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

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A convenient high-yield route to [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=CHR)] (pz = pyrazolyl; R = Ph, SiMe$_3$, Bu^n, Bu^t, CO$_2$Et or C$_6$H$_9$) has been found through the intermediary [Ru{HB(pz)$_3$}Cl(PPh$_3$)(dmf)] (dmf = dimethylformamide) which has been crystallographically characterized. This complex is readily obtained on treatment of [Ru{HB(pz)$_3$}Cl(cod)] (cod = cycloocta-1,5-diene) with 1 equivalent of PPh$_3$ in boiling dmf. The vinylidene moiety in complexes of the type [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=CHR)] is remarkably labile being easily replaced by nucleophiles L = PMe$_3$, PPh$_3$, MeCN, pyridine or CO to give [Ru{HB(pz)$_3$}Cl(PPh$_3$)L]. With the exceptions of L = PMe$_3$ or CO, these reactions are reversible. The complex [Ru{HB(pz)$_3$}Cl(PPh$_3$)(CO)] has been characterized by X-ray crystallography. On treatment of [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=CHPh)] with an excess of HC≡CR′ (R′ = SiMe$_3$, Bu^n, Bu^t, CO$_2$Et or C$_6$H$_9$) the neutral vinylidene complex [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=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 η^2-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 dienylalkynes,[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 [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=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 η^2-co-ordinated alkyne to a vinylidene ligand in [RuCl$_2$(PH$_3$)$_2$(=C=CH$_2$)] are in line with an intraligand 1,2-hydrogen shift mechanism,[3c] while vinylidene complexes of Rh^I 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*-[Mo(CO)(dmf)(Ph$_2$PCH$_2$CH$_2$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 formation of [Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)(=C=C=C=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 η^2-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 η^2-alkyne complex.[3f] Note further that the cationic complex [RuCl(=C=CH$_2$)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$]$^+$ is stable only under an acetylene atmosphere, pointing to a reversible reaction.[4b] Finally, the elimination of HC≡CPh from [RuI$_2$(=C=CHPh)(κ^1*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)] with concomitant formation of [RuI$_2$(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] at elevated temperatures, or from [RuCl(=C=CHPh)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] with CO under mild conditions (tetrahydrofuran, thf; 25 °C), has been observed.[4b] On warming above 0 °C the BF$_4^-$ salt of [Mo(η-C$_5$H$_5$)(CO){P(OMe)$_3$}$_2$(=C=CHCMe$_3$)]$^+$ decarbonylated with vinylidene tautomerization to give back the η^2-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 [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=CHR)] (R = SiMe$_3$, Bu^n, Bu^t, CO$_2$Et or C$_6$H$_9$) in which the vinylidene is readily displaceable by nucleophiles L = PMe$_3$, PPh$_3$, MeCN, pyridine (py) and CO, giving [Ru{HB(pz)$_3$}Cl(PPh$_3$)L]. Even vinylidene metathesis by HC≡CR (R = SiMe$_3$, Bu^n, Bu^t, CO$_2$Et or C$_6$H$_9$) is an extremely facile and reversible process. This is in sharp contrast to the robustness of the cationic complex [Ru{HB(pz)$_3$}(Ph$_2$PCH$_2$CH$_2$NMe$_2$)(=C=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.

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† 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, $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ 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 $[Ru\{HB(pz)_3\}Cl(cod)]$ **1** (cod = cycloocta-1,5-diene) has been prepared according to the literature.[6] Microanalyses were done by Microanalytical Laboratories, University of Vienna.

Syntheses

$[Ru\{HB(pz)_3\}Cl(PPh_3)(dmf)]$ 2. A suspension of complex **1** (130 mg, 0.284 mmol) in dimethylformamide (3 cm^3) 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. $C_{30}H_{32}BClN_6OPRu$ 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, $^1J_{CP} = 49.5$, *ipso*-C of Ph), 135.9 (borate), 135.5 (borate), 135.0 (d, $^2J_{CP} = 9.5$, $C^{2,6}$ of Ph), 134.7 (borate), 129.3 (d, $^4J_{CP} = 2.6$, C^4 of Ph), 128.1 (d, $^3J_{CP} = 8.9$ Hz, $C^{3,5}$ of Ph), 106.2 (borate), 105.9 (borate), 105.7 (borate), 38.6 (CH_3) and 32.9 (CH_3); δ_P 55.8. $\tilde{\nu}_{max}/cm^{-1}$ 2480m (B–H) and 1640s (C=O).

$[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHPh)]$ 3. A solution of complex **1** (150 mg, 0.328 mmol) and PPh_3 (86 mg, 0.328 mmol) in dimethylformamide (3 cm^3) was heated under reflux for 2 h. The solvent was then removed under vacuum and the residue, dissolved in CH_2Cl_2 (2 cm^3), was treated with HC≡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, $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectra were in agreement with the literature.[1e]

$[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHSiMe_3)]$ 4. This complex was synthesized analogously to **3** with $HC\equiv CSiMe_3$ as starting material. Yield: 80% (Found: C, 53.75; H, 4.67; N, 11.53. $C_{32}H_{35}BClN_6PRuSi$ 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, $^4J_{PH} = 3.3$, $=C=CHSiMe_3$) and −0.17 (s, 9 H, $SiMe_3$); δ_C 341.7 (d, $^2J_{CP} = 17.8$, $=C_\alpha=CHSiMe_3$), 145.8 (borate), 143.6 (borate), 136.8 (borate), 135.32 (borate), 135.30 (d, $^2J_{CP} = 10.2$, $C^{2,6}$ of Ph), 135.2 (borate), 134.9 (d, $^3J_{CP} = 3.4$, borate), 133.4 (d, $^1J_{CP} = 44.1$, *ipso*-C of Ph), 130.3 (d, $^4J_{CP} = 2.5$, C^4 of Ph), 128.5 (d, $^3J_{CP} = 9.3$, $C^{3,5}$ of Ph), 106.2 (d, $^4J_{CP} = 2.5$ Hz, borate), 106.0 (borate), 105.9 (borate), 93.1 ($=C=C_\beta HSiMe_3$) and 1.5 ($SiMe_3$); δ_P 42.4. $\tilde{\nu}_{max}/cm^{-1}$ 2493m (B–H) and 1644s (C=C).

$[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHBu^n)]$ 5. This complex was synthesized analogously to **3** with $HC\equiv CBu^n$ as starting material. Yield: 88% (Found: C, 56.77; H, 4.88; N, 11.76. $C_{33}H_{35}BClN_6PRu$ 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, $^4J_{PH} = 3.7$, $^3J_{HH} = 8.1$, $C=CHBu^n$), 2.45 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.31 (m, 4 H, $CH_2CH_2CH_2CH_3$) and 0.82 (t, 3 H, $CH_2CH_2CH_2CH_3$); δ_C 362.6 (d, $^2J_{CP} = 20.5$, $=C_\alpha=CHBu$), 145.6 (borate), 144.0 (borate), 143.4 (d, $^3J_{CP} = 1.7$ Hz, borate), 136.8 (borate), 135.3 (borate), 135.25 (d, $^2J_{CP} = 9.4$, $C^{2,6}$ of Ph), 134.7 (d, $^3J_{CP} = 2.6$ Hz, borate), 133.5 (d, $^1J_{CP} = 44.1$, *ipso*-C of Ph), 130.2 (d, $^4J_{CP} = 2.5$ Hz, C^4 of Ph), 128.4 (d, $^3J_{CP} = 9.3$, $C^{3,5}$ of Ph), 106.4 (d, $^3J_{CP} = 1.7$, $=C=C_\beta HBu$), 106.1 (d, $^4J_{CP} = 2.5$ Hz, borate), 106.0 (2C, borate), 34.6 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 18.3 (d, $^4J_{CP} = 1.7$ Hz, $CH_2CH_2CH_2CH_3$) and 14.4 ($CH_2CH_2CH_2CH_3$); δ_P 40.4. $\tilde{\nu}_{max}/cm^{-1}$ 2940m (B–H) and 1667s (C=C).

$[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHBu^t)]$ 6. This complex was synthesized analogously to **3** with $HC\equiv CBu^t$ as starting material. Yield: 74% (Found: C, 57.56; H, 5.22; N, 12.00. $C_{33}H_{35}BClN_6PRu$ requires C, 57.11; H, 5.08; N, 12.11%). NMR [$(CD_3)_2CO$, 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, $^4J_{PH} = 3.9$, $=C=CHBu^t$) and 1.08 (s, 9 H, CH_3); δ_C 365.9 (d, $^2J_{CP} = 19.5$, $=C_\alpha=CHBu^t$), 146.6 (borate), 144.6 (borate), 143.3 (borate), 138.1 (d, $^3J_{CP} = 1.7$, borate), 136.32 (borate), 136.2 (d, $^2J_{CP} = 9.3$, $C^{2,6}$ of Ph), 135.7 (d, $^3J_{CP} = 1.7$ Hz, borate), 134.3 (d, $^1J_{CP} = 44.1$, *ipso*-C of Ph), 131.3 (d, $^4J_{CP} = 2.6$, C^4 of Ph), 128.5 (d, $^3J_{CP} = 9.3$ Hz, $C^{3,5}$ of Ph), 120.1 (d, $^3J_{CP} = 1.6$, $=C=C_\beta HBu^t$), 107.1 (borate), 106.5 (d, $^4J_{CP} = 1.7$ Hz, borate), 106.4 (borate), 33.7 [$C(CH_3)_3$] and 32.7 [$C(CH_3)_3$]; δ_P 38.9. $\tilde{\nu}_{max}/cm^{-1}$ 2489m (B–H), 1670s, 1645s (C=C).

$[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHCO_2Et)]$ 7. This complex was synthesized analogously to **3** with $HC\equiv CCO_2Et$ as starting material. Yield: 86% (Found: C, 54.36; H, 4.87; N, 11.34. $C_{32}H_{31}BClN_6O_2PRu$ 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, $^4J_{PH} = 3.7$, $=C=CHCO_2Et$), 4.07 (m, 2 H, diastereotopic $CO_2CH_2CH_3$) and 1.12 (t, 3 H, $CO_2CH_2CH_3$); δ_C 353.7 (d, $^2J_{CP} = 18.7$, $=C_\alpha=CHCO_2Et$), 166.7 (CO_2Et), 146.5 (borate), 144.2 (borate), 143.5 (d, $^3J_{CP} = 1.7$, borate), 136.9 (borate), 135.8 (borate), 135.4 (d, $^2J_{CP} = 10.2$, $C^{2,6}$ of Ph), 135.0 (d, $^3J_{CP} = 3.3$, borate), 131.8 (d, $^1J_{CP} = 46.6$, *ipso*-C of Ph), 130.8 (d, $^4J_{CP} = 2.6$, C^4 of Ph), 128.6 (d, $^3J_{CP} = 10.2$, $C^{3,5}$ of Ph), 106.45 (d, $^4J_{CP} = 2.5$, borate), 106.35 (borate), 106.26 (d, $^3J_{CP} = 1.4$ Hz, $=C=C_\beta HCO_2Et$), 106.22 (borate), 60.6 ($CO_2CH_2CH_3$) and 15.0 ($CO_2CH_2CH_3$); δ_P 35.2. $\tilde{\nu}_{max}/cm^{-1}$ 2511m (B–H), 1717s (C=O), 1679s (C=C) and 1602s (C=C).

$[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHC_6H_9)]$ 8. This complex was synthesized analogously to **3** with $HC\equiv CC_6H_9$ (1-ethynylcyclohexene) as starting material. Yield: 85% (Found: C, 58.03; H, 5.08; N, 11.47. $C_{35}H_{35}BClN_6PRu$ 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 C_6H_9), 4.63 (d, 1 H, $^4J_{PH} = 3.8$, $=C=CHC_6H_9$), 2.23 (m, 2 H, C_6H_9), 1.88 (m, 2 H, C_6H_9) and 1.57 (m, 4 H, C_6H_9); δ_C 373.3 (d, $^2J_{CP} = 19.5$, $=C_\alpha=CHC_6H_9$), 145.5 (borate), 144.0 (borate), 143.5 (d, $^3J_{CP} = 1.7$, borate), 136.9 (borate), 135.36 (borate), 135.3 (d, $^2J_{CP} = 9.3$, $C^{2,6}$ of Ph), 134.8 (d, $^3J_{CP} = 2.5$, borate), 133.0 (d, $^1J_{CP} = 44.1$, *ipso*-C of Ph), 130.4 (d, $^4J_{CP} = 2.5$, C^4 of Ph), 128.5 (d, $^3J_{CP} = 9.3$, $C^{3,5}$ of Ph), 126.5, 117.5, 115.5 (d, $^3J_{CP} = 1.7$, $=C=C_\beta HC_6H_9$), 106.2 (d, $^4J_{CP} = 2.6$ Hz, borate), 106.1 (borate), 106.0 (borate), 30.3 (C_6H_9), 26.3 (C_6H_9), 23.7 (C_6H_9) and 23.0 (C_6H_9); δ_P 37.6. $\tilde{\nu}_{max}$/cm^{-1} 2483m (B–H), 1641, 1624s (C=C).

[Ru{HB(pz)$_3$}Cl(PPh$_3$)(PMe$_3$)] 9. A solution of complex **3** (75 mg, 0.105 mmol) in benzene (3 cm^3) was treated with PMe_3 (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. $C_{30}H_{34}BClN_6P_2Ru$ requires C, 52.38; H, 4.98; N, 12.22%). NMR ($CDCl_3$, 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, $^2J_{PH} = 8.1$ Hz, CH_3); δ_C 146.4 (d, $^3J_{CP} = 1.9$, borate), 145.0 (d, $^3J_{CP} = 1.0$, borate), 143.2 (d, $^3J_{CP} = 1.9$, borate), 137.0 (borate), 136.4 (borate), 136.0 (borate), 135.2 (dd, $^1J_{CP} = 33.0$, $^3J_{CP} = 1.0$, *ipso*-C of Ph), 135.0 (d, $^2J_{CP} = 9.5$, $C^{2,6}$ of Ph), 129.4 (d, $^4J_{CP} = 2.4$, C^4 of Ph), 128.4 (d, $^3J_{CP} = 8.6$, $C^{3,5}$ of Ph), 106.0 (d, $^4J_{CP} = 2.4$, borate), 105.7 (borate), 105.3 (d, $^4J_{CP} = 2.4$, borate) and 17.7 (d, $^1J_{CP} = 27.6$, CH_3); δ_P 51.0 (d, $^2J_{PP} = 36.6$) and 11.4 (d, $^2J_{PP} = 36.6$ Hz).

[Ru{HB(pz)$_3$}Cl(PPh$_3$)(CO)] 10. A solution of complex **3** (187 mg, 0.262 mmol) in benzene (6 cm^3) 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 ^{13}C-{^{1}H} NMR spectra were in agreement with the literature.[7] ^{31}P-{^{1}H} NMR ($CDCl_3$, 20 °C): δ 42.4. Crystals were grown by diffusion of diethyl ether into a solution of **10** in CH_2Cl_2.

[Ru{HB(pz)$_3$}Cl(PPh$_3$)$_2$] 11. This complex has been prepared analogously to **9** with PPh_3 as the starting material. Yield: 93%. Proton, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were in agreement with the literature.[8]

[Ru{HB(pz)$_3$}Cl(PPh$_3$)(MeCN)] 12. This complex has been prepared analogously to **9**. Yield: 93%. Proton and ^{13}C-{^{1}H} NMR spectra were in agreement with the literature.[9] δ_P 51.3. $\tilde{\nu}_{max}$/cm^{-1} 2476m (B–H) and 2279s (C≡N).

[Ru{HB(pz)$_3$}Cl(PPh$_3$)(py)] 13. This complex has been prepared analogously to **9**. Yield: 91%. Proton, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were in agreement with the literature.[1e]

Reaction of complex 3 with HC≡CR (R = SiMe$_3$, Bu^n, Bu^t, CO$_2$Et or C$_6$H$_9$). In a typical procedure, a 5 mm NMR tube was charged with a solution of complex **3** (30 mg) in C_6D_6 (0.5 cm^3) and was capped with a septum. The acetylene (5 equivalents) was added by syringe and the sample transferred to an NMR probe. Proton and ^{31}P-{^{1}H} NMR spectra were immediately recorded showing the slow formation of [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=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 C_6D_6 (0.5 cm^3) and capped with a septum. Phenylacetylene (*ca.* 10 equivalents) was added by syringe and the samples were transferred to an NMR probe. Proton and ^{31}P-{^{1}H} 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 C_6D_6 (0.5 cm^3) and capped with a septum. The acetylene was added by syringe and the samples were transferred to an NMR probe. Proton and ^{31}P-{^{1}H} 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(PMe$_3$)(=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-Kα 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(PPh$_3$)$_2$] reacts readily with terminal alkynes HC≡CR (R = Ph, SiMe$_3$, Bu^n or Bu^t) to afford the neutral vinylidene complexes [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=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 PPh_3 because of incomplete conversions. Therefore, a new synthetic approach to obtaining such complexes was developed.

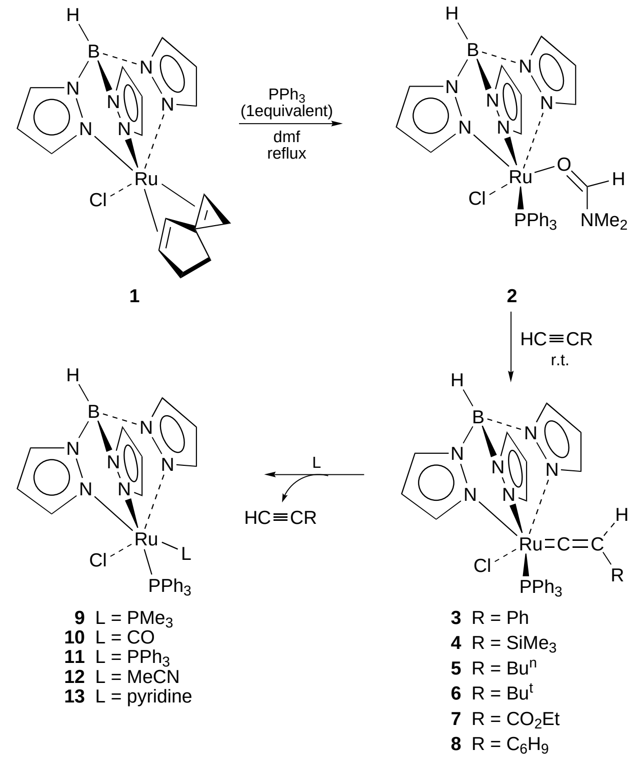
A convenient high-yield route to [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=C=CHR)] complexes proceeds through the intermediacy of [Ru{HB(pz)$_3$}Cl(PPh$_3$)(dmf)] **2**. This complex is readily obtained on treatment of [Ru{HB(pz)$_3$}Cl(cod)] **1** with 1 equivalent of PPh_3 in boiling dmf in 89% isolated yield (Scheme 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 ^{1}H and ^{13}C-{^{1}H} 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 ^{1}H NMR spectrum the NMe_2 group of dmf gives rise to a broad singlet at δ 2.68 (6 H). In the ^{13}C-{^{1}H} 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(PPh$_3$)(dmf)] **2** and [Ru{HB(pz)$_3$}Cl(PPh$_3$)(CO)] **10**

	2	**10**
Formula	$C_{30}H_{32}BClN_6OPRu$	$C_{28}H_{25}BClN_6OPRu$
M	684.93	639.84
Crystal size/mm	0.26 × 0.18 × 0.12	0.69 × 0.41 × 0.35
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	9.929(1)	31.173(3)
b/Å	15.293(2)	9.688(2)
c/Å	20.129(3)	18.545(2)
β/°	94.33(1)	93.00(1)
U/Å^3	3047.7(7)	5593.0(2)
F(000)	1400	2592
Z	4	8
D_c/g cm^{-3}	1.493	1.520
T/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	$-13 \leqslant h \leqslant 13, -18 \leqslant k \leqslant 21, -24 \leqslant l \leqslant 28$	$-39 \leqslant h \leqslant 18, -12 \leqslant k \leqslant 12, -23 \leqslant l \leqslant 23$
No. reflections measured	20 815	18 498
No. unique reflections	6977	6137
No. reflections with $F > 4\sigma(F)$	5687	5227
No. parameters	380	385
$R(F)$ [$F > 4\sigma(F)$]	0.033	0.023
(all data)	0.047	0.031
$wR(F^2)$ (all data)	0.076	0.058
Minimum, maximum Fourier-difference peaks/e Å^{-3}	−0.48, 0.46	−0.38, 0.31

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



Scheme 1 The reaction of complexes **3**–**8** with both L = PPh$_3$ 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, SiMe$_3$, Bu^n, Bu^t, CO$_2$Et or C$_6$H$_9$) at room temperature yields the respective vinylidene complexes [Ru{HB(pz)$_3$}Cl(PPh$_3$)(=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 ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR and IR spectroscopy. Characteristic NMR spectroscopic features comprise, in the ^{13}C-{^{1}H} 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 PPh$_3$ 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

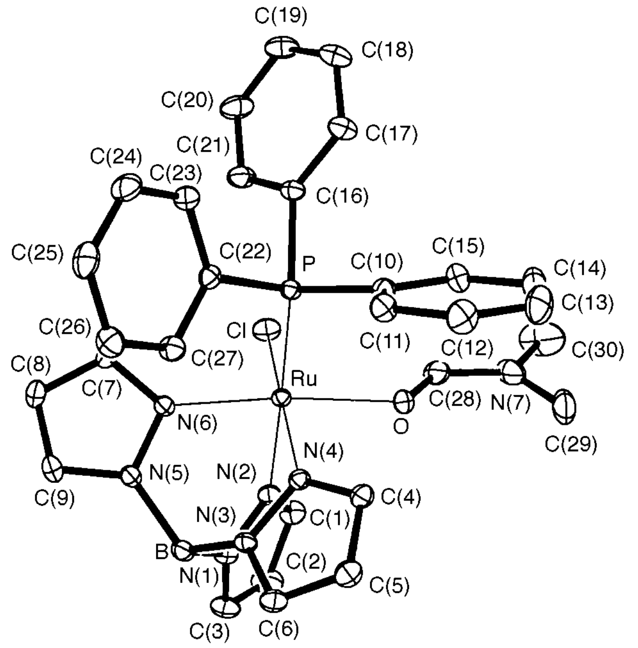


Fig. 1 Structural view of [Ru{HB(pz)$_3$}Cl(PPh$_3$)(dmf)] **2**. Selected bond lengths (Å) and angles (°): Ru–N(2) 2.139(2), Ru–N(4) 2.063(2), Ru–N(6) 2.041(2), Ru–P 2.309(1), Ru–Cl 2.424(1), Ru–O 2.154(2) and O–C(28) 1.225(4); Ru–O–C(28) 126.6(2)

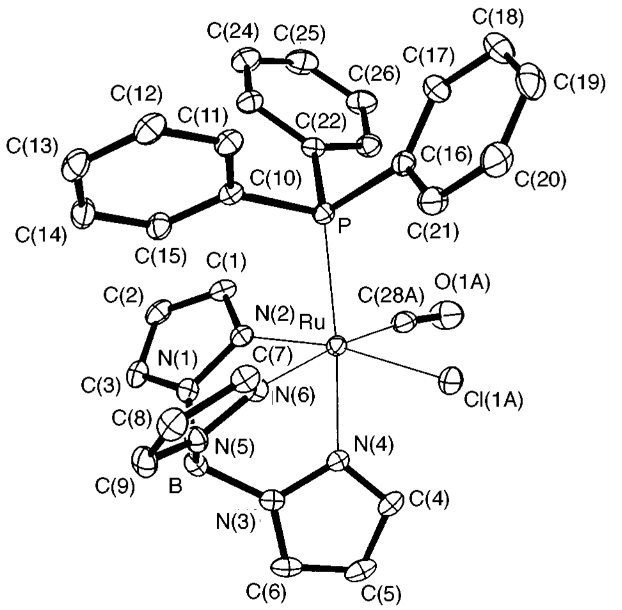
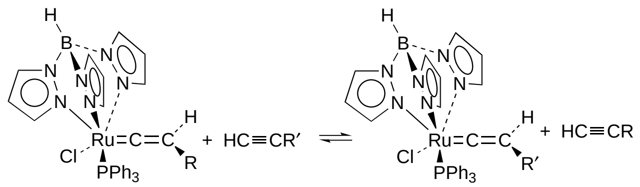


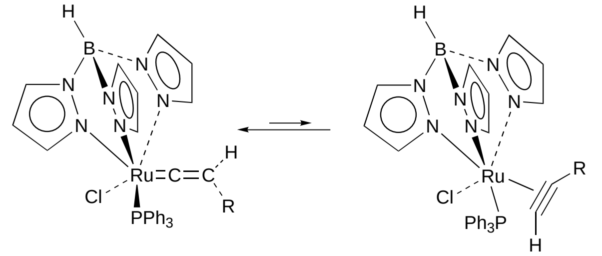
Fig. 2 Structural view of $[Ru\{HB(pz)_3\}Cl(PPh_3)(CO)]$ **10**. Selected bond lengths (Å) and angles (°): Ru–N(2) 2.116(2), Ru–N(4) 2.114(2), Ru–N(6) 2.140(2), Ru–P 2.362(1), Ru–Cl(1A) 2.418(2), Ru–C(28A) 1.848(6) and C(28A)–O(1A) 1.137(8); Ru–C(28A)–O(1A) 173.2(5), N(6)–Ru–C(28A) 173.4(2), C(28A)–Ru–Cl(1A) 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 $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)]^+$ (2.209 Å) and longer than in most other $Ru\{HB(pz)_3\}$ 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 L = PMe_3, CO, PPh_3, MeCN and pyridine. These reactions resulted in the liberation of HC≡CR and quantitative formation of the complexes $[Ru\{HB(pz)_3\}Cl(PPh_3)L]$ **9**–**13** (Scheme 1). All these are air-stable thermally robust solids and have been fully characterized by elemental analysis, ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ 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 HC≡CPh to either **11** or **13**, **3** is quantitatively regained as monitored by ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. With **9**, addition of HC≡CPh results in the liberation of PPh_3 and formation of several products including the neutral vinylidene complex $[Ru\{HB(pz)_3\}Cl(PMe_3)({=}C{=}CHPh)]$; **10** and **12**, on the other hand, are substitutionally inert with no evidence for the formation of **3** even on prolonged heating at 80 °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 =C=CHPh. Similar differences have been found with the related cationic complexes $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)(CO)]^+$ and $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)]^+$.[5] In the latter, however, the vinylidene moiety cannot be replaced by nucleophiles like CO or MeCN. Noteworthy, the vinylidene moiety in the complexes $[Ru(Pr^i{}_2PCH_2CH_2OMe)_2Cl({=}C{=}CHPh)]^+$ and $[Ru(\eta\text{-}C_5Me_5)Cl(PPh_3)({=}C{=}CHPh)]$ has recently been found to be replaceable by CO and $P(OPh)_3$.[4b,14]



Scheme 2



Scheme 3

Most remarkably, complex **3** also reacts easily with terminal acetylenes HC≡CR (R = $SiMe_3$, Bu^n, Bu^t, CO_2Et or C_6H_9) to afford reversibly the respective vinylidene complexes $[Ru\{HB(pz)_3\}Cl(PPh_3)({=}C{=}CHR)]$ **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 $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$ or $[Ru\{HB(pz)_3\}(tmen)]^+$ (tmen = $Me_2NCH_2CH_2NMe_2$) fragments to a sixth ligand was, in previous work,[5,12] found to increase in the order phosphines ≈ amines < CO ⩽ 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 $Ru\{HB(pz)_3\}Cl(PPh_3)$, reverses the stability order according to dmf < PPh_3 ≈ vinylidene < 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 $Mn(\eta\text{-}C_5H_5)(CO)_2$ is calculated to be 35 kcal mol^{-1} more stable than the acetylene one.[15a] From EH calculations, $[RhCl(PPh_3)_2({=}C{=}CH_2)]$ is more stable than $[RhCl(PPh_3)_2(\eta^2\text{-}CH{\equiv}CH)]$ by 17.1 kcal mol^{-1}.[15b] In kinetic terms, the activation enthalpy of unimolecular 1,3-hydrogen migration in d^8 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 antibonding 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 $\pi_\sigma{}^*$ (acetylene) but strong

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

	E/eV					
Fragment	$\Psi_{Ru}1$ $\sigma^*,d_{x^2-y^2}$	$\Psi_{Ru}2$ σ^*,d_{z^2}	$\Psi_{Ru}3$ π,d_{xy}	$\Psi_{Ru}4$ π,d_{xz}	$\Psi_{Ru}5$[a] π,d_{yz}	Overlap population $\langle d_{yz}\|p\rangle$
$[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$	−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 $\Psi_{Ru}5$ 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.

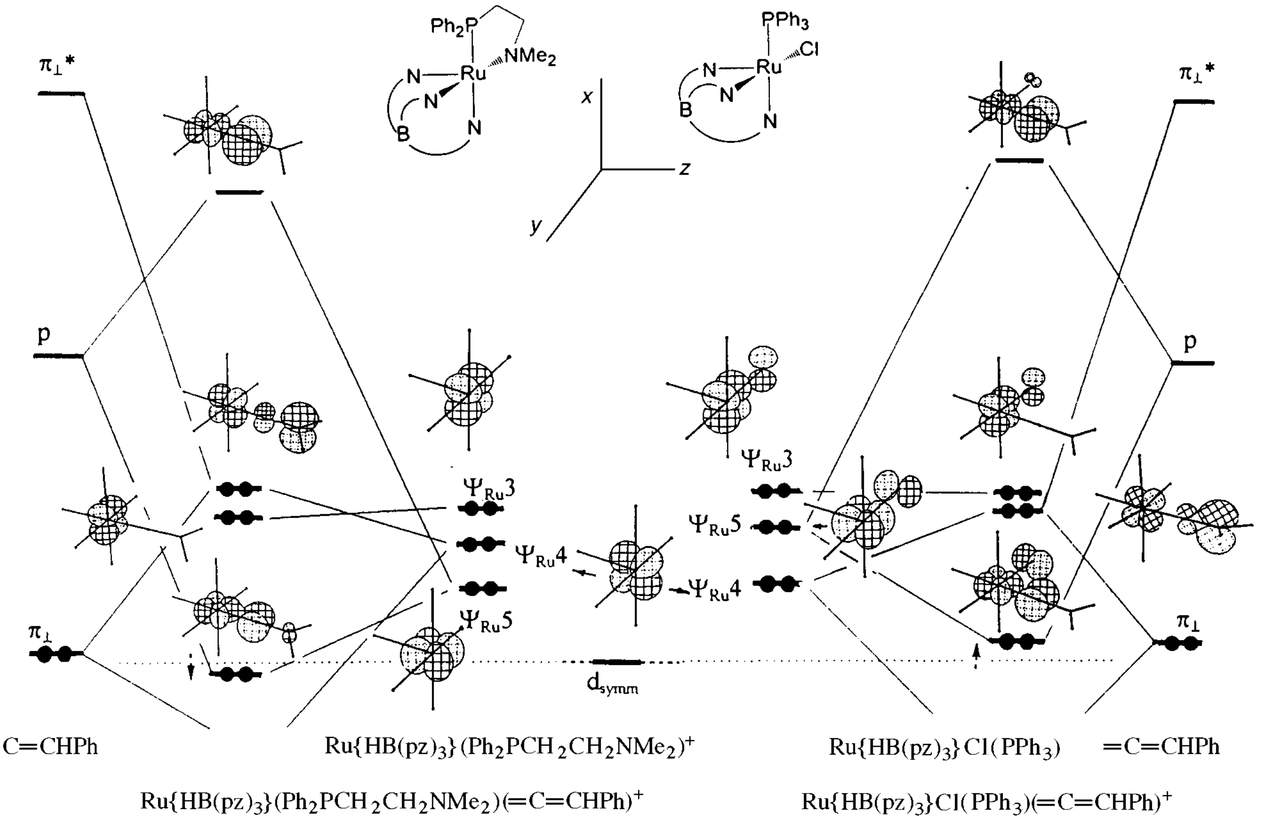


Fig. 3 Qualitative orbital-interaction diagram for the formation of $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)]^+$ and $[Ru\{HB(pz)_3\}Cl(PPh_3)({=}C{=}CHPh)]$ complexes

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(π) atomic orbitals (AOs) and both p(Cl) AOs. The orbital $\Psi_{Ru}1$ ('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 $\Psi_{Ru}3$ (1a′, or 'classical' d_{xy}). The variation of $\Psi_{Ru}1$ 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 $\Psi_{Ru}2$ ['classical' d_{z^2}, identical to 3a′ in ref. 15(*a*)] and has also appreciable π affinity *via* $\Psi_{Ru}4$ and $\Psi_{Ru}5$ ['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 $\Psi_{Ru}2$ level, likely due to the higher electronegativity of Cl over sp^3 N; (*ii*) chlorine destabilizes the d(π) orbitals $\Psi_{Ru}3$ and $\Psi_{Ru}5$, since the $p_x(Cl)$–$d_{xy}(Ru)$ and $p_z(Cl)$–$d_{yz}(Ru)$ interactions are antibonding in character (see Fig. 3). On the other hand, the $d_{xz}(Ru)$–$\pi_\perp$(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} ($\Psi_{Ru}5$) < d_{xz} ($\Psi_{Ru}4$) < d_{xy} ($\Psi_{Ru}3$) in $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$ to d_{xz} ($\Psi_{Ru}4$) < d_{yz} ($\Psi_{Ru}5$) < d_{xy}($\Psi_{Ru}3$) 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 $\Psi_{Ru}2$ and $\Psi_{Ru}5$ 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.
$[\mathrm{Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)}]^+$	1.821(5)	1.287(2)	169.6(4)	5
$[\mathrm{Ru\{HB(pz)_3\}(tmen)({=}C{=}CHPh)}]^+$	1.820(5)	1.305(6)	173.5(4)	12
$[\mathrm{Ru\{HB(pz)_3\}Cl(PPh_3)({=}C{=}CHPh)}]$	1.801(4)	1.315(6)	177.2(3)	1(*e*)
$[\mathrm{Ru(\eta\text{-}C_5Me_5)(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)}]^+$	1.81(2)	1.33(2)	173(1)	16
$[\mathrm{Ru(\eta\text{-}C_5Me_5)Cl(PPh_3)({=}C{=}CHPh)}]$	1.80(1)	1.40(2)	176(1)	14
$[\mathrm{W(\eta\text{-}C_5H_5)\{P(OMe)_3\}_2({=}C{=}CMePh)}]^+$	1.947(6)	1.330(9)	177.6(5)	4(*c*)
$[\mathrm{W(CO)(Ph_2PCH_2CH_2PPh_2)({=}C{=}CHCO_2Me)}]$	1.88(1)	1.36(1)	171.2(9)	3(*d*)
$[\mathrm{RhCl(PPr^i{}_3)_2({=}C{=}CHMe)}]$	1.775(6)	1.32(1)	177.9(6)	3(*a*)
$[\mathrm{RuBr_2(PPh_3)_2({=}C{=}CHBu^t)}]$	1.77(1)	1.36(3)	162(2)	3(*c*)
$[\mathrm{RuCl(\kappa^2}P,O\mathrm{\text{-}Pr^i{}_2PCH_2CH_2OMe)_2({=}C{=}CHPh)}]^+$	1.790(3)	1.313(5)	170.9(3)	4(*b*)

This is independent of the nature of the sixth ligand, $\mathrm{PPh_3}$ (very weak π bonder), CO (two π* MOs) and vinylidene (p and π/π* MOs). Also seen in Fig. 3, in $[\mathrm{Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)}]^+$ both the HOMO and lowest unoccupied molecular orbital (LUMO) are antibonding, whereas the HOMO in $[\mathrm{Ru\{HB(pz)_3\}Cl(PPh_3)({=}C{=}CHPh)}]$ 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 $\langle d_{yz}|p\rangle = 0.22$ 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 $\langle d_{yz}|p\rangle$ (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 $\langle d_{yz}|p\rangle$ is also displayed by the increasing $C_\alpha{=}C_\beta$ bond length from 1.287(2) Å in $[\mathrm{Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)(C{=}CHPh)}]^+$ to 1.315(6) Å in $[\mathrm{Ru\{HB(pz)_3\}Cl(PPh_3)(C{=}CHPh)}]$, similar to $\mathrm{C_5Me_5}$ analogs from 1.33(2) Å in $[\mathrm{Ru(\eta\text{-}C_5Me_5)(Ph_2PCH_2CH_2NMe_2)(C{=}CHPh)}]^+$[16] to 1.40(2) Å in $[\mathrm{Ru(\eta\text{-}C_5Me_5)Cl(PPh_3)(C{=}CHPh)}]$[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 [$\pi_\parallel$* in Fig. 4 of ref. 15(*a*)], which is perpendicular to the $C_\alpha{=}C_\beta$ π bond plane, but not to π* [$\pi_\perp$* in Fig. 4 of ref. 15(*a*)]. Consequently, two types of back bonding should be distinguished. Similar $C_\alpha{=}C_\beta$ bond-length variations are displayed when the adjacent atom is a non-metal in the series $\mathrm{CH_2{=}C_\alpha{=}C_\beta H_2}$ (1.3084)[17a] < $\mathrm{{:}C_\alpha{=}C_\beta H_2}$ (1.312)[17b] < $\mathrm{O{=}C_\alpha{=}C_\beta H_2}$ (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 ($\mathrm{{:}CH_2}$). Related changes in bond length occur in the series: $\mathrm{S{=}C_\alpha{=}C_\beta{=}PPh_3}$ (1.209) ≈ $\mathrm{O{=}C_\alpha{=}C_\beta{=}PPh_3}$ (1.210) < $\mathrm{PhN{=}C_\alpha{=}C_\beta{=}PPh_3}$ (1.248) < $\mathrm{(EtO)_2C_\alpha{=}C_\beta{=}PPh_3}$ (1.314 Å).[17c] Contrary to the marked difference between $[\mathrm{Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)({=}C{=}CHPh)}]^+$ and $[\mathrm{Ru\{HB(pz)_3\}Cl(PPh_3)({=}C{=}CHPh)}]$, 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, $\mathrm{PPh_3}$ as the sixth ligand, which is a 'classical' sp^3 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 $\Psi_{\mathrm{Ru}}5$ 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 $\mathrm{Ru{-}C_\alpha{-}C_\beta{-}Ph}$ plane.[15a] Therefore, the p(vinylidene) ⟷ $\Psi_{\mathrm{Ru}}5$ interaction should play the dominant role for this conversion. If this contribution is small, *i.e.* weak Ru=C bond, vinylidene ⟶ η^2-alkyne reconversion is feasible. Note that the $\pi_\perp$ (vinylidene) ⟷ $\Psi_{\mathrm{Ru}}4$ 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_{xz}(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, reconversion of a vinylidene complex into an η^2-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*-$[\mathrm{Mo(\eta\text{-}C_5H_5)(CO)\{P(OMe)_3\}_2({=}C{=}CHCMe_3)}]^+$ (with a *cis*-P-Mo-vinylidene construction) into the acetylene complex, whereas the $\mathrm{PPhMe_2}$ analog is stable.[4c] Actually, $\mathrm{P(OMe)_3}$ is a strong π acceptor, in contrast to $\mathrm{PPhMe_2}$. When placed in *cis* position it reduces the $\langle d_{yz}|p\rangle$. Similarly, the π interaction of the carbene's p with the $\mathrm{M(\eta\text{-}C_5H_5)(CO)_3}$ fragment is reduced by the CO ligands.[18] This gives rise to vinylidene–acetylene rearrangement in the supposed structures $[\mathrm{Mo(\eta\text{-}C_5H_5)(CO)_3(C^+{=}CHPh)}]\mathrm{BF_4}$ or $[\mathrm{W(\eta\text{-}C_5H_5)(CO)_3(C^+{=}CHPh)}]\mathrm{BF_4}$.[4a]

Acknowledgements

Financial support by the Fonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged (Project No. 11896). V. N. S. thanks D. Mendeleyev University of Chemical Technology of Russia, Moscow for leave of absence.

References

1 (*a*) C. A. Merlic and M. E. Pauly, *J. Am. Chem. Soc.*, 1996, **118**, 11 319; (*b*) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh and J. Y. Satoh, *J. Am. Chem. Soc.*, 1991, **113**, 9604; (*c*) B. M. Trost and J. A. Flygare, *J. Am. Chem. Soc.*, 1992, **114**, 5476; (*d*) B. M. Trost, G. Dyker and R. Kulawiec, *J. Am. Chem. Soc.*, 1990, **112**, 7809; (*e*) C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid and K. Kirchner, *Organometallics*, 1996, **15**, 5275; (*f*) C. Gemel, G. Kickelbick, R. Schmid and K. Kirchner, *J. Chem. Soc., Dalton Trans.*, 1997, 2113.

2 (*a*) M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; (*b*) B. M. Trost, *Angew. Chem.*, 1995, **107**, 285; (*c*) P. C. Ting, Y. C. Lin, G. H. Lee, M. C. Cheng and Y. Wang, *J. Am. Chem. Soc.*, 1996, **118**, 6433; (*d*) C. Bianchini, M. Peruzzini, A. Romerosa and F. Zanobini, *Organometallics*, 1995, **14**, 3152; (*e*) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa and F. Zanobini, *Organometallics*, 1996, **15**, 272; (*f*) H. Werner, R. Wiedmann, P. Steinert and J. Wolf,

Chem. Eur. J., 1997, **3**, 127; (*g*) R. P. Duran, V. T. Amorebieta and A. J. Colussi, *J. Am. Chem. Soc.*, 1987, **109**, 3154.

3 (*a*) Y. Wakatsuki, N. Koga, H. Werner and K. Morokuma, *J. Am. Chem. Soc.*, 1997, **119**, 360; (*b*) G. Nakamura, Y. Harada, Y. Mizobe and M. Hidai, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3305; (*c*) Y. Wakatsuki, N. Koga, H. Yamazaki and K. Morokuma, *J. Am. Chem. Soc.*, 1994, **116**, 8105; (*d*) M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1996, 1009; (*e*) P. Nombek, N. Lugan and R. Mathieu, *J. Organomet. Chem.*, 1995, **503**, C22; (*f*) G. Consiglio, F. Bangerter, C. Darpin, F. Morandini and V. Luccini, *Organometallics*, 1984, **3**, 1446.

4 (*a*) N. E. Kolobova, V. V. Skripkin, T. V. Rozanzeva, Y. T. Strukov, G. G. Alexandrov, V. A. Antonovich and V. I. Bakhumov, *Koord. Khim.*, 1982, **8**, 1655; (*b*) M. Martin, O. Gevert and H. Werner, *J. Chem. Soc., Dalton Trans.*, 1996, 2275; (*c*) P. N. Nicklas, J. P. Selegue and B. A. Young, *Organometallics*, 1988, **7**, 2248.

5 G. Trimmel, C. Slugovc, P. Wiede, K. Mereiter, V. N. Sapunov, R. Schmid and K. Kirchner, *Inorg. Chem.*, 1997, **36**, 1076.

6 C. Gemel, G. Trimmel, C. Slugovc, K. Mereiter, S. Kremel, R. Schmid and K. Kirchner, *Organometallics*, 1996, **15**, 3998.

7 N.-Y. Sun and S. J. Simpson, *J. Organomet. Chem.*, 1992, **434**, 341.

8 N. W. Alcock, I. D. Burns, K. S. Claire and A. F. Hill, *Inorg. Chem.*, 1992, **31**, 2906.

9 W.-C. Chan, C.-P. Lau, Y.-Z. Chen, Y.-Q. Fang, S.-M. Ng and G. Jia, *Organometallics*, 1997, **16**, 34.

10 G. M. Sheldrick, (*a*) SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1986; (*b*) SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

11 (*a*) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179; (*b*) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 3489; (*c*) R. Hoffman, *J. Chem. Phys.*, 1963, **39**, 1397; (*d*) C. Mealli and D. M. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399.

12 C. Gemel, P. Wiede, K. Mereiter, V. N. Sapunov, R. Schmid and K. Kirchner, *J. Chem. Soc., Dalton Trans.*, 1996, 4071.

13 (*a*) N. W. Alcock, A. F. Hill and R. B. Melling, *Organometallics*, 1991, **10**, 3898; (*b*) A. F. Hill, *J. Organomet. Chem.*, 1990, **395**, C35; (*c*) M. M. deV. Steyn, E. S. Singleton and D. C. Liles, *J. Chem. Soc., Dalton Trans.*, 1990, 2991; (*d*) A. M. McNair, D. C. Boyd and K. R. Mann, *Organometallics*, 1986, **5**, 303.

14 M. I. Bruce, B. C. Hall, N. N. Zaitseva, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1996, **522**, 307.

15 (*a*) J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, 1985, **68**, 1461; (*b*) S. K. Kang, J. S. Song, J. H. Moon and S. S. Yun, *Bull. Korean Chem. Soc.*, 1996, **17**, 1149.

16 K. Mauthner, C. Slugovc, K. Mereiter, R. Schmid and K. Kirchner, *Organometallics*, 1997, **16**, 1956.

17 (*a*) *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 75th edn., 1995, pp. 9-25, 9-34; (*b*) D. A. Plattner, Y. Li and K. N. Monk, in *Modern Acetylene Chemistry*, eds. P. J. Stang and F. Diederid, VCH, Weinheim, 1995, p. 3; (*c*) H. Burzlaff, R. Haag, E. Wilhelm and H. J. Bestmann, *Chem. Ber.*, 1985, **118**, 1720.

18 B. E. R. Schilling, R. Hoffmann and D. L. Lichtenberg, *J. Am. Chem. Soc.*, 1979, **103**, 585.

Received 1*st April* 1997; *Paper* 7/02194A