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# Facile Modification of 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane Phosphanes Coordinated to Ruthenium(II)

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Hydridotris(pyrazolyl)borate (Tp) ruthenium (II) complexes containing new phosphane ligands are described. The new complexes were obtained by electrophilic attack to a coordinated 1,3,5-triaza-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane (PTA) ligand. Thus, cationic complexes [RuX{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-R-PTA)][Y] (X = Cl, R = H (**1**), $CH_2Ph$ (**4**), $CH_2CH{=}CH_2$ (**6**), $CH_2C{\equiv}CH$ (**8**); X = I, R = $CH_2Ph$ (**5**), $CH_2CH{=}CH_2$ (**7**)) and neutral [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-$I_2$-PTA)] (**3**) have been synthesized and characterized. For complexes [RuI{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-R-PTA)][Y] (R = $CH_2Ph$, $CH_2CH{=}CH_2$) an unprecedented formal C−H activation has been observed in alcohols leading to complexes with 1-methyl-4-phenyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane, 4-(2-methoxyethyl)-1-methyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane and 1-methyl-4-[2-(propan-2-yloxi)ethyl]-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane ligands, respectively, and the mechanism explored through deuteriation experiments. The first $I_2$-charge transfer compound between $I_2$ and a nitrogen which belongs to a ligand coordinated to a transition metal, [RuI{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-$I_2$-PTA)] is described.

## Introduction

In recent years, the 1,3,5-triaza-7-phosphatricyclo[3.3.1.1$^{3,7}$]-decane[1] (PTA, Figure 1A) has become a highly appreciated ligand[2] because of its water solubility properties and the catalytic applications of its metal complexes. In addition, the clinical utility of PTA transition metal complexes binding to DNA as antitumor drugs[3] has aroused interest in this chemistry.

Since modifications on the PTA ligands affect their chemical properties, an effort has been made to functionalize the PTA phosphane to improve the water-solubility, as well as the DNA binding properties and antimicrobial activity, of the complexes. Thus, a library of water-soluble ligands such as the N-alkylated compounds [1-R-PTA]X (R = Me,[4] Et,[5] $(CH_2)_4I$,[6] $CH_2Ph$,[7] $CH_2py$ (pymePTA)[8] (Figure 1B), di-N-methylated (Figure 1C)[9] di-N-acylated (DAPTA)[10] or di-N-formylated (DFPTA),[8] (Figure 1D) can be found in the literature.

Recently, the N-boranyl adduct 1-$BH_3$-PTA has been described (Figure 1E),[11] and PTA phosphane has been modified on the P−$CH_2$−N group through lithiation reactions which allow the synthesis of a number of derivatives (Figure 1F).[12,13]

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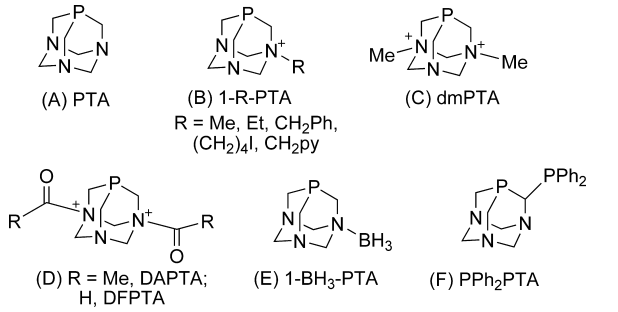
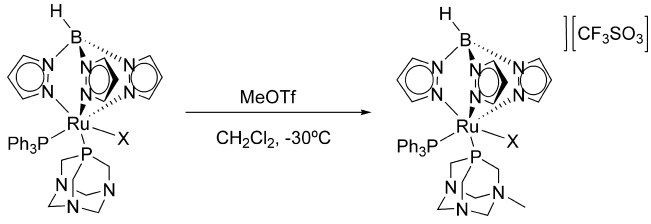



**Figure 1.** 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane (PTA) ligand and related phosphanes.

**Scheme 1**



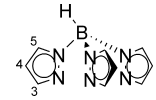

However, in spite of the high number of functionalized PTA phosphanes, the chemistry of the metal complexes of these ligands, except for the 1-Me-PTA, has been much less explored.

In this context, we have recently described the first examples of hydridotris(pyrazolyl)borate ruthenium (II) complexes containing the water-soluble PTA and 1-Me-PTA phosphane ligands and their interaction with plasmidic DNA by using a mobility shift assay.[14] In addition their antimicrobial activity was tested showing that complexes [RuX{$\kappa^3$-(*N,N,N*)-Tp}(PPh$_3$)(1-Me-PTA)][CF$_3$SO$_3$] (X = Cl, H) were quite active against prokaryotic microorganisms. The complexes were synthesized in very mild reaction conditions by electrophilic attack on one N of the coordinated PTA phosphane (Scheme 1). In our particular case, the attempts to obtain complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-Me-PTA)]-[CF$_3$SO$_3$] by reaction of the appropriate ruthenium(II) complex with the previously synthesized 1-Me-PTA phosphane ligand failed.

In this paper, we extend this synthetic method to a number of electrophiles searching for the synthesis of complexes with new hydrophilic ligands which can be tested as potential biologically active complexes. Thus, we report here the synthesis, under very mild conditions, of a series of new hydridotris(pyrazolyl)borate ruthenium(II) complexes containing modified PTA ligands obtained by electrophilic attack on the N atom of the coordinated PTA ligand. The chemistry of the obtained derivatives has also been explored.

## Experimental Section

**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 by standard methods and distilled under nitrogen before use. The compounds [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] and [RuI{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] were prepared by previously reported methods.[14] Infrared spectra were recorded on a Perkin-Elmer FT-IR Paragon 1000 spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B 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$_3$PO$_4$ as standards. DEPT experiments were carried out for all the compounds. Coupling constants *J* are given in hertz. 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. 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:



**Synthesis of [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-H-PTA)][BF$_4$] (1).** To a solution of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (100 mg, 0.13 mmol) in dichloromethane (2 mL) at −30 °C was added a diethyl ether solution of HBF$_4$·OEt$_2$ (0.13 mmol). The reaction mixture was stirred at −30 °C for 40 min. The addition of hexane (60 mL) led to the formation of a pale yellow precipitate. The solvents were decanted, and the solid residue was washed with hexane (2 × 5 mL) and dried under reduced pressure. Yield: 25 mg (42%). MS-ESI: *m*/*z* = 770 ([M]$^+$, 11%), 734 ([M − H − Cl]$^+$, 100%). Molar conductivity in nitromethane: $\Lambda_M$ = 66 S cm$^2$ mol$^{-1}$. IR (KBr): 2480 ($\nu$(BH)), 1047 ($\nu$(BF$_4$)) cm$^{-1}$. $^1$H NMR in CD$_2$Cl$_2$ ($\delta$): 8.12 (d, 1H, H$^{3,5}$ pz), 7.73 (br, 3H, H$^{3,5}$ pz), 7.48−7.34 (m, 15H, PPh$_3$), 6.67 (d, 1H, H$^{3,5}$ pz), 6.34 (d, 1H, H$^{3,5}$ pz), 6.30 (t, 1H, H$^4$ pz), 5.88 (t, 1H, H$^4$ pz), 5.84 (t, 1H, H$^4$ pz), 4.82 (br, 3H, NC*H*$_2$N), 4.52 (br, 3H, NC*H*$_2$N), 3.94 (br, 6H, NC*H*$_2$P) ppm. $^{13}$C{$^1$H} NMR in CD$_2$Cl$_2$ ($\delta$): 146.9 (s, C-3 pz), 143.9 (s, C-3 pz), 143.6 (s, C-3 pz), 136.6 (s, C-5 pz), 136.0 (s, C-5 pz), 135.9 (s, C-5 pz), 135.0 (d, $J_{CP}$ = 40 Hz, C-1 PPh$_3$), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 PPh$_3$), 129.8 (s, C-4 PPh$_3$), 128.2 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh$_3$), 106.6 (s, C-4 pz), 105.9 (s, C-4 pz), 105.2 (s, C-4 pz), 73.3 (br, N*C*H$_2$N), 49.7 (br, NCH$_2$P) ppm. $^{31}$P NMR in CD$_2$Cl$_2$ ($\delta$): 42.4 (d, $^2J_{PP}$ = 32 Hz, PPh$_3$), −18.1 (d, $^2J_{PP}$ = 32 Hz, 1-H-PTA) ppm.

**Synthesis of [{RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)}$_2${$\mu$-$\kappa^2$(*P,P*)-PTA-H-PTA}][BF$_4$] (2).** To a solution of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (100 mg, 0.13 mmol) in dichloromethane (2 mL) at −30 °C was added a diethyl ether solution of HBF$_4$·OEt$_2$ (0.07 mmol). The reaction mixture was stirred at −30 °C during 40 min. The addition of hexane (60 mL) led to the formation of a pale yellow precipitate. The solvents were decanted, and the solid residue was washed with hexane (2 × 5 mL) and dried under reduced pressure. Yield: 49 mg (43%). MS-ESI: *m*/*z* = 1539 ([M]$^+$, 7%), 770 ([RuCl(Tp)(PPh$_3$)(1-H-PTA)]$^+$, 59%). 734 ([Ru(Tp)(PPh$_3$)-(PTA)]$^+$, 100%). Molar conductivity in nitromethane: $\Lambda_M$ = 93 S cm$^2$ mol$^{-1}$. IR (KBr): 2480 ($\nu$(BH)), 1047 ($\nu$(BF$_4$)) cm$^{-1}$. $^1$H NMR in CD$_2$Cl$_2$ ($\delta$): 8.13 (d, 1H, H$^{3,5}$ pz), 7.73 (m, 3H, H$^{3,5}$ pz), 7.50−7.34 (m, 15H, PPh$_3$), 6.68 (d, 1H, H$^{3,5}$ pz), 6.30 (br, 2H, H$^{3,5}$ and H$^4$ pz), 5.88 (t, 1H, H$^4$ pz), 5.83 (t, 1H, H$^4$ pz), 4.73 (br, 3H, NC*H*$_2$N), 4.46 (br, 3H, NC*H*$_2$N), 3.92 (br, 6H, NC*H*$_2$P) ppm. $^{13}$C{$^1$H} NMR in CD$_2$Cl$_2$ ($\delta$): 146.8 (s, C-3 pz), 143.9 (s, C-3 pz), 143.5 (s, C-3 pz), 136.4 (s, C-5 pz), 135.9 (s, C-5 pz), 135.7 (s, C-5 pz), 135.4 (d, $J_{CP}$ = 46 Hz, C-1 PPh$_3$), 134.1 (d, $^2J_{CP}$ = 8 Hz, C-2,6 PPh$_3$), 129.7 (s, C-4 PPh$_3$), 128.1 (d, $^3J_{CP}$ = 9 Hz, C-3,5 PPh$_3$), 106.5 (s, C-4 pz), 105.8 (s, C-4 pz), 105.1 (s, C-4 pz), 72.5 (s, N*C*H$_2$N), 49.9 (d, $J_{CP}$ = 13 Hz, NCH$_2$P) ppm. $^{31}$P NMR in

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$CD_2Cl_2$ ($\delta$): 43.3 (d, $^2J_{PP}$ = 32 Hz, $PPh_3$), −21.1 (d, $^2J_{PP}$ = 32 Hz, PTA-H-PTA) ppm.

**Synthesis of [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$I_2$-PTA)] (3).** To a solution of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(PTA)] (100 mg, 0.13 mmol) in dichloromethane (2 mL) at −30 °C iodine (33 mg, 0.13 mmol) was added. The reaction mixture was stirred at −30 °C during 40 min. The addition of hexane afforded an orange precipitate. The solvent was decanted, and the solid residue was washed with hexane (5 × 10 mL) and dried under vacuum. Yield: 90 mg (68%). Anal. Calcd for $C_{33}H_{37}N_9BClI_2P_2Ru\cdot CH_2Cl_2$ (1107.63 g/mol): C, 36.86; H, 3.55; N, 11.38. Found: C, 36.99; H, 3.54; N, 12.54. IR (KBr): 2468 ($\nu$(BH)) $cm^{-1}$. $^1H$ NMR in $CD_2Cl_2$ ($\delta$): 8.09 (d, 1H, $H^{3,5}$ pz), 7.72 (br, 3H, $H^{3,5}$ pz), 7.50−7.33 (m, 15H, $PPh_3$), 6.64 (d, 1H, $H^{3,5}$ pz), 6.30 (br, 2H, $H^{3,5}$ and $H^4$ pz), 5.86 (d, 1H, $H^4$ pz), 5.83 (d, 1H, $H^4$ pz), 4.46 (AB spin system, $J_{HAHB}$ = 12 Hz, 3H, NC$H_2$N), 4.25 (AB spin system, $J_{HAHB}$ = 12 Hz, 3H, NC$H_2$N), 3.95−3.85 (m, 6 H, NC$H_2$P) ppm. $^{13}C\{^1H\}$ NMR in $CD_2Cl_2$ ($\delta$): 146.9 (s, C-3 pz), 143.8 (s, C-3 pz), 143.5 (s, C-3 pz), 136.6 (s, C-5 pz), 135.9 (s, C-5 pz), 135.2 (d, $J_{CP}$ = 39 Hz, C-1 $PPh_3$), 134.1 (d, $^2J_{CP}$ = 9 Hz, C-2,6 $PPh_3$), 129.8 (s, C-4 $PPh_3$), 128.1 (d, $^3J_{CP}$ = 8 Hz, C-3,5 $PPh_3$), 106.4 (s, C-4 pz), 105.7 (s, C-4 pz), 105.2 (s, C-4 pz), 73.2 (br, N$CH_2$N), 50.9 (d, $J_{CP}$ = 13 Hz, N$CH_2$P) ppm. $^{31}P$ NMR in $CD_2Cl_2$ ($\delta$): 43.9 (d, $^2J_{PP}$ = 30 Hz, $PPh_3$), −16.2 (d, $^2J_{PP}$ = 30 Hz, 1-$I_2$-PTA) ppm.

**Synthesis of [RuX{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$PhCH_2$-PTA)][I] (X = Cl (4), I (5)) and of [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$PhCD_2$-PTA)][I] ($d_2$-5).** Benzyl iodide (86 $\mu$L, 0.65 mmol) was added to a solution of complex [RuX{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(PTA)] (X = Cl, I) (100 mg, 0.13 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature during 1.5 h (X = Cl) or 4 h (X = I). The addition of hexane (60 mL) afforded complexes **4**, **5** as white solids. Solvents were decanted, and the solid residue was washed with hexane (5 × 10 mL) and dried under vacuum. Complex $d_2$-**5** was obtained by the same procedure but using dideuterated benzyl iodide. **4**: Yield: 75 mg, (64%). Anal. Calcd for $C_{40}H_{44}N_9BClIP_2Ru$: C, 48.67; H, 4.49; N, 12.77. Found: C, 48.53; H, 4.44; N, 12.73. $ESI^+$-MS (*m*/*z*): 860.2 $[M]^+$. Molar conductivity in acetonitrile: $\Lambda_M$ = 111 S $cm^2$ $mol^{-1}$. IR (KBr): 2479 ($\nu$(BH)) $cm^{-1}$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.10 (d, 1H, $H^{3,5}$ pz), 7.91 (br, 3H, $H^{3,5}$ pz), 7.88−7.12 (m, 20H, Ph), 6.89 (d, 1H, $H^{3,5}$ pz), 6.43 (d, 1H, $H^{3,5}$ pz), 6.37 (t, 1H, $H^4$ pz), 5.91 (t, 1H, $H^4$ pz), 5.89 (t, 1H, $H^4$ pz), 5.21−5.12 (m, 3H, 1-$PhCH_2$-PTA), 4.75 (AB spin system, $J_{AB}$ = 12 Hz, 1H, 1-$PhCH_2$-PTA), 4.65 (AB spin system, $J_{AB}$ = 12 Hz, 1H, 1-$PhCH_2$-PTA), 4.36 (CD spin system, $J_{CD}$ = 13 Hz, 2H, 1-$PhCH_2$-PTA), 4.28 (CD spin system, $J_{CD}$ = 13 Hz, 2H, 1-$PhCH_2$-PTA), 3.94−3.86 (m, 3H, Ph$CH_2$ and 1-$PhCH_2$-PTA), 3.75−3.70 (m, 2 H, 1-$PhCH_2$-PTA) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 149.1 (s, C-3 pz), 145.1 (s, C-3 pz), 143.7 (s, C-3 pz), 137.4 (s, C-5 pz), 136.5 (s, C-5 pz), 135.3 (d, $J_{CP}$ = 39 Hz, C-1 $PPh_3$), 134.1−126.1 (Ph and $PPh_3$), 107.3 (s, C-4 pz), 105.9 (s, C-4 pz), 105.8 (s, C-4 pz), 79.4 (s, $PhCH_2NCH_2N$), 78.0 (s, $PhCH_2NCH_2N$), 68.9 (s, N$CH_2$N), 64.1 (s, Ph$CH_2$), 53.3 (s, $PhCH_2NCH_2P$), 47.5 (d, $J_{CP}$ = 12 Hz, N$CH_2$P), 47.0 (d, $J_{CP}$ = 19 Hz, N$CH_2$P) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 42.2 (d, $^2J_{PP}$ = 30 Hz, $PPh_3$), −12.6 (d, $^2J_{PP}$ = 30 Hz, 1-$PhCH_2$-PTA) ppm. **5**: Yield: 120 mg (89%). Anal. Calcd for $C_{40}H_{44}N_9BI_2P_2Ru$: C, 44.55; H, 4.11; N, 11.69. Found: C, 44.27; H, 4.05; N, 11.54. Molar conductivity in acetonitrile: $\Lambda_M$ = 111 S $cm^2$ $mol^{-1}$. IR (KBr): 2479 ($\nu$(BH)) $cm^{-1}$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.39 (d, 1H, H pz), 7.89 (br, 2H, $H^5$ pz), 7.81 (d, 1H, $H^5$ pz), 7.49−7.22 (m, 20H, Ph and $PPh_3$), 6.55 (d, 1H, $H^3$ pz), 6.47 (d, 1H, $H^3$ pz), 6.28 (t, 1H, $H^4$ pz), 5.83 (t, 1H, $H^4$ pz), 5.79 (t, 1H, $H^4$ pz), 5.20−5.10 (m, 2H, $PhCH_2NCH_2N$), 4.76 (br, 1H, $PhCH_2NCH_2N$), 4.60 (br, 1H, $PhCH_2NCH_2N$), 4.35−4.25 (m, 3H, NC$H_2$N and Ph$CH_2$N), 4.19−4.10 (m, 2H, NC$H_2$N and $PhCH_2NCH_2P$), 3.93 (br, 1H, $PhCH_2NCH_2P$), 3.80 (br, 1H, NC$H_2$P), 3.65 (br, 2H, NC$H_2$P), 3.40 (br, 1H, NC$H_2$P) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 148.3 (s, C-3 pz), 146.6 (s, C-3 pz), 137.1 (s, C-5 pz), 136.8 (s, C-5 pz), 136.3 (s, C-5 pz), 134.6−128.3 (Ph and $PPh_3$), 107.3 (s, C-4 pz), 106.4 (s, C-4 pz), 105.6 (s, C-4 pz), 79.2 (s, $PhCH_2NCH_2N$), 78.5 (s, $PhCH_2NCH_2N$), 69.1 (s, N$CH_2$N), 64.2 (s, Ph$CH_2$N), 55.1 (s, $PhCH_2NCH_2P$), 49.9 (d, $J_{CP}$ = 15 Hz, N$CH_2$P), 49.7 (d, $J_{CP}$ = 12 Hz, N$CH_2$P) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 44.7 (d, $^2J_{PP}$ = 31 Hz, $PPh_3$), −14.5 (d, $^2J_{PP}$ = 31 Hz, 1-$PhCH_2$-PTA) ppm. $d_2$-**5**: $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 63.5 (br, Ph$CD_2$N) ppm. For full NMR spectroscopic data see Supporting Information.

**Synthesis of [RuX{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$CH_2$=$CHCH_2$-PTA)]-[I] (X = Cl (6), I (7).** Allyl iodide (12 $\mu$L, 0.13 mmol) was added to a solution of complex [RuX{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(PTA)] (X = Cl, I) (0.13 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature during 20 min (X = Cl) or 1 h (X = I). The addition of hexane (50 mL) afforded complexes **6** and **7** as yellow and orange solids, respectively. Solvents were decanted, and the solid residue was washed with hexane (5 × 5 mL) and dried under reduced pressure. **6**: Yield: 90 mg (74%). Anal. Calcd for $C_{36}H_{42}N_9BClIP_2Ru$: C, 46.15; H, 4.52; N, 13.45. Found: C, 45.76; H, 4.45; N, 13.48. $ESI^+$-MS (*m*/*z*): 810 ($[M]^+$, 100%), 770 ($[M - CH_2CH{=}CH_2]^+$, 5%), 734 ($[M - Cl{-}CH_2CH{=}CH_2]^+$, 54%). Molar conductivity in acetonitrile: $\Lambda_M$ = 124 S $cm^2$ $mol^{-1}$. IR (KBr): 2479 ($\nu$(BH)) $cm^{-1}$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.08 (d, 1H, $H^3$ pz), 7.95 (d, 1H, $H^5$ pz), 7.94 (d, 1H, $H^5$ pz), 7.86 (d, 1H, $H^5$ pz), 7.45−7.19 (m, 15H, $PPh_3$), 6.97 (d, 1H, $H^3$ pz), 6.47 (d, 1H, $H^3$ pz), 6.27 (t, 1 H, $H^4$ pz), 5.94 (t, 1 H, $H^4$ pz), 5.91 (t, 1 H, $H^4$ pz), 5.80 (m, 1H, $CH_2CH{=}CH_2$), 5.60 (m, 2H, $CH_2CH{=}CH_2$), 4.91 (AB spin system, $J_{HAHB}$ = 12 Hz, 1H, $CH_2{=}CHCH_2NCH_2N$), 4.86 (CD spin system, $J_{HCHD}$ = 12 Hz, 1H, $CH_2{=}CHCH_2NCH_2N$), 4.82 (CD spin system, $J_{HCHD}$ = 12 Hz, 1H, $CH_2{=}CHCH_2NCH_2N$), 4.69 (AB spin system, $J_{HAHB}$ = 12 Hz, 1H, $CH_2{=}CHCH_2NCH_2N$), 4.27−4.25 (m, 1H, NC$H_2$N), 4.19 (EF spin system, $J_{HEHF}$ = 14 Hz, 1H, $CH_2{=}CHCH_2NCH_2P$), 4.05 (EF spin system, $J_{HEHF}$ = 14 Hz, 1H, $CH_2{=}CHCH_2NCH_2P$), 3.99−3.94 (m, 2H, NC$H_2$N and NC$H_2$P), 3.79 (GH spin system, $J_{HGHH}$ = 15 Hz, 1H, NC$H_2$P), 3.71−3.64 (m, 3H, $CH_2{=}CHCH_2$ and NC$H_2$P), 3.03 (GH spin system, $J_{HGHH}$ = 15 Hz, 1H, NC$H_2$P) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 149.2 (s, C-3 pz), 145.1 (s, C-3 pz), 143.8 (s, C-3 pz), 137.4 (s, C-5 pz), 136.5 (s, C-5 pz), 135.4 (d, $J_{CP}$ = 39 Hz, C-1 $PPh_3$), 134.2 (d, $^2J_{CP}$ = 9 Hz, C-2,6 $PPh_3$), 130.3 (s, C-4 $PPh_3$), 129.1 (s, $CH_2{=}CHCH_2$), 128.7 (s, $^3J_{CP}$ = 9 Hz, C-3,5 $PPh_3$), 124.2 (s, $CH_2{=}CHCH_2$), 107.3 (s, C-4 pz), 105.8 (s, C-4 pz), 105.7 (s, C-4 pz), 79.0 (s, $CH_2{=}CHCH_2NCH_2N$), 78.0 (s, $CH_2{=}CHCH_2NCH_2N$), 70.0 (s, N$CH_2$N), 63.3 (s, $CH_2{=}CHCH_2$), 53.8 (s, $CH_2{=}CHCH_2NCH_2P$), 47.8 (d, $J_{CP}$ = 13 Hz, N$CH_2$P), 47.2 (d, $J_{CP}$ = 16 Hz, N$CH_2$P) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 42.3 (d, $^2J_{PP}$ = 31 Hz, $PPh_3$), −13.2 (d, $^2J_{PP}$ = 31 Hz, 1-$CH_2$=$CHCH_2$-PTA) ppm. **7**: Yield: 118 mg (88%). Anal. Calcd for $C_{36}H_{42}N_9BI_2P_2Ru$: C, 42.04; H, 4.12; N, 12.26. Found: C, 41.99; H, 4.05; N, 12.19. $ESI^+$-MS (*m*/*z*): 934.14 $[M]^+$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.40 (d, 1H, $H^3$ pz), 7.94 (br, 2H, $H^5$ pz), 7.85 (d, 1H, $H^5$ pz), 7.43−7.31 (m, 15H, $PPh_3$), 6.66 (d, 1H, $H^3$ pz), 6.63 (d, 1H, $H^3$ pz), 6.28 (t, 1H, $H^4$ pz), 5.90 (t, 1H, $H^4$ pz), 5.86 (t, 1H, $H^4$ pz), 5.77−5.74 (m, 1H, $CH_2{=}CHCH_2$), 5.56−5.51 (m, 2H, $CH_2{=}CHCH_2$), 4.92−4.90 (m, 2H, $CH_2{=}CHCH_2NCH_2N$), 4.81 (m, 1H, $CH_2{=}CHCH_2NCH_2N$), 4.73 (m, 1H, $CH_2{=}CHCH_2NCH_2N$), 4.29 (spin system AB, $J_{HAHB}$ = 13 Hz, 1H, NC$H_2$N), 4.16 (spin system AB, $J_{HAHB}$ = 13 Hz, 1H, NC$H_2$N), 4.07−4.00 (m, 3H, 2H $CH_2{=}CHCH_2NCH_2P$ and 1H NC$H_2$P), 3.79−3.75 (m, 2H, NC$H_2$P), 3.65 (d, $^3J_{HH}$ = 7 Hz, 2H,

$CH_2$=CHC$H_2$), 3.40−3.35 (m, 1H, NC$H_2$P) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 148.5 (s, C-3 pz), 148.4 (s, C-3 pz), 146.6 (s, C-3 pz), 137.1 (s, C-5 pz), 136.8 (s, C-5 pz), 136.4 (s, C-5 pz),135.2 (d, $J_{CP}$ = 40 Hz, C-1 $PPh_3$), 134.6 (d, $^2J_{CP}$ = 9 Hz, C-2,6 $PPh_3$), 130.2 (s, C-4 $PPh_3$), 129.3 (s, $CH_2$=CHC$H_2$), 128.5 (d, $^3J_{CP}$ = 9 Hz, C-3,5 $PPh_3$), 123.9 (s, $CH_2$=C$H$C$H_2$), 107.3 (s, C-4 pz), 106.2 (s, C-4 pz), 105.7 (s, C-4 pz), 79.0 (s, $CH_2$=CHC$H_2$NC$H_2$N), 78.1 (s, $CH_2$=CHC$H_2$NC$H_2$N), 69.0 (s, NC$H_2$N), 63.1 (s, $CH_2$=CHC$H_2$), 55.3 (d, $J_{CP}$ = 7 Hz, $CH_2$=CHC$H_2$NC$H_2$P), 50.1 (d, $J_{CP}$ = 15 Hz, NC$H_2$P), 49.9 (d, $J_{CP}$ = 18 Hz, NC$H_2$P) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 44.0 (d, $^2J_{PP}$ = 31 Hz, $PPh_3$), −15.6 (d, $^2J_{PP}$ = 31 Hz, 1-$CH_2$=CHC$H_2$-PTA) ppm.

**Synthesis of [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-CH≡CC$H_2$-PTA)][Br] (8).** Propargyl bromide (58 $\mu$L, 0.65 mmol) was added to a solution of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(PTA)] (100 mg, 0.13 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature during 4 h. The addition of hexane (60 mL) afforded a white solid precipitate. Solvents were decanted, and the solid residue was washed with hexane (5 × 10 mL) and dried under vacuum. Yield: 80 mg (69%). Anal. Calcd for $C_{36}H_{40}N_9BBrClP_2Ru\cdot 1/2CH_2Cl_2$: C, 47.12; H, 4.44; N, 13.55. Found: C, 46.69; H, 4.97; N, 13.56. ESI$^+$-MS (*m*/*z*): 808 $[M]^+$. Molar conductivity in acetonitrile: $\Lambda_M$ = 103 S cm$^2$ mol$^{-1}$. IR (KBr): 3272 ($\nu$(C(sp)-H)), 2479 ($\nu$(BH)), 2117 ($\nu$(C≡C)) cm$^{-1}$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.12 (d, 1H, H$^3$ pz), 7.91 (br, 2H, H$^5$ pz), 7.85 (d, 1 H, H$^5$ pz), 7.41−7.29 (m, 15H, Ph), 6.70 (d, 1H, H$^3$ pz), 6.54 (d, 1H, H$^3$ pz), 6.29 (t, 1H, H$^4$ pz), 5.90 (t, 1H, H$^4$ pz), 5.89 (t, 1H, H$^4$ pz), 5.06−4.99 (m, 2H, 1-1-CH≡CC$H_2$-PTA), 4.90−4.78 (m, 2H, 1-CH≡CC$H_2$-PTA), 4.40−4.21 (m, 3H, 1-CH≡CC$H_2$-PTA), 4.13−4.08 (m, 4H, 1-CH≡CC$H_2$-PTA and C$H_2$C≡CH), 3.74−3.64 (m, 3H, 1-CH≡CC$H_2$-PTA). $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 148.6 (s, C-3 pz), 144.8 (s, C-3 pz), 143.8 (s, C-3 pz), 137.3 (s, C-5 pz), 136.5 (s, C-5 pz), 136.4 (s, C-5 pz), 135.4 (d, $J_{CP}$ = 39 Hz, C-1 $PPh_3$), 134.0 (d, $^2J_{CP}$ = 9 Hz, C-2,6 $PPh_3$), 130.2 (s, C-4 $PPh_3$), 128.7 (d, $^2J_{CP}$ = 9 Hz, C-3,5 $PPh_3$), 107.3 (s, C-4 pz), 106.1 (s, C-4 pz), 105.7 (s, C-4 pz), 84.5 (s, $CH_2C$≡CH), 79.0 (s, $CH_2C$≡CHNC$H_2$N), 78.8 (s, $CH_2C$≡CHNC$H_2$N), 70.7 (s, $CH_2C$≡C$H$), 69.0 (s, NC$H_2$N), 54.0 (s, C$H_2$C≡CH), 50.8 (s, $CH_2C$≡CHNC$H_2$P), 47.8 (d, $J_{CP}$ = 14 Hz, NC$H_2$P), 47.5 (d, $J_{CP}$ = 16 Hz, NC$H_2$P) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 42.4 (d, $^2J_{PP}$ = 31 Hz, $PPh_3$), −11.2 (d, $^2J_{PP}$ = 31 Hz, 1-CH≡CC$H_2$-PTA) ppm.

**Synthesis of [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$CH_3$-4-Ph-PTA)][I] (9) and of [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$CH_3$-4-Ph-$d_2$-PTA)][I] ($d_2$-9).** A solution of complex [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-Ph$CH_2$-PTA)][I] (**5**) (100 mg, 0.09 mmol) in methanol (35 mL) was heated at reflux temperature during 13 h. The solution was concentrated and then transferred to a silica gel chromatography column and eluted with dichloromethane/methanol (10:1). The obtained solution was concentrated. The addition of diethyl ether afforded a pale orange solid precipitate. The solid was washed with diethyl ether and dried under reduced pressure. The same procedure was used to obtain complex $d_2$-**9** from $d_2$-**5**. Yield: 52 mg (52%). IR (KBr): 2478 ($\nu$(BH)) cm$^{-1}$. Molar conductivity in methanol: $\Lambda_M$ = 79 S cm$^2$ mol$^{-1}$ ESI$^+$-MS (*m*/*z*): 952 $[M]^+$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.25 (br, 1H, H$^3$ pz), 7.81 (d, 1H, H$^5$ pz), 7.76 (d, 1H, H$^5$ pz), 7.72 (d, 1H, H$^5$ pz), 7.45−6.99 (m, 20H, Ph and $PPh_3$), 6.56 (d, 1H, H$^3$ pz), 6.28 (t, 1H, H$^4$ pz), 6.17 (t, 1H, H$^4$ pz), 5.80 (t, 1H, H$^4$ pz), 5.62 (s, 1H, NC$H$N), 5.39−5.27 (m, 1H, $CH_3$NC$H_2$N), 5.24−5.17 (m, 1H, $CH_3$NC$H_2$N), 5.09 (br, 2H, H$^3$ pz and $CH_3$NC$H_2$N), 5.01−4.89 (m, 1H, $CH_3$NC$H_2$N), 4.75 (br, 2H, $CH_3$NC$H_2$P), 3.70−3.57 (m, 1H, NC$H_2$P), 3.50 (br, 1H, NC$H_2$P), 3.08 (s, 3H, C$H_3$N), 3.01 (br, 1H, NC$H_2$P), 2.93−2.81 (m, 1H, NC$H_2$P) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 147.7 (s, C-3 pz), 146.5 (s, C-3 pz), 145.8 (s, C-3 pz), 136.7 (s, C-5 pz), 136.2 (s, C-5 pz), 135.1 (d, $J_{CP}$ = 39 Hz, C-1 $PPh_3$), 134.6−126.7 (Ph and $PPh_3$), 106.5 (s, C-4 pz), 106.4 (s, C-4 pz), 105.4 (s, C-4 pz), 81.7 (s, 2C, $CH_3$NC$H_2$N), 75.2 (s, NC$H$N), 62.1 (s, $CH_3$NC$H_2$P), 49.0 (s, C$H_3$N), 43.0 (d, $J_{CP}$ = 14 Hz, NC$H_2$P), 41.6 (d, $J_{CP}$ = 18 Hz, NC$H_2$P) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 46.4 (d, $^2J_{PP}$ = 32 Hz, $PPh_3$), −17.7 (d, $^2J_{PP}$ = 32 Hz, 1-$CH_3$-4-Ph-PTA) ppm. $d_2$-**9**: $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 81.3 (br, HC(D)NMe), 74,8 (br, PhCD) ppm. For full NMR spectroscopic data see Supporting Information.

**Synthesis of [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$){1-$CH_3$-4-{RO($CH_2$)$_2$}-PTA}][I] (R = $CH_3$ (10a), $CH(CH_3)_2$ (10b)).** A solution of complex [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$CH_2$=CHC$H_2$-PTA)][I] (**7**) (50 mg, 0.05 mmol) in the corresponding alcohol (methanol or 2-propanol) (10 mL) was heated at reflux temperature during 9 h. The solution was concentrated and then transferred to a silica gel chromatography column and eluted with dichloromethane/methanol (10:1). The obtained solution was concentrated. The addition of diethyl ether afforded a pale orange solid precipitate. The solid was washed with diethyl ether and dried under reduced pressure. **10a**: Yield: 27 mg (49%). ESI$^+$-MS (*m*/*z*): 934 $[M]^+$. Molar conductivity in acetonitrile: $\Lambda_M$ = 144 S cm$^2$ mol$^{-1}$. IR (KBr): 2480 ($\nu$(BH)) cm$^{-1}$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 7.88 (d, 1H, H$^3$ pz), 7.38 (br, 2H, H$^5$ pz), 7.28 (d, 1H, H$^5$ pz), 6.85−6.73 (m, 15H, $PPh_3$), 6.12 (d, 1H, H$^3$ pz), 6.07 (d, 1H, H$^3$ pz), 5.71 (t, 1H, H$^4$ pz), 5.33 (br, 2H, H$^4$ pz), 4.41−4.35 (m, 2H, NC$H_2$N), 4.07−4.04 (m, 1H, NC$H_2$N), 3.81−3.78 (m, 3H, NC$H$N and $CH_3$NC$H_2$P), 3.48−3.44 (m, 1H, NC$H_2$P), 2.97−2.94 (m, 2H, NC$H_2$P), 2.67−2.62 (m, 6H, NC$H_2$N, OC$H_2$ and OC$H_3$), 2.22 (s, 3H, C$H_3$N), 2.10−2.06 (m, 1H, NC$H_2$P), 1.39−1.28 (m, 2H, C$H_2$CH) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 148.5 (s, C-3 pz), 148.0 (s, C-3 pz), 146.7 (s, C-3 pz), 137.3 (s, C-5 pz), 136.9 (s, C-5 pz), 136.8 (s, C-5 pz), 135.3 (d, $J_{CP}$ = 40 Hz, C-1 $PPh_3$), 134.6 (d, $^2J_{CP}$ = 8 Hz, C-2,6 $PPh_3$), 130.2 (s, C-4 $PPh_3$), 128.5 (d, $^3J_{CP}$ = 8 Hz, C-3,5 $PPh_3$), 107.3 (s, C-4 pz), 106.3 (s, C-4 pz), 105.8 (s, C-4 pz), 81.4 (s, NC$H_2$N), 71.7 (s, NC$H$N), 68.3 (s, OC$H_2$), 67.7 (s, NC$H_2$N), 59.9 (s, $CH_3$NC$H_2$P), 58.5 (s, OC$H_3$), 48.8 (s, C$H_3$N), 44.0 (d, $J_{CP}$ = 16 Hz, NC$H_2$P), 42.1 (d, $J_{CP}$ = 17 Hz, NC$H_2$P), 29.9 (s, C$H_2$CH) ppm. $^{31}P$ NMR in dmso-$d_6$ ($\delta$): 42.8 (d, $^2J_{PP}$ = 31 Hz, $PPh_3$), −21.9 (d, $^2J_{PP}$ = 31 Hz, 1-$CH_3$-4-{$CH_3O(CH_2)_2$}-PTA) ppm. **10b**: Yield: 34 mg (62%). ESI$^+$-MS (*m*/*z*): 962 $[M]^+$. Molar conductivity in acetonitrile: $\Lambda_M$ = 112 S cm$^2$ mol$^{-1}$. IR (KBr): 2477 ($\nu$(BH)) cm$^{-1}$. $^1H$ NMR in dmso-$d_6$ ($\delta$): 8.45 (d, 1 H, H$^3$ (pz)), 7.94 (d, 1 H, H$^5$ (pz)), 7.86 (d, 1 H, H$^5$ (pz)), 7.81 (d, 1 H, H$^5$ (pz)), 7.43−7.30 (m, 15 H, $PPh_3$), 6.70 (d, 1 H, H$^3$ (pz)), 6.66 (d, 1 H, H$^3$ (pz)), 6.29 (t, 1 H, H$^4$ (pz)), 5.90 (t, 1 H, H$^4$ (pz)), 5.87 (t, 1 H, H$^4$ (pz)), 4.92 (AB spin system, 1 H, $J_{HAHB}$ = 13 Hz, $CH_3$NC$H_2$N), 4.84 (CD spin system, 1 H, $J_{HCHD}$ = 11 Hz, $CH_3$NC$H_2$N), 4.75 (CD spin system, 1 H, $J_{HCHD}$ = 11 Hz, $CH_3$NC$H_2$N), 4.70 (AB spin system, 1 H, $J_{HAHB}$ = 13 Hz, $CH_3$NC$H_2$N), 4.51−4.53 (m, 2 H, $CH_3$NC$H_2$P), 4.20−4.19 (m, 1 H, OC$H_2$), 4.14−4.11 (m, 1 H, OC$H_2$), 3.84 (EF spin system, 1 H, $J_{HEHF}$ = 18 Hz, NC$H_2$P), 3.54 (EF spin system, 1 H, $J_{HEHF}$ = 18 Hz, NC$H_2$P), 3.48 (GH spin system, 1 H, $J_{HGHH}$ = 17 Hz, NC$H_2$P), 3.40−3.30 (m, 2 H, NC$H$N and C$H$(CH$_3$)$_2$), 3.25 (GH spin system, 1 H, $J_{HGHH}$ = 17 Hz, NC$H_2$P), 2.81 (s, 3 H, C$H_3$N), 2.25−2.18 (m, 1 H, $OCH_2CH_2$), 1.84−1.78 (m, 1 H, $OCH_2CH_2$), 1.06 (d, 6 H, $^3J_{HH}$ = 6 Hz, CH(C$H_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR in dmso-$d_6$ ($\delta$): 148.6 (s, C-3 (pz)), 148.5 (s, C-3 (pz)), 146.7 (s, C-3 (pz)), 137.1 (s, C-5 (pz)), 136.8 (s, C-5 (pz)), 136.4 (s, C-5 (pz)), 135.4 (d, $J_{CP}$ = 41 Hz, C-1 $PPh_3$), 134.7 (d, $^2J_{CP}$ = 9 Hz, C-2,6 $PPh_3$), 130.2 (s, C-4 $PPh_3$), 128.5 (d, $^3J_{CP}$ = 8 Hz, C-3,5 $PPh_3$), 107.3 (s, C-4 (pz)), 106.3 (s, C-4 (pz)), 105.7 (s, C-4 (pz)), 79.8 (s, $CH_3$NC$H_2$N), 79.6 (s, $CH_3$NC$H_2$N), 71.2 (d, $^3J_{CP}$ = 7 Hz, NC$H$N), 68.7 (s, OC$H_2$),

**Table 1.** Crystal Data and Structure Refinement for Compounds **3**·0.5($Cl_2CH_2$), **7′**, and **10a′**·2($CH_3OH$)

| | **3·0.5($Cl_2CH_2$),** | **7′** | **10a′·2($CH_3OH$)** |
|---|---|---|---|
| empirical formula | $C_{33}H_{37}N_9BClI_2P_2Ru$, 0.5($Cl_2$ C $H_2$) | $C_{36}H_{42}N_9BIP_2Ru$, $CF_3SO_3$ | $C_{37}H_{46}N_9BIOP_2Ru$,$CF_3SO_3$, 2(C $H_3$ OH) |
| formula weight | 1065.25 | 1050.58 | 1146.7 |
| temperature/K | 150(2) | 150(2) | 150(2) |
| wavelength/Å | 1.5418 | 1.5418 | 1.5418 |
| crystal system | triclinic | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| *a*/Å | 9.9698(3) | 10.2618(3) | 10.3449(3) |
| *b*/Å | 10.8518(4) | 12.3332(4) | 15.3597(4) |
| *c*/Å | 18.2308(6) | 16.6379(4) | 16.3835(4) |
| α/deg | 94.407(3) | 78.219(2) | 77.787(2) |
| *β*/deg | 92.830(3) | 89.921(2) | 72.564(2) |
| *γ*/deg | 100.590(3) | 89.491(3) | 72.630(2) |
| *Z* | 2 | 2 | 2 |
| volume/Å$^3$ | 1929.01(11) | 2061.27(10) | 2348.97(11) |
| calculated density/g cm$^{-3}$ | 1.834 | 1.693 | 1.621 |
| $\mu$/mm$^{-1}$ | 18.224 | 10.701 | 9.492 |
| *F*(000) | 1038 | 1052 | 1160 |
| crystal size/mm | 0.18 × 0.10 × 0.04 | 0.12 × 0.07 × 0.03 | 0.11 × 0.07 × 0.05 |
| $\theta$ range/deg | 4.16 to 74.34 | 2.71 to 73.95 | 2.85 to 73.86 |
| no. of reflns. collected | 18045 | 19081 | 24250 |
| no. of unique reflns. | 7392 [R(int) = 0.0476] | 7740 [R(int) = 0.0254] | 8953 [R(int) = 0.0237] |
| completeness to $\theta_{max}$ | 93.7% | 92.5% | 94.1% |
| no. of parameters/restraints | 458/0 | 527/1 | 557/0 |
| Goodness-of-fit on $F^2$ | 1.103 | 1.092 | 1.129 |
| weight function (a, b) | 0.0784, 14.8638 | 0.1041, 16.0608 | 0.1521, 1.9749 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0503 | 0.0591 | 0.0643 |
| $wR_2$ [$I > 2\sigma(I)$][a] | 0.1451 | 0.1777 | 0.1909 |
| $R_1$ (all data) | 0.0586 | 0.0683 | 0.0775 |
| $wR_2$ (all data) | 0.1564 | 0.1874 | 0.2172 |
| largest diff. peak and hole/e Å$^{-3}$ | 1.186 and −1.637 | 2.375 and −3.277 | 2.486 and −2.630 |

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg) for [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$CH_2$=$CHCH_2$-PTA)][$CF_3SO_3$] (**7′**) and [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$){1-$CH_3$-4-{$CH_3O(CH_2)_2$}-PTA}][$CF_3SO_3$] (**10a′**)

| | | | | | |
|---|---|---|---|---|---|
| | | Selected Bond Lengths (Å) for **7′** | | | |
| Ru(1)−N(4) | 2.143(6) | Ru(1)−N(6) | 2.147 (6) | Ru(1)−N(8) | 2.106 (6) |
| Ru(1)−P(1) | 2.2691(16) | Ru(1)−P(2) | 2.3414(16) | Ru(1)−I(1) | 2.6978(7) |
| C(1)−N(1) | 1.507(8) | C(4)−N(1) | 1.547(8) | C(6)−N(1) | 1.533(9) |
| C(2)−N(2) | 1.464(9) | C(4)−N(2) | 1.420(9) | C(5)−N(2) | 1.467(10) |
| C(3)−N(3) | 1.482(8) | C(5)−N(3) | 1.472(9) | C(6)−N(3) | 1.406(10) |
| C(7)−N(1) | 1.514(9) | C(7)−C(8) | 1.489(12) | C(8)−C(9) | 1.319(13) |
| | | Selected Bond Angles (deg) for **7′** | | | |
| C(9)−C(8)−C(7) | 123.2(8) | C(8)−C(7)−N(1) | 114.3(6) | P(1)−Ru(1)−I(1) | 92.46(4) |
| P(2)−Ru(1)−I(1) | 96.48(4) | P(1)−Ru(1)−P(2) | 98.82(6) | | |
| | | Selected Bond Lengths (Å) for **10a′** | | | |
| Ru(1)−N(4) | 2.158(5) | Ru(1)−N(6) | 2.096 (5) | Ru(1)−N(8) | 2.139 (5) |
| Ru(1)−P(1) | 2.2776(16) | Ru(1)−P(2) | 2.3343(16) | Ru(1)−I(1) | 2.6935(6) |
| C(1)−N(1) | 1.529(9) | C(4)−N(1) | 1.509(11) | C(6)−N(1) | 1.541(10) |
| C(2)−N(2) | 1.487(9) | C(4)−N(2) | 1.406(11) | C(5)−N(2) | 1.471(11) |
| C(3)−N(3) | 1.457(9) | C(5)−N(3) | 1.471(10) | C(6)−N(3) | 1.428(11) |
| C(10)−N(1) | 1.483(11) | C(6)−C(7) | 1.468(15) | C(7)−C(8) | 1.520(15) |
| C(8)−O(1) | 1.465(15) | C(9)−O(1) | 1.419(14) | | |
| | | Selected Bond Angles (deg) for **10a′** | | | |
| C(9)−O(1)−C(8) | 109.4(10) | O(1)−C(8)−C(7) | 108.0(10) | C(5)−C(7)−C(8) | 116.4(10) |
| P(1)−Ru(1)−I(1) | 91.93(4) | P(2)−Ru(1)−I(1) | 95.14(4) | P(1)−Ru(1)−P(2) | 97.18(6) |

60.0 (d, $J_{CP}$ = 8 Hz, $CH_3NCH_2P$), 49.8 (d, $J_{CP}$ = 17 Hz, $NCH_2P$), 49.0 (s, $CH_3N$), 48.5 (d, $J_{CP}$ = 15 Hz, $NCH_2P$), 45.2 (s, br, $CH(CH_3)_2$), 22.5 (s, $CH(CH_3)_2$) ppm. $^{31}$P NMR in dmso-$d_6$ ($\delta$): 43.8 (d, $^2J_{PP}$ = 30 Hz, $PPh_3$), −18.6 (d, $^2J_{PP}$ = 30 Hz, 1-$CH_3$-4-{$(CH_3)_2CHO(CH_2)_2$}-PTA) ppm.

**Anion Exchange Reactions: Synthesis of [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$CH_2CH$=$CH_2$-PTA)][$CF_3SO_3$] (7′) and [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$){1-$CH_3$-4-{$CH_3O(CH_2)_2$}-PTA}][$CF_3SO_3$] (10a′).** A solution of complexes **7** or **10a** was stirred with $NaCF_3SO_3$ during 30 min in MeOH at room temperature. The solution was concentrated and diethyl ether added to yield **7′** or **10a′**. Spectroscopic data for these complexes are as the former complexes **7** and **10a** except for the $CF_3SO_3$ absorptions on the IR spectra. **7′**: IR (KBr): 1258, 1159, 1031 ($\nu(CF_3SO_3)$) cm$^{-1}$. **10a′**: IR (KBr): 1260, 1165, 1030 ($\nu(CF_3SO_3)$) cm$^{-1}$.

**X-ray Crystal Structure Determination of Complexes 3·0.5($Cl_2CH_2$), 7′, and 10a′·2($CH_3OH$).** Crystals suitable for X-ray diffraction analysis were obtained, by slow evaporation of saturated dichloromethane (**3** and **7′**) or methanol (**10a′**) solutions. The most relevant crystal and refinement data are collected in Table 1.

Data collection was performed at 150(2) K on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu Kα radiation ($\lambda$ = 1.5418 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (10−20 s). Data collection strategy was calculated with the program CrysAlis Pro

CCD.[15] Data reduction and cell refinement were performed with the program CrysAlis Pro RED.[15] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[15]

In all cases the software package WINGX[16] was used for space group determination, structure solution, and refinement. The structure for the complex **3** was solved by direct methods using SIR92.[17] For **7′** and **10a′** the structures were solved by Patterson interpretation and phase expansion using DIRDIF.[18]

In the crystal of **3**, one dichloromethane molecule solvation per two formula units of the complex was found to be disordered over two positions related by the center of symmetry. In the crystal of **10a′** two methanol molecules of solvation per two formula units of the complex were found.

Isotropic least-squares refinement on $F^2$ using SHELXL97[19] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined (except dichloromethane solvent molecule in **3**. This highly disordered group was found and isotropically refined). Except for H−B, in all cases the H atoms were geometrically located, and their coordinates were refined riding on their parent atoms. The coordinates of H atoms were found from different Fourier maps, and included in a refinement with isotropic parameters.

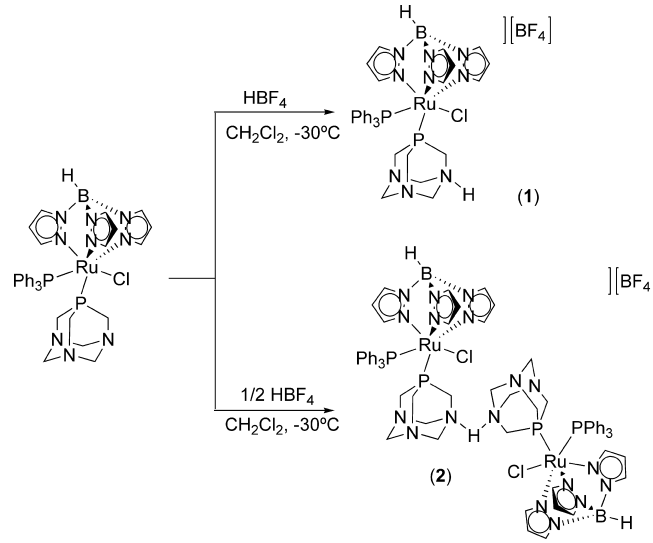
Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[20] The crystallographic plots were made with PLATON.[21]

## Results and Discussion

**Reaction of [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] with Protic Acids. Synthesis of [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-H-PTA)][BF$_4$] (1).** Addition of an equimolecular amount of $HBF_4$ acid to a solution of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] in dichloromethane at −30 ° produces the complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-H-PTA)][BF$_4$] (**1**), which precipitates upon addition of diethyl ether. The formation of complex **1** comes from the protonation of one nitrogen of the coordinated PTA ligand leading to the 3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1$^{3,7}$]decane ligand (Scheme 2).

Complex **1** is isolated as a pale yellow powder in 43% yield. The molar conductivity value found for complex **1** in nitromethane (66 S cm$^2$ mol$^{-1}$) is lower than expected for a 1:1 electrolyte (75−95).[22] Complex **1** has been analytically and spectroscopically characterized (IR and $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR). In particular, it must be noted that: i) the IR spectrum (KBr) shows the characteristic $\nu$(BH) absorption for the Tp ligand at 2489 cm$^{-1}$; ii) $^{31}$P{$^1$H} spectrum exhibits two doublets at 42.4 (PPh$_3$) and −18.1 (1-H-PTA) ($^2J_{PP}$ = 32 Hz), the last one clearly shifted low field from the value found for [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (−35.6 ppm);[11] iii) the $^1$H NMR spectum shows two broad signals for the hydrogen atoms of the NCH$_2$N groups of the PTA ligand at 4.82 and 4.52 ppm and a broad signal at 3.94 ppm for the NCH$_2$P protons; iv) $^{13}$C{$^1$H} NMR spectrum reveals the CH$_2$ groups of the PTA ligand as broad signals at 73.2 ppm (NCH$_2$N) and 51.8 ppm (NCH$_2$P).

**Scheme 2**




**Synthesis of [{RuCl[$\kappa^3$(*N,N,N*)-Tp](PPh$_3$)}$_2${$\mu$-$\kappa^2$(*P,P*)-PTA-H-PTA}][BF$_4$] (2).** When the reaction of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] with $HBF_4$ acid is carried out using a 2:1 molar ratio at −30 °C, a different complex [{RuCl[$\kappa^3$(*N,N,N*)-Tp](PPh$_3$)}$_2${$\mu$-$\kappa^2$(*P,P*)-PTA-H-PTA}][BF$_4$] (**2**) is isolated in 43% yield. (Scheme 2)

Complex **2** is postulated as a dinuclear complex according with the analytical and spectroscopic data and conductance measurements in solution. The electrospray mass spectrum performed for complex **2** shows a significant peak at $m/z$ = 1539 (7%) with the isotopic distribution expected for the dinuclear complex **2**. Significant spectroscopic data are given: (i) the $\nu$(BH) appears at 2476 cm$^{-1}$ in the IR spectrum (KBr); (ii) the $^{31}$P{$^1$H} NMR spectrum shows two doublets at 43.3 (PPh$_3$) and −21.1 (PTA-H-PTA) ($^2J_{PP}$ = 32 Hz) ppm indicating a high symmetry in the molecule and/or free rotation around the N−H bonds which leads to the equivalence for the phosphanes; (iii) the $^1$H NMR spectrum shows three broad signals at 4.73 and 4.46 for the NCH$_2$N hydrogen atoms and at 3.92 ppm for the six NCH$_2$P hydrogen atoms; (iv) the $^{13}$C{$^1$H} spectrum agrees with the proposed structure.

PGSE NMR experiments do not allow one to confirm the dimeric nature for the species in solution but point to more complicated associations depending on the concentration of the sample. In a recent paper, Peruzzini et al.[23] reported a study on the self-aggregation tendency of RAPTA complexes

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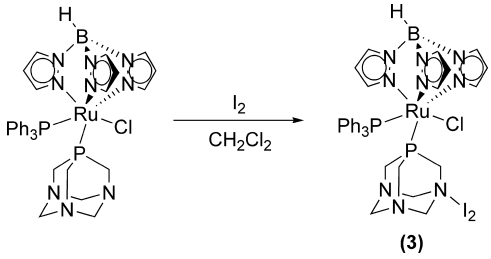
(19) Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
(20) *Tables for X-Ray Crystallography*; Kynoch Press: Birminghan, U.K., 1974; Vol. IV (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands).
(21) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht, The Netherlands, 2007.
(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
(23) Bolaño, S.; Ciancaleoni, G.; Bravo, J.; Gonsalvi, L.; Macchioni, A.; Peruzzini, M. *Organometallics* **2008**, *27*, 1649–1652.

**Scheme 3**




**(3)**

$[RuCl_2(\eta^6\text{-}p\text{-cymene})(1\text{-H-PTA})]^+$ through NMR spectroscopy that conclude the existence of H-bonded dicationic species in solution, which can be compared to the structure proposed for complex **2** in the solid state.

**Reaction of [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(PTA)] with $I_2$: Synthesis of [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$I_2$-PTA)] (3).** The reaction of complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(PTA)] with iodine at −30 °C leads to the isolation of the complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$I_2$-PTA)] (**3**) as an orange solid in 68% yield (Scheme 3).

Elemental analyses as well as $^1$H, $^{31}$P{$^1$H}, and $^{13}$C{$^1$H} NMR spectra for complex **3** agree with the proposed structure. The most remarkable features for this complex are as follows: (i) the IR spectrum (KBr) shows the characteristic $\nu$(BH) absorption for the Tp ligand at 2468 cm$^{-1}$; (ii) the $^{31}$P{$^1$H} spectrum shows two doublet resonances at $\delta = 43.9$ ($PPh_3$) and −16.2 ppm ($J_{PP} = 30$ Hz) (1-$I_2$-PTA). The clear deshielding of the last signal indicates the coordination of $I_2$ to the phosphane; (iii) the $^1$H NMR spectrum show the signals for the 6 hydrogen atoms of the $NCH_2N$ group of the ligand which appear as AB spin system at 4.46 and 4.25 ($J_{HAHB} = 12$ Hz). The $NCH_2P$ protons appear as a multiplet at 3.95−3.85 ppm; (iv) the $^{13}$C{$^1$H} NMR spectrum show resonances for the $NCH_2N$ and $NCH_2P$ carbon atoms at 73.2 (s) and 50.9 (d, $J_{CP} = 13$ Hz), respectively.

Slow evaporation of a $CH_2Cl_2$/hexane solution of complex **3** allows for crystals suitable for X-ray diffraction studies. Oak Ridge Thermal Ellipsoid Plot (ORTEP) type representation is shown in Figure 2. Selected bonding data are collected in the caption.

The ruthenium atom exhibits a distorted octahedral coordination geometry bonded $\kappa^3$(*N,N,N*) to the hydridotris(pyrazolyl)borate ligand, to one chlorine atom and to the phosphorus atom of the 1-$I_2$-PTA and $PPh_3$ ligands. The interligand N−Ru−N angles are in the range of 80.8−87.9°, and the Ru−N bond distances (2.142(6)−2.079(6) Å) are in the range of those found for other ruthenium (II) complexes like [RuCl{$\kappa^3$(*N,N,N*)-Tp}(NCMe)($PPh_3$)][24] (Ru−N 2.088−2.159 Å). The Ru−N bond distances trans to the phosphane ligands (2.133(6) and 2.142(6) Å) are significatively longer

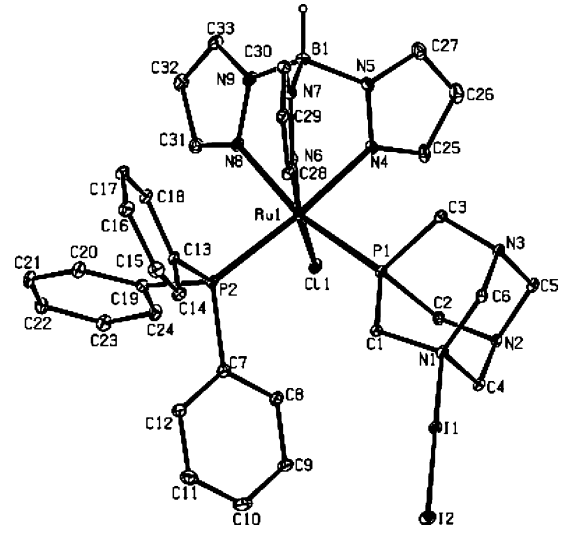



**Figure 2.** Molecular structure and atom-labeling scheme for complex [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-$I_2$-PTA)] (**3**). Hydrogen atoms, except B−H, and solvent molecules have been omitted for clarity. Non-hydrogen atoms are represented by their 20% probability ellipsoids. Selected bond lengths (Å): Ru(1)−N(4) = 2.142(6), Ru(1)−N(8) = 2.133(6), Ru(1)−N(6) = 2.079(6), Ru(1)−P(1) = 2.2702(17), Ru(1)−P(2) = 2.3305(18), Ru(1)−Cl(1) = 2.4440(17), C(1)−N(1) = 1.492(9), C(4)−N(1) = 1.487(9), C(6)−N(1) = 1.496(9), C(2)−N(2) = 1.473(8), C(4)−N(2) = 1.445(9), C(5)−N(2) = 1.470(10), C(3)−N(3) = 1.475(8), C(5)−N(3) = 1.466(9), C(6)−N(3) = 1.446(9), N(1)−I(1) = 2.422(6), I(1)−I(2) = 2.8134(6). Selected bond angles (deg): N(1)−I(1)−I(2) = 178.71(15), P(1)−Ru(1)−Cl(1) = 92.80(6), P(2)−Ru(1)−Cl(1) = 93.66(6), P(1)−Ru(1)−P(2) = 99.15(6).

than the Ru−N trans to the chlorine atom (Ru(1)−N(6) = 2.079(6) Å) according with the higher trans influence for the phosphane ligands.[25]

The corresponding I−I bond distance 2.8134(6) Å is longer than the I−I distance either in the gas phase (2.677)[26] or in crystalline diiodine[27] (2.717(6) at 110 K) as a result of the presence of the N···I interaction. The N(1)−I(1)−I(2) bond angle is slightly bent (178.71(15)°), as expected for a N−$I_2$ charge transfer complex. According with the classification of Bigoli et al.,[28] the compound can be classified as an A type adduct ($d$(I−I) < 2.85 Å), consistent with a weak N···I−I interaction.

The observed packing along the *x*-axis (see Figure 3) may be ascribed to intermolecular interactions between the central I(1) and C(26)H atoms. Thus, the C(26)−H···I(1) shows a distance of 3.797Å and a bond angle of 138° which are in accord with a hydrogen interaction C(26)H(26)···I. Also, hydrogen interactions can be observed along the *y*-axis through the Cl(1) atom bonded to the ruthenium atom and the C(29)H atoms. The C(29)H(29)···Cl(1) distance (3.4409 Å) and the bond angle (127°) agree with a hydrogen interaction C(29)H(29)···Cl(1) (Figure 3). These interactions between iodine and chlorine atoms and the hydrogens in the pyrazol rings lead to an overall ordering in the crystal where opposite orientations can be found for the molecules.

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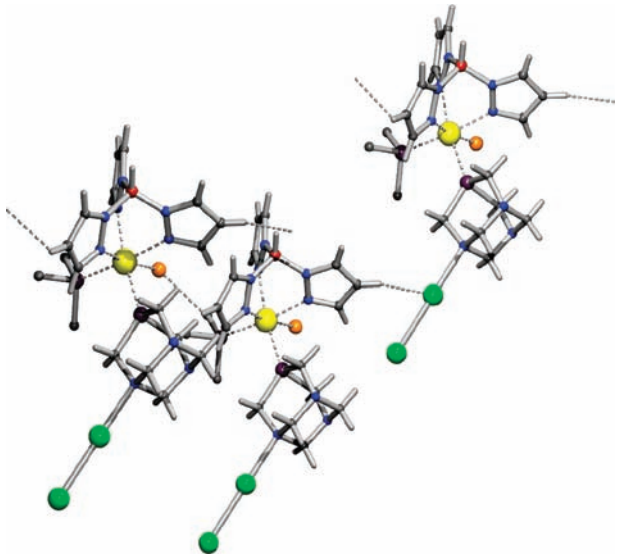


**Figure 3.** C(26)−H···I(1) and C(29)−H···Cl(1) interactions on complex [RuCl{$\kappa^3$(N,N,N)-Tp}(PPh$_3$)(1-I$_2$-PTA)] (**3**).

The charge-transfer complexes between iodine and aromatic nitrogen heterocycles are well-known,[29] but to the best of our knowledge, this is the first example in which the nitrogen belongs to a ligand coordinated to a transition metal.

**Reaction of [RuX{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(PTA)] with Organic Halides: Synthesis of [RuX{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-R-PTA)][Y] (R = CH$_2$Ph, Y = I, X = Cl, (4), X = I (5); R = CH$_2$CH=CH$_2$, Y = I, X = Cl (6), I (7); R = CH$_2$C≡CH, Y = Br, X = Cl (8).** The reaction of complexes [RuX{$\kappa^3$-(*N,N,N*)-Tp}(PPh$_3$)(PTA)] (X = Cl, I) with organic halides such as benzyl iodide, allyl iodide or propargyl bromide in dichloromethane at room temperature leads to the synthesis of the complexes [RuX{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-R-PTA)][Y] (R = CH$_2$Ph, Y = I, X = Cl (**4**), X = I (**5**); R = CH$_2$CH=CH$_2$, Y = I, X = Cl (**6**), X = I (**7**); R = CH$_2$C≡CH, Y = Br, X = Cl (**8**) which contain modified PTA ligands (Scheme 4). The complexes are isolated in 64−74% yields.

The molar conductivities in nitromethane (103−124 S cm$^2$ mol$^{-1}$) are in the range found for electrolytes 1:1.

The spectroscopic data agree with the proposed stoichiometries. The more remarkable features are as follows: (i) IR spectra show the characteristic $\nu$(BH) absorptions at 2479 cm$^{-1}$ for all the complexes and $\nu$(C(sp)H) and $\nu$(C≡C) absorptions at 3272 and 2117 cm$^{-1}$, respectively, for complex **8**; (ii) the $^{31}$P{$^1$H} NMR spectra show two doublets in the ranges 42.2−42.4 (PPh$_3$) and −11.2 to −13.2 ppm (1-R-PTA); (iii) the signals on the $^1$H NMR spectra have been fully assigned through COSY HH, HSQC, HMBC experiments and agree with the proposed complexes (see Experimental Section); (iv) the $^{13}$C{$^1$H} NMR spectra show the characteristic signals for the N−CH$_2$ carbon at 64.1 (**4**), 64.2 (**5**), 129.1 (**6**), 129.3 (**7**), and 54.0 (**8**), as well as the signals corresponding for the benzyl, allyl, and propargyl groups.

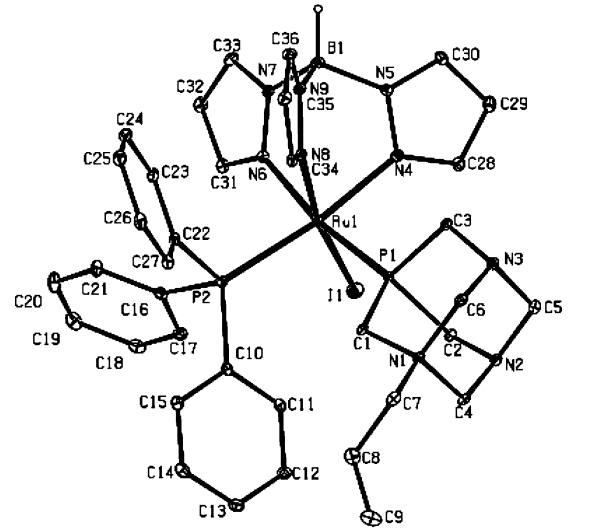
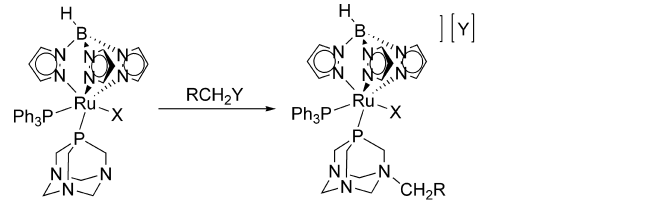


**Figure 4.** Molecular structure and atom-labeling scheme for the cation of complex [RuI{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$)(1-CH$_2$=CHCH$_2$-PTA)][CF$_3$SO$_3$] (**7′**). Hydrogen atoms, except B−H, and solvent molecules have been omitted for clarity. Non-hydrogen atoms are represented by their 20% probability ellipsoids.

**Scheme 4**



X = Cl, R = Ph, Y = I (**4**), X = I, R = Ph, Y = I (**5**)
X = Cl, R = CH=CH$_2$, Y = I (**6**), X = I, R = CH=CH$_2$, Y = I (**7**)
X = Cl, R = C≡CH, Y = Br (**8**)

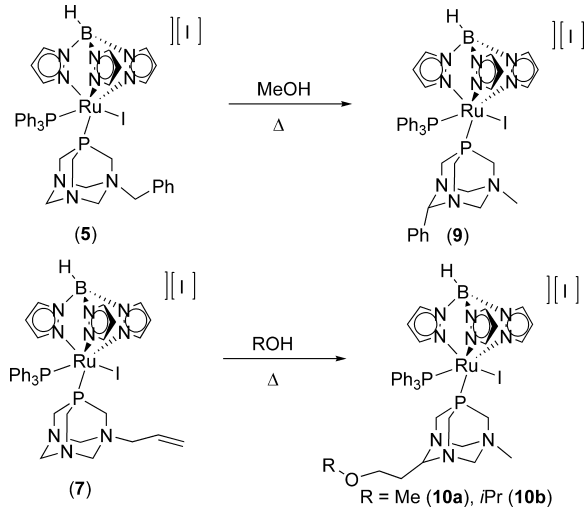
Slow evaporation of CH$_2$Cl$_2$ solutions of complex **7′** (obtained from **7** via exchange of the iodide anion by CF$_3$SO$_3$) enables to obtain crystals suitable for X-ray diffraction studies of **7′**. ORTEP type representation of the cation complex is shown in Figure 4. Selected bonding data are collected in Table 2.

The ruthenium atom exhibits a distorted octahedral coordination geometry bonded $\kappa^3$(*N,N,N*) to the hydridotris(pyrazolyl)borate ligand, to one iodine atom and to the phosphorus atoms of the 1-allyl-PTA and PPh$_3$ ligands. The interligand N−Ru−N angles and Ru−N bond distances are in the range of those found for other divalent ruthenium complexes.[24] The Ru−N bond distances trans to the phosphane ligands (2.143(6) and 2.147(6) Å) are significantly longer than the Ru−N trans to the chlorine atom (Ru(1)−N(8) = 2.106(6) Å) according with the higher trans influence for the phosphane ligands.[25]

As commented in the introduction, the complex [RuCl{$\kappa^3$-(*N,N,N*)-Tp}(PPh$_3$)(1-Me-PTA)][CF$_3$SO$_3$] could not be synthesized by direct reaction between a metallic precursor and free 1-Me-PTA ligand.[14] To check if the direct synthesis was a competitive method for the synthesis of derivatives **4** and

(29) For I$_2$ charge transfer complexes, see, for example, (a) Dolder, S.; Liu, S.; Beurer, E.; Ouahab, L.; Decurtins, S. *Polyhedron* **2006**, *25*, 1514–1518. (b) Corban, G. J.; Hadjiliadis, S. K.; Kubicki, M.; Tiekink, E. R. T.; Butler, I. S.; Drougas, E.; Kosmas, A. M. *Inorg. Chem.* **2005**, *44*, 8617–8627. (c) Rimmer, E. L.; Bailey, R. D.; Hanks, T. W.; Pennington, W. T. *Chem.—Eur. J.* **2000**, *6*, 4071–4081. (d) Engel, P. S.; Duan, S.; Whitmmire, K. H. *J. Org. Chem.* **1998**, *63*, 5666–5667. (e) Bailey, R. D.; Grabarczyk, M. T.; Hanks, W.; Pennington, W. T. *J. Chem. Soc., Perkin Trans.* **1997**, *2*, 2781–2786.

**Scheme 5**




**6**, the reactions of the 1-benzyl-PTA[7] and 1-allyl-PTA phosphanes[30] with [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)$_2$] were carried out. However, after 3 h in refluxing toluene, only the starting material was present in the reaction mixtures.

**C−H Activation Reactions: Synthesis of [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-Me-4-Ph-PTA)][I] (9) and [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$){1-Me-4-{RO($CH_2$)$_2$}-PTA}][I] (R = Me (10a), *i*Pr (10b)).** By heating alcoholic solutions of complexes **5** and **7**, new complexes [RuCl{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$)(1-Me-4-Ph-PTA)][I] (**9**) and [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$){1-Me-4-{RO($CH_2$)$_2$}-PTA}][I] (R = Me (**10a**), *i*Pr (**10b**)) have been prepared (Scheme 5).

The characterization of the complexes has been carried out by analytical and spectroscopic methods (see Experimental Section). Thus, IR spectra for both complexes show the characteristic $\upsilon$(BH) absorption at 2478 (**9**), 2480 (**10a**), and 2477 (**10b**) $cm^{-1}$ and $^1H$ NMR spectra show the signals corresponding to the hydridotris(pyrazolyl)borate and for the methyl group bonded to the nitrogen atom at 3.08 (**9**), 2.22 (**10a**), and 2.81 (**10b**) ppm. For complex **9** the $^{13}C\{^1H\}$ spectrum shows the signal corresponding to the methyl group bonded to the nitrogen at 49.0 ppm, and the $^{31}P\{^1H\}$ spectrum shows two doublets at 46.4 ($PPh_3$) and −17.7 (1-methyl-4-phenyl-PTA) ppm. For complexes **10a,b** the signals corresponding to the PTA substituents appear in the $^{13}C\{^1H\}$ spectrum at 48.8 (**10a**) and 49.0 (**10b**) ppm (methyl group bonded to the nitrogen) and 68.3 ($OCH_2$) and 58.5 ($OCH_3$) ppm for complex (**10a**) and 68.7 ($OCH_2$) and 22,5 and 45.2 ($OCH(CH_3)_2$) ppm for complex (**10b**). The $^{31}P\{^1H\}$ spectrum show two doublets corresponding to the $PPh_3$ phosphorus atom at 42.8 (**10a**), 43.8 (**10b**) ppm and at −21.9 (**10a**) and −18.6 (**10b**) ppm for the modified PTA ligand.

Slow evaporation of $CH_2Cl_2$ solutions of complex [RuI{$\kappa^3$-(*N,N,N*)-Tp}($PPh_3$){1-$CH_3$-4-{$CH_3O(CH_2)_2$}-PTA}][$CF_3SO_3$] **10a′** (obtained from **10a** via exchange of the iodide anion by $CF_3SO_3$) enable crystals that are suitable for X-ray diffraction studies of **10a′**. ORTEP type representation of the cation is shown in Figure 5. Selected bonding data are collected in Table 2.

(30) For the synthesis and X-ray structure of 1-allyl PTA, see the Supporting Information.

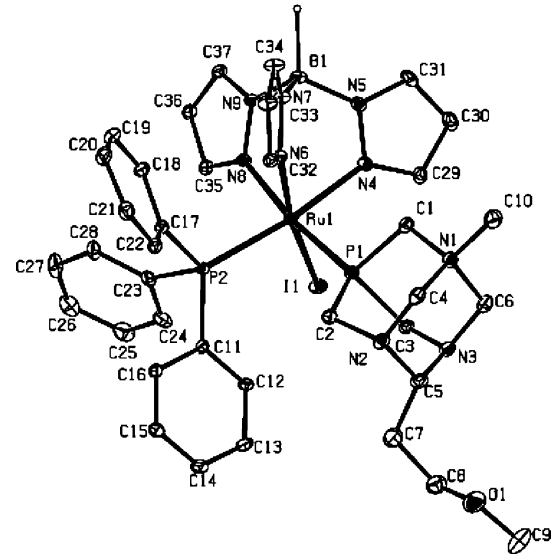
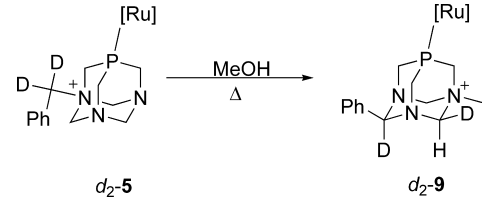



**Figure 5.** Molecular structure and atom-labeling scheme for the cation of complex [RuI{$\kappa^3$(*N,N,N*)-Tp}($PPh_3$){1-$CH_3$-4-{$CH_3O(CH_2)_2$}-PTA}][$CF_3SO_3$] (**10a′**). Hydrogen atoms, except B−H, and solvent molecules have been omitted for clarity. Non-hydrogen atoms are represented by their 10% probability ellipsoids.

**Scheme 6**




The ruthenium atom exhibits a distorted octahedral coordination geometry bonded $\kappa^3$(*N,N,N*) to the hydridotris(pyrazolyl)borate ligand, to one iodine atom, and to the phosphorus atoms of the 1-methyl-4-metoxyethyl-PTA and $PPh_3$ ligands. The interligand N−Ru−N angles and the Ru−N bond distances are in the range found in complex **7′**. The ORTEP view shows the methoxy ethyl chain bonded to the C(5) of the PTA ligand and a methyl group on the N(1).

To get insight into the reaction mechanism, a deuteration experiment was carried out using α,α-$d_2$-benzyl iodide as the electrophile. Thus, heating a solution of the dideuterated complex $d_2$-**5** in methanol, resulted in the regioselective formation of the dideuterated complex $d_2$-**9** (Scheme 6).

On the basis of this finding, the following mechanism is proposed for the observed rearrangement (Chart 1).

The first step would involve the ring opening of PTA to generate the iminium intermediate I. Then, intramolecular deuteride transfer to the iminium group, probably favored by an additional stabilization of the incipient carbocation by the nitrogen atom, would provide intermediate II, which in turn would undergo nucleophilic cyclization to intermediate III. The same pathway involving intermediates IV and V and a posterior hydride migration would explain the transformation of intermediate III into the observed complex **9**.

**Chart 1.** Proposed Mechanism for the Synthesis of Complex [RuI{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$){1-CH$_3$-4-Ph-PTA}][I] (**9**)

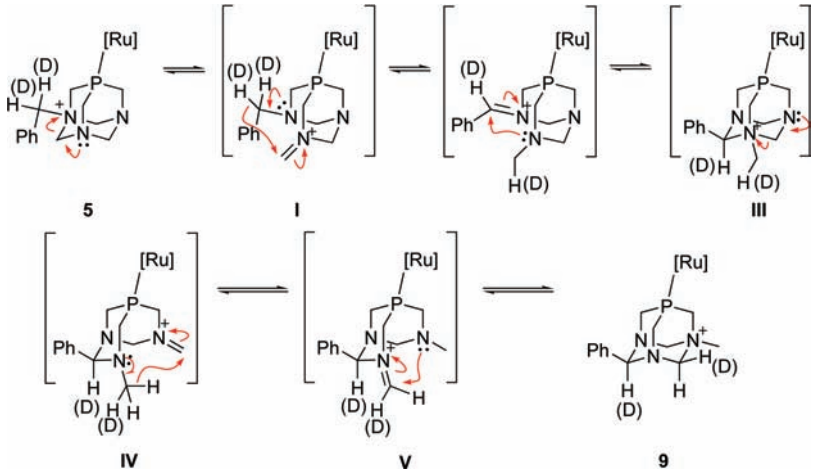
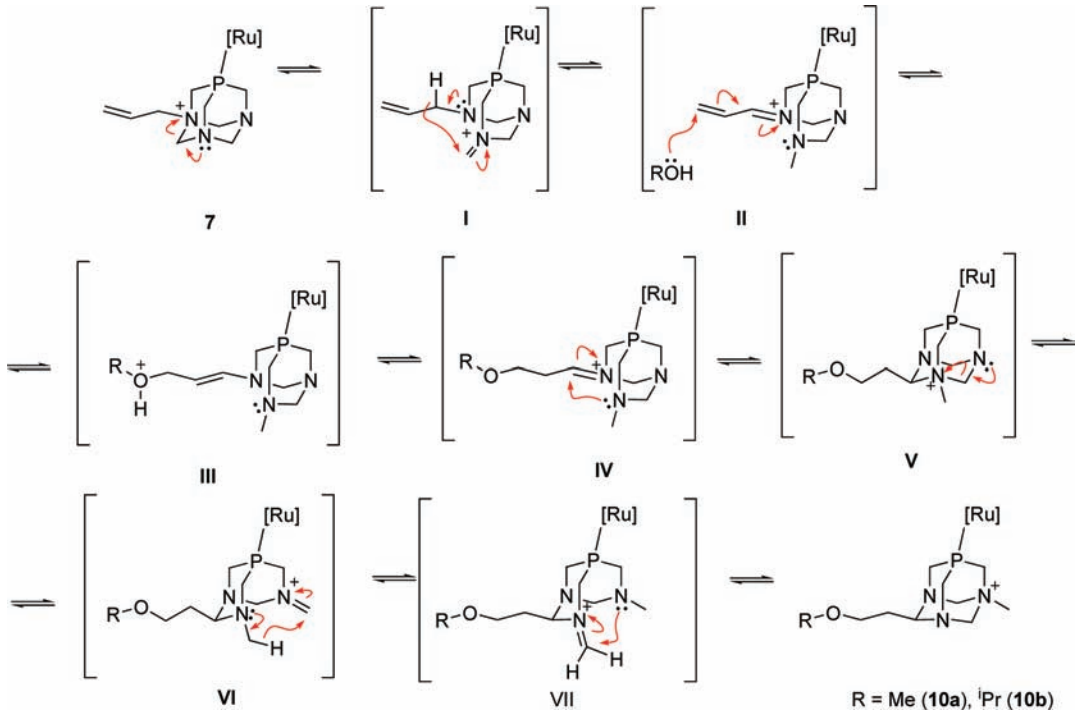



**Chart 2.** Proposed Mechanism for the Synthesis of Complexes [RuI{$\kappa^3$(*N,N,N*)-Tp}(PPh$_3$){1-Me-4-{RO(CH$_2$)$_2$}-PTA}][I] (**10a,b**)




Accordingly, a similar proposal can be assumed for the reaction of complex **7** with MeOH and *i*PrOH to give complexes **10a,b** (Chart 2). Thus, the initial ring opening/hydride transfer (intermediates I, II) would be followed by conjugate addition of the corresponding alcohol and proton transfer (intermediates III, IV). Then, cyclization to intermediate V followed by ring opening (intermediate VI), hydride transfer (intermediate VII), and cyclization would complete the whole transformation.

The proposed mechanism agrees with the intermediates assumed for Duff and Sommelet reactions[31] in which the key step is transfer of hydrogen from a $-CH_2$ group of one amine to an imine intermediate.

A PTA ring opening has been recently described by Romerosa et al. by treatment of the di-N-methylated PTA ligand (dmPTA) with KOH obtaining a 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane derivative (dmoPTA).[9]

To check if these activation reactions occur only with the metal-bound phosphanes, the 1-benzyl and 1-allyl-PTA phosphanes were heated in refluxing MeOH, but a mixture of unidentified compounds, which could not be separated, was obtained, pointing out the role of the metal atom in these transformations.

## Conclusions

Electrophilic attack on one of the nitrogen atoms of a coordinated PTA ligand allows the synthesis of new complexes with modified PTA phosphane ligands in very mild conditions. The reaction with iodine allows the isolation of

(31) (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 5th ed.; Wiley Interscience: New York, 2001; pp 717 and 1536. (b) Ogata, Y.; Kawasaki, A.; Sugiura, F. *Tetrahedron* **1968**, *24*, 5001–5010. (c) Angyal, S. J. *Org. React.* **1954**, *8*, 197–217.

the first charge transfer complex of iodine with a N atom from a ligand bonded to a transition metal complex. Interestingly, complexes with 1-benzyl and 1-allyl PTA ligands bonded to ruthenium can undergo ring opening and C−H activation reactions which lead to unprecedented substituted 1-methyl-4-phenyl-PTA, 4-(2-methoxyethyl)-1-methyl-PTA and 1-methyl-4-[2-(propan-2-yloxi)ethyl]-PTA ligands, respectively. Deuteration experiments have been performed which lead us to outline a reaction pathway closely related to that of the Duff and Sommelet reactions.

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**Supporting Information Available:** Experimental data for the synthesis and X-ray crystallographic analyses of 1-allyl-PTA phosphane, additional information on the analysis of the structure of complex **3** and spectroscopic data for the deuteration experiments. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC: 696033 (**3**), 696034 (**7′**), 696035 (**10a′**), and 696036 (1-allyl-PTA) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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