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FULL PAPER

Synthesis and characterization of ruthenium quinolin-8-olate complexes. Unexpected formation of a κ^1-hydrotris(pyrazolyl)borate complex

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The complex $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)Cl_2]_2$ reacted with K[quin] (quin = quinolin-8-olate) to yield the half-sandwich complex $Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)Cl$ **1**. Chloride abstraction from **1** with $AgCF_3SO_3$ affords the neutral complex $Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)(\kappa^1O\text{-}CF_3SO_3)$. The lability of the $CF_3SO_3^-$ ligand in **2** is apparent by the reaction with CH_3CN giving $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)(CH_3CN)]CF_3SO_3$ **3**. Refluxing RuTp(COD)Cl in the presence of K[quin] resulted in the formation of $Ru(COD)(quin)_2$ **4** containing no Tp ligand; **4** has also been obtained in good yield by treating $[Ru(COD)Cl_2]_n$ with K[quin] in boiling methanol. Treatment of either **1** or **3** with 1 equivalent of KTp resulted in the formation of the unusual complex $Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)(\kappa^1N\text{-Tp})$ (**5**) featuring a κ^1-co-ordinated Tp ligand. However, if **1** is treated with KTp in the presence of $AgCF_3SO_3$ the cationic complex $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)(\kappa^1\text{-Hpz})]CF_3SO_3$ **6** is obtained containing a pyrazole ligand as a result of B–N bond cleavage. Complexes **1**, **4**, **5**, and **6** have been characterized by X-ray crystallography.

Introduction

The organometallic chemistry of late transition metals has traditionally been associated with low oxidation states. Thus, mainly π-acceptor ligands requiring at least some back donation from the metal to bind well have been used such as CO, polyenes, or tertiary phosphines.[1] Compared to this, σ donor and σ/π donor ligands such as amines, alkoxides, or amides are less commonly used. We have recently shown that on going from σ-donor/π-acceptor ligands to pure σ-donor ligands the changes in reactivity can be quite drastic. For instance, in the presence of the nitrogen σ-donor ligand Tp (Tp = hydrotris(pyrazolyl)borate), π ligands such as COD are substitutionally inert in sharp contrast to its lability in the neighborhood of Cp and Cp*.[2] In fact, the substitution of COD in RuTp(COD)Cl needs boiling dmf solutions while in RuCp(COD)Cl this takes place at ambient temperature. It is also remarkable that the rate for CH_3CN self-exchange is more than 8 orders of magnitude slower in $[RuTp(CH_3CN)_3]^+$ (1.2×10^{-8} s^{-1})[3] than in the isoelectronic complex $[RuCp(CH_3CN)_3]PF_6$(5.6 s^{-1}).[4]

In the present work we report on the synthesis and characterization of some organoruthenium complexes containing the hard anionic κ^2-N,O-co-ordinated quinolin-8-olate (quin) in conjunction with the π ligand *p*-cymene. Crystal structures of representative complexes are given including the first featuring the parent κ^1-Tp ligand.

Experimental

General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade used without further purification. The solvents were purified according to standard procedures.[5] The deuteriated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$,[6] KTp,[7] and $[RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)]_2$[8] were prepared according to the literature. ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer and referenced to $SiMe_4$, $^{11}B\text{-}\{^1H\}$ spectra on a Bruker AMX-300 spectrometer and referenced to $BF_3{\cdot}Et_2O$ and infrared spectra on a Bruker Vector 22 spectrometer.

Synthesis

$Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)Cl$ 1. To a solution of $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)Cl_2]_2$ (100 mg, 1.63 mmol) in thf (8 mL), K[quin] (71 mg, 3.27 mmol) was added and the reaction mixture stirred for 2 h at room temperature. The volume was reduced to 2 mL whereupon a orange precipitate formed. Precipitation was completed by addition of Et_2O (5 mL). The solid was transferred to a glass frit and extracted with CH_2Cl_2 (10 mL). The CH_2Cl_2 solution was evaporated to dryness, and the residue dissolved in CH_2Cl_2 (1 mL). Upon addition of Et_2O again a orange precipitate formed, which was washed with Et_2O (4 × 2 mL) and dried in vacuum. Yield: 128 mg (94%) (Found: C, 55.22; H, 4.76; N, 3.17. $C_{19}H_{20}ClNORu$ requires: C, 55.00; H, 4.86; N, 3.38%). DC: R_f (CH_2Cl_2–acetone 1:1 (v/v) = 0.47). NMR ($CDCl_3$, 20 °C): ^1H, δ 8.93 (bs, 1 H, hc^2), 8.09 (d, $^3J_{HH}$ = 8.6, 1 H, hc^4), 7.34 (vt, $^3J_{HH}$ = 7.8, 1 H, hc^6), 7.33 (bs, 1 H, hc^3), 7.05 (bd, $^3J_{HH}$ = 7.8, 1 H, hc^5), 6.85 (d, $^3J_{HH}$ = 7.8, 1 H, hc^7), 5.63 (m, 1 H, cy), 5.52 (m, 1 H, cy), 5.47 (m, 1 H, cy), 5.34 (m, 1 H, cy), 2.81 (m, 1 H, $CH(Me)_2$), 2.32 (s, 3 H, Me), 1.19 (d, $^3J_{HH}$ = 6.2, 3 H, $CH(Me)_2$) and 1.16 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, $CH(Me)_2$); $^{13}C\text{-}\{^1H\}$, δ 169.0 (hc^8), 149.7 (hc^2), 144.8 (hc^{8a}), 138.1 (hc^4), 130.9 (hc^6), 130.7 (hc^{4a}), 122.5 (hc^3), 115.6 (hc^5), 111.1 (hc^7), 101.8 (cy^1), 99.3 (cy^4), 83.1, 82.5, 81.8, 81.3 ($cy^{2,3,5,6}$), 31.6 ($CHMe_2$), 23.1, 22.7 ($CHMe_2$) and 19.3 (Me).

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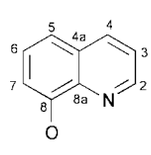
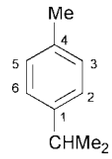




Ru(η⁶-*p*-MeC$_6$H$_4$Pr^i)(quin)(κ¹*O*-CF$_3$SO$_3$) 2. Complex **1a** (100 mg, 0.241 mmol) and AgCF$_3$SO$_3$ (65 mg, 0.252 mmol) were dissolved in thf and stirred at room temperature for 2 h. After evaporation of the solvent, the residue was redissolved in CH_2Cl_2 and the solution filtered. The white precipitate was filtered off and the product crystallized by addition of Et_2O. Yield: 79 mg (77%) (Found: C, 45.60; H, 3.73; N, 2.49. $C_{20}H_{20}F_3NO_4RuS$ requires: C, 45.45; H, 3.81; N, 2.65%). ^{1}H NMR (CD_3NO_2, 20 °C): δ 8.58 (d, 1 H, $^3J_{HH}$ = 5.1, hc^2), 7.93 (d, 1 H, $^3J_{HH}$ = 8.7, hc^4), 7.44 (m, 2 H, hc^6, hc^3), 7.06 (m, 2 H, hc^5, hc^7), 6.59 (m, 2 H, cy), 4.77 (m, 2 H, cy), 2.76 (s, 3 H, CH_3), 2.36 (m, 1 H, C*H*(Me)$_2$), 1.02 (d, 3 H, $^3J_{HH}$ = 7.0, CH(*Me*)$_2$) and 0.79 (d, 3 H, $^3J_{HH}$ = 7.00 Hz, CH(*Me*)$_2$) ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 164.4(hc^8), 156.2(hc^2), 143.0(hc^{8a}), 140.2(hc^4), 130.6(hc^6), 130.1 (hc^{4a}), 124.6(hc^3), 120.5(hc^5), 120.4(hc^7), 106.4 (cy^1), 97.1(cy^4), 87.1, 86.3, 84.5, 78.9(cy^{2,3,5,6}), 32.1(*C*HMe$_2$), 22.3, 22.2 (CH*Me*$_2$) and 20.0 (Me).

[Ru(η⁶-*p*-MeC$_6$H$_4$Pr^i)(quin)(CH$_3$CN)]CF$_3$SO$_3$ 3. Complex **1** (100 mg, 0.241 mmol) and AgCF$_3$SO$_3$ (65 mg, 0.252 mmol) were dissolved in CH_3CN (5 mL) and stirred for 30 min at room temperature. The solvent was removed *in vacuo*, the residue redissolved in CH_2Cl_2 (1 mL) and the product precipitated by addition of Et_2O. Yield: 121 mg (88%) (Found: C, 46.53; H, 3.98; N, 5.08. $C_{22}H_{23}F_3N_2O_4RuS$ requires: C, 46.39; H, 4.07; N, 4.92%). NMR ($CDCl_3$, 20 °C): ^{1}H, δ 9.46 (d, 1 H, $^3J_{HH}$ = 4.4, hc^2), 8.22 (d, 1 H, $^3J_{HH}$ = 8.5, hc^4), 7.61 (dd, 1 H, ^3J(H^{3}H^4) = 8.5, ^3J(H^{3}H^4)24;= 4.4, hc^3), 7.38 (dd, 1 H, ^3JH^{5}H^6 = ^3JH^{6}H^7 = 7.9, hc^6), 7.10 (d, 1 H, *J* = 7.9, hc^5), 7.0 (d, 1 H, $^3J_{HH}$ = 7.9, hc^7), 5.94 (m, 4 H, cy), 2.65 (s, 1 H, $^3J_{HH}$ = 7.0, C*H*(Me)$_2$), 2.28 (s, 3 H, CH_3), 2.21 (bs, 3 H, CH_3CN) and 1.07 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, CH(*Me*)$_2$); ^{13}C-{^{1}H}, δ 166.9 (hc^8), 153.1 (hc^2), 143.4 (hc^{8a}), 139.5 (hc^4), 130.7 (hc^6), 130.4 (hc^{4a}), 124.0 (CN), 123.8 (hc^3), 118.7 (hc^5), 113.4 (hc^7), 103.8 (cy^1), 102.6 (cy^4), 86.8, 85.9, 83.4, 83.3, 31.7 (*C*HMe$_2$), 22.9 (CH*Me*$_2$), 22.5 (CH*Me*$_2$), 19.3 (CH_3) and 4.4 (*C*H$_3$CN).

Ru(COD)(quin)$_2$ 4. *Method 1.* A suspension of [Ru(COD)Cl$_2$]$_n$ (300 mg, 1.071 mmol) and K[quin] (418 mg, 2.142 mmol) in methanol (10 mL) was heated under reflux for 2 h. The volume of the solution was reduced to 2 mL and the resulting bright brown precipitate transferred to a glass frit and washed with methanol (3 × 1 mL) to remove an impurity (green spot on DC; R_f (CH_2Cl_2–acetone 1:1 (v/v)) = 0.69). The residue was extracted with Et_2O (250 mL) to remove another impurity (yellow spot on DC; R_f (CH_2Cl_2–acetone 1:1 (v/v)) = 0.45). An analytically pure material was obtained after removal of Et_2O under reduced pressure. Yield: 275 mg (52%) (Found: C, 62.85; H, 4.74; N, 5.77. $C_{26}H_{24}N_2O_2Ru$ requires: C, 62.76; H, 4.86; N, 5.63%). DC: R_f (CH_2Cl_2–acetone 1:1 (v/v)) = 0.85). NMR ($CDCl_3$, 20 °C): ^{1}H, δ 8.53 (dd, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 1.6, 2 H, hc^2), 7.85 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.6, 2 H, hc^4), 7.42 (dd, $^3J_{HH}$ = 8.1, $^3J_{HH}$ = 7.8, 2 H, hc^6), 7.26 (dd, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.1, 2 H, hc^5), 7.12 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 5.0, 2 H, hc^3), 6.85 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.2 Hz, 2 H, hc^7), 4.41 (m, 2 H, COD), 3.40 (m, 2 H, COD), 2.85–2.69 (m, 2 H, COD), 2.60–2.43 (m, 2 H, COD) and 2.41–2.23 (m, 4 H, COD); ^{13}C-{^{1}H}, δ 170.0 (hc^8), 145.1 (hc^{2,8a}), 136.0 (hc^4), 131.1 (hc^{4a}), 130.1 (hc^6), 121.9 (hc^5), 115.6 (hc^3), 111.0 (hc^7), 93.0 (COD), 92.9 (COD), 30.4 (COD) and 30.3 (COD).

Method 2. To a solution of RuTp(COD)Cl (150 mg, 0.328 mmol) in dmf K[quin] (120 mg, 0.655 mmol) was added and the mixture heated at reflux for 2 h. After evaporation of the solvent under reduced pressure the residue was dissolved in CH_2Cl_2 and the product precipitated by addition of Et_2O. The product was collected on a glass frit, washed with Et_2O and dried *in vacuo*. Yield: 129 mg (79%).

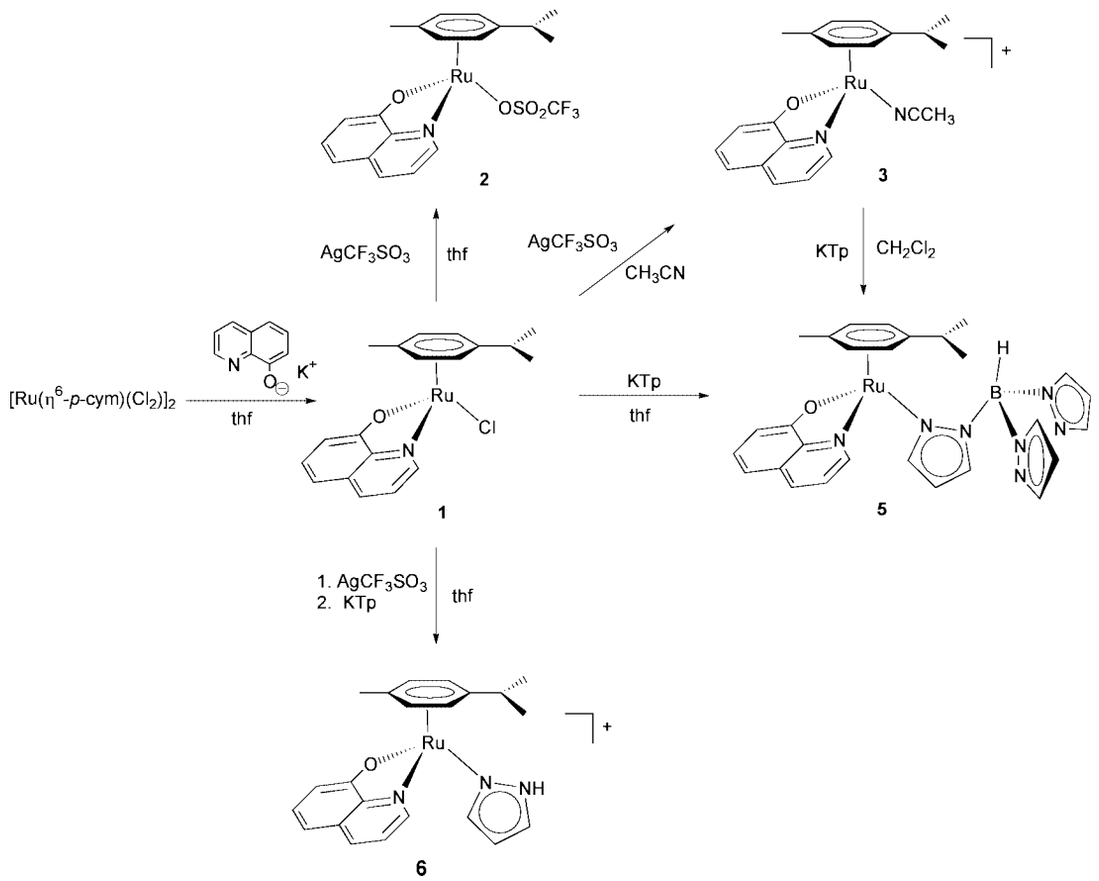
Ru(η⁶-*p*-MeC$_6$H$_4$Pr^i)(quin)(κ¹*N*-Tp) 5. *Method (a).* To a solution of complex **1** (100 mg, 0.241 mmol) in thf (4 mL) KTp (60.8 mg, 0.241 mmol) was added and the mixture heated at 50 °C for 2 h. After that time the solution was evaporated to dryness and the resulting residue transferred to a glass frit and extracted with CH_2Cl_2 (15 mL). The filtrate was reduced to about 1 mL and upon addition of Et_2O (2 mL) and *n*-hexane (2 mL) a bright yellow precipitate was formed, which was collected on a glass frit, washed with *n*-hexane (2 × 2 mL) and dried in vacuum. Yield: 117 mg (82%).

Method (b). To a solution of complex **3** (200 mg, 0.351 mmol) in CH_2Cl_2 (4 mL) KTp (88.5 mg, 0.351 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. After that time the solution was filtered and the volume of the filtrate reduced to about 1 mL. Upon addition of Et_2O (2 mL) and *n*-hexane (2 mL) a bright yellow precipitate was formed, which was collected on a glass frit, washed with *n*-hexane (2 × 2 mL) and dried under vacuum. Yield: 90 mg (63%) (Found: C, 56.86; H, 4.86; N, 16.32. $C_{28}H_{30}BN_7ORu$ requires: C, 56.76; H, 5.10; N, 16.55%). NMR ($CDCl_3$, 20 °C): ^{1}H, δ 9.31 (d, $^3J_{HH}$ = 4.9, 1 H, hc^2), 7.87 (d, $^3J_{HH}$ = 8.4, 1 H, hc^4), 7.69 (d, $^3J_{HH}$ = 1.5, 1 H, Tp), 7.64 (d, $^3J_{HH}$ = 2.1, 1 H, Tp), 7.51 (m, 2 H, Tp), 7.27 (dd, $^3J_{HH}$ = 8.0, $^3J_{HH}$ = 7.7, 1 H, hc^6), 7.18 (d, $^3J_{HH}$ = 2.1, 1 H, Tp), 7.06 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 4.9, 1 H, hc^3), 7.00 (dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.1, 1 H, hc^5), 6.77 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.1, 1 H, hc^7), 6.23 (dd, $^3J_{HH}$ = 2.1, $^3J_{HH}$ = 1.7, 1 H, Tp), 6.20 (d, $^3J_{HH}$ = 2.1, 1 H, Tp), 6.15 (vt, $^3J_{HH}$ = 2.4, 1 H, Tp), 5.85 (d, $^3J_{HH}$ = 5.8, 2 H, cy), 5.81 (vt, $^3J_{HH}$ = 2.1, 1 H, Tp), 5.73 (d, $^3J_{HH}$ = 5.8, 2 H, cy), 2.40 (m, 1 H, C*H*(Me)$_2$), 2.19 (s, 3 H, Me), 1.19 (d, $^3J_{HH}$ = 7.0, 3 H, CH(*Me*)$_2$) and 0.83 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH(*Me*)$_2$); ^{13}C-{^{1}H}, δ 168.2 (hc^8), 152.1 (hc^2), 144.0 (hc^{8a}), 141.8 (Tp), 141.1 (Tp), 140.9 (Tp), 139.4 (Tp), 138.1 (hc^4), 133.1 (Tp), 132.5 (Tp), 130.3 (hc^6), 130.2 (hc^{4a}), 122.5 (hc^3), 114.8 (hc^5), 112.1 (hc^7), 107.0 (Tp), 104.8 (Tp), 104.5 (cy^1), 104.4 (Tp), 100.8 (cy^4), 84.9, 84.6, 84.4, 83.5 (cy^{2,3,5,6}), 31.3 (*C*HMe$_2$), 23.6, 21.7 (CH*Me*$_2$), 18.5 (Me); ^{11}B-{^{1}H}, δ −1.8. IR (Nujol, cm^{-1}): 2434.8, 2398.0, 2362.0 and 2341.5 ν(B–H).

[Ru(η⁶-*p*-MeC$_6$H$_4$Pr^i)(quin)(κ¹-Hpz)]CF$_3$SO$_3$ 6. A solution of complex **1** (100 mg, 0.241 mmol) and AgCF$_3$SO$_3$ (65 mg, 0.252 mmol) in thf (5 mL) was stirred at room temperature for 2 h. After that time KTp (60.7 mg, 0.241 mmol) was added. After stirring for 2 h, the solution was filtered and the solvent removed under vacuum. After redissolving the residue in CH_2Cl_2 (2 mL), the yellow product was precipitated by addition of Et_2O, collected on a glass frit, washed twice with Et_2O and dried *in vacuo*. Yield: 99 mg (69%) (Found: C, 46.43; H, 3.92; N, 6.88. $C_{23}H_{24}F_3N_3O_4RuS$ requires C, 46.31; H, 4.06; N, 7.04%). NMR ($CDCl_3$, 20 °C): ^{1}H, δ 12.91 (bs, 1H, pz NH), 9.58 (d, 1 H, $^3J_{HH}$ = 4.8, hc^2), 8.07 (d, 1 H, $^3J_{HH}$ = 7.4, hc^4), 7.39 (m, 4 H, hc^6, hc^3, pz^5, pz^3), 7.02 (d, 1 H, $^3J_{HH}$ = 8.2, hc^5), 6.84 (d, 1 H, $^3J_{HH}$ = 7.8, hc^7), 6.11 (m, pz^4), 6.03 (m, 1 H, cy), 5.82 (m, 3 H, cy), 2.38 (m, 1 H, *CH*(Me$_2$)), 1.09 (s, 3 H, CH_3) and 0.89 (d, 6 H, *J* = 7.0 Hz, CH(*Me*$_2$)); ^{13}C-{^{1}H}, δ 167.6 (hc^8), 151.6 (hc^2), 143.3 (hc^{8a}), 140.1 (pz^3), 138.5 (hc^4), 133.4 (pz^5), 130.5 (hc^6), 130.4 (hc^{4a}), 123.1 (hc^3), 114.8 (hc^5), 112.3 (hc^7), 106.8 (pz^4), 103.7 (cy^1), 101.3 (cy^4), 85.1, 82.3, 82.2, 68.1 (cy^{2,3,5,6}), 31.2 (*C*HMe$_2$), 22.8, 21.7 (CH*Me*$_2$) and 18.2 (Me).

X-Ray crystallography

Crystal data and experimental details are given in Table 1. X-Ray data for complex **1** were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated



Scheme 1

Mo-Kα radiation ($\lambda = 0.71073$ Å) and the θ–2θ scan technique; for **4**, **5** and **6**·$CHCl_3$ on a Siemens Smart CCD area detector diffractometer using graphite monochromated Mo-Kα radiation and 0.3° ω-scan frames. Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. All structures were solved by direct methods using the program SHELXS 97.[9] Structure refinement on F^2 was carried out with SHELXL 97.[10] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were in most cases inserted in idealized positions and refined riding with the atoms to which they were bonded.

CCDC reference number 186/2037.

See http://www.rsc.org/suppdata/dt/b0/b002490m/ for crystallographic files in .cif format.

Results and discussion

Treatment of $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)Cl_2]_2$ with 2 equivalents of K[quin] in thf at room temperature for 2 h affords the half-sandwich complex $Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)Cl$ **1** in 94% isolated yield (Scheme 1) as an orange air-stable complex. Complex **1** has been characterized by ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy as well as elemental analysis. The ^1H NMR spectrum shows six distinct multiplets for the quin ligand with the chemical shifts and multiplicities in the expected range for N,Oco-ordination. The *p*-cymene ligand gives rise to four multiplets centered at δ 5.61, 5.50, 5.46, and 5.35, respectively, assigned to the aromatic hydrogen atoms. The methyl groups of the *i*-Pr moiety are diastereotopic exhibiting two distinct doublets centered at δ 1.19 and 1.16. The $^{13}C\text{-}\{^1H\}$ NMR spectrum does not bear any unusual features and is not discussed here.

The solid state structure of complex **1** was determined by single-crystal X-ray diffraction. An ORTEP[11] diagram is depicted in Fig. 1. Selected bond distances and angles are reported in Table 2. Accordingly, **1** adopts a three legged piano stool conformation with Cl and the N and O atoms of the bidentate quin ligand as the legs. The Ru–Cl, Ru–N, and Ru–O distances are 2.422(1), 2.094(2), and 2.073(2) Å, respectively, with Cl–Ru–N, Cl–Ru–O, and N–Ru–O angles of 84.3(1), 86.5(1), and 78.8(1)°. The *p*-cymene ring is essentially planar with C–C bond distances in the range 1.385(2)–1.429(2) Å, giving a mean value of 1.413 Å. The Ru–C distances range from 2.162(2) to 2.203(2) Å (mean 2.181 Å).

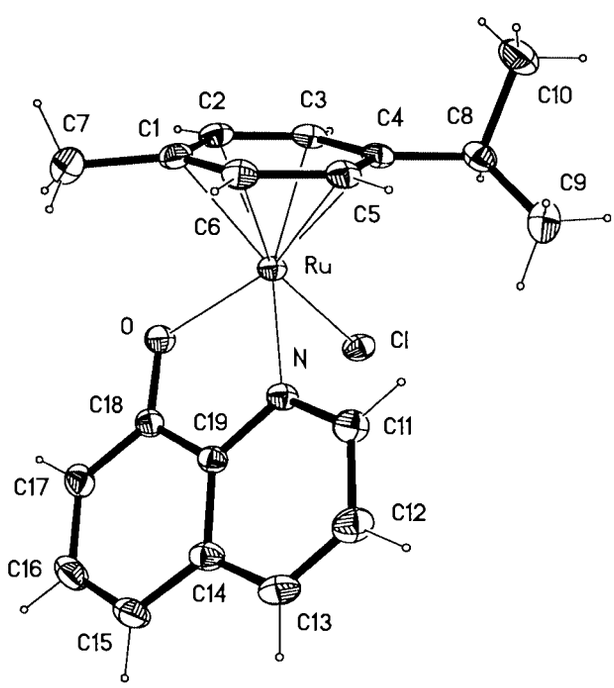


Fig. 1 Structural view of $Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)(quin)Cl$ **1** showing 20% probability thermal ellipsoids (as in all cases).

Table 1 Crystallographic data for complexes **1**, **4**, **5**, and **6**·$CHCl_3$

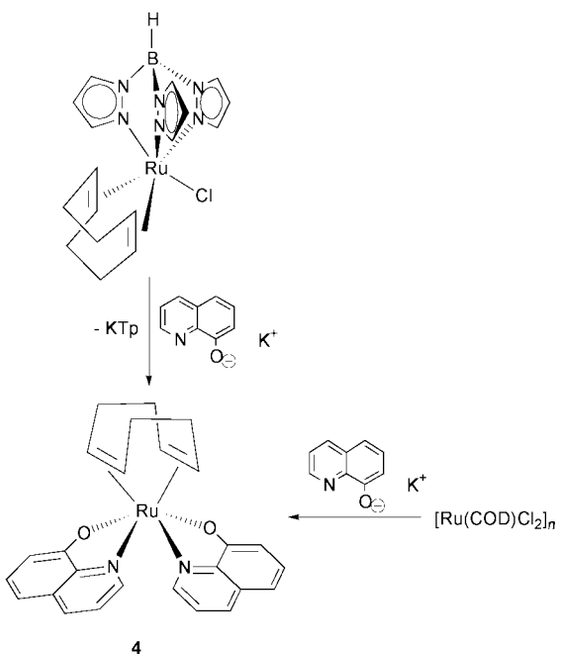
	1	**4**	**5**	**6**·$CHCl_3$
Formula	$C_{19}H_{20}ClNORu$	$C_{26}H_{24}N_2O_2Ru$	$C_{28}H_{30}BN_7ORu$	$C_{24}H_{25}Cl_3F_3N_3O_4RuS$
M	414.88	497.54	592.47	715.95
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	10.757(2)	8.412(4)	9.980(1)	9.899(4)
b/Å	13.287(3)	12.927(5)	10.672(1)	12.855(6)
c/Å	12.309(2)	19.141(8)	12.548(2)	12.936(6)
α/°			92.58(1)	115.46(2)
β/°	102.97(1)	92.47(2)	91.70(1)	99.12(2)
γ/°			98.78(1)	93.28(2)
V/Å^3	1714.4(6)	2080(1)	1318.5(3)	1453(1)
Z	4	4	2	2
T/K	300(2)	295(2)	301(2)	223(2)
μ/mm^{-1}(Mo-Kα)	1.074	0.781	0.631	0.942
Total reflections	3164	16365	15883	20908
Independent reflections	3023	3651	7617	8201
R_{int}	0.013	0.035	0.021	0.017
*R*1 (all data)	0.027	0.043	0.038	0.037
*wR*2 (all data)	0.048	0.070	0.062	0.089

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**, **5**, and **6**·$CHCl_3$

	1 X = Cl	**5** X = N (Tp)	**6**·$CHCl_3$ X = N (Hpz)
Ru–O(1)	2.073(2)	2.066(1)	2.063(2)
Ru–N(1)	2.094(2)	2.090(1)	2.091(2)
Ru–X	2.422(1)	2.127(1)	2.118(2)
Ru–C(1–6)$_{av}$	2.181(2)	2.194(2)	2.195(2)
C(1–6)$_{av}$	1.413(4)	1.418(2)	1.410(4)
O(1)–Ru–N(1)	78.8(1)	79.0(1)	79.4(1)
O(1)–Ru–X	86.5(1)	84.7(1)	82.8(1)
N(1)–Ru–X	84.3(1)	86.0(1)	85.1(1)

Substitution of the Cl atom in complex **1** for the weakly nucleophilic $CF_3SO_3^-$ anion was investigated with the intention of generating a reactive complex bearing a weakly co-ordinating ligand occupying a latent co-ordination site. In fact, chloride abstraction from **1** with $AgCF_3SO_3$ (1 equivalent) affords, on work-up, a complex with the formula Ru(η^6-*p*-$MeC_6H_4Pr^i$)(quin)(CF_3SO_3) **2** (Scheme 1). This formulation is consistent with the elemental analysis and the close similarities between the ^{1}H and ^{13}C-{^{1}H} NMR spectra of the 18e$^-$ complex **1**. However, in view of the ability of $CF_3SO_3^-$ to co-ordinate to Ru^{II}, as well as the orange color of the complex (all known 16e half-sandwich compexes of Ru^{II} are dark blue to dark violet), we believe that the formula should be Ru(η^6-*p*-$MeC_6H_4Pr^i$)(quin)(κ^1*O*-CF_3SO_3). In fact, several ruthenium complexes with the κ^1-OSO_2CF_3 ligand are known and have even been structurally characterized.[12] The lability of the $CF_3SO_3^-$ ligand in **2** is apparent by the reaction with CH_3CN giving [Ru(η^6-*p*-$MeC_6H_4Pr^i$)(quin)(CH_3CN)]CF_3SO_3 **3** in 88% yield (Scheme 1). It has to be noted, however, that **2** does not react with the strong π-acceptor ligand CO to afford [Ru(η^6-*p*-$MeC_6H_4Pr^i$)(quin)(CO)]CF_3SO_3 indicating that the [Ru(η^6-*p*-$MeC_6H_4Pr^i$)(quin)]$^+$ moiety is apparently a very good Lewis acid but a poor π base.

As part of our current interest in RuTp chemistry,[13] we have attempted to prepare complexes of the type RuTp(quin)(solv) (solv = *e.g.* dmf, thf or CH_3CN). The general route to complexes containing the RuTp(quin) moiety is refluxing RuTp(COD)Cl in the presence of quin in the appropriate solvent. This approach, however, resulted in the formation of several not identified materials together with Ru(COD)(quin)$_2$ **4** in low yield regardless of whether quin was used stoichiometrically or in excess. Noteworthy, **4** can be obtained



4

Scheme 2

in good yield by treating [Ru(COD)Cl_2]$_n$ with K[quin] in boiling methanol (Scheme 2). The structure of **4** is shown in Fig. 2 with selected bond distances and angles given in the caption. This compound is the *trans*(O,O), *cis*(N,N) isomer related to the complex *trans*(O,O), *cis*(N,N)-Ru(quin)$_2$(PPh_3)$_2$.[14]

In an other attempt to prepare the neutral compound RuTp(quin)(thf), **1**, **2**, and **3** have been treated with 1 equivalent of KTp in thf. Arene ligands have been shown to be displaced easily by 6e donor ligands such as Cp or Tp.[15] Surprisingly, this approach failed in all these cases and instead the unusual complex Ru(η^6-*p*-$MeC_6H_4Pr^i$)(quin)(κ^1*N*-Tp) **5** featuring a κ^1-co-ordinated Tp ligand was isolated as the major product (Scheme 1). Complex **5** is air-stable in the solid state yet decomposes in solution on exposure to air. Characterization has been accomplished by ^{1}H, ^{13}C-{^{1}H}, and ^{11}B-{^{1}H} NMR and IR spectroscopy as well as elemental analysis. While ^{1}H and ^{13}C-{^{1}H} NMR spectra are not very informative as to the co-ordination mode of Tp, a κ^1 denticity is suggested from a ^{11}B-{^{1}H} NMR spectrum exhibiting a resonance at δ −1.8 (*cf.* δ −2.0 for [Rh(κ^1-Tp^{Me2})(C_2H_4)$_2$] and also free,

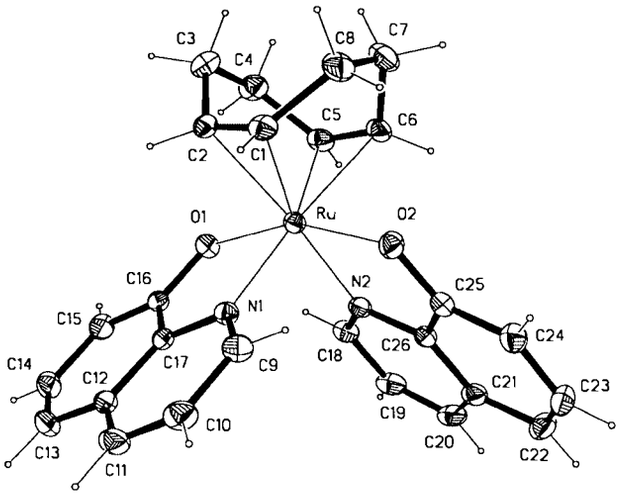


Fig. 2 Structural view of Ru(COD)(quin)$_2$ **4** selected bond distances (Å) and angles (°): Ru–O(1) 2.085(2), Ru–O(2) 2.093(2), Ru–N(1) 2.094(2), Ru–N(2) 2.086(2), Ru–C(1) 2.184(3), Ru–C(2) 2.198(3), Ru–C(5) 2.182(3) and Ru–C(6) 2.186(3); O(1)–Ru–N(1) 79.7(1), O(2)–Ru–N(2) 79.5(1), O(1)–Ru–O(2) 159.2(1) and N(1)–Ru–N(2) 91.7(1).

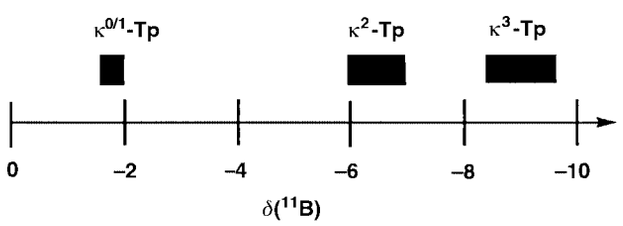


Fig. 3 ^{11}B chemical shifts as a function of the Tp denticity.

i.e. "κ°"-Tp[16]). For comparison, κ^3- and κ^2-Tp complexes exhibit more upfield shifted resonances as shown in Fig. 3.[17]

In some cases also the *ν*(B–H) stretching frequency has been used as criterion for establishing the denticity of Tp.[18] In the present case, however, the situation is more complicated since not a single absorption but four bands at 2435, 2398, 2362, and 2342 cm^{-1} are observed. Similar observations have been made for other κ^1-Tp complexes and the presence of isomers such as κ^2*N*,*H* or κ^2*N*,*N*′ species has been suggested.[19] In the present case, however, such species are very unlikely since **5** is both co-ordinatively saturated and kinetically inert.

According to our knowledge, complex **5** is the first example of an isolated and fully characterized metal complex bearing the parent κ^1-co-ordinated Tp ligand. It has to be noted, however, that there are several examples of complexes featuring a κ^1-co-ordinated Tp derivative.[19] Therefore, the structure of **5** has been determined by X-ray crystallography. (Fig. 4 with selected bond distances and angles in Table 2). Complex **5** adopts a three legged piano stool conformation with the N(1), O, and N(3) atoms as the legs. The Ru–N(1), Ru–O, and Ru–N(3) distances are 2.090(1), 2.066(1), and 2.127(1) Å, respectively, with N(1)–Ru–N(3), N(1)–Ru–O, and N(3)–Ru–O angles of 86.0(1), 79.0(1), and 84.7(1)°. The borate moiety is κ^1-co-ordinated to ruthenium with two pyrazolyl groups oriented away from the metal center. The hydride substituent of the Tp ligand is pointing towards the ruthenium. However, the distance between them is 3.121(2) Å, excluding any agostic interaction. The *p*-cymene ring is again planar with C–C bond distances in the range 1.398(2)–1.435(2) Å, giving a mean value of 1.418 Å. The Ru–C distances range from 2.173(2) to 2.219(2)Å (mean 2.194 Å).

Since two pyrazolyl groups of the Tp ligand in complex **5** are oriented away from the metal center this complex may act as a bidentate ligand forming a binuclear complex with a bridging Tp ligand co-ordinated in κ^1 and κ^2 fashion. Thus, **5** was treated

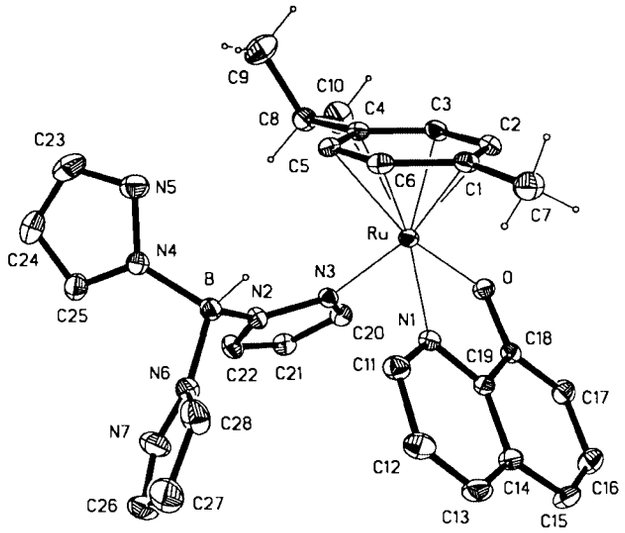


Fig. 4 Structural view of Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(quin)(κ^1*N*-Tp) **5**.

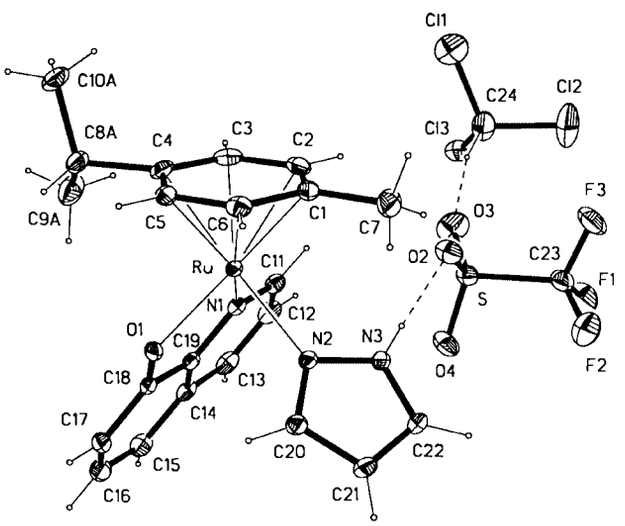


Fig. 5 Structural view of [Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(quin)(κ^1*N*-Hpz)]CF$_3$SO$_3$·CHCl$_3$ **6**·CHCl$_3$.

with the substitutionally labile complex [RuCp(PPh$_3$)(CH$_3$CN)$_2$]PF$_6$.[20] The reaction was monitored by ^{1}H NMR spectroscopy revealing the formation of several intractable materials and no evidence for a Tp-bridged complex.

In another attempt to obtain a binuclear complex, **2** was prepared *in situ* by adding AgCF$_3$SO$_3$ and then 0.5 equivalent of KTp in thf as the solvent. The solution changed immediately from orange to pale yellow and on work-up the cationic complex [Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(quin)(κ^1-Hpz)]CF$_3$SO$_3$ **6** was obtained albeit in low yield. The same complex was obtained in 63% isolated yield on using stoichiometric amounts of KTp. There was no evidence for a species containing a bridging Tp ligand. Complex **6** contains a pyrazole ligand as a result of B–N bond cleavage as is readily apparent from a characteristic resonance of the pz N–H proton at *δ* 12.91. However, similar B–N cleavage reactions have been reported.[21] In this particular case traces of Ag$^+$ may play an important role. It has to be noted that **2** reacts with KTp to give not only **5** (60%) but also substantial amounts of **6** (40%), while with **1** and also **3** the formation of **6** has not been observed. Furthermore, **5** reacts with 1 equivalent of AgCF$_3$SO$_3$ to give quantitatively **6** together with free pyrazole as monitored by ^{1}H NMR spectroscopy. The fate of the remaining pyrazolyl borate moiety remains unclear.

The solid state structure of complex **6** has been confirmed by single-crystal X-ray diffraction. An ORTEP diagram is depicted in Fig. 5. Selected bond distances and angles are reported in

Table 2. Complex **6** adopts a three legged piano stool conformation. The Ru–N(Hpz), Ru–N, and Ru–O distances are 2.118(2), 2.091(2), and 2.063(2) Å, respectively, with N(Hpz)–Ru–N, N(Hpz)–Ru–O, and N–Ru–O angles of 85.1(1), 82.8(1), and 79.4(1)°. In crystalline state the compound exhibits an orientationally disordered isopropyl group (not shown in Fig. 5), and more importantly an interesting stabilization by hydrogen bonds from the pyrazole ligand and the $CHCl_3$ molecule to the CF_3SO_3 group with N(3)···O(2) 2.841(3) Å, N(3)–H(3)···O(2) 178°, and C(24)···O(3) 3.090(5) Å, C(24)–H(24)···O(3) 167° (Fig. 5).

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