

Ruthenium(II) tris(pyrazolyl)borate complexes.† Reversible vinylidene complex formation

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A convenient high-yield route to $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHR})]$ (pz = pyrazolyl; R = Ph, SiMe₃, Buⁿ, Bu^t, CO₂Et or C₆H₉) has been found through the intermediary $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(\text{dmf})]$ (dmf = dimethylformamide) which has been crystallographically characterized. This complex is readily obtained on treatment of $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{cod})]$ (cod = cycloocta-1,5-diene) with 1 equivalent of PPh₃ in boiling dmf. The vinylidene moiety in complexes of the type $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHR})]$ is remarkably labile being easily replaced by nucleophiles L = PMe₃, PPh₃, MeCN, pyridine or CO to give $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)\text{L}]$. With the exceptions of L = PMe₃ or CO, these reactions are reversible. The complex $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(\text{CO})]$ has been characterized by X-ray crystallography. On treatment of $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHPh})]$ with an excess of HC≡CR' (R' = SiMe₃, Buⁿ, Bu^t, CO₂Et or C₆H₉) the neutral vinylidene complex $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHR}')]$ was reversibly formed. Comparative studies and extended-Hückel molecular orbital calculations have been performed to elucidate the nature of the bonding in the various vinylidene complexes. The bonding between the metal center and the vinylidene ligand is dominated by the d_{yz} (metal)–p (vinylidene) interaction. If this contribution is small, reconversion of the vinylidene complex into an η²-alkyne complex can be accomplished.

The chemistry of vinylidene transition-metal complexes has attracted increasing attention in recent years especially because of their appearance as key intermediates in stoichiometric and catalytic transformations of organic molecules.^{2a–f} Representative examples of ruthenium catalysis involving vinylidene complexes have been reported for the cyclization of dienyl-alkynes,^{1a} the dimerization of HC≡CBu^t,^{1b} the tandem cyclization–reconstructive addition of propargyl (prop-2-ynyl) alcohols with allyl alcohols,^{1c} and the reconstitutive condensation of acetylenes and allyl alcohols.^{1d} In developing the chemistry of the tris(pyrazolyl)borate ligand, HB(pz)₃, we have recently shown^{1e} that also the novel neutral vinylidene complex $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHPh})]$ is an efficient catalyst precursor in the dimerization of terminal acetylenes to yield enynes. The catalytic cycles proposed for all of these processes have in common the assumption of reversible vinylidene complex formation, but a definite proof must await further study.

The formation of vinylidene complexes from terminal alkynes is well studied.^{3a–f} The tautomerization of free acetylene into vinylidene has been the subject of a number of theoretical and physicochemical studies.^{3a} There are a variety of mechanistic suggestions for the formation of vinylidene complexes depending on the nature of the alkyne, the coligands, and the metal.^{3b} *Ab initio* molecular orbital (MO) calculations on the transformation of an η²-co-ordinated alkyne to a vinylidene ligand in $[\text{RuCl}_2(\text{PH}_3)_2(=\text{C}=\text{CH}_2)]$ are in line with an intraligand 1,2-hydrogen shift mechanism,^{3c} while vinylidene complexes of Rhⁱ are typically formed *via* an alkynylhydrido complex (oxidative-addition step) followed by a 1,3-hydrogen shift.^{3a} In similar fashion dimethylformamide (dmf) is replaced with PhC≡CH in *trans*- $[\text{Mo}(\text{CO})(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ to give the corresponding vinylidene complex.^{3d} In this context, also the 1,4-hydrogen shift mechanism claimed to operate in the form-

ation of $[\text{Ru}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)(=\text{C}=\text{C}=\text{CH}_2)]^+$ from CH≡C–C≡CH may be noted.^{3b}

On the other hand, the reverse process, *i.e.* the conversion of a vinylidene complex into an η²-alkyne complex, has not been paid much attention. Nevertheless, such a reaction has been postulated to occur in some cationic vinylidene complexes of W and Mo.^{4a} Also, the epimerization of vinylidene upon heating is likely to proceed *via* an η²-alkyne complex.^{3f} Note further that the cationic complex $[\text{RuCl}(=\text{C}=\text{CH}_2)(\kappa^2P, O\text{-Pr}^i\text{PCH}_2\text{CH}_2\text{OMe})_2]^+$ is stable only under an acetylene atmosphere, pointing to a reversible reaction.^{4b} Finally, the elimination of HC≡CPh from $[\text{RuI}_2(=\text{C}=\text{CHPh})(\kappa^1P\text{-Pr}^i\text{PCH}_2\text{CH}_2\text{OMe})(\kappa^2P, O\text{-Pr}^i\text{PCH}_2\text{CH}_2\text{OMe})]$ with concomitant formation of $[\text{RuI}_2(\kappa^2P, O\text{-Pr}^i\text{PCH}_2\text{CH}_2\text{OMe})_2]$ at elevated temperatures, or from $[\text{RuCl}(=\text{C}=\text{CHPh})(\kappa^2P, O\text{-Pr}^i\text{PCH}_2\text{CH}_2\text{OMe})_2]$ with CO under mild conditions (tetrahydrofuran, thf; 25 °C), has been observed.^{4b} On warming above 0 °C the BF₄[–] salt of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}_2(=\text{C}=\text{CHCMe}_3)]^+$ decarbonylated with vinylidene tautomerization to give back the η²-alkyne complex.^{4c} It would be worthwhile to analyse in more detail the structural conditions under which the ruthenium–vinylidene bond becomes labile.

Here we report on the synthesis of a series of new ruthenium vinylidene complexes of the type $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHR})]$ (R = SiMe₃, Buⁿ, Bu^t, CO₂Et or C₆H₉) in which the vinylidene is readily displaceable by nucleophiles L = PMe₃, PPh₃, MeCN, pyridine (py) and CO, giving $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)\text{L}]$. Even vinylidene metathesis by HC≡CR (R = SiMe₃, Buⁿ, Bu^t, CO₂Et or C₆H₉) is an extremely facile and reversible process. This is in sharp contrast to the robustness of the cationic complex $[\text{Ru}\{\text{HB}(\text{pz})_3\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(=\text{C}=\text{CHPh})]^+$ described previously.⁵ The question is whether this is an ordinary effect of charge due to different Coulomb forces or due to some other effects, treatable by the concepts of MO theory. For this purpose we include extended Hückel (EH) calculations, although these cannot account for charge effects.

† Ruthenium tris(pyrazolyl)borate complexes. Part 6.^{1f}
Non-SI units employed: cal = 4.184 J, eV ≈ 1.60 × 10^{–19} J.

Experimental

General

All reactions were performed under an inert atmosphere of purified argon by using Schlenk techniques. All chemicals were standard reagent grade used without further purification. The solvents were purified and dried according to standard procedures and stored over 4 Å molecular sieves. The deuteriated solvents from Aldrich were dried over 4 Å molecular sieves. Proton, ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86 and 101.26 MHz, respectively, and were referenced to SiMe_4 and to H_3PO_4 (85%). Diffuse-reflectance Fourier-transform IR spectra were recorded on a Mattson RS 2 spectrometer. The complex $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{cod})]$ **1** (cod = cycloocta-1,5-diene) has been prepared according to the literature.⁶ Microanalyses were done by Microanalytical Laboratories, University of Vienna.

Syntheses

[Ru{HB(pz)₃}Cl(PPh₃)(dmf)] 2. A suspension of complex **1** (130 mg, 0.284 mmol) in dimethylformamide (3 cm³) was treated with PPh_3 (74.5 mg, 0.284 mmol) and the mixture heated under reflux for 1 h after which the solvent was removed under vacuum. The yellow solid was washed with *n*-hexane and dried under vacuum. Yield: 170 mg (89%) (Found: C, 54.00; H, 5.13; N, 12.71. $\text{C}_{30}\text{H}_{32}\text{BClN}_6\text{OPRu}$ requires C, 53.71; H, 4.81; N, 12.53%). NMR (CDCl_3 , 20 °C): δ_{H} 7.89 (s, 1 H, dmf), 7.87 (d, 1 H, $J = 2.0$, borate), 7.73 (m, 2 H, borate), 7.70 (d, 1 H, $J = 2.4$, borate), 7.39–7.23 (m, 15 H, Ph), 6.92 (d, 1 H, $J = 2.0$, borate), 6.86 (d, 1 H, $J = 2.0$, borate), 6.25 (m, 1 H, borate), 5.83 (dd, 1 H, $J = 2.4$, 2.4, borate), 5.80 (dd, 1 H, $J = 2.4$, 2.4, borate) and 2.68 (br s, 6 H, CH_3); δ_{C} 169.72 (C=O), 148.0 (borate), 145.8 (borate), 141.6 (borate), 136.4 (d, $^1J_{\text{CP}} = 49.5$, *ipso*-C of Ph), 135.9 (borate), 135.5 (borate), 135.0 (d, $^2J_{\text{CP}} = 9.5$, $\text{C}^{2,6}$ of Ph), 134.7 (borate), 129.3 (d, $^4J_{\text{CP}} = 2.6$, C^4 of Ph), 128.1 (d, $^3J_{\text{CP}} = 8.9$ Hz, $\text{C}^{3,5}$ of Ph), 106.2 (borate), 105.9 (borate), 105.7 (borate), 38.6 (CH_3) and 32.9 (CH_3); δ_{P} 55.8. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2480m (B–H) and 1640s (C=O).

[Ru{HB(pz)₃}Cl(PPh₃)(=C=CHPh)] 3. A solution of complex **1** (150 mg, 0.328 mmol) and PPh_3 (86 mg, 0.328 mmol) in dimethylformamide (3 cm³) was heated under reflux for 2 h. The solvent was then removed under vacuum and the residue, dissolved in CH_2Cl_2 (2 cm³), was treated with $\text{HC}\equiv\text{CPh}$ (200 μl) and stirred for 3 h. After removal of the solvent, the oily residue was stirred in *n*-hexane until the oil was converted into a fine pink powder, which was collected on a glass frit and dried under vacuum. Yield: 206 mg (88%). Proton, ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ NMR spectra were in agreement with the literature.^{1e}

[Ru{HB(pz)₃}Cl(PPh₃)(=C=CHSiMe₃)] 4. This complex was synthesized analogously to **3** with $\text{HC}\equiv\text{CSiMe}_3$ as starting material. Yield: 80% (Found: C, 53.75; H, 4.67; N, 11.53. $\text{C}_{32}\text{H}_{35}\text{BClN}_6\text{PRuSi}$ requires C, 54.13; H, 4.97; N, 11.84%). NMR (CDCl_3 , 20 °C): δ_{H} 8.20 (d, 1 H, $J = 2.4$, borate), 7.64–7.53 (m, 9 H, Ph, borate), 7.41–7.27 (m, 9 H, Ph, borate), 6.61 (d, 1 H, $J = 1.9$, borate), 6.31 (d, 1 H, $J = 2.3$, borate), 6.22 (m, 1 H, borate), 5.87 (dd, 1 H, $J = 2.3$, 2.3, borate), 5.76 (dd, 1 H, $J = 2.4$, 2.4, borate), 3.73 (d, 1 H, $^4J_{\text{PH}} = 3.3$, =C=CHSiMe₃) and –0.17 (s, 9 H, SiMe₃); δ_{C} 341.7 (d, $^2J_{\text{CP}} = 17.8$, =C=CHSiMe₃), 145.8 (borate), 143.6 (borate), 136.8 (borate), 135.32 (borate), 135.30 (d, $^2J_{\text{CP}} = 10.2$, $\text{C}^{2,6}$ of Ph), 135.2 (borate), 134.9 (d, $^3J_{\text{CP}} = 3.4$, borate), 133.4 (d, $^1J_{\text{CP}} = 44.1$, *ipso*-C of Ph), 130.3 (d, $^4J_{\text{CP}} = 2.5$, C^4 of Ph), 128.5 (d, $^3J_{\text{CP}} = 9.3$, $\text{C}^{3,5}$ of Ph), 106.2 (d, $^4J_{\text{CP}} = 2.5$ Hz, borate), 106.0 (borate), 105.9 (borate), 93.1 (=C=C β HSiMe₃) and 1.5 (SiMe₃); δ_{P} 42.4. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2493m (B–H) and 1644s (C=C).

[Ru{HB(pz)₃}Cl(PPh₃)(=C=CHBuⁿ)] 5. This complex was

synthesized analogously to **3** with $\text{HC}\equiv\text{CBu}^n$ as starting material. Yield: 88% (Found: C, 56.77; H, 4.88; N, 11.76. $\text{C}_{33}\text{H}_{35}\text{BClN}_6\text{PRu}$ requires C, 57.11; H, 5.08; N, 12.11%). NMR (CDCl_3 , 20 °C): δ_{H} 7.90 (d, 1 H, $J = 2.6$), 7.70 (d, 1 H, $J = 2.3$), 7.63–7.56 (m, 8 H), 7.40–7.31 (m, 9 H), 6.72 (d, 1 H, $J = 2.3$), 6.18 (m, 1 H), 5.95 (d, 1 H, $J = 2.3$), 5.91 (dd, 1 H, $J = 2.0$, 2.0), 5.74 (dd, 1 H, $J = 2.3$, 2.3), 4.11 (td, 1 H, $^4J_{\text{PH}} = 3.7$, $^3J_{\text{HH}} = 8.1$, =C=CHBuⁿ), 2.45 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.31 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and 0.82 (t, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); δ_{C} 362.6 (d, $^2J_{\text{CP}} = 20.5$, =C α =CHBu), 145.6 (borate), 144.0 (borate), 143.4 (d, $^3J_{\text{CP}} = 1.7$ Hz, borate), 136.8 (borate), 135.3 (borate), 135.25 (d, $^2J_{\text{CP}} = 9.4$, $\text{C}^{2,6}$ of Ph), 134.7 (d, $^3J_{\text{CP}} = 2.6$ Hz, borate), 133.5 (d, $^1J_{\text{CP}} = 44.1$, *ipso*-C of Ph), 130.2 (d, $^4J_{\text{CP}} = 2.5$ Hz, C^4 of Ph), 128.4 (d, $^3J_{\text{CP}} = 9.3$, $\text{C}^{3,5}$ of Ph), 106.4 (d, $^3J_{\text{CP}} = 1.7$, =C=C β HBu), 106.1 (d, $^4J_{\text{CP}} = 2.5$ Hz, borate), 106.0 (2C, borate), 34.6 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 22.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.3 (d, $^4J_{\text{CP}} = 1.7$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and 14.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); δ_{P} 40.4. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2940m (B–H) and 1667s (C=C).

[Ru{HB(pz)₃}Cl(PPh₃)(=C=CHBu^t)] 6. This complex was synthesized analogously to **3** with $\text{HC}\equiv\text{CBu}^t$ as starting material. Yield: 74% (Found: C, 57.56; H, 5.22; N, 12.00. $\text{C}_{33}\text{H}_{35}\text{BClN}_6\text{PRu}$ requires C, 57.11; H, 5.08; N, 12.11%). NMR [$(\text{CD}_3)_2\text{CO}$, 20 °C]: δ_{H} 8.01 (d, 1 H, $J = 1.9$, borate), 7.81 (m, 2 H, borate), 7.68 (m, 1 H, borate), 7.57–7.42 (m, 9 H, Ph), 7.42–7.30 (m, 6 H, Ph), 6.72 (d, 1 H, $J = 2.3$, borate), 6.26 (d, 1 H, $J = 2.3$, borate), 6.21 (m, 1 H, borate), 5.92 (dd, 1 H, $J = 2.3$, 2.0, borate), 5.82 (dd, 1 H, $J = 2.3$, 2.3, borate), 3.82 (d, 1 H, $^4J_{\text{PH}} = 3.9$, =C=CHBu^t) and 1.08 (s, 9 H, CH_3); δ_{C} 365.9 (d, $^2J_{\text{CP}} = 19.5$, =C α =CHBu^t), 146.6 (borate), 144.6 (borate), 143.3 (borate), 138.1 (d, $^3J_{\text{CP}} = 1.7$, borate), 136.32 (borate), 136.2 (d, $^2J_{\text{CP}} = 9.3$, $\text{C}^{2,6}$ of Ph), 135.7 (d, $^3J_{\text{CP}} = 1.7$ Hz, borate), 134.3 (d, $^1J_{\text{CP}} = 44.1$, *ipso*-C of Ph), 131.3 (d, $^4J_{\text{CP}} = 2.6$, C^4 of Ph), 128.5 (d, $^3J_{\text{CP}} = 9.3$ Hz, $\text{C}^{3,5}$ of Ph), 120.1 (d, $^3J_{\text{CP}} = 1.6$, =C=C β HBu^t), 107.1 (borate), 106.5 (d, $^4J_{\text{CP}} = 1.7$ Hz, borate), 106.4 (borate), 33.7 [$\text{C}(\text{CH}_3)_3$] and 32.7 [$\text{C}(\text{CH}_3)_3$]; δ_{P} 38.9. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2489m (B–H), 1670s, 1645s (C=C).

[Ru{HB(pz)₃}Cl(PPh₃)(=C=CHCO₂Et)] 7. This complex was synthesized analogously to **3** with $\text{HC}\equiv\text{CCO}_2\text{Et}$ as starting material. Yield: 86% (Found: C, 54.36; H, 4.87; N, 11.34. $\text{C}_{32}\text{H}_{31}\text{BClN}_6\text{O}_2\text{PRu}$ requires C, 54.14; H, 4.40; N, 11.84%). NMR (CDCl_3 , 20 °C): δ_{H} 7.90 (d, 1 H, $J = 2.0$, borate), 7.71 (d, 1 H, $J = 2.0$, borate), 7.69 (d, 1 H, $J = 2.4$, borate), 7.63–7.56 (m, 7 H, Ph, borate), 7.47–7.29 (m, 9 H, Ph), 6.68 (d, 1 H, $J = 2.0$, borate), 6.33 (d, 1 H, $J = 2.0$, borate), 6.19 (m, 1 H, borate), 5.93 (dd, 1 H, $J = 2.0$, 2.0, borate), 5.77 (dd, 1 H, $J = 2.3$, 2.3, borate), 4.70 (d, 1 H, $^4J_{\text{PH}} = 3.7$, =C=CHCO₂Et), 4.07 (m, 2 H, diastereotopic $\text{CO}_2\text{CH}_2\text{CH}_3$) and 1.12 (t, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$); δ_{C} 353.7 (d, $^2J_{\text{CP}} = 18.7$, =C α =CHCO₂Et), 166.7 (CO₂Et), 146.5 (borate), 144.2 (borate), 143.5 (d, $^3J_{\text{CP}} = 1.7$, borate), 136.9 (borate), 135.8 (borate), 135.4 (d, $^2J_{\text{CP}} = 10.2$, $\text{C}^{2,6}$ of Ph), 135.0 (d, $^3J_{\text{CP}} = 3.3$, borate), 131.8 (d, $^1J_{\text{CP}} = 46.6$, *ipso*-C of Ph), 130.8 (d, $^4J_{\text{CP}} = 2.6$, C^4 of Ph), 128.6 (d, $^3J_{\text{CP}} = 10.2$, $\text{C}^{3,5}$ of Ph), 106.45 (d, $^4J_{\text{CP}} = 2.5$, borate), 106.35 (borate), 106.26 (d, $^3J_{\text{CP}} = 1.4$ Hz, =C=C β HCO₂Et), 106.22 (borate), 60.6 (CO₂CH₂CH₃) and 15.0 (CO₂CH₂CH₃); δ_{P} 35.2. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2511m (B–H), 1717s (C=O), 1679s (C=C) and 1602s (C=C).

[Ru{HB(pz)₃}Cl(PPh₃)(=C=CHC₆H₉)] 8. This complex was synthesized analogously to **3** with $\text{HC}\equiv\text{CC}_6\text{H}_9$ (1-ethynylcyclohexene) as starting material. Yield: 85% (Found: C, 58.03; H, 5.08; N, 11.47. $\text{C}_{35}\text{H}_{35}\text{BClN}_6\text{PRu}$ requires C, 58.55; H, 4.91; N, 11.70%). NMR (CDCl_3 , 20 °C): δ_{H} 8.00 (d, 1 H, $J = 2.1$, borate), 7.69 (d, 1 H, $J = 2.1$, borate), 7.64 (d, 1 H, $J = 2.1$, borate), 7.61–7.53 (m, 7 H, Ph, borate), 7.44–7.27 (m, 9 H, Ph), 6.76 (d, 1 H, $J = 2.1$, borate), 6.19 (m, 1 H, borate), 6.04 (d, 1 H, $J = 2.1$, borate), 5.93 (dd, 1 H, $J = 2.1$, 2.1, borate), 5.77 (dd, 1 H, $J = 2.1$, 2.4, borate), 5.21 (m, 1 H, olefinic H of C₆H₉), 4.63 (d, 1 H, $^4J_{\text{PH}} = 3.8$, =C=CHC₆H₉), 2.23 (m, 2 H, C₆H₉), 1.88 (m,

2 H, C₆H₉) and 1.57 (m, 4 H, C₆H₉); δ_{C} 373.3 (d, $^2J_{\text{CP}}$ = 19.5, =C=CHC₆H₉), 145.5 (borate), 144.0 (borate), 143.5 (d, $^3J_{\text{CP}}$ = 1.7, borate), 136.9 (borate), 135.36 (borate), 135.3 (d, $^2J_{\text{CP}}$ = 9.3, C^{2,6} of Ph), 134.8 (d, $^3J_{\text{CP}}$ = 2.5, borate), 133.0 (d, $^1J_{\text{CP}}$ = 44.1, *ipso*-C of Ph), 130.4 (d, $^4J_{\text{CP}}$ = 2.5, C⁴ of Ph), 128.5 (d, $^3J_{\text{CP}}$ = 9.3, C^{3,5} of Ph), 126.5, 117.5, 115.5 (d, $^3J_{\text{CP}}$ = 1.7, =C=C₆H₉), 106.2 (d, $^4J_{\text{CP}}$ = 2.6 Hz, borate), 106.1 (borate), 106.0 (borate), 30.3 (C₆H₉), 26.3 (C₆H₉), 23.7 (C₆H₉) and 23.0 (C₆H₉); δ_{P} 37.6. $\tilde{\nu}_{\text{max}}$ /cm⁻¹ 2483m (B–H), 1641, 1624s (C=C).

[Ru{HB(pz)₃}Cl(PPh₃)(PMe₃)] 9. A solution of complex **3** (75 mg, 0.105 mmol) in benzene (3 cm³) was treated with PMe₃ (excess) and stirred for 36 h at room temperature. After removal of the solvent, the oily residue was stirred with diethyl ether until a fine yellow powder was obtained, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 41 mg (57%) (Found: C, 52.57; H, 5.10; N, 11.99. C₃₀H₃₄BCIN₆P₂Ru requires C, 52.38; H, 4.98; N, 12.22%). NMR (CDCl₃, 20 °C): δ_{H} 8.04 (d, 1 H, J = 1.8, borate), 7.69–7.55 (m, 8 H, Ph, borate), 7.54 (d, 1 H, J = 2.7, borate), 7.28–7.18 (m, 9 H, Ph), 6.61 (d, 1 H, J = 2.2, borate), 6.15 (m, 1 H, borate), 5.76 (m, 1 H, borate), 5.68 (d, 1 H, J = 2.3, borate), 5.56 (dd, 1 H, J = 2.3, 2.3, borate) and 1.12 (d, 9 H, $^2J_{\text{PH}}$ = 8.1 Hz, CH₃); δ_{C} 146.4 (d, $^3J_{\text{CP}}$ = 1.9, borate), 145.0 (d, $^3J_{\text{CP}}$ = 1.0, borate), 143.2 (d, $^3J_{\text{CP}}$ = 1.9, borate), 137.0 (borate), 136.4 (borate), 136.0 (borate), 135.2 (dd, $^1J_{\text{CP}}$ = 33.0, $^3J_{\text{CP}}$ = 1.0, *ipso*-C of Ph), 135.0 (d, $^2J_{\text{CP}}$ = 9.5, C^{2,6} of Ph), 129.4 (d, $^4J_{\text{CP}}$ = 2.4, C⁴ of Ph), 128.4 (d, $^3J_{\text{CP}}$ = 8.6, C^{3,5} of Ph), 106.0 (d, $^4J_{\text{CP}}$ = 2.4, borate), 105.7 (borate), 105.3 (d, $^4J_{\text{CP}}$ = 2.4, borate) and 17.7 (d, $^1J_{\text{CP}}$ = 27.6, CH₃); δ_{P} 51.0 (d, $^2J_{\text{PP}}$ = 36.6) and 11.4 (d, $^2J_{\text{PP}}$ = 36.6 Hz).

[Ru{HB(pz)₃}Cl(PPh₃)(CO)] 10. A solution of complex **3** (187 mg, 0.262 mmol) in benzene (6 cm³) was saturated with CO and stirred for 3 h at reflux. On removal of the volatiles the oily residue was stirred in diethyl ether until a yellow powder was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 130 mg (77%). Proton and ¹³C-¹H NMR spectra were in agreement with the literature.⁷ ³¹P-¹H NMR (CDCl₃, 20 °C): δ 42.4. Crystals were grown by diffusion of diethyl ether into a solution of **10** in CH₂Cl₂.

[Ru{HB(pz)₃}Cl(PPh₃)₂] 11. This complex has been prepared analogously to **9** with PPh₃ as the starting material. Yield: 93%. Proton, ¹³C-¹H and ³¹P-¹H NMR spectra were in agreement with the literature.⁸

[Ru{HB(pz)₃}Cl(PPh₃)(MeCN)] 12. This complex has been prepared analogously to **9**. Yield: 93%. Proton and ¹³C-¹H NMR spectra were in agreement with the literature.⁹ δ_{P} 51.3. $\tilde{\nu}_{\text{max}}$ /cm⁻¹ 2476m (B–H) and 2279s (C≡N).

[Ru{HB(pz)₃}Cl(PPh₃)(py)] 13. This complex has been prepared analogously to **9**. Yield: 91%. Proton, ¹³C-¹H and ³¹P-¹H NMR spectra were in agreement with the literature.^{1e}

Reaction of complex 3 with HC≡CR (R = SiMe₃, Buⁿ, Bu^t, CO₂Et or C₆H₉). In a typical procedure, a 5 mm NMR tube was charged with a solution of complex **3** (30 mg) in C₆D₆ (0.5 cm³) and was capped with a septum. The acetylene (5 equivalents) was added by syringe and the sample transferred to an NMR probe. Proton and ³¹P-¹H NMR spectra were immediately recorded showing the slow formation of [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHR)].

Reaction of complexes 4–8 with HC≡CPh. A series of 5 mm NMR tubes were charged with solutions of complexes **4–8** (*ca.* 30 mg) in C₆D₆ (0.5 cm³) and capped with a septum. Phenylacetylene (*ca.* 10 equivalents) was added by syringe and the

samples were transferred to an NMR probe. Proton and ³¹P-¹H NMR spectra were recorded showing the formation of **3**.

Reaction of complexes 9–13 with HC≡CPh. A series of 5 mm NMR tubes were charged with solutions of complexes **9–13** (*ca.* 30 mg) in C₆D₆ (0.5 cm³) and capped with a septum. The acetylene was added by syringe and the samples were transferred to an NMR probe. Proton and ³¹P-¹H NMR spectra were immediately recorded showing, in the cases of **11** and **13**, the slow formation of **3**. Complex **9** formed in addition to the vinylidene complex [Ru{HB(pz)₃}Cl(PMe₃)(=C=CHPh)] (<10%) several unidentified products, while **10** and **12** did not react with HC≡CPh even after prolonged stirring at 80 °C.

Crystallography

Crystal data and experimental details for complexes **2** and **10** are given in Table 1. X-Ray data were collected with a Siemens Smart CCD area-detector diffractometer using graphite-monochromated Mo-K α radiation (λ 0.710 73 Å), a nominal crystal-to-detector distance of 3.85 cm and 0.3° ω -scan frames. Corrections for Lorentz-polarization effects, crystal decay and absorption were applied. The structure was solved with direct methods.^{10a} All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.^{10b} The structures were refined against F^2 .

CCDC reference number 186/709.

EHMO Calculations

The extended-Hückel molecular orbital calculations were conducted by using the program developed by Hoffmann and Lipscomb,^{11a,c} and modified by Mealli and Proserpio.^{11d} The atomic parameters used in this study were taken from the CACAO program.^{11d} All bond lengths and angles of the complexes analysed were those determined crystallographically.

Results and Discussion

As we have previously reported,^{1e} [Ru{HB(pz)₃}Cl(PPh₃)₂] reacts readily with terminal alkynes HC≡CR (R = Ph, SiMe₃, Buⁿ or Bu^t) to afford the neutral vinylidene complexes [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHR)]. Of these, however, only the phenyl derivative **3** could be isolated in pure form, while the others were persistently contaminated with the starting material and PPh₃ because of incomplete conversions. Therefore, a new synthetic approach to obtaining such complexes was developed.

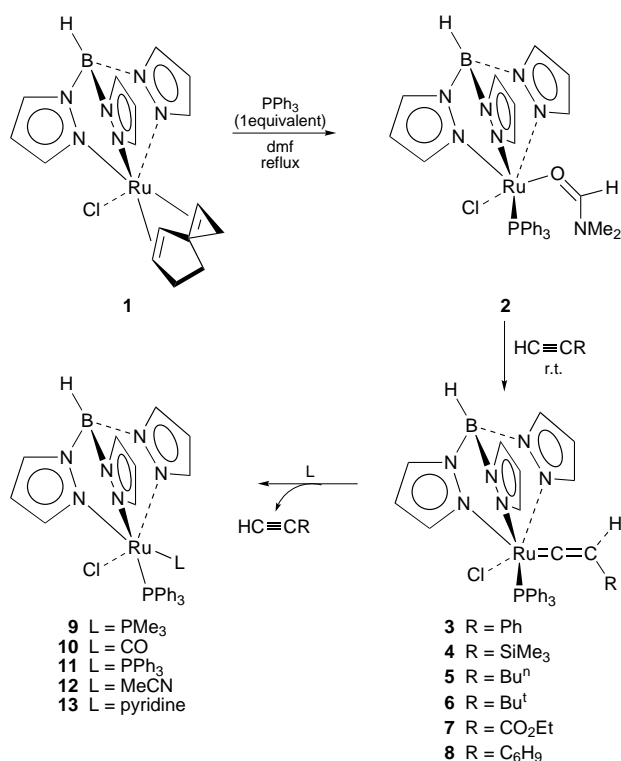
A convenient high-yield route to [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHR)] complexes proceeds through the intermediacy of [Ru{HB(pz)₃}Cl(PPh₃)(dmf)] **2**. This complex is readily obtained on treatment of [Ru{HB(pz)₃}Cl(cod)] **1** with 1 equivalent of PPh₃ in boiling dmf in 89% isolated yield (Scheme 1). A structural view of **2** is depicted in Fig. 1 with important bond distances and angles in the caption. While **2** is air stable in the solid state, it decomposes slowly in solution. Its solution ¹H and ¹³C-¹H NMR spectra exhibit three distinct sets of pyrazol-1-yl resonances due to the existence of three types of pyrazol-1-yl rings. In the ¹H NMR spectrum the NMe₂ group of dmf gives rise to a broad singlet at δ 2.68 (6 H). In the ¹³C-¹H NMR spectrum co-ordinated dmf exhibits characteristic resonances at δ 169.7, 38.6 and 32.9 which can be assigned to the ketonic carbonyl carbon and the methyl groups, respectively. There is no evidence for free dmf in solution. In the IR spectrum the ν (C=O) band is observed at 1640 cm⁻¹, in line with other ruthenium dmf complexes.^{5,12} This value is below that of free dmf observed at 1675 cm⁻¹, implying, as expected, that co-ordination decreases the C=O bond strength. The ν (B–H) vibration is found at 2480 cm⁻¹ which is characteristic of HB(pz)₃ when terdentate *N,N',N''*-bonded to a metal center.

The dmf molecule is co-ordinated to the metal as an η^1 -oxygen donor ligand. The Ru–O distance is 2.154(2) Å. The

Table 1 Crystallographic data for [Ru{HB(pz)₃}Cl(PPh₃)(dmf)] **2** and [Ru{HB(pz)₃}Cl(PPh₃)(CO)] **10**

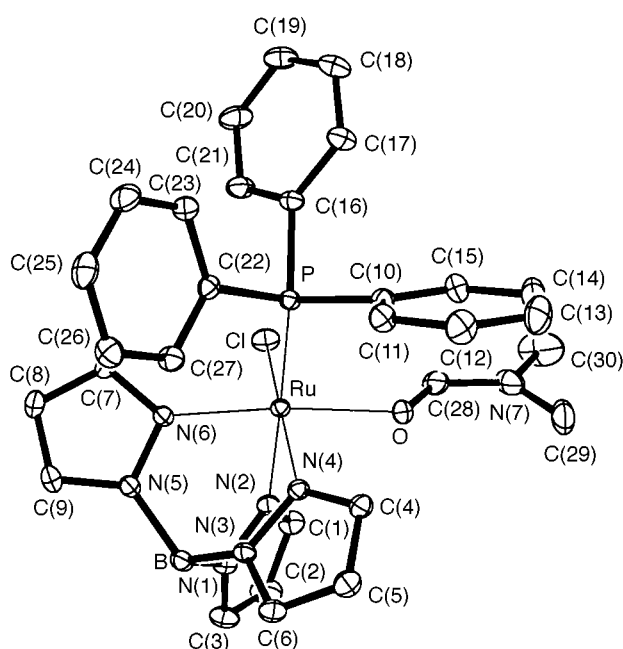
	2	10
Formula	C ₃₀ H ₃₂ BClN ₆ OPRu	C ₂₈ H ₂₅ BClN ₆ OPRu
<i>M</i>	684.93	639.84
Crystal size/mm	0.26 × 0.18 × 0.12	0.69 × 0.41 × 0.35
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> /Å	9.929(1)	31.173(3)
<i>b</i> /Å	15.293(2)	9.688(2)
<i>c</i> /Å	20.129(3)	18.545(2)
β/°	94.33(1)	93.00(1)
<i>U</i> /Å ³	3047.7(7)	5593.0(2)
<i>F</i> (000)	1400	2592
<i>Z</i>	4	8
<i>D</i> /g cm ⁻³	1.493	1.520
<i>T</i> /K	297	300
μ(Mo-Kα)/mm ⁻¹	0.428	0.747
Minimum, maximum transmission factors	0.829, 0.928	0.769, 0.862
θ _{max} /°	27.5	27
Index ranges	-13 ≤ <i>h</i> ≤ 13, -18 ≤ <i>k</i> ≤ 21, -24 ≤ <i>l</i> ≤ 28	-39 ≤ <i>h</i> ≤ 18, -12 ≤ <i>k</i> ≤ 12, -23 ≤ <i>l</i> ≤ 23
No. reflections measured	20 815	18 498
No. unique reflections	6977	6137
No. reflections with <i>F</i> > 4σ(<i>F</i>)	5687	5227
No. parameters	380	385
<i>R</i> (<i>F</i>) [<i>F</i> > 4σ(<i>F</i>)]	0.033	0.023
(all data)	0.047	0.031
<i>wR</i> (<i>F</i> ²) (all data)	0.076	0.058
Minimum, maximum Fourier-difference peaks/e Å ⁻³	-0.48, 0.46	-0.38, 0.31

$$R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|, wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

**Scheme 1** The reaction of complexes **3–8** with both L = PPh₃ and pyridine is reversible. r.t. = Room temperature

Ru–O–C(28) angle is 126.6(2)°. The co-ordination geometry of complex **2** is approximately octahedral. The Ru–N(6) and Ru–N(4) distances are 2.041(2) and 2.063(2) Å, respectively, while the Ru–N(2) distance is slightly longer being 2.139(1) Å, but are within the range for other ruthenium HB(pz)₃ complexes.^{1e,5,6,12,13a–d} The Ru–P and Ru–Cl bond distances are 2.309(1) and 2.424(1) Å. In sum, there are no unusual distortions.

Treatment of complex **2** (either as a pure sample or prepared *in situ*) with HC≡CR (R = Ph, SiMe₃, Buⁿ, Bu^t, CO₂Et or C₆H₉)

**Fig. 1** Structural view of [Ru{HB(pz)₃}Cl(PPh₃)(dmf)] **2**. Selected bond lengths (Å) and angles (°): Ru–N(2) 2.139(2), Ru–N(4) 2.063(2), Ru–N(6) 2.041(2), Ru–P 2.309(1), Ru–Cl 2.424(1), Ru–O 2.154(2) and O–C(28) 1.225(4); Ru–O–C(28) 126.6(2)

at room temperature yields the respective vinylidene complexes [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHR)] **3–8** in high yields (Scheme 1). All these complexes are air stable in the solid state. Characterization was by elemental analysis and by ¹H, ¹³C-¹H and ³¹P-¹H NMR and IR spectroscopy. Characteristic NMR spectroscopic features comprise, in the ¹³C-¹H NMR spectrum, a marked low-field resonance in the range of δ 373.3 to 341.7 (d, *J*_{CP} = 18–20 Hz) assignable to the α-carbon of the vinylidene moiety. The resonances of HB(pz)₃ and PPh₃ are in the expected ranges. Based on the structural data reported previously^{1e} for **3**, all of these neutral vinylidene complexes should be particularly stable thermodynamically. Note the Ru–C bond

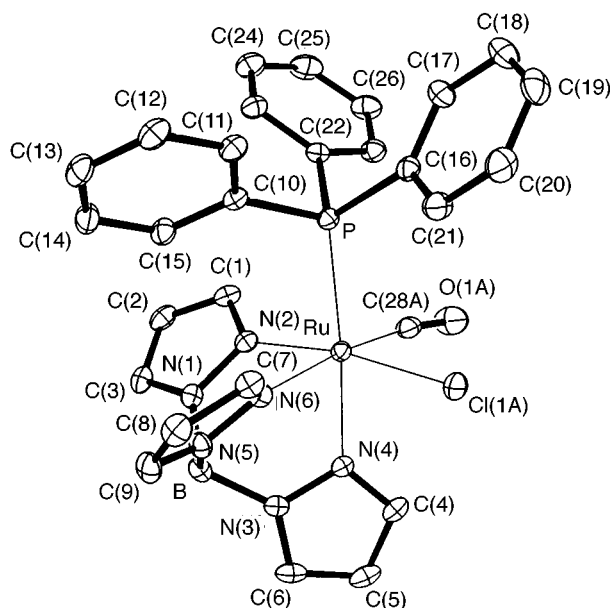
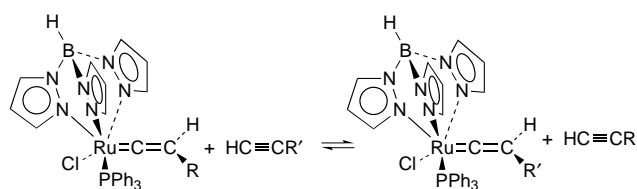


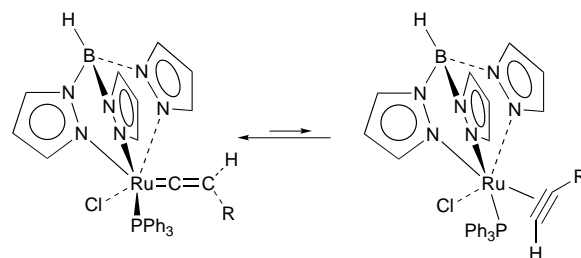
Fig. 2 Structural view of $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(\text{CO})]$ **10**. Selected bond lengths (Å) and angles ($^\circ$): Ru–N(2) 2.116(2), Ru–N(4) 2.114(2), Ru–N(6) 2.140(2), Ru–P 2.362(1), Ru–Cl(1A) 2.418(2), Ru–C(28A) 1.848(6) and C(28A)–O(1A) 1.137(8); Ru–C(28A)–O(1A) 173.2(5), N(6)–Ru–C(28A) 173.4(2), C(28A)–Ru–Cl(1A) 87.8(2) and P–Ru–Cl(1A) 97.0(1)

distance of 1.801(4) Å which is relatively short for a ruthenium vinylidene complex.^{2a,4b,14} Furthermore, the Ru–N(*trans*) bond distance of 2.199(3) Å is similar to that in the cationic analog $[\text{Ru}\{\text{HB}(\text{pz})_3\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(=\text{C}=\text{CHPh})]^+$ (2.209 Å) and longer than in most other $\text{Ru}\{\text{HB}(\text{pz})_3\}$ complexes. This strong *trans* influence may reflect both strong σ or/and π interactions between N(*trans*) and the vinylidene ligand *via* Ru.^{5,12} It is thus surprising that the vinylidene moiety in **3–8** is labile, being readily replaced by a variety of monodentate ligands $\text{L} = \text{PMe}_3$, CO, PPh_3 , MeCN and pyridine. These reactions resulted in the liberation of $\text{HC}\equiv\text{CR}$ and quantitative formation of the complexes $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)\text{L}]$ **9–13** (Scheme 1). All these are air-stable thermally robust solids and have been fully characterized by elemental analysis, ^1H , ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ NMR spectroscopy. It is worth noting that **10–13** have already been synthesized by another method.^{1e,7–9} With the exception of **11** and **13**, all complexes are formed irreversibly. On addition of an excess of $\text{HC}\equiv\text{CPh}$ to either **11** or **13**, **3** is quantitatively regained as monitored by ^1H and ^{31}P - $\{^1\text{H}\}$ NMR spectroscopy. With **9**, addition of $\text{HC}\equiv\text{CPh}$ results in the liberation of PPh_3 and formation of several products including the neutral vinylidene complex $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PMe}_3)(=\text{C}=\text{CHPh})]$; **10** and **12**, on the other hand, are substitutionally inert with no evidence for the formation of **3** even on prolonged heating at 80 $^\circ\text{C}$.

For comparison with complex **3**, the structure of **10** has been determined by X-ray crystallography as depicted in Fig. 2 with important bond distances in the caption. It is interesting that the ruthenium–carbon bond distance [1.848(6) Å] is significantly longer than in **3** [1.801(4) Å]. Moreover, the *trans* influence in **10** [Ru–N(6) 2.140(2) Å] is not as pronounced as in **3** [Ru–N(6) 2.199(3) Å] suggesting that CO is a weaker σ donor and/or π acceptor than $=\text{C}=\text{CHPh}$. Similar differences have been found with the related cationic complexes $[\text{Ru}\{\text{HB}(\text{pz})_3\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(\text{CO})]^+$ and $[\text{Ru}\{\text{HB}(\text{pz})_3\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(=\text{C}=\text{CHPh})]^+$.⁵ In the latter, however, the vinylidene moiety cannot be replaced by nucleophiles like CO or MeCN. Noteworthy, the vinylidene moiety in the complexes $[\text{Ru}(\text{Pr}^i_2\text{PCH}_2\text{CH}_2\text{OMe})_2\text{Cl}(=\text{C}=\text{CHPh})]^+$ and $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHPh})]$ has recently been found to be replaceable by CO and $\text{P}(\text{OPh})_3$.^{4b,14}



Scheme 2



Scheme 3

Most remarkably, complex **3** also reacts easily with terminal acetylenes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3$, Bu^n , Bu^t , CO_2Et or C_6H_9) to afford reversibly the respective vinylidene complexes $[\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)(=\text{C}=\text{CHR})]$ **4–8** (Scheme 2). Although no products other than vinylidene complexes could be detected by NMR spectroscopy, it is likely that these are in equilibrium with their respective η^2 -co-ordinated acetylene complexes as shown in Scheme 3.

A point of particular concern is the dramatic coligand effect on the vinylidene complex stability. Thus the binding tendency of the $[\text{Ru}\{\text{HB}(\text{pz})_3\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)]^+$ or $[\text{Ru}\{\text{HB}(\text{pz})_3\}(\text{tmen})]^+$ ($\text{tmen} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) fragments to a sixth ligand was, in previous work,^{5,12} found to increase in the order phosphines \approx amines $<$ CO \leq vinylidene. This means that vinylidene is ordinarily non-replaceable by nucleophiles. In the present work, in contrast, we have seen that the presence of chloride in a basal position of the fragment, in $\text{Ru}\{\text{HB}(\text{pz})_3\}\text{Cl}(\text{PPh}_3)$, reverses the stability order according to $\text{dmf} < \text{PPh}_3 \approx \text{vinylidene} < \text{CO}$ with the consequence that vinylidene becomes easily replaceable by acetylenes or even phosphines.

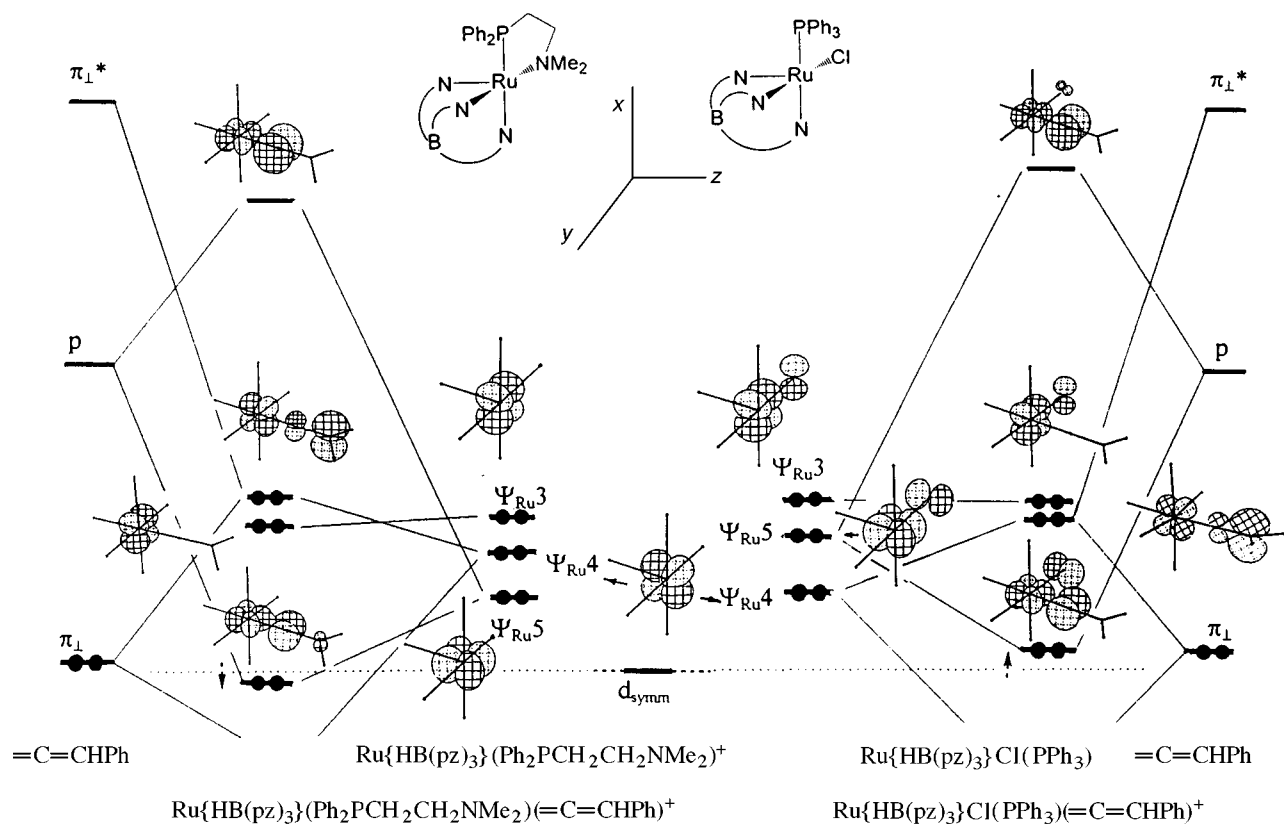
Let us at first review previous energetic considerations. While the formation of vinylidene from free acetylene is endothermic by 44–47 kcal mol^{–1},^{2a,g} upon co-ordination to a transition metal the thermodynamic stabilities are reversed, e.g. the vinylidene complex of $\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2$ is calculated to be 35 kcal mol^{–1} more stable than the acetylene one.^{15a} From EH calculations, $[\text{RhCl}(\text{PPh}_3)_2(=\text{C}=\text{CH}_2)]$ is more stable than $[\text{RhCl}(\text{PPh}_3)_2(\eta^2\text{-CH}\equiv\text{CH})]$ by 17.1 kcal mol^{–1}.^{15b} In kinetic terms, the activation enthalpy of unimolecular 1,3-hydrogen migration in d⁸ rhodium(i) systems was calculated to be about 33 kcal mol^{–1}. The free energy of activation should exceed this value, since the process is certainly entropically disfavoured. On the other hand, for a bimolecular hydrogen exchange, the free energy of activation was estimated to be ca. 17 kcal mol^{–1}.^{3a} Bruce^{4c} has claimed that the energy difference between η^2 -alkyne and vinylidene tautomers should be small for divalent molybdenum. In conclusion, the free energy of activation of the back reaction should be relatively low, of the order of 10 kcal mol^{–1}, implying that vinylidene–acetylene conversion might be achieved just by a small variation in the σ or π metal–vinylidene interactions.

Based on a Walsh analysis, Silvestre and Hoffmann^{15a} suggest that the metal–acetylene complex is less stable than the vinylidene variant because of the different natures of the highest occupied molecular orbital (HOMO), which is anti-bonding in the former but more non-bonding in the latter. However, two other features should not be forgotten: (i) metal d(σ) [termed 3a' in Fig. 4 of ref. 15(a)] interacts weakly with the low-lying occupied bonding π_σ orbital of acetylene but strongly with the high-lying occupied sp orbital of vinylidene; (ii) the interaction of metal d(π) is weak with π_σ^* (acetylene) but strong

Table 2 Relevant MO energy levels of ruthenium in some fragments and their transformations in the complexes

Fragment	<i>E/eV</i>					Overlap population ($d_{yz} p$)
	Ψ_{Ru1} $\sigma^*, d_{x^2-y^2}$	Ψ_{Ru2} σ^*, d_{z^2}	Ψ_{Ru3} π, d_{xy}	Ψ_{Ru4} π, d_{xz}	Ψ_{Ru5}^a π, d_{yz}	
$[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$	-6.52	-9.82	-11.37	-11.52	-11.74	
$[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)(CO)]^+$	-6.76	-4.48	-11.38	-11.67	-8.01 (-12.06)	0.29
$[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)(C=CHPh)]^+$	-6.82	-4.47	-11.39	-11.24	-9.10 (-12.26)	0.22
$[Ru\{HB(pz)_3\}Cl(PPh_3)]$	-5.57	-9.72	-11.20	-11.69	-11.39	
$[Ru\{HB(pz)_3\}Cl(PPh_3)]^b$	-7.31	-9.84	-11.51	-11.66	-11.79	
$[Ru\{HB(pz)_3\}Cl(PPh_3)(C=CHPh)]$	-5.54	-4.91	-11.19	-11.27	-12.02 (-8.95)	0.13
$[Ru\{HB(pz)_3\}Cl(PPh_3)(C=CHPh)]$	-7.63	-4.97	-11.52	-11.29	-9.13 (-12.33)	0.23
$[Ru\{HB(pz)_3\}Cl(PPh_3)(CO)]$	-5.84	-4.86	-11.27	-11.97	-7.82 (-11.76)	0.22
$[Ru\{HB(pz)_3\}Cl(PPh_3)_2]$	-5.62	-5.34	-11.24	-11.40	-11.32	

^a Two entries signify a splitting of Ψ_{Ru5} due to overlap with p orbitals of π ligands. The value for the ligand-centered MO is parenthesized. ^b Ru-Cl distance arbitrarily taken as 2.85 Å.

**Fig. 3** Qualitative orbital-interaction diagram for the formation of $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)(=C=CHPh)]^+$ and $[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHPh)]$ complexes

with p (vinylidene), providing the M=C double bond. The respective MOs are termed in turn Φ_2 , Φ_1' [for (i)] and Φ_3 , Φ_3' [for (ii)] in Fig. 4 of ref. 15(a).

The results of the present EHMO analysis, done as before,^{5,12} are presented in Table 2 and are illustrated in the comparative interaction diagram in Fig. 3, with the apex-metal line chosen as the *z* axis. Whereas the construction of the $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$ fragment, similar to $[Ru\{HB(pz)_3\}(tmen)]^+$,¹² is mainly by σ bonds, in $[Ru\{HB(pz)_3\}Cl(PPh_3)]$ there is an additional π interaction between the ruthenium $d(\pi)$ atomic orbitals (AOs) and both p(Cl) AOs. The orbital Ψ_{Ru1} ('classical' $d_{x^2-y^2}$ or σ^*) is responsible for the interactions in the square base of fragments and, because of symmetry, is not affected by a sixth ligand, similar to Ψ_{Ru3} (1a', or 'classical' d_{xy}). The variation of Ψ_{Ru1} in Table 2 shows that the presence of chloride strengthens the pyramidal structure of the fragment. The vacant site of the fragment is both a good σ acceptor through Ψ_{Ru2} ['classical' d_{z^2} , identical to 3a' in ref. 15(a)] and has also appreciable π affinity via Ψ_{Ru4} and Ψ_{Ru5} ['classical' d_{xz}

and d_{yz} , identical to 2a' and a'' in ref. 15(a)]. Whether the sixth position is ultimately a π donor or a π acceptor will depend on the nature of the ligand added and the electron population of the two MOs.

The effect of Cl in $[Ru\{HB(pz)_3\}(PPh_3)Cl]$, relative to $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$, is two-fold: (i) the σ affinity of the fragment is reduced as reflected by an increase in the Ψ_{Ru2} level, likely due to the higher electronegativity of Cl over sp^3 N; (ii) chlorine destabilizes the $d(\pi)$ orbitals Ψ_{Ru3} and Ψ_{Ru5} , since the $p_x(Cl)-d_{xy}(Ru)$ and $p_z(Cl)-d_{yz}(Ru)$ interactions are anti-bonding in character (see Fig. 3). On the other hand, the $d_{xz}(Ru)-\pi_1(\text{vinylidene})$ interaction, claimed to be important for the η^2 -alkyne-vinylidene rearrangement,^{15a} is not sensitive to chloride, because of symmetry. In sum, chloride brings about an inversion in energy from $d_{yz}(\Psi_{Ru5}) < d_{xz}(\Psi_{Ru4}) < d_{xy}(\Psi_{Ru3})$ in $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$ to $d_{xz}(\Psi_{Ru4}) < d_{yz}(\Psi_{Ru5}) < d_{xy}(\Psi_{Ru3})$ in $[Ru\{HB(pz)_3\}Cl(PPh_3)]$ (Fig. 3) and weakens both the σ and π affinity of the ruthenium fragment, seen in the changes in Ψ_{Ru2} and Ψ_{Ru5} upon complex formation.

Table 3 Comparison of bond distances (Å) and angles (°) in some vinylidene complexes

Complex	M=C	C=C	M=C=C	Ref.
[Ru{HB(pz) ₃ }(Ph ₂ PCH ₂ CH ₂ NMe ₂)(=C=CHPh)] ⁺	1.821(5)	1.287(2)	169.6(4)	5
[Ru{HB(pz) ₃ }(tmen)(=C=CHPh)] ⁺	1.820(5)	1.305(6)	173.5(4)	12
[Ru{HB(pz) ₃ }Cl(PPh ₃)(=C=CHPh)]	1.801(4)	1.315(6)	177.2(3)	1(e)
[Ru(η-C ₅ Me ₅)(Ph ₂ PCH ₂ CH ₂ NMe ₂)(=C=CHPh)] ⁺	1.81(2)	1.33(2)	173(1)	16
[Ru(η-C ₅ Me ₅)Cl(PPh ₃)(=C=CHPh)]	1.80(1)	1.40(2)	176(1)	14
[W(η-C ₅ H ₅){P(OMe) ₃ } ₂](=C=CMePh)] ⁺	1.947(6)	1.330(9)	177.6(5)	4(c)
[W(CO)(Ph ₂ PCH ₂ CH ₂ PPh ₂)(=C=CHCO ₂ Me)]	1.88(1)	1.36(1)	171.2(9)	3(d)
[RhCl(PPr ⁱ) ₃](=C=CHMe)]	1.775(6)	1.32(1)	177.9(6)	3(a)
[RuBr ₂ (PPh ₃) ₂](=C=CHBu ^t)]	1.77(1)	1.36(3)	162(2)	3(c)
[RuCl(κ ² -P,O-Pr ⁱ ₂ PCH ₂ CH ₂ OMe) ₂](=C=CHPh)] ⁺	1.790(3)	1.313(5)	170.9(3)	4(b)

This is independent of the nature of the sixth ligand, PPh₃ (very weak π bondor), CO (two π* MOs) and vinylidene (p and π/π* MOs). Also seen in Fig. 3, in [Ru{HB(pz)₃}(Ph₂PCH₂CH₂NMe₂)(=C=CHPh)]⁺ both the HOMO and lowest unoccupied molecular orbital (LUMO) are antibonding, whereas the HOMO in [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHPh)] is essentially non-bonding and the LUMO is antibonding. Consequently, electronic excitation should have little effect on the Ru–C bond in the former complex but will weaken it in the latter.

The destabilization by chloride of the d_{yz}(Ru)–p(vinylidene) interaction is reflected by the decrease in the corresponding overlap population from ⟨d_{yz}|p⟩ = 0.22 in the cationic complex to 0.13 in the neutral one. That this is due to the presence of chloride is corroborated by a computer simulation extending the Ru–Cl distance from the crystallographic value of 2.42 to 2.85 Å. As a result, the overlap population ⟨d_{yz}|p⟩ (Table 2) increases to the value of the cationic complex with concomitant increase in the rotational barrier of vinylidene from 0.5 to 2 eV (*cf.* with the 1.53 eV calculated for the cationic complex).

The Cl-initiated diminished overlap population ⟨d_{yz}|p⟩ is also displayed by the increasing C_α=C_β bond length from 1.287(2) Å in [Ru{HB(pz)₃}(Ph₂PCH₂CH₂NMe₂)(=C=CHPh)]⁺ to 1.315(6) Å in [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHPh)], similar to C₅Me₅ analogs from 1.33(2) Å in [Ru(η-C₅Me₅)(Ph₂PCH₂CH₂NMe₂)(=C=CHPh)]⁺ 16 to 1.40(2) Å in [Ru(η-C₅Me₅)Cl(PPh₃)(=C=CHPh)] 14 (see Table 3). This unusual effect of back bonding provoking C–C bond strengthening (towards a triple bond) results from the fact that electron density is shifted onto p [π_{||}* in Fig. 4 of ref. 15(a)], which is perpendicular to the C_α=C_β π bond plane, but not to π* [π_⊥* in Fig. 4 of ref. 15(a)]. Consequently, two types of back bonding should be distinguished. Similar C_α=C_β bond-length variations are displayed when the adjacent atom is a non-metal in the series CH₂=C_α=C_βH₂ (1.3084) 17a < C_α=C_βH₂ (1.312) 17b < O=C_α=C_βH₂ (1.317 Å). 17a Here, the p AO of oxygen is an acceptor rather than a donor compared to the p MO of singlet carbene (:CH₂). Related changes in bond length occur in the series: S=C_α=C_β=PPh₃ (1.209) ≈ O=C_α=C_β=PPh₃ (1.210) < PhN=C_α=C_β=PPh₃ (1.248) < (EtO)₂C_α=C_β=PPh₃ (1.314 Å). 17c Contrary to the marked difference between [Ru{HB(pz)₃}(Ph₂PCH₂CH₂NMe₂)(=C=CHPh)]⁺ and [Ru{HB(pz)₃}Cl(PPh₃)(=C=CHPh)], Table 2 reveals only minor differences in the d(π) orbitals of Ru between the two CO variants. Of course, CO co-ordination is governed by ordinary back donation. Finally, PPh₃ as the sixth ligand, which is a 'classical' sp³ electron-pair donor with little conjugation with adjacent π bonds, does not noticeably split the ruthenium d(π) orbitals (Table 2). The labilization of the vinylidene ligand in the presence of the Cl coligand can be interpreted in terms of a decrease in both the σ and π property of the ruthenium fragment, above all destabilizing the Ru=C double bond. The diminished overlap between p(vinylidene) and Ψ_{Ru}5 stimulates the electrophilic character of the α-carbon of the vinylidene ligand for nucleophilic addition to occur, *e.g.* by epoxide 3e involving an ene–vinylidene equilibrium. In either the 1,2- or 1,3-hydrogen shift vinylidene → alkene isomerization

mechanism, hydrogen migration proceeds in the Ru–C_α–C_β–Ph plane. 15a Therefore, the p(vinylidene) ↔ Ψ_{Ru}5 interaction should play the dominant role for this conversion. If this contribution is small, *i.e.* weak Ru=C bond, vinylidene → η²-alkyne reversion is feasible. Note that the π_⊥ (vinylidene) ↔ Ψ_{Ru}4 interaction occurs in the perpendicular plane and thus should be ineffective.

Conclusion

The different stabilities of the vinylidene and acetylene complexes are due to changes in both the σ- and π-bonding interactions. The nature of the bonding between a metal center and the vinylidene ligand cannot be understood adequately without distinguishing two types of π interactions, *viz.* d_{yz}(metal)–π(vinylidene) and d_{yz}(metal)–p(vinylidene) back bonding, where the latter turns out to be essential to the stability of the vinylidene complex. If this contribution is small, reversion of a vinylidene complex into an η²-alkyne complex can be accomplished. This is effected by either of two ways: (i) destabilization of the d_{yz} orbital by the presence of halide in a *cis* position, as is the case of the present ruthenium complexes, and (ii) weak π donor strength of the metal fragment by using strong π-acceptor (or weak π-donor) coligands. An example is the conversion of *trans*-[Mo(η-C₅H₅)(CO){P(OMe)₃}₂](=C=CHCMe₃)]⁺ (with a *cis*-P-Mo-vinylidene construction) into the acetylene complex, whereas the PPhMe₂ analog is stable. 4c Actually, P(OMe)₃ is a strong π acceptor, in contrast to PPhMe₂. When placed in *cis* position it reduces the ⟨d_{yz}|p⟩. Similarly, the π interaction of the carbene's p with the M(η-C₅H₅)(CO)₃ fragment is reduced by the CO ligands. 18 This gives rise to vinylidene–acetylene rearrangement in the supposed structures [Mo(η-C₅H₅)(CO)₃(C⁺=CHPh)]BF₄ or [W(η-C₅H₅)(CO)₃(C⁺=CHPh)]BF₄. 4a

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