DALTON

Ruthenium tris(pyrazolyl)borate complexes. Formation and characterization of acetone, dimethylformamide and vinylidene complexes containing N,N-donor co-ligands

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Chloride abstraction from $[Ru\{HB(pz)_3\}(tmen)Cl]$ (pz = pyrazolyl, tmen = $Me_2NCH_2CH_2NMe_2$) with $NaBPh_4$ in the solvents acetone and dimethylformamide led to the formation of the respective cationic $[Ru\{HB(pz)_3\}(tmen)(solv)]^+$ complexes. In the presence of phenylacetylene, these are easily transformed into the first example of a ruthenium $HB(pz)_3$ vinylidene complex. Extended-Hückel molecular-orbital calculations have been performed to establish the nature of the bonding involved. From $[Ru\{HB(pz)_3\}(py)_2Cl]$ (py = pyridine) the corresponding vinylidene complex could be prepared in the same way, although the intermediate solvent complexes could not be isolated. Selected crystal structures were determined.

In contrast to the isoelectronic $(\eta\text{-}C_5H_5)Ru^+$ or $(\eta\text{-}C_5Me_5)Ru^+$ fragments, $\{HB(pz)_3\}Ru^+$ (pz = pyrazolyl) has been found to bind nitrogen-donor ligands very easily.[1] This different behaviour is due to the different geometries of the orbitals involved in constructing the complexes, with $HB(pz)_3$ being a σ donor, and C_5H_5 as well as C_5Me_5 π donors. The presence of electron-rich nitrogen ligands, in connection with the steric demand of the $HB(pz)_3$ ligand, may promote the generation of co-ordinatively unsaturated complexes. In the present paper we will investigate such a possibility by analysing the reaction products formed through chloride abstraction from the two starting species $[Ru\{HB(pz)_3\}(tmen)Cl]$ **1** (tmen = $Me_2NCH_2CH_2NMe_2$) and $[Ru\{HB(pz)_3\}(py)_2Cl]$ **2** (py = pyridine) reported previously.[1] Chloride abstraction was effected by $NaBPh_4$, NH_4PF_6 or TlO_3SCF_3 in the weakly co-ordinating solvents acetone and tetrahydrofuran (thf).

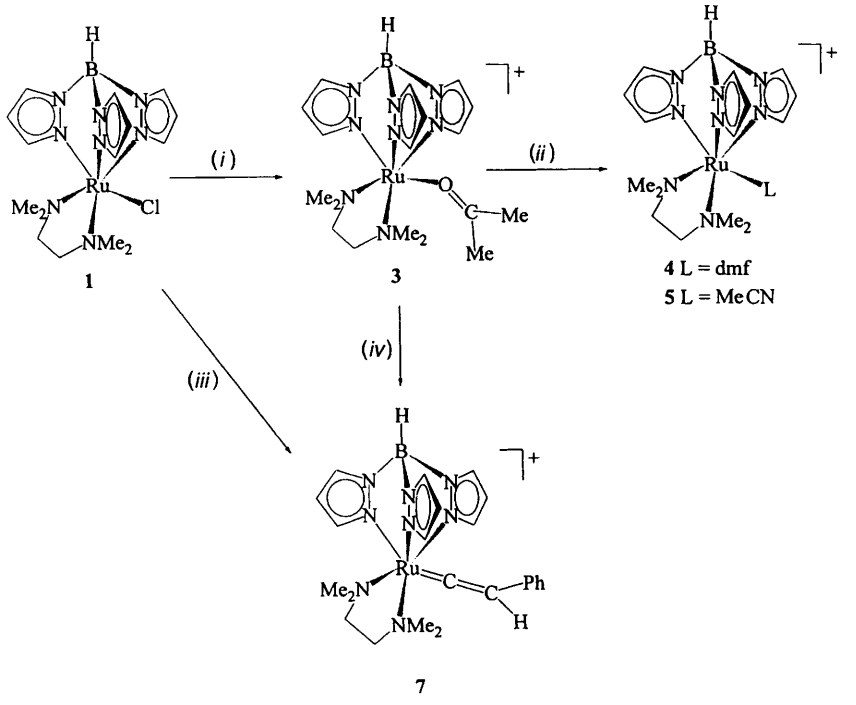
Results and Discussion

When treated with $NaBPh_4$ (1 equivalent) in acetone complex **1** readily loses chloride resulting in the formation of the cationic complex $[Ru\{HB(pz)_3\}(tmen)(Me_2CO)]BPh_4$ **3** in 91% yield (Scheme 1). A structural view of **3** is depicted in Fig. 1 with important bond distances and angles reported in the caption. While this complex is air stable in the solid state, it decomposes slowly in solution. The ^1H and $^{13}C\text{-}\{^1H\}$ solution NMR spectra exhibit two distinct sets of pyrazol-1-yl resonances pointing to the existence of two types of pyrazol-1-yl rings in 2:1 ratio. In the ^1H NMR spectrum the two NMe_2 groups of tmen give rise to two singlets at δ 2.54 (6 H) and 1.60 (6 H), *i.e.* the methyl groups are diastereotopic. The methyl protons of acetone give a singlet at δ 2.34 (6 H). In the $^{13}C\text{-}\{^1H\}$ NMR spectrum co-ordinated acetone exhibits characteristic resonances at δ 226.5 and 31.8 which can be assigned to the ketonic carbonyl carbon and the methyl groups, respectively (*cf.* free acetone exhibits respective resonances at δ 205.1 and 30.5). There is no evidence for free acetone in solution. In the IR spectrum the ν(C=O) band is observed at 1649 cm^{-1}, in line with other ruthenium acetone complexes.[2-5] This value is lower than the frequency for free acetone observed at 1710 cm^{-1}. Thus, as expected, co-ordination leads to a decrease in C=O bond strength. The ν(B–H) vibration is found at 2476 cm^{-1} which is characteristic for $HB(pz)_3$ when terdentate N,N′,N″-bonded to a metal centre.

The acetone molecule is co-ordinated as an oxygen-donor ligand. The Ru–O distance of 2.103(2) Å is relatively short indicating a strong interaction, while C(18)–O [1.243(4) Å] is longer than that observed for the free acetone molecule (1.20 Å).[6] For comparison, the Ru–O (acetone) distances in $[Ru\{C(=CHPh)OC(O)Me\}(PPr^i_3)_2(CO)(Me_2CO)]^+$,[2] $[Ru(PPh_3)_2(CO)(SnCl_3)Cl(Me_2CO)]$[3] and $[Ru_2(\mu\text{-}O_2CEt)_4(Me_2CO)_2]$[4] are 2.205(6), 2.194(8) and 2.363(5) Å, respectively. The Ru–O–C(18) angle of 136.5(2)° is considerably smaller than literature values. For instance, in $[Ru\{C(=CHPh)OC(O)Me\}(PPr^i_3)_2(CO)(Me_2CO)]^+$ and $[Ru(PPh_3)_2(CO)(SnCl_3)Cl(Me_2CO)]$ the Ru–O–C angles are reported to be 164.7(6) and 153.0(5)°, respectively. The co-ordination geometry of **3** is approximately octahedral with all angles at ruthenium between 86 and 96 and 177 and 178°. The three Ru–N (pyrazolyl) bond lengths show only minor variations [average 2.083(2) Å] and are within the range for other $Ru\text{–}HB(pz)_3$ complexes.[7] The Ru–N (tmen) bond distances are 2.188(2) and 2.210(3) Å. In sum, there are no structural features implying unusual deviations or distortions.

The acetone molecule of complex **3** is easily displaced by other donor molecules such as dmf (dimethylformamide) and MeCN entailing quantitative formations of the cationic complexes $[Ru\{HB(pz)_3\}(tmen)(dmf)]^+$ **4** and $[Ru\{HB(pz)_3\}(tmen)(MeCN)]^+$ **5** (Scheme 1). The synthesis and characterization of the latter has been reported before[1] and is not discussed here. As for **5**, the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra bear no unusual features and it is sufficient to mention the characteristic resonance of the ketonic carbonyl carbon of the dmf ligand at δ 169.0 compared to 162.5 of free dmf. The IR spectrum of **4** shows the expected strong ν(C=O) absorption of dmf at 1651 cm^{-1} very similar to that of free dmf (1675 cm^{-1}).

The solid-state structure of complex **4** is depicted in Fig. 2 with selected bond distances and angles given in the caption. The overall structure is very similar to that of **3**. The Ru–O and O–C(18) distances are 2.117(2) and 1.243(4) Å, respectively. The Ru–O–C(18) angle is 123.7(3)°. There is only a marginal *trans*-labilizing influence. The Ru–N(2) and Ru–N(4) distances are



Scheme 1 (*i*) $NaBPh_4$, Me_2CO; (*ii*) L; (*iii*) $NaBPh_4$, HC≡CPh; (*iv*) HC≡CPh

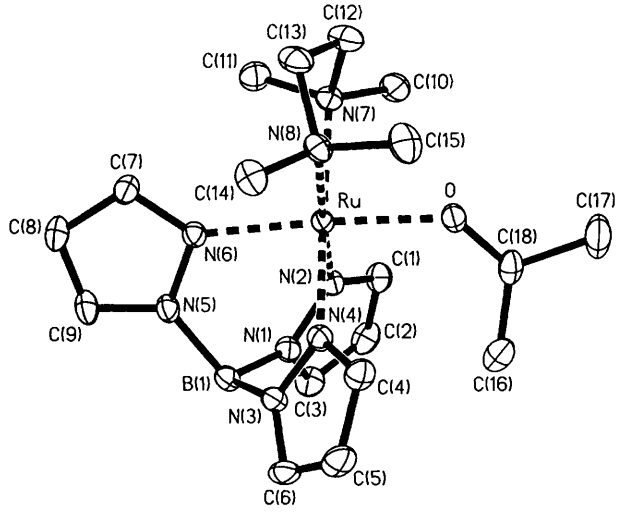


Fig. 1 Structural view of $[Ru\{HB(pz)_3\}(tmen)(Me_2CO)]BPh_4$ **3** showing 20% probability thermal ellipsoids (BPh_4^- omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–N(2) 2.086(2), Ru–N(4) 2.073(3), Ru–N(6) 2.090(2), Ru–N(7) 2.210(3), Ru–N(8) 2.188(2), Ru–O 2.103(2) and O–C(18) 1.243(5); N(4)–Ru–N(2) 87.6(1), N(4)–Ru–N(6) 85.7(1), N(2)–Ru–N(6) 87.5(1), O–Ru–N(6) 175.2(1) and Ru–O–C(18) 136.5(2)

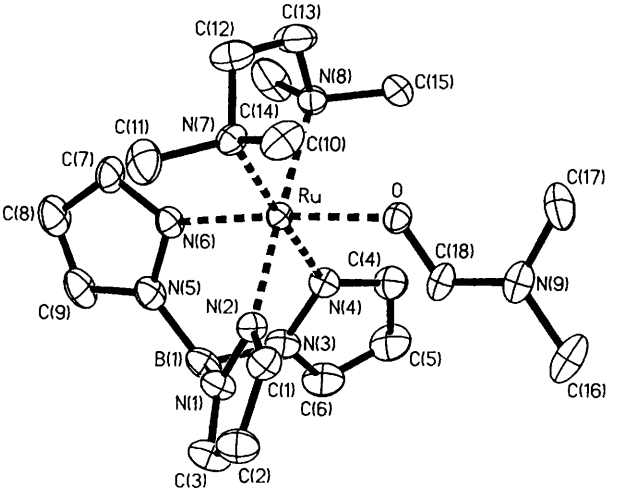


Fig. 2 Structural view of $[Ru\{HB(pz)_3\}(tmen)(dmf)]BPh_4{\cdot}CH_2Cl_2$ showing 20% probability thermal ellipsoids (BPh_4^- and CH_2Cl_2 omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–N(2) 2.070(3), Ru–N(4) 2.070(3), Ru–N(6) 2.089(3), Ru–N(7) 2.171(3), Ru–N(8) 2.194(3), Ru–O 2.117(2), O–C(18) 1.243(4) and C(17)–N(9) 1.443(6); N(4)–Ru–N(2) 85.8(1), N(4)–Ru–N(6) 87.3(1), N(2)–Ru–N(6) 88.1(1), O–Ru–N(6) 176.0(1) and Ru–O–C(18) 123.7(3)

both 2.070(3) Å, while Ru–N(6) is only slightly longer [2.089(3) Å].

Next we changed the solvent and performed chloride abstraction from complex **1** with both $NaBPh_4$ and TlO_3SCF_3 in thf instead of acetone. Whereas in the case of $NaBPh_4$ complete decomposition of the starting material takes place, with TlO_3SCF_3 (1 equivalent), instead of the expected unsaturated complex cation $[Ru\{HB(pz)_3\}(tmen)]^+$, there is quantitative formation of the 18e$^-$ complex $[Ru\{HB(pz)_3\}(tmen)(OSO_2CF_3)]$ **6**. This formulation is based on the elemental analysis and the close similarity between the ^1H NMR spectrum of the cationic 18e$^-$ complexes **3**–**5** and (neutral) **1** advocating against an ionic $[Ru\{HB(pz)_3\}(tmen)]^+CF_3SO_3^-$ composition. Thus we conclude that $CF_3SO_3^-$ is directly bound, weakly of course, to the metal, adding to the small number known of ruthenium complexes bearing the OSO_2CF_3 ligand.[8,10] There is no evidence of thf co-ordination. In this context, quite different reactivity has been observed in an otherwise similar system. Thus, highly reactive five-co-ordinate ruthenium(II) complexes could be prepared with the sterically demanding spectator ligands C_5Me_5 and $C_6H_3(CH_2NMe_2)_2$-2,6 in conjunction with bulky co-ligands such as tertiary phosphines. For instance, the synthesis of the 16e$^-$ complexes $[Ru(\eta\text{-}C_5Me_5)(PR_3)Cl]$ (R = C_6H_{11} or Pr^i),[11] $[Ru(\eta\text{-}C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]^+$,[12] $[Ru(\eta\text{-}C_5Me_5)\{(C_6H_{11})_2PCH_2CH_2OMe\}Cl]$[13] and $[Ru\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(PPh_3)Cl]$[8] has recently been reported.

Both complexes **1** and **3** are excellent precursors for the synthesis of vinylidene complexes as depicted in Scheme 1. The reaction of **1** with phenylacetylene in the presence of $NaBPh_4$ or NH_4PF_6 in CH_2Cl_2 yields the cationic vinylidene complex $[Ru\{HB(pz)_3\}(tmen)(=C=CHPh)]^+$ as the BPh_4^- salt **7a** and the PF_6^- salt **7b** each in high yields as air-stable red solids (Scheme 1). Likewise, treatment of **3** with 1 equivalent of phenylacetylene in CH_2Cl_2 or acetone affords **7a** in essentially quantitative yield as monitored by ^1H NMR spectroscopy.

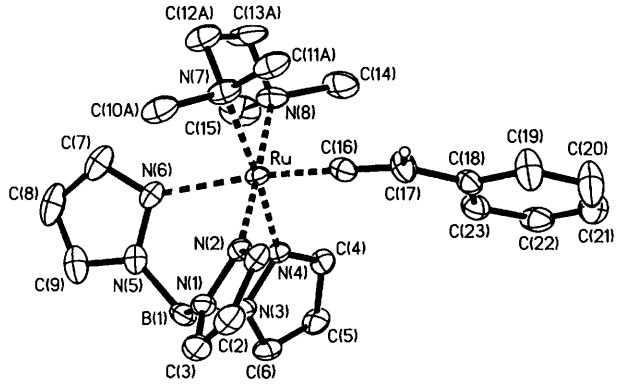
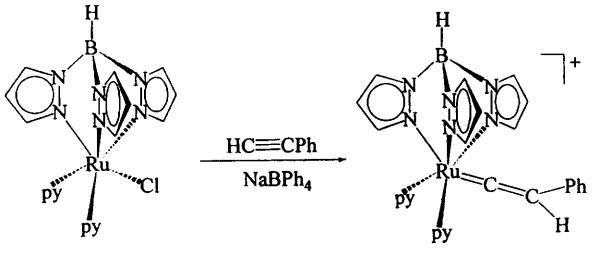


Fig. 3 Structural view of $[Ru\{HB(pz)_3\}(tmen)(=C=CHPh)]BPh_4 \cdot CH_2Cl_2$ **7a**·CH_2Cl_2 showing 20% probability thermal ellipsoids (only one orientation of the disordered tmen ligand shown, BPh_4 and CH_2Cl_2 omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–N(2) 2.082(3), Ru–N(4) 2.097(3), Ru–N(6) 2.266(4), Ru–N(7) 2.155(4), Ru–N(8) 2.169(3), Ru–C(16) 1.820(5), C(16)–C(17) 1.305(6) and C(17)–C(18) 1.458(6); Ru–C(16)–C(17) 173.5(4), C(16)–C(17)–C(18) 130.5(4), C(16)–Ru–N(6) 173.0(2), N(2)–Ru–N(6) 85.5(1) and N(4)–Ru–N(6) 83.4(1)



2 **8**

Scheme 2

Since **7** appears to be the first vinylidene ruthenium complex with $HB(pz)_3$ as a co-ligand, the molecular structure of **7a** has been determined (Fig. 3). Selected bond distances and angles are given in the caption. The characteristic NMR spectroscopic features comprise, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum, a marked low-field resonance at δ 369.9 and a signal at δ 114.3 assignable to the α- and β-carbons of the vinylidene moiety, respectively. The C_β-hydrogen atom gives rise to a singlet at δ 5.57 (1 H). Finally, the resonances of $HB(pz)_3$ and tmen are in the expected ranges.

The overall octahedral structure of complex **7a**·CH_2Cl_2 is very similar to those of **3** and **4**. However, the two Ru–N (pyrazolyl) bond lengths *cis* to the vinylidene moiety are significantly shorter [Ru–N(2) 2.082(3), Ru–N(4) 2.097(3) Å] than that *trans* to the vinylidene moiety [Ru–N(6) 2.266(4) Å]. The two Ru–N (tmen) bond lengths [2.155(4) and 2.169(3) Å] are very similar. The Ru–C(16) bond distance [1.820(5) Å] is somewhat shorter than in other vinylideneruthenium complexes.[14] For instance, in $[Ru(\eta\text{-}C_5H_5)(PMe_3)_2(=C=CHMe)]^+$ and $[Ru(\eta\text{-}C_5H_5)(Ph_2PCH_2CH_2PPh_2)\{=C=CPh(C_7H_7)\}]^+$ the Ru–C distances are 1.845(7) and 1.848(9) Å, respectively.[15,16] The Ru=C=C group is essentially linear, the angle Ru–C(16)–C(17) being 173.5(4)°. The C(16)–C(17) bond distance is 1.305(6) Å corresponding to a bond order between two and three.

Let us now turn to describe the reaction of complex **2**. In contrast to **1**, chloride abstraction from **2** gave only intractable material, no matter whether $NaBPh_4$ or TlO_3SCF_3 are used in either thf or acetone. In the presence of phenylacetylene, however, halide abstraction with TlO_3SCF_3 (1 equivalent) in CH_2Cl_2 gives, on work-up, the cationic vinylidene complex $[Ru\{HB(pz)_3\}(py)_2(=C=CHPh)]CF_3SO_3$ **8** in 84% isolated yield (Scheme 2). This complex exhibits similar NMR spectroscopic features to those of **7**. The characteristic resonances of the C_α and C_β carbons of the vinylidene moiety

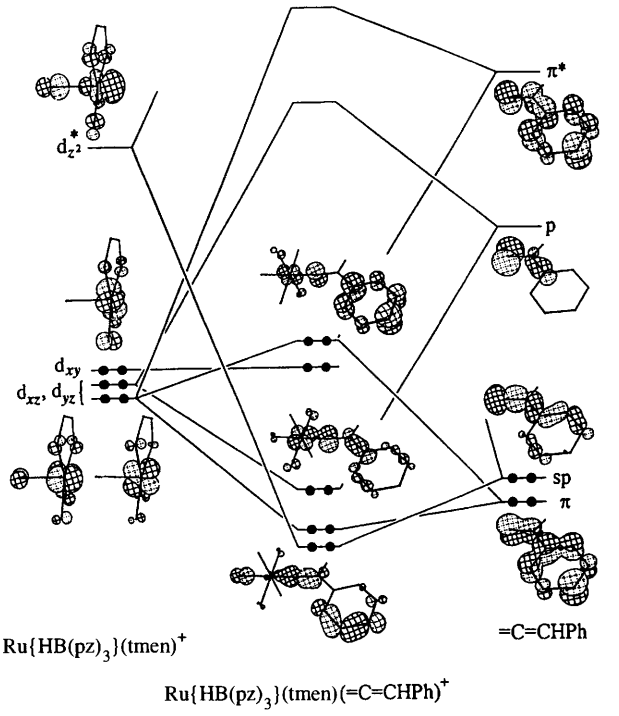


Fig. 4 Qualitative orbital-interaction diagram for the formation of $[Ru\{HB(pz)_3\}(tmen)(=C=CHPh)]^+$ **7**

are found at δ 376.6 and 113.5. In the ^1H NMR spectrum the C_β hydrogen atom gives rise to a singlet at δ 5.96 (1 H).

To characterize further the complexes prepared in this work, we also performed extended-Hückel molecular-orbital (EHMO) calculations.[17,18] The $Ru\{HB(pz)_3\}(tmen)^+$ fragment is to be considered as a practically regular square pyramid (C_{4v}) held together by mainly σ bonds without any significant participation of the d_π atomic orbitals (AOs) (d_{xy}, d_{xz}, d_{yz}) of ruthenium. It should be remarked here that the $HB(pz)_3$ ligand itself has been classified as a good π donor.[19] This property, however, becomes noticeable only in the presence of appropriate, *i.e.* π-accepting, co-ligands such as CO. In addition, such a π–π resonance between the ligands through the metal centre is particularly effective in the case of C_{3v} symmetry where all three π orbitals of the metal are equally participating in the metal–ligand bondings as in $[Mo\{HB(pz)_3\}(CO)_3]$.[19] In our case, then, with tmen as the co-ligand, the interactions between d_π and π or π* of the pyrazolyl rings of the $HB(pz)_3$ ligand remain insignificant. The $Ru\{HB(pz)_3\}(tmen)^+$ has a high affinity to co-ordinate a sixth ligand *trans* to N(6) of $HB(pz)_3$ (Fig. 3) provided it is π overlapping. Of the ligands considered, vinylidene is most strongly bound because of its high π acidity. According to the orbital interaction diagram shown in Fig. 4, the bonding between Ru and vinylidene is due to both d_σ–sp and d_π–p interactions. The strong Ru–C_α bond originating from the p (vinylidene)–d_π (Ru) interaction is further strengthened by the participation of the empty π* orbital of vinylidene. The empty p orbital (lowest unoccupied molecular orbital, LUMO) of vinylidene takes electron density from the π AOs of Ru and hence the formal oxidation state of Ru should be considered as +IV. The d_σ–sp interaction brings about a notable destabilization of the Ru–N(6) bond as reflected in the crystal structure. This *trans* influence is reinforced by the d_π–p overlap.

In the other complexes of $Ru\{HB(pz)_3\}(tmen)^+$ with acetone, MeCN, and dmf, π–π interactions are of minor importance, of course, with only a marginal *trans* effect observed. Nevertheless some involvement of d_π–π (or p) interactions can be implied from the EHMO calculations done so far on the complexes with ligated MeCN and acetone. This is also consistent with the unusual rank of ligand strengths

observed, in particular the order thf < $CF_3SO_3^-$ < Me_2CO < MeCN, which is not the order of the σ basicity as measured by the donor numbers (D_N).[20] According to these, thf is a stronger donor than acetone, and MeCN is weaker than both acetone and thf.

A final remark concerns a comparison between the C_5H_5 and $HB(pz)_3$ analogues. In the $(\eta\text{-}C_5H_5)Ru^+$ fragment all AOs of Ru are mixed implying that the d_π orbitals are no longer non-bonding. Consequently, its interactions with both p and π* orbitals of the vinylidene moiety are weaker, and the Ru=C bond slightly longer, compared to $\{HB(pz)_3\}Ru^+$.[14–16]

Experimental

General information

All reactions were performed under an inert atmosphere of purified argon by using Schlenk techniques and/or a glove-box. All chemicals were standard reagent grade and used without further purification. The solvents were purified and dried according to standard procedures and stored over 4 Å molecular sieves.[21] The deuteriated solvents were obtained from Aldrich and dried over 4 Å molecular sieves. The complexes [Ru{$HB(pz)_3$}(tmen)Cl] **1** and [Ru{$HB(pz)_3$}$(py)_2$Cl] **2** were prepared according to the literature.[1] Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and referenced to $SiMe_4$, diffuse reflectance Fourier-transform IR spectra on a Mattson RS 2 spectrometer. Microanalyses were by Microanalytical Laboratories, University of Vienna.

Syntheses

[Ru{$HB(pz)_3$}(tmen)(Me_2CO)]BPh_4 3. A solution of complex **1** (192 mg, 0.412 mmol) in acetone (5 cm^3) was treated with $NaBPh_4$ (141 mg, 0.412 mmol). After the mixture was stirred at room temperature for 8 h the solvent was removed under vacuum. The residue was dissolved in acetone and insoluble materials were filtered off. On addition of diethyl ether a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 302 mg (91%) (Found: C, 62.3; H, 6.65; N, 13.75. $C_{42}H_{52}B_2N_8ORu$ requires C, 62.45; H, 6.50; N, 13.85%). NMR (CD_2Cl_2, 20 °C): δ_H 7.87 (d, 4 H, J = 2.5), 7.43 (d, 2 H, J = 1.9 Hz), 7.36 (m, 8 H), 7.05 (m, 8 H), 6.90 (m, 4 H), 6.32 (m, 3 H), 2.54 (s, 6 H), 2.34 (s, 6 H) and 1.60 (s, 6 H); δ_C 226.5 (C=O), 163.3 [q, J(BH) = 49.1], 147.1, 144.2, 138.5, 137.5, 136.2 [q, J(BH) = 1.4], 126.0 [q, J(BH) = 2.9 Hz], 122.1, 107.1, 106.8, 63.1, 52.5, 52.0 and 31.8 (O=CMe_2). $\tilde{\nu}_{max}/cm^{-1}$ 2476w (B–H) and 1649s (C=O).

[Ru{$HB(pz)_3$}(tmen)(dmf)]BPh_4 4. To a solution of complex **3** (100 mg, 0.124 mmol) in CH_2Cl_2 (5 cm^3) was added dmf (10 equivalents) and stirred at room temperature for 8 h. Addition of diethyl ether resulted in the precipitation of **4** which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 97 mg (95%) (Found: C, 61.15; H, 6.55; N, 15.2. $C_{42}H_{53}B_2N_9ORu$ requires C, 61.3; H, 6.50; N, 15.3%). NMR ($CDCl_3$, 20 °C): δ_H 7.82 (m, 3 H), 7.62 (d, 1 H, J = 2.3), 7.43 (m, 8 H), 7.38 (d, 2 H, J = 2.3), 7.04 (m, 8 H), 6.89 (m, 4 H), 6.28 (m, 3 H), 6.21 (s, 1 H), 2.68 (d, 6 H, J = 5.0), 2.45 (s, 10 H) and 2.23 (s, 6 H); δ_C 169.0 (C=O), 164.9 [q, J(BH) = 49.1], 147.6, 143.7, 138.6, 137.7, 137.0, 126.3 [q, J(BH) = 2.4 Hz], 122.4, 107.8, 107.0, 63.2, 53.0, 38.6 (HCONMe_2) and 33.7 (HCONMe_2). $\tilde{\nu}_{max}/cm^{-1}$ 2473w (B–H) and 1651s (C=O).

[Ru{$HB(pz)_3$}(tmen)(MeCN)]BPh_4 5. This complex was synthesized analogously to **4** with **3** as starting material in the presence of MeCN (10 equivalents). Yield: 93% (Found: C, 62.35; H, 6.20; N, 16.1. $C_{41}H_{49}B_2N_9Ru$ requires C, 62.3; H, 6.25; N, 15.95%). The solution NMR spectra are in full agreement with those previously reported.[1]

[Ru{$HB(pz)_3$}(tmen)(OSO_2CF_3)] 6. A solution of complex **1** (101 mg, 0.217 mmol) in tetrahydrofuran (5 cm^3) was treated with TlO_3SCF_3 (77 mg, 0.217 mmol) and stirred at room temperature for 8 h. Then the solution was evaporated to dryness and the residue dissolved in tetrahydrofuran. Insoluble materials were filtered off. On addition of diethyl ether a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 111 mg (82%) (Found: C, 38.5; H, 3.40; N, 17.75. $C_{20}H_{20}BF_3N_8O_3RuS$ requires C, 38.65; H, 3.25; N, 18.05%). NMR: δ_H(CD_2Cl_2, 20 °C) 8.02 (d, 1 H, J = 2.2), 7.84 (d, 1 H, J = 2.6), 7.79 (d, 2 H, J = 2.6), 7.65 (d, 2 H, J = 2.2), 6.31 (dd, 2 H, J = 2.2, 2.6), 6.23 (dd, 1 H, J = 2.2, 2.6 Hz), 2.99 (m, 4 H), 2.85 (s, 6 H) and 2.37 (s, 6 H).

[Ru{$HB(pz)_3$}(tmen)(=C=CHPh)]BPh_4 7a. *Method 1.* A solution of complex **1** (188 mg, 0.404 mmol) in CH_2Cl_2 (5 cm^3) was treated with phenylacetylene (0.2 cm^3, 1.82 mmol) in the presence of $NaBPh_4$ (138 mg, 0.404 mmol) and stirred at room temperature for 8 h. Then the solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of diethyl ether a red precipitate was formed which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 254 mg (74%).

Method 2. A solution of complex **3** (65 mg, 0.140 mmol) was treated with phenylacetylene (48 mg, 0.140 mmol) at room temperature for 3 h. On addition of diethyl ether a red precipitate was formed which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 107 mg (95%) (Found: C, 66.15; H, 6.30; N, 12.95. $C_{47}H_{52}B_2N_8Ru$ requires C, 66.3; H, 6.15; N, 13.15%). NMR [$(CD_3)_2CO$, 20 °C]: δ_H 8.66 (d, 1 H, J = 2.4), 8.14 (d, 1 H, J = 2.0), 7.98 (d, 2 H, J = 2.0), 7.95 (d, 2 H, J = 2.4), 7.37 (m, 8 H), 7.08 (m, 3 H), 6.96 (m, 8 H), 6.81 (m, 4 H), 6.63 (m, 1 H), 6.56 (m, 2 H), 6.32 (m, 2 H), 5.57 (s, 1 H), 3.13 (m, 10 H) and 2.37 (s, 6 H); δ_C 369.9 (C_α), 164.9 [q, J(BH) = 48.8], 146.2, 145.5, 139.0, 138.7, 137.7, 130.1, 127.7, 127.6, 127.5, 126.7 [q, J(BH) = 3.1 Hz], 114.3 (C_β), 108.6, 108.3, 64.2, 58.6 and 53.3.

[Ru{$HB(pz)_3$}(tmen)(=C=CHPh)]PF_6 7b. This complex was prepared analogously to **7a** with **1** and NH_4PF_6 as the starting materials (Method 1). Yield: 77% (Found: C, 40.65; H, 4.95; N, 16.4. $C_{23}H_{32}BF_6N_8PRu$ requires C, 40.8; H, 4.75; N, 16.55%). NMR (CD_3CN, 20 °C): δ_H 8.59 (d, 1 H, J = 2.1), 8.18 (d, 1 H, J = 2.1), 7.99 (d, 2 H, J = 2.4), 7.95 (d, 2 H, J = 2.1), 7.16 (m, 3 H), 6.73 (m, 1 H), 6.61 (m, 2 H), 6.41 (m, 2 H), 5.60 (s, 1 H), 3.19 (m, 10 H) and 2.44 (s, 6 H); δ_C 369.0 (C_α), 145.6, 144.9, 138.5, 138.3, 129.7, 127.6, 127.1, 127.0, 113.7 (C_β), 108.1, 107.7, 63.6, 58.0 and 52.8.

[Ru{$HB(pz)_3$}$(py)_2$(=C=CHPh)]CF_3SO_3 8. A solution of complex **2** (92 mg, 0.198 mmol), TlO_3SCF_3 (70 mg, 0.198 mmol) and phenylacetylene (0.2 cm^3, 1.82 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 8 h. The TlCl formed was filtered off, the filtrate evaporated to dryness and the resulting residue redissolved in CH_2Cl_2. Addition of diethyl ether resulted in the formation of a yellow precipitate which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 120 mg (84%) (Found: C, 43.5; H, 3.95; N, 16.1. $C_{25}H_{26}BF_3N_8O_3RuS$ requires C, 43.7; H, 3.80; N, 16.3%). NMR [$(CD_3)_2CO$, 20 °C]: δ_H 8.74 (d, 4 H, J = 5.3), 8.32 (d, 1 H, J = 2.3), 8.08 (m, 4 H), 7.83 (d, 1 H, J = 2.3 Hz), 7.59 (m, 4 H), 7.18 (m, 4 H), 7.05 (m, 1 H), 6.93 (m, 2 H), 6.63 (m, 1 H), 6.29 (m, 2 H) and 5.96 (s, 1 H); δ_C 376.6 (C_α), 156.0, 146.2, 144.8, 140.7, 138.9, 138.7, 130.5, 127.7, 113.5 (C_β), 109.4 and 108.9.

Table 1 Crystallographic data

	3	**4**·CH_2Cl_2	**7a**·CH_2Cl_2
Formula	$C_{42}H_{52}B_2N_8ORu$	$C_{43}H_{55}B_2Cl_2N_9ORu$	$C_{48}H_{54}B_2Cl_2N_8Ru$
M	807.61	907.57	936.58
Crystal system	Orthorhombic	Triclinic	Triclinic
Crystal size/mm	0.20 × 0.30 × 0.40	0.40 × 0.25 × 0.10	0.08 × 0.27 × 0.65
Space group	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	16.190(2)	12.561(2)	11.512(2)
b/Å	15.508(4)	14.069(3)	12.286(2)
c/Å	32.460(4)	14.577(3)	18.598(2)
α/°		96.78(1)	70.74(1)
β/°		96.66(1)	81.63(1)
γ/°		97.62(1)	67.68(1)
U/Å^3	8150(3)	2512.7(8)	2298.2(6)
$F(000)$	3376	944	972
Z	8	2	2
D_c/g cm^{-3}	1.316	1.200	1.353
T/K	298	298	296
μ(Mo-Kα)/mm^{-1}	0.428	0.483	0.501
Minimum, maximum transmission factors	0.95, 1.07	0.93, 1.07	0.94, 1.10
θ_{max}/°	25	23.3	23.3
hkl Ranges	0–19, 0–18, 0–38	−13 to 13, −15 to 15, 0–16	−12 to 12, −12 to 13, 0–20
No. reflections measured	7146	9740	9317
No. unique reflections	7146	6858	6460
R_{merge}	0.000	0.026	0.060
No. observed reflections [$F > 4\sigma(F)$]	4988	6231	5715
No. parameters	487	546	553
$R(F)$ [$F > 4\sigma(F)$]	0.037	0.041	0.044
(all data)	0.069	0.047	0.058
$wR(F^2)$ (all data)	0.084	0.095	0.113
Minimum, maximum Fourier-difference peaks/e Å^{-3}	−0.32, 0.34	−0.36, 0.43	−0.51, 0.48

Crystallography

Crystal data and experimental details for complexes **3**, **4**·CH_2Cl_2 and **7a**·CH_2Cl_2 are given in Table 1. X-Ray data for **3** were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation and the θ–2θ scan technique. For **4**·CH_2Cl_2 and **7a**·CH_2Cl_2 a Siemens Smart CCD area detector diffractometer, graphite-monochromated Mo-Kα radiation, a nominal crystal-to-detector distance of 6 cm, and 0.3° ω-scan frames were used. Corrections for Lorentz-polarization effects, crystal decay and absorption (empirically) were applied. The structures were solved by direct methods.[22] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[23] The structures were refined against F^2 using the weighting scheme $w = 1/[\sigma^2(F_o^2) + AP^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$. In **7a**·CH_2Cl_2 an orientation ambiguity of the tmen ligand with split positions for the ethylene bridge and two methyl groups in a 53:47 ratio was found. This disorder was modelled in the least-squares refinement by applying distance restraints. No attempts were made to resolve the severe disorder of the methylene chloride solvent molecules in **4**·CH_2Cl_2 and **7a**·CH_2Cl_2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/209.

Extended-Hückel orbital calculations

The EHMO calculations were conducted by using the original program developed by Hoffmann and Lipscomb,[17] and modified by Mealli and Proserpio.[18] The AO parameters used were taken from the CACAO program.[18]

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