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Neutral and cationic ruthenium hydrotris(pyrazolyl)borate derivatives containing bulky monodentate phosphines. Crystal structures of $[RuTp(H_2O)(PPr^i_2Me)_2][CF_3SO_3]\cdot EtOH$ and $[RuTp(N_2)(PEt_3)_2][BPh_4]$

Miguel A. Jiménez Tenorio, Manuel Jiménez Tenorio, M. Carmen Puerta * and Pedro Valerga

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain. E-mail: carmen.puerta@uca.es

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The complexes $[RuTp(Cl)(PPr^i_2Me)_2]$ **1** and $[RuTp(Cl)(PEt_3)_2]$ **2** were prepared by thermal displacement of PPh_3 from $[RuTp(Cl)(PPh_3)_2]$ by the corresponding phosphine. A series of cationic complexes of the type $[RuTp(L)(PR_3)_2]^+$ (L = H_2O, N_2 or $CNBu^t$; PR_3 = PPr^i_2Me or PEt_3) was obtained by chloride abstraction from **1** or **2** in the presence of L. As consequence of the steric crowding, one of the PPr^i_2Me ligands in **1** is labile, and it was readily replaced by neutral molecules such as MeCN or $CNBu^t$ to yield the neutral complexes $[RuTp(Cl)L(PPr^i_2Me)]$ (L = MeCN or $CNBu^t$). The monohydrides $[RuTp(H)(PPr^i_2Me)_2]$ and $[RuTp(H)(PEt_3)_2]$ were obtained by treatment of **1** or **2** with $NaBH_4$ in MeOH. Protonation of these monohydrides led to the cationic dihydrogen complexes $[RuTp(H_2)(PPr^i_2Me)_2]^+$ and $[RuTp(H_2)(PEt_3)_2]^+$ which were isolated as $[BPh_4]^-$ salts, and characterized by determination of their $(T_1)_{min}$ and $^1J_{HD}$ coupling constants in the corresponding isotopomers. The neutral hydride(dihydrogen) complex $[RuTp(H)(H_2)(PPr^i_2Me)]$, which resulted from the reaction of $[RuTp(Cl)(MeCN)(PPr^i_2Me)]$ with $NaBH_4$ in MeOH, was characterized in analogous fashion. The crystal structures of the complexes $[RuTp(H_2O)(PPr^i_2Me)_2][CF_3SO_3]\cdot EtOH$ and $[RuTp(N_2)(PEt_3)_2][BPh_4]$ were determined.

Introduction

The chemistry of ruthenium hydrotris(pyrazolyl)borate (Tp) complexes, which had been rather underdeveloped compared to that of the related and formally homologous cyclopentadienyl and pentamethylcyclopentadienyl ruthenium derivatives, has attracted increasing attention in recent years. New TpRu complexes containing a variety of co-ligands, particularly nitrogen donors such as $Me_2NCH_2CH_2NMe_2$, MeCN, pyridine, *etc*. as well as cycloocta-1,5-diene (COD) and hemilabile phosphino amine ligands of the type $Ph_2PCH_2CH_2NR_2$, have been reported very recently,[1–6] and many of these have shown to be active catalysts for processes such as the dimerization of terminal acetylenes or the coupling of phenylacetylene with benzoic acid or allyl alcohols.[1,7] Tertiary phosphines have also been used as co-ligands,[8–15] and complexes such as $[RuTp(X)(PPh_3)_2]$ (X = Cl or H)[8,12,15] and $[RuTp(MeCN)(PPh_3)_2][BF_4]$[12] shown to be quite efficient catalyst precursors.[7,12,16] Interestingly, complexes containing bidentate phosphine ligands, *e.g.* [RuTp(Cl)(dppe)],[1] are catalytically inactive.[7] It seems that the catalyst precursor must contain at least one weakly bound ligand which upon dissociation generates the co-ordinatively unsaturated, catalytically active species. We have previously prepared TpRu complexes containing the bulky diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe), and studied its reactivity towards small molecules,[15] and also towards terminal alkynes and alkynols.[17] Although these complexes exhibit a chemical reactivity similar to that of their half-sandwich homologues,[18] they are catalytically inactive. For this reason, and continuing our studies on the chemistry of ruthenium complexes with bulky phosphine ligands, we have now focused our attention on PPr^i_2Me, a bulky phosphine which can be considered as the monodentate equivalent of dippe. Dissociation of one monodentate PPr^i_2Me ligand is expected to occur more easily than the chelate ring opening in complexes containing bidentate phosphines such as dippe or dppe, and hence such derivatives are more likely to act as suitable precursors for catalytically active species. In this work we describe the synthesis, properties and chemical reactivity of a range of neutral and cationic TpRu complexes containing PPr^i_2Me, including dinitrogen adducts as well as "classical" and "non-classical" hydrides, and also related derivatives with PEt_3, a less sterically demanding phosphine ligand having electron-donating capabilities similar to those of PPr^i_2Me.

Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or dry-box techniques. Tetrahydrofuran, diethyl ether and light petroleum (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. Triethylphosphine was purchased from Aldrich, whereas PPr^i_2Me was obtained by reaction of $PClPr^i_2$ (Aldrich) with MgMeI in diethyl ether; KTp[19] and $[RuTp(Cl)(PPh_3)_2]$[8] were obtained according to published procedures. Infrared spectra were recorded in Nujol mulls on Perkin-Elmer FTIR Spectrum 1000 spectrophotometers, NMR spectra on Varian Unity 400 MHz or Gemini 200 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^1H and ^{13}C-{^1H}) or 85% H_3PO_4 (^{31}P-{^1H}). The coupling constants $^3J_{HH}$ for the Tp ligand were all in the range 2–2.5 Hz. Microanalyses were by the Serveis Científico-Tècnics, Universitat de Barcelona.

Preparations

$[RuTp(Cl)(PPr^i_2Me)_2]$ 1. To a solution of $[RuTp(Cl)(PPh_3)_2]$ (1.75 g, 2 mmol) in toluene (15 ml), PPr^i_2Me (0.75 ml, *ca*. 5 mmol) was added *via* a syringe. The mixture was refluxed for 1 h, then allowed to cool to room temperature and light petrol-

eum (15 ml) added. A pale yellow, crystalline precipitate was obtained. It was filtered off, washed with diethyl ether and light petroleum, and dried *in vacuo*. Yield: 0.74 g, 60% (Found: C, 45.2 ; H, 7.28; N, 13.4. Calc. for $C_{23}H_{44}BClN_6P_2Ru$: C, 45.0; H, 7.17; N, 13.7%). IR: ν(BH) 2456 cm^{-1}. NMR (C_6D_6): ^1H, δ (298 K) −0.23, 0.74, 1.34, 1.54 {m, P[CH(CH_3)$_2$]$_2$}; 1.14 (d, J_{HP} = 3.2 Hz, PCH_3); 2.31, 2.95 {m, P[CH(CH_3)$_2$]$_2$}; 5.85 (t, 1 H), 5.93 (t, 2 H), 7.29 (d, 1 H), 7.51 (d, 2 H), 7.54 (d, 1 H) and 8.39 (d, 2 H); δ (198 K, CD_2Cl_2) −0.63, 0.78, 0.92, 1.14, 1.25, 1.32, 1.39, 2.10, 3.35 (br, PPr^i_2Me); 6.05 (s, 1 H), 6.13 (br, 2 H), 7.14 (s, 1 H), 7.65 (br, 2 H), 7.70 (s, 1 H) and 7.91 (br, 2 H); ^{31}P-{^1H}, δ (298 K) 27.5 (s); δ (183 K, CD_2Cl_2) 23.9 (d), 25.9 (d), $^2J_{PP}$ = 30.9 Hz; ^{13}C-{^1H}, δ (298 K) 6.8 (m, PCH_3); 16.2, 17.7, 19.1, 19.2 {s, P[CH(*C*H_3)$_2$]$_2$}; 24.1, 28.1 {m, P[*C*H(CH$_3$)$_2$]$_2$}; 104.7, 105.0, 134.5, 136.2, 145.1 and 147.1 [s, $HB(C_3H_3N_2)_3$].

[RuTp(Cl)(PEt_3)$_2$] 2. Complex **2** was prepared in a fashion analogous to that for **1**, starting from [RuTp(Cl)(PPh_3)$_2$] (1.75 g, 2 mmol) and PEt_3 (0.75 ml, *ca*. 5 mmol). Yield: 0.68 g, 65% (Found: C, 43.0; H, 6.96; N, 14.1. Calc. for $C_{21}H_{40}BClN_6P_2Ru$: C, 43.1; H, 6.83; N, 14.4%). IR: ν(BH) 2469 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.75 [m, P(CH_2CH_3)$_3$], 1.87 [m, P(CH_2CH_3)$_3$]; 6.07 (t, 1 H), 6.13 (t, 2 H), 7.41 (d, 1 H), 7.61 (d, 2 H), 7.71 (d, 1 H) and 7.97 (d, 2 H); ^{31}P-{^1H}, δ 26.8 (s); ^{13}C-{^1H}, δ 7.8 [s, P(CH_2CH_3)$_3$], 18.4 [m, P(CH_2CH_3)$_3$]; 104.0, 105.2, 134.9, 136.2, 143.9 and 147.6 [s, $HB(C_3H_3N_2)_3$].

[RuTp(H_2O)(PPr^i_2Me)$_2$][CF_3SO_3]·EtOH 3. To a tetrahydrofuran solution (15 ml) of complex **1** (0.3 g, 0.5 mmol) under argon, AgO_3SCF_3 (0.12 g, *ca*. 0.5 mmol) was added. The mixture was stirred at room temperature for 1 h, then, filtered through Celite in order to remove the precipitate of AgCl. The solvent was removed *in vacuo*, and the residue dissolved in 96% EtOH. Concentration and cooling to −20 °C for several days afforded well formed crystals, which were filtered off, washed with light petroleum and dried *in vacuo*. Yield: 0.29 g, 77% (Found: C, 41.0; H, 6.83; N, 10.9. Calc. for $C_{26}H_{52}F_3N_6O_5P_2RuS$: C, 41.1; H, 6.85; N, 11.1%). IR: ν(BH) 2463 cm^{-1}. NMR ($CDCl_3$): ^1H, δ −0.23, 1.01, 1.23, 1.34 {m, P[CH(CH_3)$_2$]$_2$}; 1.45 (d, J_{HP} = 6 Hz, PCH_3); 2.26, 2.44 {m, P[CH(CH$_3$)$_2$]$_2$}; 3.10 (br, H_2O); 6.08 (t, 1 H), 6.25 (t, 2 H), 7.29 (d, 1 H), 7.63 (d, 1 H), 7.73 (br, 2 H) and 7.84 (br, 2 H); ^{31}P-{^1H}, δ 28.5 (s); ^{13}C-{^1H}, δ 7.7 (m, PCH_3); 16.9, 18.7, 19.8, 20.0 {s, P[CH(*C*H_3)$_2$]$_2$}; 25.1, 28.9 {m, P[*C*H(CH$_3$)$_2$]$_2$}; 105.6, 106.0, 135.6, 137.3, 145.5 and 148.6 [s, $HB(C_3H_3N_2)_3$].

[RuTp(H_2O)(PEt_3)$_2$][BPh_4] 4. Complex **4** was obtained following a procedure identical to that for **3**, starting from **2** (0.29 g, 0.5 mmol). It was converted into its tetraphenylborate salt by addition of $NaBPh_4$ (0.3 g, excess) to an ethanol solution. Cooling to −20 °C afforded white crystals, which were filtered off, washed with light petroleum and dried *in vacuo*. Yield: 0.35 g, 80% (Found: C, 61.0; H, 7.14; N, 9.2. Calc. for $C_{45}H_{62}B_2N_6OP_2Ru$: C, 60.9; H, 6.99; N, 9.5%). IR: ν(BH) 2479 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.70 [m, P(CH_2CH_3)$_3$], 1.68 [m, P(CH_2CH_3)$_3$]; 5.30 (s, H_2O); 6.19 (t, 1 H), 6.24 (t, 2 H), 7.38 (d), 7.44 (s br), 7.69 (d, 2 H) and 7.77 (d, 1 H); ^{31}P-{^1H}, δ 25.0 (s); ^{13}C-{^1H} [$(CD_3)_2CO$], δ 6.9 [s, P(CH_2CH_3)$_3$], 17.9 [m, P(CH_2CH_3)$_3$]; 106.0, 106.2, 136.0, 137.2, 143.2 and 147.9 [s, $HB(C_3H_3N_2]_3$.

[RuTp(N_2)(PPr^i_2Me)$_2$][BPh_4] 5. To a tetrahydrofuran solution (15 ml) of complex **1** (0.3 g, 0.5 mmol) under dinitrogen, AgO_3SCF_3 (0.12 g, *ca*. 0.5 mmol) was added. The mixture was stirred at room temperature for 2 h then filtered through Celite or centrifuged. The solvent was removed *in vacuo*, and the residue dissolved in MeOH. Addition of solid $NaBPh_4$ (0.3 g, excess), concentration and cooling to −20 °C for several days afforded red crystals, which were filtered off, washed with ethanol and light petroleum and dried *in vacuo*. They were recrystallized from a mixture of dichloromethane and light petroleum. Yield: 0.31 g, 68% (Found: C, 61.2; H, 7.03; N, 11.8. Calc. for $C_{47}H_{64}B_2N_8P_2Ru$: C, 61.0; H, 6.92; N, 12.1%). IR: ν(BH) 2491, ν(N≡N) 2159 cm^{-1}. NMR [$(CD_3)_2CO$]: ^1H, δ −0.32, 1.04, 1.32 {m, P[CH(CH_3)$_2$]$_2$}; 1.68 (d, J_{HP} = 7.2 Hz, PCH_3); 2.36, 2.72 {m, P[CH(CH$_3$)$_2$]$_2$}; 6.23 (t, 1 H), 6.33 (t, 2 H), 7.75 (d, 1 H), 7.84 (d, 2 H), 7.92 (d, 1 H) and 7.99 (d, 2 H); ^{31}P-{^1H}, δ 25.4 (s); ^{13}C-{^1H}, δ 6.9 (m, PCH_3); 16.5, 18.2, 18.8, 19.4 {s, P[CH(*C*H_3)$_2$]$_2$}; 24.8, 27.0 {m, P[*C*H(CH$_3$)$_2$]$_2$}; 106.9, 107.5, 137.3, 139.0, 146.5 and 150.7 [s, $HB(C_3H_3N_2)_3$].

[RuTp(N_2)(PEt_3)$_2$][BPh_4] 6. A procedure identical to that for the preparation and recrystallization of complex **5** was followed, starting from **2** (0.29 g, 0.5 mmol). Yield: 0.33 g, 73% (Found: C, 59.9; H, 7.01; N, 12.1. Calc. for $C_{45}H_{60}B_2N_8P_2Ru$: C, 60.2; H, 6.69; N, 12.5%). IR: ν(BH) 2505 ν(N≡N) 2163 cm^{-1}. NMR [$(CD_3)_2CO$]: ^1H, δ 0.78 (m, PCH_2CH_3), 1.93 (m, PCH_2CH_3); 6.20 (t, 1 H), 6.34 (t, 2 H), 7.70 (d, 1 H), 7.82 (d, 2 H), 7.91 (d, 1 H) and 7.98 (d, 2 H); ^{31}P-{^1H}, δ 25.8 (s); ^{13}C-{^1H}, δ (CD_2Cl_2) 7.9 [s, P(CH_2CH_3)$_3$], 18.5 [m, P(CH_2CH_3)$_3$]; 107.5, 106.5, 137.5, 138.8, 143.2 and 143.3 [s, $HB(C_3H_3N_2)_3$].

[RuTp($CNBu^t$)(PPr^i_2Me)$_2$][BPh_4] 7. *Method A.* To a suspension of complex **1** (0.15 g, *ca*. 0.25 mmol) in EtOH (10 ml), $NaBPh_4$ (0.2 g, excess) and a few drops of $CNBu^t$ were added. The mixture was heated smoothly for *ca*. 2 h using a water-bath. Then, the resulting yellow solution was concentrated and cooled to −20 °C. The white solids were collected by filtration, washed with EtOH and light petroleum and dried *in vacuo*. Yield: 0.2 g, 82%.

Method B. A dichloromethane solution (10 ml) of complex **5** (0.1 g, *ca*. 0.11 mmol) was treated with a few drops of $CNBu^t$. The solution became pale yellow. It was stirred at room temperature for 10 min. Concentration and addition of light petroleum yielded a white precipitate, which was filtered off, washed with light petroleum and dried *in vacuo*. Yield: 0.1 g, quantitative (Found: C, 63.8; H, 7.55; N, 9.8. Calc. for $C_{52}H_{73}B_2N_7P_2Ru$: C, 63.7; H, 7.45; N, 10.0%). IR: ν(BH) 2487, ν(C≡N) 2124 cm^{-1}. NMR ($CDCl_3$): ^1H, δ −0.33, 0.91 1.28, 1.36 {m, P[CH(CH_3)$_2$]$_2$}; 1.29 (d, J_{HP} = 6.8 Hz, PCH_3); 1.44 [s, RuCNC(CH$_3$)$_3$]; 1.94, 2.41 {m, P[CH(CH$_3$)$_2$]$_2$}; 6.20 (t, 2 H), 6.33 (t, 1 H), 7.63 (d, 2 H), 7.65 (d, 2 H), 7.69 (d, 1 H) and 7.83 (d, 1 H); ^{31}P-{^1H}, δ 26.0 (s); ^{13}C-{^1H}, δ 7.2 (m, PCH_3); 19.5, 19.1, 18.1, 16.2 {s, P[CH(*C*H_3)$_2$]$_2$}; 30.8, 24.9 {m, P[*C*H(CH$_3$)$_2$]$_2$}; 31.1 [s, RuCNC(*C*H_3)$_3$]; 49.3 [s, CN*C*(CH$_3$)$_3$]; 106.7, 136.8, 137.5, 144.6, 145.7 [s, $HB(C_3H_3N_2)_3$]; Ru*C*NC(CH$_3$)$_3$ not observed.

[RuTp($CNBu^t$)(PEt_3)$_2$][BPh_4] 8. This complex was obtained by either of the two procedures outlined for the preparation of **7**, starting either from **2** (method A) or from **6** (method B), with similar yields (Found: C, 63.1; H, 7.33; N, 10.1. Calc. for $C_{50}H_{69}B_2N_7P_2Ru$: C, 63.1; H, 7.25; N, 10.3%). IR: ν(BH) 2471, ν(C≡N) 2123 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.72 [m, P(CH_2CH_3)$_3$]; 1.43 [s, CNC(CH_3)$_3$]; 1.69 [m, P(CH_2CH_3)$_3$]; 6.02 (t, 2 H), 6.31 (t, 1 H), 7.48 (d, 2 H), 7.62 (d, 1 H), 7.66 (d, 2 H) and 7.84 (d, 1 H); ^{31}P-{^1H}, δ 24.0 (s); ^{13}C-{^1H}, δ 7.5 [s, P(CH_2CH_3)$_3$], 19.1 [m, P(CH_2CH_3)$_3$]; 30.8 [s, RuCNC(*C*H_3)$_3$]; 49.5 [s, RuCN*C*(CH$_3$)$_3$]; 106.4, 106.5, 136.5, 137.1, 143.4 and 145.5 [s, $HB(C_3H_3N_2)_3$]; Ru*C*NC(CH$_3$)$_3$ not observed.

[RuTp(Cl)(MeCN)(PPr^i_2Me)] 9. A solution of complex **1** (0.3 g, 0.5 mmol) in MeCN (15 ml) was heated under reflux for 2 h. Then, the solvent was removed *in vacuo*. The resulting yellow microcrystalline material was washed with several portions of light petroleum and dried thoroughly. Yield: 0.24 g, 95% (Found: C, 41.2; H, 5.89; N, 18.5. Calc. for $C_{18}H_{30}BClN_7PRu$: C, 41.4; H, 5.74; N, 18.8%). IR: ν(BH) 2479; ν(C≡N) 2269, 2245 cm^{-1}. NMR [$(CD_3)_2CO$]: ^1H, δ 0.15, 1.10, 1.35 {m, P[CH(CH_3)$_2$]$_2$}; 1.52 (d, J_{HP} = 8 Hz, PCH_3); 2.24 {m, P[CH(CH$_3$)$_2$]$_2$}; 2.56 (s, $RuNCCH_3$); 6.11 (t, 1 H), 6.16 (t, 1 H), 6.17 (t, 1 H),

7.56 (d, 1 H), 7.68 (d, 1 H), 7.69 (d, 1 H), 7.74 (d, 1 H), 7.80 (d, 1 H) and 7.88 (d, 1 H); ^{31}P-{^{1}H}, δ 42.1 (s); ^{13}C-{^{1}H}, δ 4.1 (s, RuNC*C*H$_3$); 4.2 (d, J_{CP} = 21.7, PCH$_3$); 16.5 (d, J_{HP} = 1.3), 16.7 (d, J_{HP} = 1.3), 17.8, 17.9 {s, P[CH(*C*H$_3$)$_2$]$_2$}; 24.7 {d, J_{CP} = 22.7 Hz, P[*C*H(CH$_3$)$_2$]$_2$}; 105.6, 105.7, 106.6, 134.4, 136.2, 136.5, 142.1, 146.0 and 146.2 [s, HB(C$_3$H$_3$N$_2$)$_3$].

[RuTp(Cl)(CNBu^t)(PPr$^i_2$Me)] 10. To a solution of complex **1** (0.15 g, *ca*. 0.25 mmol) in tetrahydrofuran a few drops of CNBu^t were added. The mixture was heated at 60 °C for 2 h. Then the solvent was removed *in vacuo*, leaving a yellow powder which was washed with several portions of light petroleum and dried *in vacuo*. Yield: 0.14 g, quantitative (Found: C, 44.3; H, 6.40; N, 17.1. Calc. for $C_{21}H_{36}BClN_7PRu$: C, 44.7; H, 6.38; N, 17.4%). IR: ν(BH) 2460, ν(C≡N) 2071, 2099 cm^{-1}. NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 0.31, 1.00, 1.04, 1.14 {m, P[CH(C*H*$_3$)$_2$]$_2$}; 0.85 (d, J_{HP} = 3.2 Hz, PCH$_3$); 1.51 [s, CNC(CH$_3$)$_3$]; 1.99, 2.19 {m, P[C*H*(CH$_3$)$_2$]$_2$}; 6.15 (t, 1 H), 6.16 (t, 1 H), 6.24 (t, 1 H), 7.50 (d, 1 H), 7.65 (d, 1 H), 7.79 (d, 1 H), 7.82 (d, 1 H), 7.84 (br, 1 H) and 7.94 (d, 1 H); ^{31}P-{^{1}H}, δ 42.5 (s); ^{13}C-{^{1}H} (C$_6$D$_6$), δ 4.2 (d, J_{CP} = 40, PCH$_3$); 15.9, 17.1, 17.7, 19.2 {s, P[CH(*C*H$_3$)$_2$]$_2$}; 24.1 (d, J_{CP} = 41), 28.5 {d, J_{CP} = 49 Hz, P[*C*H(CH$_3$)$_2$]$_2$}; 31.0 [s, RuCNC(*C*H$_3$)]; 48.3 [s, RuCN*C*(CH$_3$)$_3$]; 105.0, 105.1, 105.5, 134.8, 135.5, 142.6, 143.9, 145.3 [s, HB(C$_3$H$_3$N$_2$)$_3$]; 233 [br, Ru*C*NC(CH$_3$)$_3$].

[RuTp(Cl)(PPr$^i_2$Me)(PEt$_3$)] 11. To a tetrahydrofuran solution of complex **1** (0.15 g, 0.25 mmol) neat PEt$_3$ (0.05 ml, slight excess) was added. The mixture was heated at 60 °C for 1 h. Removal of the solvent and washing with light petroleum afforded a yellow solid, which was dried *in vacuo*. Yield: 0.13 g, quantitative (Found: C, 43.9; H, 7.15; N, 14.0. Calc. for $C_{22}H_{42}BClN_6P_2Ru$: C, 44.1; H, 7.01; N, 14.0%). IR: ν(BH) 2473 cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 0.78 [m, P(CH$_2$C*H*$_3$)$_3$], 1.88 [m, P(C*H*$_2$CH$_3$)$_3$]; −0.39, 0.97, 1.39, 1.47 {m, P[CH(C*H*$_3$)$_2$]$_2$}; 1.37 (d, J_{HP} = 7.2 Hz, PCH$_3$); 2.71, 2.26 {m, P[C*H*(CH$_3$)$_2$]$_2$}; 6.08 (t, 1 H), 6.13 (br, 2 H), 7.44 (d, 1 H), 7.61 (d, 1 H), 7.71(br, 2 H), 8.00 (d, 2 H) and 8.03 (d, 2 H); ^{31}P-{^{1}H}, δ 31.1 (d); 23.3 (d), $^{2}J_{PP}$ = 32.3 Hz; ^{13}C-{^{1}H}, δ 6.8 (d, J_{CP} = 34.8, PCH$_3$); 6.9 [s, P(CH$_2$*C*H$_3$)$_3$]; 18.5 [d, J_{CP} = 45.4, P(*C*H$_2$CH$_3$)$_3$]; 19.3, 19.2, 17.8, 15.7 {s, P[CH(*C*H$_3$)$_2$]$_2$}; 24.0, 28.9 {d, J_{CP} = 42.4 Hz, P[*C*H(CH$_3$)$_2$]$_2$}; 104.0, 105.1, 105.3, 134.8, 134.9, 136.4, 144.0, 144.4 and 147.4 [s, HB(C$_3$H$_3$N$_2$)$_3$].

[RuTp(H)(PPr$^i_2$Me)$_2$] 12. To a slurry of complex **1** (0.3 g, 0.5 mmol) in MeOH (15 ml) an excess of NaBH$_4$ (0.15 g) was added. The mixture was heated using a water-bath, until efervescence ceased. After 45 min a yellow-orange solution was obtained. Removal of the solvent yielded an oily residue, which was dissolved in light petroleum and filtered through Celite. Concentration and cooling to −20 °C afforded a yellow solid which was filtered off and dried *in vacuo*. This compound slowly turns green on standing under dinitrogen or argon, even when stored in a freezer. Yield: 0.16 g, 58% (Found: C, 47.3; H, 7.92; N, 14.1. Calc. for $C_{23}H_{45}BN_6P_2Ru$: C, 47.7; H, 7.77; N, 14.5%). IR: ν(BH) 2456, ν(RuH) 1917 cm^{-1}. NMR (C$_6$D$_6$): ^{1}H, δ −15.36 (t, $^{2}J_{HP}$ = 28.8, RuH); 0.02, 0.64, 1.15, 1.24 {m, P[CH(C*H*$_3$)$_2$]$_2$}, 1.05 (d, J_{HP} = 5.8 Hz, PCH$_3$); 2.16 {m, P[C*H*(CH$_3$)$_2$]$_2$}; 5.70 (s br, 2 H), 5.99 (s br, 1 H), 7.00 (s br, 2 H), 7.37 (s br, 1 H), 7.59 (s br, 1 H) and 7.76 (s br, 2 H); ^{31}P-{^{1}H}, δ 47.8 (s); ^{13}C-{^{1}H}, δ 9.2 (m, PCH$_3$); 17.8, 18.1, 18.2, 19.3 {s, P[CH(*C*H$_3$)$_2$]$_2$}; 25.3, 31.9 {m, P[*C*H(CH$_3$)$_2$]$_2$}; 104.5, 104.6, 135.0, 145.4 and 146.9 [s, HB(C$_3$H$_3$N$_2$)$_3$].

[RuTp(H)(PEt$_3$)$_2$] 13. Complex **13** was obtained in a fashion analogous to that for **12**, starting from **2** (0.29 g, 0.5 mmol). Yield: 0.16 g, 60% (Found: C, 45.4; H, 7.27; N, 14.9. Calc. for $C_{21}H_{41}BN_6P_2Ru$: C, 45.8; H, 7.44; N, 15.3%). IR: ν(BH) 2456, ν(RuH) 1915 cm^{-1}. NMR (C$_6$D$_6$): ^{1}H, δ −15.11 (t, $^{2}J_{HP}$ = 29.2 Hz, RuH); 0.74 [m, P(CH$_2$C*H*$_3$)$_3$]; 1.50 [m, P(C*H*$_2$CH$_3$)$_3$]; 5.86 (t, 2 H), 6.14 (t, 1 H), 7.52 (d, 2 H), 7.75 (s br, 3H) and 8.25 (d, 1 H); ^{31}P-{^{1}H}, δ 45.9 (s); ^{13}C-{^{1}H}, δ 8.1 [s, P(CH$_2$*C*H$_3$)$_3$], 21.2 [m, P(*C*H$_2$CH$_3$)$_3$]; 105.0, 105.8, 135.2, 145.8 and 146.9 [s, HB(C$_3$H$_3$N$_2$)$_3$].

[RuTp(H$_2$)(PPr$^i_2$Me)$_2$][BPh$_4$] 14. To a solution of complex **12** (0.15 g, 0.26 mmol) in diethyl ether (10 ml) at −80 °C under argon, HBF$_4$·OEt$_2$ (2–3 drops, excess) was added. The mixture was allowed to warm to room temperature. Then the solvent was removed *in vacuo*, and the residue treated with a MeOH solution containing NaBPh$_4$ (0.2 g, excess). A white, microcrystalline precipitate was obtained. It was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. This compound was recrystallized from a dichloromethane–ethanol mixture under argon. The isotopomer [RuTp(HD)(PPr$^i_2$Me)$_2$]$^+$ was generated *in situ*, by reaction of **12** with DBF$_4$·OEt$_2$ (obtained from D$_2$O–HBF$_4$·OEt$_2$ 3:1). Yield: 0.19 g, 81% (Found: C, 62.5; H, 7.46; N, 9.1. Calc. for $C_{47}H_{66}B_2N_6P_2Ru$: C, 62.8; H, 7.34; N, 9.35%). IR: ν(BH) 2489 cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H, δ −9.55 [s br, Ru(H$_2$); $(T_1)_{min}$ 16 ms at 203 K, 400 MHz, $^{1}J_{HD}$ = 31.1, J_{HP} = 7.3 Hz]; −0.08, 0.90, 1.35 {m, P[CH(C*H*$_3$)$_2$]$_2$}; 1.42 (d, PCH$_3$); 2.00, 2.22 {m, P[C*H*(CH$_3$)$_2$]$_2$}; 6.23 (t, 2 H), 6.45 (t, 1 H), 7.68 (d, 2 H), 7.72 (d, 2 H), 7.77 (d, 1 H) and 7.96 (d, 1 H); ^{31}P-{^{1}H}, δ 30.6 (s); ^{13}C-{^{1}H}, δ 7.0 (m, PCH$_3$); 16.6, 17.6, 18.5, 19.4 {s, P[CH(*C*H$_3$)$_2$]$_2$}; 25.1, 30.3 {m, P[*C*H(CH$_3$)$_2$]$_2$}; 107.0, 107.5, 137.4, 138.2, 146.7 and 147.0 [s, HB(C$_3$H$_3$N$_2$)$_3$].

[RuTp(H$_2$)(PEt$_3$)$_2$][BPh$_4$] 15. A procedure identical to that for complex **14** was followed for **15**, starting from **13** (0.15 g, 0.27 mmol). Yield: 0.17 g, 75% (Found: C, 61.9; H, 7.18; N, 9.4. Calc. for $C_{45}H_{62}B_2N_6P_2Ru$: C, 62.0; H, 7.12; N, 9.65%). IR: ν(BH) 2495 cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H, δ −9.83 [s br, Ru(H$_2$), $(T_1)_{min}$ 18 ms at 203 K, 400 MHz, $^{1}J_{HD}$ = 30.9, J_{HP} = 7.1 Hz]; 0.78 [m, P(CH$_2$C*H*$_3$)$_3$]; 1.74 [m, P(C*H*$_2$CH$_3$)$_3$]; 6.23 (t, 2 H), 6.41 (t, 1 H), 7.59 (d, 2 H), 7.71 (d, 2 H), 7.78 (d, 1 H) and 7.93 (d, 1 H); ^{31}P-{^{1}H}, δ 28.1 (s); ^{13}C-{^{1}H}, δ 7.3 [s, P(CH$_2$*C*H$_3$)$_3$], 19.4 [m, P(*C*H$_2$CH$_3$)$_3$]; 107.0, 107.2, 146.9, 146.2, 137.2 and 138.0 [s, HB(C$_3$H$_3$N$_2$)$_3$].

[RuTpH$_3$(PPr$^i_2$Me)] 16. A solution of complex **9** (0.15 g, 0.29 mmol) in MeOH (10 ml) was treated with an excess of NaBH$_4$ (0.15 g). The mixture was heated at 60 °C for 1 h. Then the solvent was removed *in vacuo*, the residue extracted with light petroleum, and the solution filtered through Celite. A sticky residue was obtained upon solvent removal and dissolved in warm MeOH. Filtration, concentration and cooling to −20 °C afforded pale yellow crystals, which were filtered off and dried *in vacuo*. A mixture of the isotopomers [RuTpH$_2$D(PPr$^i_2$Me)] and [RuTp(H)D$_2$(PPr$^i_2$Me)] was obtained by gentle heating of a CD$_3$OD solution of **16**. Yield: 0.1 g, 77% (Found: C, 42.3; H, 6.91; N, 18.5. Calc. for $C_{16}H_{30}BN_6PRu$: C, 42.8; H, 6.68; N, 18.7%). IR: ν(BH) 2475, ν(RuH) 1946 cm^{-1}. NMR (C$_6$D$_6$): ^{1}H, δ −10.45 [d, $^{2}J_{HP}$ = 19.6, RuH$_3$, $(T_1)_{min}$ 41 ms at 201 K, CD$_2$Cl$_2$, 400 MHz, $^{1}J_{HD}$ = 7.4]; 0.69, 0.83 {m, P[CH(C*H*$_3$)$_2$]$_2$}; 1.03 (d, J_{HP} = 7.2 Hz, PCH$_3$); 5.99 (s br), 7.56 (s br) and 7.84 (s br); ^{31}P-{^{1}H}, δ 62.9 (s); ^{13}C-{^{1}H}, δ 13.3 (d, J_{CP} = 44, PCH$_3$); 15.0, 18.3, 18.4, 18.5 {s, P[CH(*C*H$_3$)$_2$]$_2$}; 22.6, 26.5 {d, J_{CP} = 44 Hz, P[*C*H(CH$_3$)$_2$]$_2$}; 105.7, 135.6 and 146.2 [s br, HB(C$_3$H$_3$N$_2$)$_3$].

Crystallography

Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer (T = 290 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix in each case were determined by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 1. Data were collected by the ω–2θ scan method in both cases. Lorentz-polarization corrections

were applied. Decay was monitored by measuring three standard reflections every 100 measurements. Decay and semiempirical absorption correction (ψ method) were also applied. The structures were solved by Patterson methods and subsequent expansion of the models using DIRDIF.[20] Reflections having $I > 3\sigma(I)$ were used for structure refinement. For complex **3** all non-hydrogen atoms were anisotropically refined; H(1), H(2) and H(52) were localized in Fourier-difference maps and the remaining hydrogen atoms included at idealized positions and not refined. In the case of compound **6** all the non-hydrogen atoms in the cation except the phosphine ethyl groups were anisotropically refined, and the remaining non-hydrogen atoms were isotropically refined. Hydrogen atoms were included at idealized positions and not refined. Since the space groups were non-centrosymmetrical in both cases, the two possible enantiomorphs were checked and no significant differences found. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[21] software system and ORTEP[22] for plotting. Maximum and minimum peaks in the final Fourier-difference maps were +1.42 and −0.97 e Å^{-3} for **3**, and +0.56 and −0.43 e Å^{-3} for **6**.

CCDC reference number 186/1139.

See http://www.rsc.org/suppdata/dt/1998/3601/ for crystallographic files in .cif format.

Results and discussion

The complexes [RuTp(Cl)(PPr$^{i}_{2}$Me)$_2$] **1** and [RuTp(Cl)(PEt$_3$)$_2$] **2** were obtained by thermal displacement of PPh_3 from [RuTp(Cl)(PPh$_3$)$_2$] by the corresponding phosphine in refluxing toluene, a procedure which has been previously used for the synthesis of [RuTp(Cl)(dippe)].[15] The physical properties of these pale yellow, crystalline compounds match those of the dippe derivative. The presence of six separate pyrazole ring proton resonances in the ^{1}H NMR spectra, and of one singlet in the ^{31}P-{^{1}H} NMR spectra, of these complexes at room temperature suggest an octahedral structure analogous to that found for the parent complex [RuTp(Cl)(PPh$_3$)$_2$] by X-ray crystallography. It is interesting that the complexes [Ru(C$_5$R$_5$)Cl(PEt$_3$)$_2$] (R = H or Me), formal homologues of **2**, are known. However, attempts made to synthesize organometallic counterparts of complex **1**, namely [Ru(C$_5$R$_5$)Cl(PPr$^{i}_{2}$Me)$_2$] (R = H or Me), have been unsuccessful.[23] It seems that the bulk of PPr$^{i}_{2}$Me makes difficult, or even prevents, the formation of half-sandwich species containing two of these phosphine ligands in a cisoid disposition, an observation which is consistent with the fact that complexes of the type [Ru(C$_5$R$_5$)Cl(PR$_3$)$_2$] (R = H or Me; PR$_3$ = PPr$^{i}_{3}$ or PCy$_3$) are also unknown.[24] Instead, 16-electron species [(C$_5$Me$_5$)RuCl(PR$_3$)] (PR$_3$ = PCy$_3$, PPr$^{i}_{3}$, PPhPr$^{i}_{2}$) have shown to be stable, yet reactive.[25] Given the increased bulk of the Tp ligand compared to C$_5$H$_5$ or C$_5$Me$_5$, the formation of a complex containing two *cis*-PPr$^{i}_{2}$Me ligands such as **1** is remarkable. Compound **1** shows in its ^{1}H NMR spectrum one multiplet at δ −0.23 attributable to CH$_3$ protons of isopropyl groups of the PPr$^{i}_{2}$Me ligand, which is somewhat unusual, since such a high-field resonance has not been observed in the ^{1}H NMR spectra of other TpRu phosphine complexes, *e.g.* **2** or [RuTp(Cl)(dippe)]. This anomalous chemical shift for isopropyl groups casts some doubts on whether **1** is really a plain six-co-ordinate species having a κ^3-Tp ligand (**A**), or a highly fluxional five-co-ordinate molecule containing a κ^2-Tp group and phosphines in a *trans* disposition, being stabilized by means of an "agostic" interaction with the isopropyl group of one of the phosphine ligands (**B**).

Ruthenium derivatives containing one κ^2-Tp ligand and two *trans* phosphine ligands have recently been reported, *i.e.* [Ru(κ^2-Tp)H(CO)(PPr$^{i}_{3}$)$_2$][26] and [Ru(κ^2-Tp)H(CO)(PPh$_3$)$_2$],[27] so this is a real possibility to be considered in our case. When the temperature is lowered the ^{31}P-{^{1}H} NMR resonance observed in the spectrum of **1** broadens, and splits into two separate signals which resolve into doublets at 183 K [Fig. 1(A)], suggesting the non-equivalence of the phosphorus atoms at this temperature. At this temperature, three of the pyrazole ring resonances in the ^{1}H NMR spectrum broaden [Fig. 1(B)], although they do not split as would be expected if the slow exchange limit were reached to give rise to nine separate signals, indicative of the non-equivalence of the three pyrazole rings of the Tp ligand. Apart from broadening and shifting to δ −0.63, lowering the temperature causes no effect on the high-field phosphine proton resonance. Apparently, this spectral behaviour might be consistent with a formulation as a κ^2-Tp complex with "agostic" interaction. However, no reduced $^1J_{CH}$ coupling constants were observed in the proton-coupled ^{13}C NMR spectrum, as would be expected if "agostic" hydrogen atoms were present. If instead we assume that **1** is just a sterically crowded six-co-ordinate complex, the unusual chemical shift observed might be caused by anisotropy due to the fact that some of the isopropyl hydrogen atoms of the phosphine, as result of the steric pressure, are forced near the magnetic ring current influence of a pyrazole ring. The inequivalent phosphines at low temperature may arise from freezing out conformers around single M–P and P–C bonds. No crystals of **1** suitable for X-ray diffraction could be obtained. However, crystals of the aqua complex [RuTp(H$_2$O)(PPr$^{i}_{2}$Me)$_2$][CF$_3$SO$_3$]·EtOH **3** were serendipitously obtained during an attempt to prepare the co-ordinatively unsaturated complex [RuTp(PPr$^{i}_{2}$Me)$_2$][CF$_3$SO$_3$] by reaction of **1** with AgO$_3$SCF$_3$ in EtOH, and its structure was determined.

A structural ORTEP view of complex **3** is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. Com-

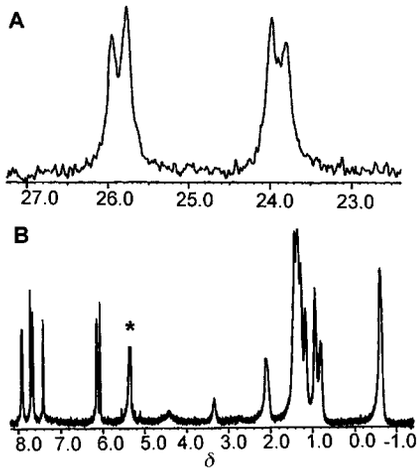


Fig. 1 The NMR spectra of complex **1** at 183 K (CD_2Cl_2): (A) ^{31}P-{^{1}H}, (B) ^{1}H. The peak marked with * corresponds to the solvent.

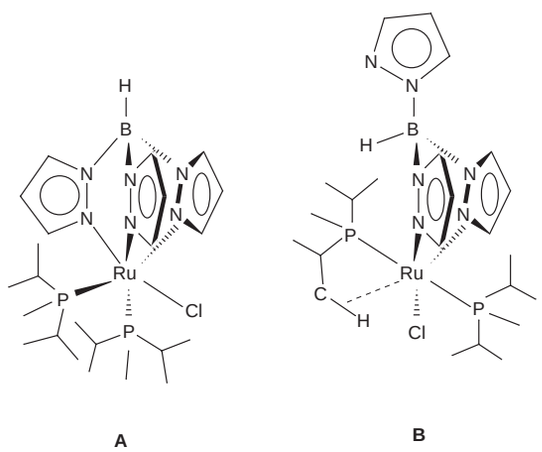


Table 1 Summary of data for the crystal structure analysis of complexes **3** and **6**

	3	**6**
Formula	$C_{26}H_{52}N_6BF_3O_5P_2RuS$	$C_{45}H_{60}B_2N_8P_2Ru$
M	791.62	897.66
Crystal size/mm	0.32 × 0.25 × 0.14	0.40 × 0.36 × 0.22
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)
a/Å	14.337(5)	15.908(4)
b/Å	22.077(6)	11.550(3)
c/Å	13.204(6)	22.555(4)
β/°	90.44(2)	
U/Å^3	3734(1)	4637(2)
Z	4	4
D_c/g cm^{-3}	1.408	1.286
μ(Mo-Kα)/cm^{-1}	6.03	4.37
F(000)	1648	1880
Unique reflections	6012	3754
Observed reflections ($I > 3\sigma_I$)	3434	1998
Number of parameters	406	338
R	0.062	0.066
R' ($w = \sigma_F^{-2}$)	0.075	0.077

Table 2 Selected bond distances (Å) and angles (°) for [RuTp(H_2O)(PPr^i_2Me)$_2$][CF_3SO_3]·EtOH

Ru(1)–P(1)	2.342(3)	O(1)···O(5)	2.59(1)
Ru(1)–P(2)	2.362(3)	O(1)–H(1)	1.21
Ru(1)–O(1)	2.142(6)	O(1)–H(2)	0.95
Ru(1)–N(12)	2.049(7)	O(5)–H(3)	0.97
Ru(1)–N(22)	2.147(8)	O(1)–H(3)	1.70
Ru(1)–N(32)	2.140(7)	O(2)–H(1)	1.83
O(1)···O(2)	2.82(1)		
P(1)–Ru(1)–P(2)	98.54(10)	O(1)–Ru(1)–N(12)	169.7(3)
P(1)–Ru(1)–O(1)	92.3(2)	O(1)–Ru(1)–N(22)	85.1(3)
P(1)–Ru(1)–N(12)	92.6(2)	O(1)–Ru(1)–N(32)	83.6(3)
P(1)–Ru(1)–N(22)	170.8(2)	N(12)–Ru(1)–N(22)	88.6(3)
P(1)–Ru(1)–N(32)	91.5(2)	N(12)–Ru(1)–N(32)	87.3(3)
P(2)–Ru(1)–O(1)	96.1(2)	N(22)–Ru(1)–N(32)	79.4(3)
P(2)–Ru(1)–N(12)	92.1(2)	Ru(1)–O(1)–H(1)	120.6
P(2)–Ru(1)–N(22)	90.5(2)	Ru(1)–O(1)–H(2)	110.0
P(2)–Ru(1)–N(32)	170.0(2)	H(1)–O(1)–H(2)	88.4

pound **3**, which also shows a high field phosphine proton resonance at δ −0.23, has a six-coordinate distorted octahedral structure, with phosphines in a cisoid arrangement showing no evidence for "agostic" interaction with the metal. The water molecule appears bound to ruthenium, and linked to an oxygen atom of the $[CF_3SO_3]^-$ anion *via* a hydrogen bond. The OH group of the ethanol solvate also forms a hydrogen bond with the co-ordinated water molecule. The hydrogen bond distances O···O are 2.59(1) and 2.82(1) Å. Strong hydrogen bonds between water and the $[CF_3SO_3]^-$ anion have also been observed in the recently reported crystal structures of [RuTp(H_2O){$Ph_2P(CH_2)_2NMe_2$}][CF_3SO_3]·0.5CH_2Cl_2[3] and [RuTp(H_2O)(COD)][CF_3SO_3],[2] which consist of neutral dimeric units linked by hydrogen bonds. In these compounds the hydrogen bond O···O distances range from 2.714 Å to 2.966 Å, comparing well with the O(1)···O(2) separation, although the O(1)···O(5) bond distance of 2.59(1) Å is indicative of a much stronger hydrogen bond between the water ligand and the ethanol solvate molecule. The Ru(1)–O(1) bond distance 2.142(6) Å is similar to the Ru–O separations observed for [RuTp(H_2O){$Ph_2P(CH_2)_2NMe_2$}][CF_3SO_3]·0.5CH_2Cl_2 [2.190(2) Å][3] and [RuTp(H_2O)(COD)][CF_3SO_3] [2.151(4) Å],[2] and also for the complex [Ru{$HC(pz)_3$}(H_2O)$_3$][p-$MeC_6H_4SO_3$]$_2$·1.5 H_2O [2.131(1) Å; $HC(pz)_3$ = tris(pyrazolyl)methane)].[28] The angle P(1)–Ru(1)–P(2) of 98.54(10)° is significantly larger than the values of *ca.* 85° found for complexes containing the bidentate phosphine dippe, such as [RuTp{=C(OMe)CH_2CO_2Me}(dippe)][BPh_4][17] or [RuTp(H_2)(dippe)][BPh_4],[15] since the phosphine ligands are monodentate in **3** and do not have the "bite angle" imposed by the backbone ethane chain in dippe. In this fashion the steric repulsions between the two PPr^i_2Me are minimized, but this forces some of the methyl groups on the isopropyl substituents [C(11) and C(3)] to move towards the gap between two pyrazole rings. As consequence, the hydrogen atoms attached to these methyl groups fall into the the magnetic ring current influence of the pyrazole rings, giving rise to the anomalous high field chemical shift observed for these protons in the ^{1}H NMR spectra. From the crystal structure of **3** it is clear that two bulky PPr^i_2Me can appear simultaneously bound to a TpRu centre, and therefore the absence of known complexes of the type [Ru(C_5Me_5)Cl(PR_3)$_2$] (PR_3 = bulky phosphine ligand: PPr^i_3, PCy_3, PPr^i_2Me, PPr^i_2Ph *etc.*) might be due to electronic rather than to steric reasons.[24,25]

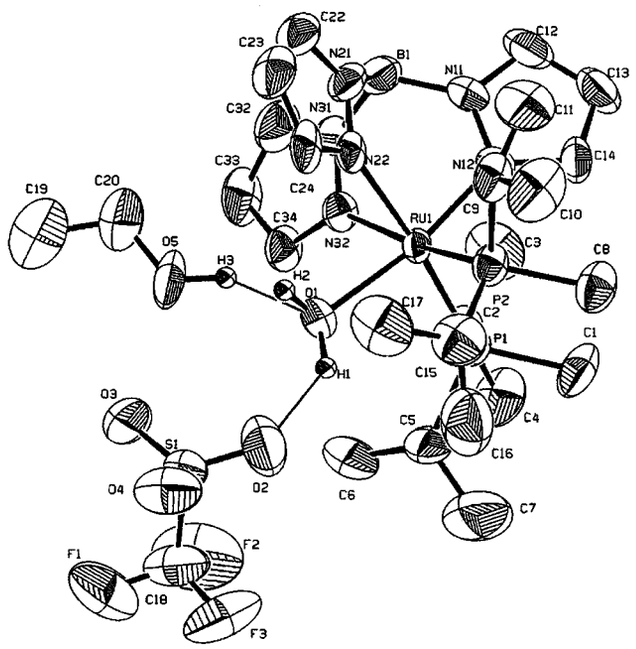


Fig. 2 An ORTEP drawing of the compound [RuTp(H_2O)(PPr^i_2-Me)$_2$][CF_3SO_3]·EtOH with 50% probability thermal ellipsoids. Hydrogen atoms, except those of the water ligand, are omitted.

The aqua complex [RuTp(H_2O)(PEt_3)$_2$][BPh_4] **4** was also obtained by chloride abstraction from **2** under argon in the presence of water, using AgO_3SCF_3. The water protons in **3** and **4** appear respectively at δ 3.1 and 5.30 respectively. If the chloride abstraction from complexes **1** and **2** is performed under dinitrogen instead of argon, then the dinitrogen adducts [RuTp(N_2)(PPr^i_2Me)$_2$]$^+$ and [RuTp(N_2)(PEt_3)$_2$]$^+$ are obtained, which were isolated as their respective tetraphenylborate salts **5** and **6**. These compounds display one strong $\nu(N_2)$ band at 2159 and 2163 cm^{-1} respectively. Since our initial report of the synthesis of the dinitrogen complex [RuTp(N_2)(dippe)][BPh_4] [$\nu(N_2)$ 2165 cm^{-1}],[15] two other TpRu dinitrogen adducts have been described: [RuTp(N_2){$Ph_2P(CH_2)_2NMe_2$}][CF_3SO_3] [$\nu(N_2)$ 2182 cm^{-1}][3] and [RuTp(N_2)(PPh_3)$_2$][BF_4] [$\nu(N_2)$ 2177 cm^{-1}],[12] which suggest that, at variance with their cyclopentadienyl or pentamethylcyclopentadienyl homologues,[18a] TpRu dinitrogen complexes seem to be a well established class of compounds. The crystal structure of **6** was determined. An ORTEP view of the complex cation is shown in Fig. 3. Selected bond lengths and angles are listed in Table 3. As for compound **3**, the co-ordination around the Ru atom is distorted octahedral. The dinitrogen ligand is bound in the end-on manner, with a Ru(1)–N(1)–N(2) angle of 166(3)°. The Ru(1)–N(1) and N(1)–N(2) separations are 1.91(2) and 1.01(2) Å respectively, which are fully consistent with the dimensions obtained for other ruthenium dinitrogen complexes including [RuTp(N_2){Ph_2P-$(CH_2)_2NMe_2$}][CF_3SO_3] (Ru–N 1.943(4), N–N 1.097(5) Å].[3] As

Table 3 Selected bond distances (Å) and angles (°) for $[RuTp(N_2)(PEt_3)_2][BPh_4]$

Ru(1)–P(1)	2.362(5)	Ru(1)–N(22)	2.15(2)
Ru(1)–P(2)	2.365(6)	Ru(1)–N(32)	2.07(1)
Ru(1)–N(1)	1.91(2)	N(1)–N(2)	1.01(2)
Ru(1)–N(12)	2.17(1)		
P(1)–Ru(1)–P(2)	99.8(2)	P(2)–Ru(1)–N(32)	88.9(5)
P(1)–Ru(1)–N(1)	91.8(7)	N(1)–Ru(1)–N(12)	90(1)
P(1)–Ru(1)–N(12)	90.7(5)	N(1)–Ru(1)–N(22)	87.5(9)
P(1)–Ru(1)–N(22)	172.7(5)	N(1)–Ru(1)–N(32)	176.5(9)
P(1)–Ru(1)–N(32)	91.6(5)	N(12)–Ru(1)–N(22)	82.0(7)
P(2)–Ru(1)–N(1)	91.2(9)	N(12)–Ru(1)–N(32)	88.7(7)
P(2)–Ru(1)–N(12)	169.3(5)	N(22)–Ru(1)–N(32)	89.0(7)
P(2)–Ru(1)–N(22)	87.5(5)	Ru(1)–N(1)–N(2)	166(3)

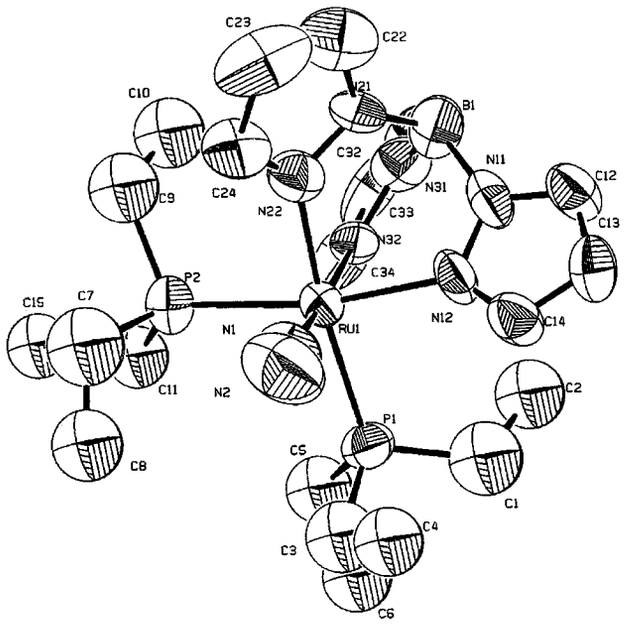


Fig. 3 An ORTEP drawing of the cation $[RuTp(N_2)(PEt_3)_2]^+$ with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

in most other cases, the observed N(1)–N(2) bond distance is identical within the experimental error to that of the free N_2 molecule, a fact which in the case of $[RuTp(N_2)\{Ph_2P(CH_2)_2NMe_2\}]^+$ has been interpreted in terms of a delicate compensatory influence of σ-bond strengthening and π-bond weakening in the N_2 molecule, as inferred from extended Hückel molecular orbital (EHMO) calculations.[3] This also accounts for the high frequency at which the $\nu(N_2)$ IR band appears in these complexes. The dinitrogen ligand in **5** and **6** is labile, and easily replaceable by good neutral donors such as $CNBu^t$, leading to the cationic complexes $[RuTp(CNBu^t)(PPr^i{}_2Me)_2][BPh_4]$ **7** [ν(CN) 2124 cm^{-1}] and $[RuTp(CNBu^t)(PEt_3)_2][BPh_4]$ **8** [ν(CN) 2123 cm^{-1}], which have octahedral structures as inferred from spectral data and do not require further comment.

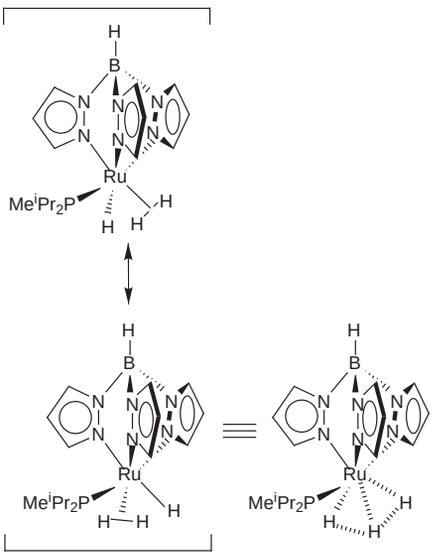
As a consequence of its bulkiness, $PPr^i{}_2Me$ in complex **1** is substitutionally labile, at variance with PEt_3 in **2**. Thus, **1** reacts smoothly with neutral donors such as MeCN or $CNBu^t$ furnishing the neutral complexes $[RuTp(Cl)L(PPr^i{}_2Me)]$ (L = MeCN **9** or $CNBu^t$ **10**). These compounds display strong bands in their respective IR spectra at 2269 and 2245 cm^{-1}, and at 2071 and 2099 cm^{-1}, attributable to ν(CN) in the ligands MeCN and $CNBu^t$. The three pyrazole rings of the Tp ligand in these species are inequivalent, and hence nine separate proton and carbon resonances appear in their ^1H and ^{13}C-$\{^1H\}$ NMR spectra. The characteristic high-field phosphine proton resonance observed for compounds of the type $[RuTp(X)(PPr^i{}_2Me)_2]$ is absent in the ^1H NMR spectra of **9** and **10**. The steric crowding around the metal decreases upon replacement of one of the $PPr^i{}_2Me$ by a less bulky ligand, so the methyl protons of the isopropyl substituents are not forced any more to remain under the magnetic ring current influence of the pyrazole rings. Triethylphosphine also displaces one $PPr^i{}_2Me$ from **1**, affording the mixed phosphine derivative $[RuTp(Cl)(PPr^i{}_2Me)(PEt_3)]$ **11**, which is characterized by the presence of two doublets in its ^{31}P-$\{^1H\}$ NMR spectrum corresponding to an AB spin system, as expected. In this particular compound the substitution of one $PPr^i{}_2Me$ by one PEt_3 does not relieve the steric pressure and the high field Pr^i proton resonance is still observed in the ^1H NMR spectrum. Other compounds of the type $[RuTp(Cl)L(PR_3)]$ (L = MeCN, py, CO, $P(OMe)_3$ or PMe_3; $PR_3 = PPh_3$ or PCy_3) have been described recently, these being prepared either by displacement of DMF from $[RuTp(Cl)(DMF)(PPh_3)]$ by L,[1] or by reaction of L with the ruthenium(III) complex $[RuTp(Cl)(OR)(PCy_3)]$ (R = Me or Et).[9]

Synthesis and characterization of hydride complexes

Complex **1** and **2** reacted with $NaBH_4$ in MeOH affording the neutral monohydride complexes $[RuTp(H)(PPr^i{}_2Me)_2]$ **12** and $[RuTp(H)(PEt_3)_2]$ **13**. These air-sensitive compounds display one strong ν(RuH) IR band near 1915 cm^{-1}, and one triplet in their ^1H NMR spectra attributable to the hydride proton. As result of the smaller size of hydrogen compared to chloride or other atoms, there is less steric pressure in the hydride complexes containing two $PPr^i{}_2Me$ ligands than in other $[RuTp(X)(PPr^i{}_2Me)_2]$ derivatives, and therefore all phosphine proton resonances in the ^1H NMR spectrum of **12** have positive chemical shifts relative to tetramethylsilane.

Both complexes **12** and **13** are protonated by $HBF_4{\cdot}OEt_2$ furnishing the dihydrogen adducts $[RuTp(H_2)(PPr^i{}_2Me)_2]^+$ and $[RuTp(H_2)(PEt_3)_2]^+$ which were isolated as their tetraphenylborate salts **14** and **15**. The dihydrogen ligand in these complexes is characterized by a broad resonance in the corresponding ^1H NMR spectra, having short minimum longitudinal relaxation times $(T_1)_{min}$ of 16 and 18 ms respectively (400 MHz). The coupling constants $^1J_{HD}$ observed for the isotopomers $[RuTp(HD)(PPr^i{}_2Me)_2]^+$ and $[RuTp(HD)(PEt_3)_2]^+$ are 31.1 and 30.9 Hz. These values of $(T_1)_{min}$ and $^1J_{HD}$ compare well with those previously found for other cationic TpRu dihydrogen complexes such as $[RuTp(H_2)(dippe)][BPh_4]$,[15] $[RuTp(H_2)(PPh_3)_2][BF_4]$,[12] and also $[RuTp(H_2)(CO)(PPr^i{}_3)][BF_4]$,[26] being consistent with the presence of a co-ordinated dihydrogen molecule. From the values of $(T_1)_{min}$, a separation d(H–H) of 0.95 Å for both **14** and **15** has been estimated, assuming fast spinning of the dihydrogen ligand. Complexes **14** and **15** are white, crystalline solids, indefinitely stable at room temperature under argon. Under dinitrogen the dihydrogen ligand is displaced very slowly by N_2 to yield the corresponding dinitrogen complex **5** or **6**. As for other cationic TpRu derivatives, equilibrium or irreversible tautomerization to the ruthenium(IV) dihydride form has not been observed, this being attributed to the particular electron donating capabilities of the Tp group (*e.g.* in comparison with those of the formally related C_5H_5 or C_5Me_5 ligands), as well as to the fact that this ligand favours six- over seven-co-ordinate species.[12,15,26]

We attempted to prepare the neutral monohydride complex $[RuTp(H)(MeCN)(PPr^i{}_2Me)]$ by treatment of **9** with $NaBH_4$ in MeOH. However, in the course of the reaction the MeCN ligand was lost, and the ultimate product obtained turned out to be the hydride(dihydrogen) complex $[RuTp(H)(H_2)(PPr^i{}_2Me)]$ **16**, which was isolated in the form of pale yellow crystals. This compound displays one strong IR band at 1946 cm^{-1} attributable to ν(RuH). The ^1H NMR spectrum shows one doublet at δ −10.45 ($^2J_{HP}$ = 19.6 Hz, 3 H) corresponding to the hydridic protons. No decoalescence of this resonance is observed as the temperature is lowered, suggesting that there is rapid atom exchange between hydride and dihydrogen sites, leading to the equivalence of these protons.



Only three rather broad proton and carbon pyrazole ring resonances are observed for complex **16** even at low temperature, indicative of the equivalence of the three pyrazole rings of the Tp ligand due to fluxional behaviour. Accordingly, the ^{31}P-{^{1}H} NMR spectrum shows one singlet. The value of $(T_1)_{min}$ for the hydride resonance is 40.8 ms (208 K, 400 MHz). As consequence of rapid chemical exchange with the terminal hydride, this relaxation time is averaged, but in agreement with the presence of one η^2-H_2 ligand within the complex. Complex **16** undergoes H–D exchange with CD_3OD, leading to the isotopomers [RuTp(H)(HD)(PPr^i_2Me)] and [RuTp(D)(HD)-(PPr^i_2Me)]. A $^{1}J_{HD}$ coupling constant of 7.4 Hz is observed, which is also averaged. Assuming a rapid hydride–dihydrogen fluxionality in a $MH(H_2)$ system, $^{1}J_{HD}$ of the dihydrogen ligand is equal to 3 times the observed $^{1}J_{HD}$ coupling constant,[14] and hence in our case turns out to be 22.2 Hz, a value which is typical for dihydrogen co-ordinated to a transition metal. The values of $(T_1)_{min}$ and $^{1}J_{HD}$ for **16** are very similar to those found for the compounds [RuTp(H)(H_2)(PR_3)] ($PR_3 = PCy_3$ [13] or PPh_3 [29]). The derivatives [RuTp*(H)(H_2)(PCy_3)] [Tp* = tris(3,5-dimethylpyrazolyl)hydroborate or tris(4-bromo-3-isopropylpyrazolyl)hydroborate] have also been described,[14] and their spectral properties match those of **16**. It is interesting that the compounds [RuTp*(H)(H_2)(PCy_3)][14] and [RuTp(H)(H_2)-(PPh_3)][29] have been obtained by hydrogenation of suitable precursor complexes, using pressures of H_2 ranging from *ca.* 3 ($PR_3 = PCy_3$) to 6–40 atm ($PR_3 = PPh_3$). In our case the hydride–dihydrogen complex is formed smoothly just by reaction of **9** with $NaBH_4$ in MeOH, the use of a H_2 atmosphere not being required. Under similar conditions, but with longer reaction times, the reaction of [RuTp(Cl)(MeCN)(PPh_3)] with $NaBH_4$ in MeOH leads to the hydrido carbonyl complex [RuTp(H)(CO)(PPh_3)]. In general, the reaction of [RuTp(H)-(MeCN)(PPh_3)] with $NaBH_4$ and alcohols RCH_2OH (R = Me, Et, Ph or tolyl) yields alkyl or aryl TpRu carbonyl derivatives [RuTp(R)(CO)(PPh_3)] resulting from the decarbonylation of the alcohol.[29] However, we have not detected similar species so far in our system.

The chemical reactivity of hydride complexes **12**–**16** is currently being investigated in detail. In a forthcoming paper we will describe stoichiometric and catalytic C–C coupling reactions in 1-alkynes mediated by the complexes described in this work.

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