160, 1031 (OTf). ^{1}H NMR (600.1 MHz, dichloromethane-d_2): 8.17 (d, 1H, H^{3,5} (pz)), 8.11 (d, 1H, H^{3,5} (pz)), 7.91 (d, 1H, H^{3,5} (pz)), 7.77 (d, 1H, H^{3,5} (pz)), 7.74–7.72 (m, 3H, Ph), 37.63–7.61

(m, 4H, Ph), 7.55 (d, 1H, $H^{3,5}$ (pz)), 7.52–7.18 (m, 18H, Ph), 6.62 (t, 1H, H^4 (pz)), 6.61 (d, 1H, $H^{3,5}$ (pz)), 6.21 (t, 1H, H^4 (pz)), 5.95 (t, 1H, H^4 (pz)), 5.23 (AB spin system, J_{HAHB} = 12 Hz, 1H, CH_3NCH_2N), 5.18 (AB spin system, J_{HAHB} = 12 Hz, 1H, CH_3NCH_2N), 4.73 (CD spin system, J_{HCHD} = 12 Hz, 1H, CH_3NCH_2N), 4.69 (CD spin system, J_{HCHD} = 12 Hz, 1H, CH_3NCH_2N), 4.38–4.29 (m, 2H, NCH_2N), 4.22 (EF spin system, J_{HEHF} = 14 Hz, 1H, CH_3NCH_2P), 4.09 (EF spin system, J_{HEHF} = 14 Hz, 1H, CH_3NCH_2P), 3.79–3.69 (m, 2H, NCH_2P), 3.35 (GH spin system, J_{HGHH} = 15 Hz, 1H, NCH_2P), 3.28 (GH spin system, J_{HGHH} = 15 Hz, 1H, NCH_2P), 2.61 (s, 3H, CH_3N). $^{13}C\{^1H\}$ NMR (150.9 MHz, dichloromethane-d_2): 312.3 (t, $^2J_{CP} = {}^2J_{CP'}$ = ! 18 Hz, C_α), 194.4 (s, C_β), 167.4 (s, C_γ), 147.2 (s, C-3 (pz)), 144.4 (s, C-3 (pz)), 144.3 (s, C-3 (pz)), 143.6 (s, C-1 Ph), 137.8 (s, C-5 (pz)), 137.0 (s, C-5 (pz)), 136.9 (s, C-5 (pz)), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh_3), 133.4 (d, J_{CP} = 45 Hz, C-1 PPh_3), 133.3 (s, C-4 Ph), 132.1 (s, C-3,5 Ph), 130.8 (s, C-4 PPh_3), 129.3 (s, C-2,6 Ph), 128.7 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh_3), 120.6 (q, J_{CF} = 320 Hz, CF_3SO_3), 108.8 (s, C-4 (pz)), 107.3 (s, C-4 (pz)), 106.3 (s, C-4 (pz)), 79.9 (s, CH_3NCH_2N), 79.6 (s, CH_3NCH_2N), 69.2 (s, NCH_2N), 55.5 (d, J_{CP} = 9 Hz, CH_3NCH_2P), 48.9 (s, CH_3N), 48.4 (d, J_{CP} = 18 Hz, NCH_2P), 47.0 (d, J_{CP} = 15 Hz, NCH_2P). $^{31}P\{^1H\}$ NMR (161.9 MHz, dichloromethane-d_2): 31.8 (d, $^2J_{PP}$ = 29 Hz, PPh_3), −23.7 (d, $^2J_{PP}$ = 29 Hz, 1-CH_3-PTA). MS (ESI, *m/z*): 840 $[M]^+$. Anal. Calc. for $C_{51}H_{50}BF_6N_9O_6P_2RuS_2{\cdot}1.5CH_2Cl_2$: C, 46.22; H, 3.92; N, 9.24; S, 4.70. Found: C, 46.54; H, 3.53; N, 9.15; S, 4.63%.

3. Results and discussion

3.1. Synthesis of [Ru(C≡CR){κ³(N,N,N)-Tp}(PPh₃)(PTA)] (R = Ph (1a), ⁿBu (1b), 1-cyclopentenyl (1c), p-methoxyphenyl (1d), 6-methoxynaft-2-yl (1e))

The reaction of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] with terminal alkynes in the presence of NEt_3 in refluxing methanol produces the alkynyl complexes [Ru(C≡CR){κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] (**1a–e**) which are isolated as air-stable, yellow solids in 40–69% yield [17] (see Scheme 1).

Complexes **1a–e** are soluble in acetone and dichloromethane and are insoluble in methanol, diethyl ether, and hexane. They have been analytically and spectroscopically characterized (see Section 2 for details). Particular note must be taken of the fact that: (i) IR spectra (KBr) show the characteristic ν(C≡C) absorption at 2082 (**1a**), 2095 (**1b**), 2066 (**1c**), 2082 (**1d**), and 2065 (**1d**) cm^{-1} and the ν(BH) absorption of the Tp ligand in the range 2464–2491 cm^{-1}; (ii) $^{31}P\{^1H\}$ NMR spectra show two doublets ($^2J_{PP}$ = 32–34 Hz) in the range δ = 53.3–54.2 (PPh_3) and −32.2–30.7 (PTA) ppm; (iii) the α-carbon appears in the $^{13}C\{^1H\}$ NMR spectra as a triplet ($J_{C,P} = J_{C,\ P'}$ = 16–22 Hz) at δ = 126.7 (**1a**), 101.6 (**1b**), 124.7 (**1c**), 121.8 (**1d**), and 125.7 (**1e**) ppm and the β-carbon as a singlet in the range of 107.7–111.2 ppm; (iv) for all the complexes, ^1H NMR spectra concur with the proposed stoichiometry.

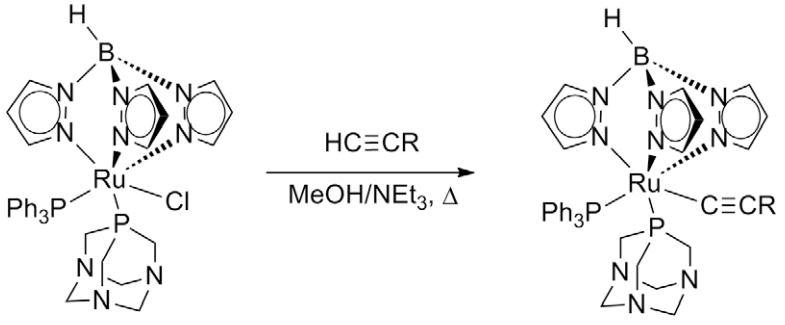
3.2. Synthesis of [Ru{κ³(N,N,N)-Tp}(PPh₃)(PTA)(C=C=CPh₂)][X] (X = PF₆ (2a), CF₃SO₃ (2b)), and [Ru{κ³(N,N,N)-Tp}(PPh₃)(PTA)(C=C=CC₁₂H₈)][PF₆] (3)

The reaction of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] with 1,1-diphenyl-2-propyn-1-ol in the presence of an halide extractor such as $NaPF_6$ or $NaCF_3SO_3$ in refluxing methanol produces the allenylidene complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)-(C=C=CPh_2)][X] (X = PF_6 (**2a**), CF_3SO_3 (**2b**)) which are isolated as air-stable violet-colored solids in 85% (**2a**) and 60% (**2b**) yield (Scheme 2).

Complexes **2a, b** have been analytically and spectroscopically characterized (IR and ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$NMR; see Section 2 for details). Both complexes present similar spectroscopic features except for those corresponding to the PF_6 (IR 840 cm^{-1} and $^{31}P\{^1H\}$ −144.4 ppm) and CF_3SO_3 (IR 1278, 1154, and 1031 cm^{-1}) counteranions. Thus, the IR spectra (KBr) show bands for the ν(BH) at 2488 cm^{-1} (**2a**) and 2486 (**2b**) cm^{-1} and for ν(=C=C=C) at 1941 (**2a**) and 1940 (**2b**) cm^{-1}. The signal for the phosphorous atom of the PTA ligand appears as a doublet at δ = −45.1 (**2a**) and −46.5 (**2b**) due to the coupling with the PPh_3 (39.6 (**2a**), 40.2 (**2b**) ppm). The $^{13}C\{^1H\}$ NMR spectra show the signals due to the C_α (δ = 308.9 (**2a**), 309.0 (**2b**)), C_β (δ = 202.7 (**2a**), 203.7 (**2b**)) and C_γ (δ = 163.4 (**2a**), 162.8 (**2b**)) of the allenylidene group. All these spectroscopic data agree with the reported data for ruthenium allenylidene complexes with the Tp ring [18].

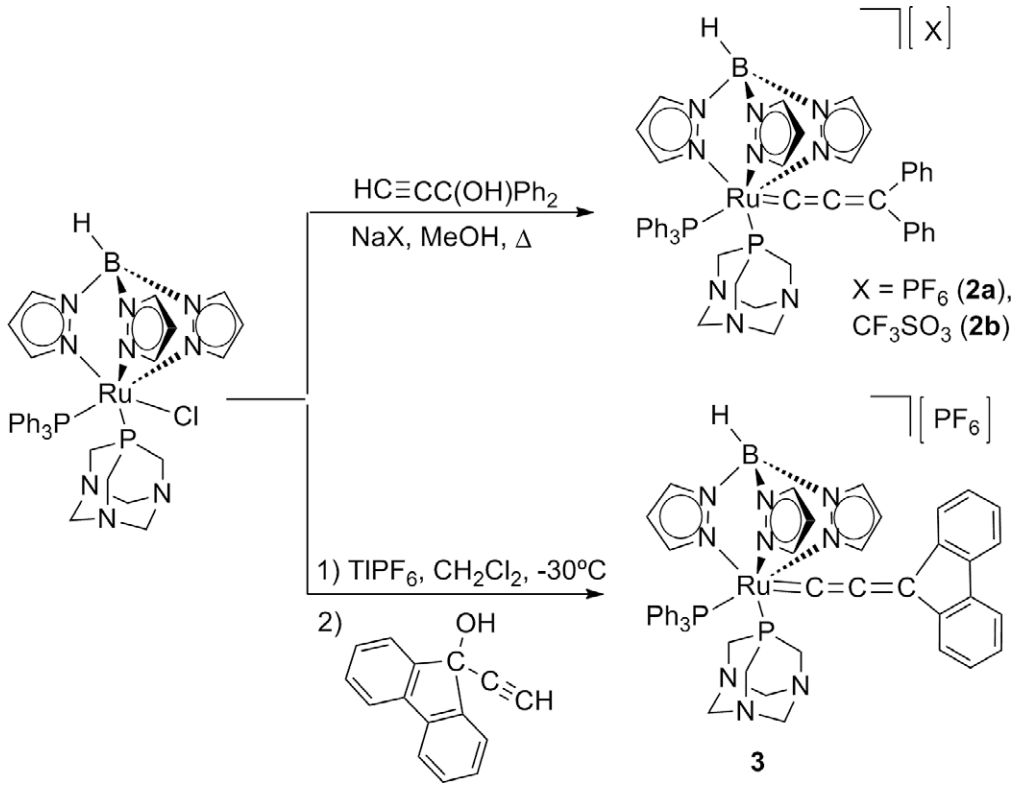
When the same reaction is carried out using 9-ethynyl-9H-fluoren-9-ol, a complex mixture of products is obtained. However, when a solution of complex [RuCl{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] in dichloromethane is treated with $TlPF_6$ at low temperature, a white solid precipitates. Posterior addition of the propargyl alcohol 9-ethynyl-9H-fluoren-9-ol to this suspension, and stirring over a 48 h period leads to the formation of the allenylidene complex [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(C=C=$CC_{12}H_8$)][PF_6] (**3**) as a violet-colored solid in 80% yield.

Elemental analyses corroborate the proposed stoichiometry and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra support the proposed structure for complex **3**. The most remarkable features of this complex are: (i) $^{13}C\{^1H\}$ NMR shows one triplet ($^2J_{CP} = {}^2J_{CP'}$ = 20 Hz) corresponding to the C_α at δ = 309.4 ppm and two singlets at δ = 210.6 and 156.2 ppm, corresponding to the C_β and C_γ, respectively; (ii) $^{31}P\{^1H\}$ NMR spectrum confirms the existence of the two

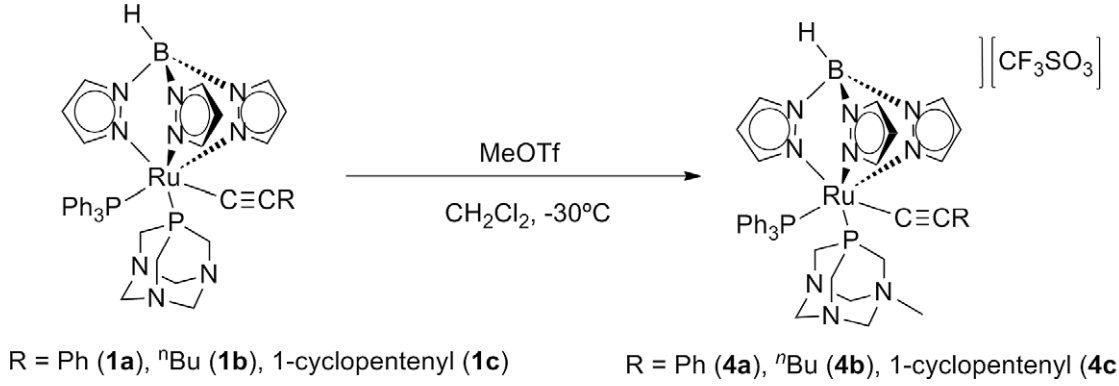


R = Ph (**1a**), ^{n}Bu (**1b**), 1-cyclopentenyl (**1c**), *p*-methoxyphenyl (**1d**), 6-methoxynaft-2-yl (**1e**)

Scheme 1.



Scheme 2.



Scheme 3.

phosphane ligands by two doublets ($^2J_{PP}$ = 33 Hz) at 37.9 (PPh_3) and −48.3 (PTA) as well as the PF_6 group which appears at δ = −144.4 ppm; (iii) the IR spectrum (KBr) exhibit the characteristic absorptions for the ν(BH) of the Tp ligand at 2490, ν(=C=C=C) at 1941 and for the PF_6 group at 841 cm^{-1}.

The nature of the white solid obtained by treating [RuCl-{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] with $TlPF_6$ remains unknown, due to its high insolubility which prevents its characterization. A polymeric species formed by coordination of the electrophilic thalium cation to one of the nitrogen atoms of the PTA ligand might account for this insolubility [19].

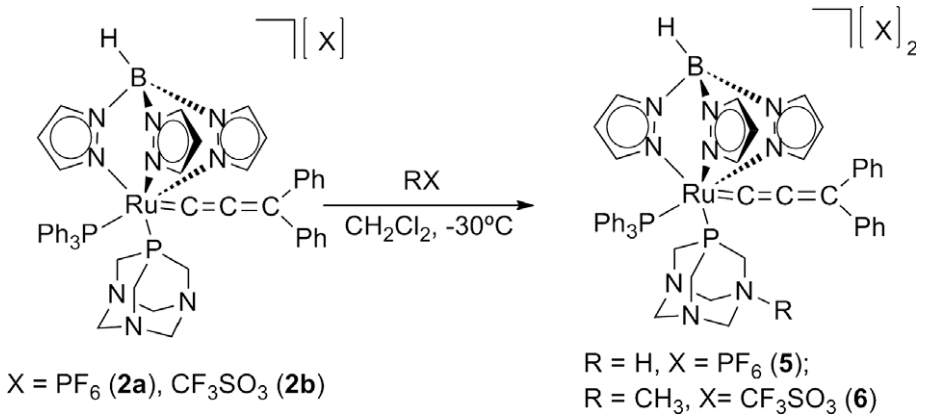
This polymer would evolve slowly through halide extraction in the presence of 9-ethynyl-9H-fluoren-9-ol, leading to complex **3**. Also, this white solid reacts with isopropylamine or pyridine, to produce the cationic complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(N-H_2*i*Pr)][PF_6] and [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(py)][PF_6] [20] (see Supplementary material).

3.3. Electrophilic attacks on the coordinated PTA ligands

It is well known that σ-alkynyl complexes undergo electrophilic additions to the β-carbon of the alkynyl group to yield vinylidene complexes [21]. In the same way, allenylidene complexes can also react with electrophiles to yield vinylcarbine complexes [22–25]. These reactions could compete with the electrophilic attack to one of the nitrogen atoms of the PTA phosphane ligand. The reaction with electrophiles was conducted in order to determine the selectivity of this reaction in the former complexes.

3.3.1. Synthesis of cationic alkynyl complexes [Ru(C≡CR){κ^3(N,N,N)-Tp}(PPh_3)(1-CH_3-PTA)][CF_3SO_3] (R = Ph (**4a**), ^{n}Bu (**4b**), 1-cyclopentenyl (**4c**))

The treatment of complexes **1a–c** at −30 °C with MeOTf in CH_2Cl_2 leads chemoselectively to the methylation of one of the nitrogen atoms of the PTA phosphane, resulting in the complexes



Scheme 4.

[Ru(C≡CR){κ^3(*N,N,N*)-Tp}(PPh_3)(1-CH_3-PTA)][CF_3SO_3] (R = Ph (**4a**), ^{n}Bu (**4b**), 1-cyclopentenyl (**4c**)), which contain a 1-methyl-3,5-diaza-1-azonia-7-phosphaadamantane (1-CH_3-PTA) ligand (Scheme 3).

The molar conductivities in acetone (109–115 Ω^{-1} cm^2 mol^{-1}) are in the range found for electrolytes 1:1 [26]. Elemental analysis and spectroscopic data agree with the proposed formulations (see Section 2). Thus, the chemical shift of the phosphorous atom of the 1-CH_3-PTA ligand in the $^{31}P\{^1H\}$ NMR spectra (δ = −10.3 (**4a**), −10.0 (**4b**), −11.3 (**4c**)) appears in all cases at lower fields than the PTA phosphane in the former complexes (δ = −31.5 (**1a**), −30.7 (**1b**), −32.2 (**1c**)) as observed for previously reported ruthenium(II) complexes [15,16]. The typical AB spin system observed for the NCH_2N groups in the ^1H NMR spectra of complexes **1a–c** disappears and a large number of doublets and triplets in the range of 3.35–5.15 ppm are observed for complexes **4a–c**. The methyl group of the 1-CH_3-PTA ligand for these complexes appears as a singlet in the ranges of 2.58–2.95 and at 49.3–50.0 in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively.

All the attempts made to obtain the dicationic vinylidene complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(1-CH_3-PTA)(C=C(CH_3)R)][CF_3SO_3]$_2$ formed by electrophilic addition of a methyl group to the β-carbon of the alkynyl failed even when a large excess of reagent was used.

*3.3.2. Synthesis of dicationic ruthenium(II) allenylidene complexes [Ru{κ^3(N,N,N)-Tp}(PPh_3)(1-H-PTA)(C=C=CPh$_2$)][PF_6]$_2$ (**5**) and [Ru{κ^3(N,N,N)-Tp}(PPh_3)(1-CH_3-PTA)(C=C=CPh$_2$)][CF_3SO_3]$_2$ (**6**)*

The addition of an equimolecular amount of HPF_6 acid to a solution of complex [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(C=C=CPh$_2$)][PF_6] (**2a**) in dichloromethane at −30°C chemoselectively produces the complex [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(1-H-PTA)(C=C=CPh$_2$)][PF_6]$_2$ (**5**). Likewise, the addition of $MeCF_3SO_3$ to complex [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(C=C=CPh$_2$)][CF_3SO_3] (**2b**) results in the complex [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(1-CH_3-PTA)(C=C=CPh$_2$)][CF_3SO_3]$_2$ (**6**) (see Scheme 4). The formation of complexes **5** and **6** comes from the protonation or methylation of one nitrogen atom from the coordinated PTA ligand in complexes **2a** and **2b,** respectively. The molar conductivity values found in acetone (208 (**5**) 217 (**6**) Ω^{-1} cm^2 mol^{-1}) are in the range found for electrolytes 1:2 [26].

Complexes **5** and **6** have been analytically and spectroscopically characterized (IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR). In particular, it must be noted that: (i) the IR spectra (KBr) show the characteristic ν(BH) absorption for the Tp ligand at 2488 cm^{-1}; (ii) $^{31}P\{^1H\}$ NMR spectra exhibit two doublets ($^2J_{PP}$ = 29–32 Hz) at δ = 42.4 (**5**) and 31.8 (**6**) for the phosphorous atom of the PPh_3 ligand and −18.1 (**5**) and −23.7 (**6**) ppm for the phosphorous atoms of the 1-H-PTA and 1-CH_3-PTA phosphanes, respectively; (iii) $^{13}C\{^1H\}$ NMR spectra reveal the presence of the allenylidene group as a triplet (t, $^2J_{CP} = {}^2J_{CP'}$ = 18 Hz,) for the C_α at δ = 308.0 (**5**) and 312.3 (**6**) ppm, and two singlets for C_β (194.1 (**5**), 194.4 (**6**)) and C_γ (168.3 (**5**), 167.4 (**6**)), respectively. The methyl group bound to the adamantane ring in complex **6** appears in the $^{13}C\{^1H\}$ NMR spectrum at δ = 48.9 ppm.

4. Summary

In summary, we have reported the synthesis of novel hydridotris(pyrazolyl)borate ruthenium(II) alkynyl complexes [Ru(C≡CR)-{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)] containing the water-soluble 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (PTA) ligand by alkyne activation in the presence of NEt_3. Furthermore, new allenylidene [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(C=C=CR$_2$)][X] derivatives have been isolated and characterized by reaction with the corresponding propargyl alcohols. For 9-ethynyl-9H-fluoren-9-ol, the use of $TlPF_6$ was necessary and the reaction probably occurs through a polymeric species in which the Tl atom is coordinated to the nitrogen of PTA phosphane. The electrophilic attacks to the former complexes are chemoselectives producing the alkylation of the PTA ligand and no electrophilic attack on the alkynyl or allenylidene chain has been detected.

Acknowledgements

This work was supported by the Spanish Ministerio de Educación, Cultura y Deporte (BQU2003-0255) and Consolider Ingenio 2010 (CSD2007-00006). A. García-Fernández thanks the Spanish Ministerio de Educación, Cultura y Deporte for a scholarship.

Appendix A. Supplementary material

The synthesis of the complexes [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(N-$H_2{}^i$Pr)][PF_6] and [Ru{κ^3(*N,N,N*)-Tp}(PPh_3)(PTA)(py)][PF_6] is included as supplementary data associated with this article and can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.017.

References

[1] F. Joó, Aqueous Organometallic Catalysis, Kluwer, Dordrecht, 2001.
[2] B. Cornils, W.A. Herrmann (Eds.), Aqueous Phase Organometallic Catalysis. Concepts and Applications, second ed., Wiley-VCH, Weinheim, 2004.
[3] W.H. Ang, P.J. Dyson, Eur. J. Inorg. Chem. (2006) 4003–4018.
[4] P.J. Dyson, G. Sava, Dalton Trans. (2006) 1929–1933.
[5] A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Viza, M. Peruzzini, Coord. Chem. Rev. 248 (2004) 955–993.
[6] S. Bolaño, J. Bravo, J.A. Castro, M. Rodriguez-Rocha, M.F.C. Guedes da Silva, A.J.L. Pombeiro, L. Gonsalvi, M. Peruzzini, Eur. J. Inorg. Chem. (2007) 5523–5532.
[7] C.A. Mebi, P.N. Radhika, B.J. Frost, Organometallics 26 (2007) 429–438.
[8] C.A. Mebi, B.J. Frost, Organometallics 24 (2005) 2339–2346.

[9] W. Kandioller, C.G. Hartinger, A.A. Nazarov, J. Kasser, R. John, M.A. Jakupec, V.B. Arion, P.J. Dyson, B.K. Keppler, J. Organomet. Chem. 694 (2009) 922–929.
[10] M.H. Garcia, T.S. Morais, P. Florindo, M.F.M. Piedade, V. Moreno, C. Ciudad, V. Noe, J. Inorg. Biochem. 103 (2009) 354–361.
[11] A.K. Renfrew, A.D. Phillips, A.E. Egger, C.G. Hartinger, S.S. Bosquain, A.A. Nazarov, B.K. Keppler, L. Gonsalvi, M. Peruzzini, P.J. Dyson, Organometallics 28 (2009) 1165–1172.
[12] C. Scolaro, C.G. Hartinger, C.S. Allardyce, B.K. Keppler, P.J. Dyson, J. Inorg. Biochem. 102 (2008) 1743–1748.
[13] T. Bugarcic, A. Habtemariam, J. Stepankova, P. Heringova, J. Kasparkova, R.J. Deeth, R.D.L. Johnstone, A. Prescimone, A. Parkin, S. Parsons, V. Brabec, P.J. Sadler, Inorg. Chem. 47 (2008) 11470–11486.
[14] C.A. Vock, A.K. Renfrew, R. Scopelliti, L. Juillerat-Jeanneret, P.J. Dyson, Eur. J. Inorg. Chem. (2008) 1661–1671.
[15] A. García-Fernandez, J. Díez, A. Manteca, J. Sánchez, M.P. Gamasa, E. Lastra, Polyhedron 27 (2008) 1214–1228.
[16] A. García-Fernandez, J. Díez, M.P. Gamasa, E. Lastra, Inorg. Chem. 48 (2009) 2471–2481.
[17] Posterior to the submission of this manuscript, the synthesis of complex [Ru(C≡CPh){κ^3(*N*,*N*,*N*)-Tp}(PPh_3)(PTA)] by means of a different synthetic procedure has been reported: S. Bolaño, M. Rodríguez-Rocha, J. Bravo, J. Castro, E. Oñate, M. Peruzzini, Organometallics, Article ASAP, doi: 10.1021/om9005142.
[18] B. Buriez, I.D. Burns, A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 18 (1999) 1504–1516.
[19] A related polymer formed by a coordination of Ag to the nitrogen of PTA phosphane has been reported: C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruíz, L. Gonsalvi, M. Peruzzini, Angew. Chem. Int. Ed. 44 (2005) 2568–2572.
[20] See supplementary material for the synthesis and spectroscopic data of the complexes [Ru{κ^3(*N*,*N*,*N*)-Tp}(PPh_3)(PTA)(NH_2*i*Pr)][PF_6] and [Ru{κ^3(*N*,*N*,*N*)-Tp}(PPh_3)(PTA)(py)][PF_6].
[21] C. Puerta, P. Valerga, Coord. Chem. Rev. 193–195 (1999) 977–1025.
[22] V. Cadierno, J. Gimeno, Chem. Rev. 109 (2009) 3512–3560.
[23] E.A. Shaffer, C. Chen, A.M. Beatty, E.J. Valente, H. Schanz, J. Organomet. Chem. 692 (2007) 5221–5233.
[24] E. Bustelo, M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 25 (2006) 4019–4025;
E. Bustelo, M. Jimenez-Tenorio, K. Mereiter, M.C. Puerta, P. Valerga, Organometallics 21 (2002) 1903–1911.
[25] R.C. Harbort, S. Hartmann, R.F. Winter, K.W. Klinkhammer, Organometallics 22 (2003) 3171–3174.
[26] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81–122.