DALTON

Synthesis and reactivity of [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(OCH$_2$R)] (pz = pyrazolyl, R = H or Me)†

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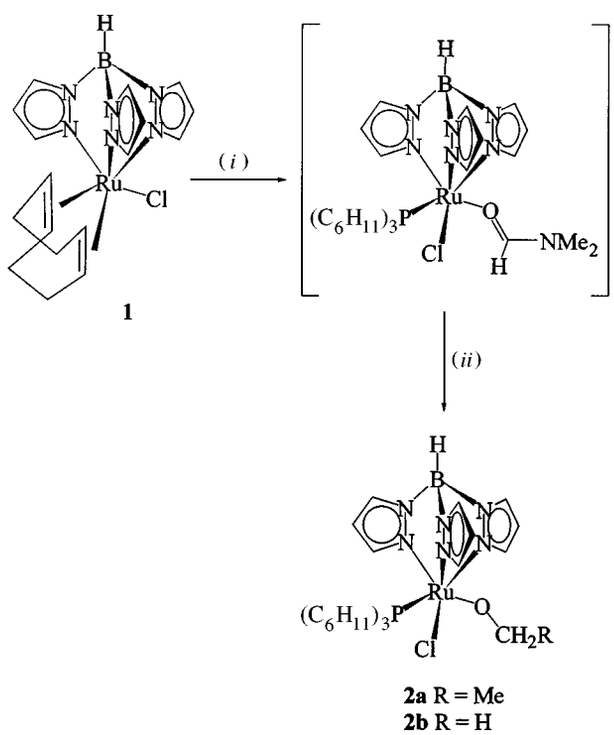
The complex [Ru{HB(pz)$_3$}(cod)Cl] **1** (cod = cycloocta-1,5-diene) reacted with P(C$_6$H$_{11}$)$_3$ (≥1 equivalent) in boiling dimethylformamide (dmf) to give the highly air-sensitive intermediate [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(dmf)] which, on exposure to air in either ethanol or methanol as the solvent, was converted to the ruthenium(III) complexes [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(OCH$_2$R)] (R = Me **2a** or H **2b**) in good yields. Complex **2b** has been characterized by X-ray crystallography. Treatment of **2a** or **2b** with L = MeCN, pyridine, CO, P(OMe)$_3$, or PMe$_3$ in CH$_2$Cl$_2$ afforded the (diamagnetic) ruthenium(II) compounds [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}(Cl)L] **3**–**7**. Most remarkably, **2a** or **2b** reacted also with terminal alkynes HC≡CR (R = Ph, CO$_2$Et, Bu^n or SiMe$_3$) giving the neutral vinylidene complexes [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl (=C=CHR)] **8**–**11**. Preliminary results of a study of the catalytic activity of **2** are also presented. Thus, **2a** and **2b** catalysed the dimerization of some terminal alkynes HC≡CR (R = Ph, CO$_2$Et or SiMe$_3$).

In our continuing systematic studies of the chemistry of ruthenium tris(pyrazolylborate) complexes[1–5] we have recently shown that [Ru{HB(pz)$_3$}(PPh$_3$)Cl(dmf)] (pz = pyrazolyl, dmf = dimethylformamide) is a very usable precursor for the easy production of a variety of complexes of the types [Ru{HB(pz)$_3$}(PPh$_3$)(Cl)L] and [Ru{HB(pz)$_3$}(PPh$_3$)Cl(=C=CHR)] (R = CO$_2$Et, Bu^n or SiMe$_3$).[1] The method fails, however, when bulkier phosphines such as P(C$_6$H$_{11}$)$_3$ or PPr$^i_3$ are used instead of PPh$_3$. The reason is that the corresponding complex [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(dmf)] is extremely air-sensitive and, in addition, dmf is highly labilized obviously due to both the greater steric demand as well as the higher basicity of P(C$_6$H$_{11}$)$_3$ relative to PPh$_3$. When [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(dmf)] was used *in situ* in the presence of an alcohol (MeOH or EtOH) the novel complexes [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(OCH$_2$R)] (R = H or Me) were formed. In making a virtue of necessity, the complexes appear to be useful precursors for new complexes of the types [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}(Cl)L] [L = MeCN, pyridine, CO, P(OMe)$_3$ or PMe$_3$] and [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(=C=CHR)] (R = Ph, CO$_2$Et, SiMe$_3$ or Bu^n).

Results and Discussion

Synthesis of [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(OCH$_2$R)] (R = Me or H)

The complexes [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$Cl(OCH$_2$R)] (R = Me **2a** or H **2b**) were synthesized in a one-pot reaction with [Ru{HB(pz)$_3$}(cod)Cl] **1** (cod = cycloocta-1,5-diene) used as the starting material. This reaction appears to proceed *via* the highly reactive intermediate [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(dmf)]. Though the latter complex could not be isolated in pure form, the PPh$_3$ analogue [Ru{HB(pz)$_3$}(PPh$_3$)Cl(dmf)] has recently been isolated and crystallographically characterized.[2] When **1** is refluxed in dmf in the presence of P(C$_6$H$_{11}$)$_3$ (≥1 equivalent) and the resulting solid residue is exposed to air in ethanol or methanol as the solvent, complexes **2a** and **2b** are, on work-up, obtained in 65 and 49% yields (Scheme 1). It should be noted that even in the presence of P(C$_6$H$_{11}$)$_3$ in excess



2a R = Me
2b R = H

Scheme 1 (*i*) P(C$_6$H$_{11}$)$_3$, dmf, reflux; (*ii*) RCH$_2$OH, O$_2$

there was no evidence of the formation of [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}$_2$Cl], apparently for steric reasons. A similar observation has been made in the case of Ru(η^5-C$_5$Me$_5$) complexes.[6] Complexes **2a** and **2b** are thermally robust red solids which are stable to air both in the solid state and in solution.

Characterization was by elemental analysis. The NMR spectra exhibited severe line broadening due to the paramagnetic nature of the complexes. The measured magnetic moment of **2b** is μ_{eff} = 1.83μ_B at 295 K, consistent with a d^5 (Ru^{III}) low-spin configuration with one unpaired electron. The molecular structure of **2b** is depicted in Fig. 1 with important bond distances. The co-ordination geometry is approximately octahedral with all angles at ruthenium being between 88 and 96

† Ruthenium tris(pyrazolyl)borate complexes. Part 5.[1]

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

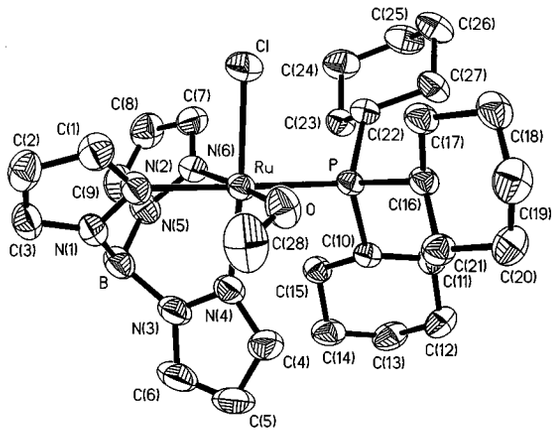


Fig. 1 Structural view of $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl(OMe)]$ **2b**. Selected bond lengths (Å) and angles (°): Ru–O 1.943(1), Ru–N(2) 2.133(2), Ru–N(4) 2.084(2), Ru–N(6) 2.109(2), Ru–Cl 2.370(1), Ru–P 2.394(1) and O–C(28) 1.370(4); C(28)–O–Ru 123.8(2), Cl–Ru–N(4) 174.7(1), N(6)–Ru–O 175.4(1) and N(2)–Ru–P 177.3(1)

and 175 and 177°. The three Ru–N (pz) bond lengths show only small deviations from the average distance of 2.108(2) Å, which is within the range of related ruthenium complexes.[1–5,7] The Ru-O distance and the Ru-O-C(28) angle is 1.943(1) Å and 123.8(2)°, respectively. This means that there are no structural features implying unusual deviations or distortions. It should be noted that the Ru-Cl distance is only 2.370(1) Å, which is somewhat shorter than those found in many other $HB(pz)_3$ complexes of Ru^{II}, *e.g.* 2.409(3) Å in $[Ru\{HB(pz)_3\}(PPh_3)_2Cl]$,[8] 2.401(1) Å in $[Ru\{HB(pz)_3\}(PPh_3)Cl(=C=CHPh]$[1] and 2.418(2) Å in $[Ru\{HB(pz)_3\}(PPh_3)Cl(CO)]$.[9]

Complexes **2a** and **2b** turned out to be useful reagents for the preparation of compounds of the types $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}(Cl)L]$ and $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl(=C=CHR)]$ as will be outlined in the following paragraphs.

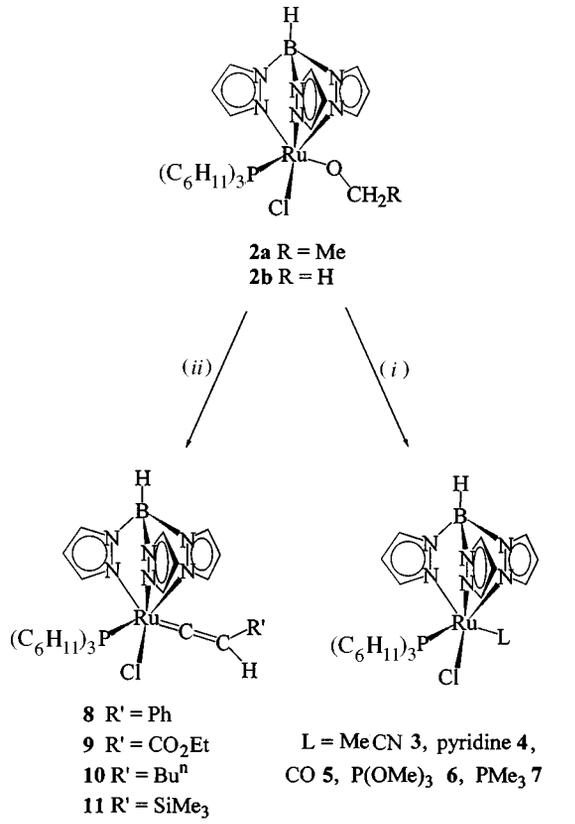
Reaction of $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl(OCH_2R)]$ with MeCN, pyridine, CO, $P(OPh)_3$, PMe_3 and HC≡CR′ (R′ = Ph, CO_2Et, Bu^n or $SiMe_3$)

Treatment of complex **2a** or **2b** with L = MeCN, pyridine, CO, $P(OMe)_3$ and PMe_3 in CH_2Cl_2 affords the diamagnetic ruthenium(II) compounds $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}(Cl)L]$ **3–7** each in high yields (Scheme 2). All these compounds are thermally robust solids which are stable to air both in the solid state and in solution. Characterization was by elemental analysis, ^1H and ^{31}P-$\{^1H\}$ NMR spectroscopy, and in the case of **4–6** also by ^{13}C-$\{^1H\}$ NMR spectroscopy, noting no unusual features.

The reaction of complex **2a** with L = MeCN, py, CO, $P(OMe)_3$ and PMe_3 has been monitored by ^1H NMR spectroscopy showing the formation **3–7** together with 0.5 equivalent of acetaldehyde and 0.5 equivalent of ethanol according to equation (1). In the absence of kinetic data it should just

$$2[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl(OEt)] + 2\,L \longrightarrow \underset{\mathbf{2a}}{} \quad 2[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}(Cl)L] + MeCHO + EtOH \quad (1)$$
$$\underset{\mathbf{3–7}}{}$$

be noted that the reaction rate seems to increase with the basicity of L. In the same way the reaction of **2b** is found to release 0.5 equivalent of each formaldehyde and methanol. Overall, reaction (1) represents the recombination of two alkoxy radicals. In order to see whether a free-radical pathway operates, we treated **2a** in $CDCl_3$ with a five-fold excess of $P(OMe)_3$ in the presence of an eight-fold excess of Pr^iOH. Since in the ^1H NMR spectrum no acetone could be detected (but a small amount of acetaldehyde) homolytic Ru–O bond cleavage can be ruled out. An alternative, although speculative, pathway could be initial β elimination in **2a** with the ruthenium(III) hydride complex formed reacting with another molecule of **2a**.



Scheme 2 (*i*) L; (*ii*) HC≡CR′

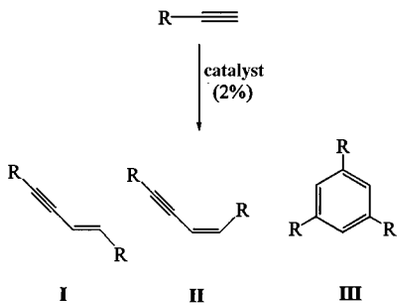
Most remarkably, complex **2a** (**2b**) reacts also with terminal alkynes HC≡CR′ (R′ = Ph, CO_2Et, Bu^n or $SiMe_3$) in CH_2Cl_2 giving the neutral vinylidene complexes $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl(=C=CHR')]$ **8–11** according to equation (1) (Scheme 2) in high yields, except for **8**. All of these solids are pale red, air stable in the solid state, but decompose slowly in aerobic solutions to the carbonyl complex $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl(CO)]$ **5**, adding to the known cases of the oxidation of ruthenium(II) vinylidene complexes by dioxygen.[10] In another type of conversion, complex **11** reacts with MeOH as the solvent at room temperature to give the alkoxycarbene complex $[Ru\{HB(pz)_3\}\{P(C_6H_{11})_3\}Cl\{=C(OMe)Me\}]$ **12** in almost quantitative yield. All other vinylidene complexes are stable in this solvent.

All the vinylidene complexes have been characterized by ^1H and ^{31}P-$\{^1H\}$ NMR and, in the case of sufficient stability as for **10** and **11**, ^{13}C-$\{^1H\}$ NMR spectra. In the latter there are characteristic low-field resonances at δ 361.0 and 340.2 assignable to the α-carbon of the vinylidene moiety. The C_β hydrogen atom gives rise to a resonance in the range from δ 4.06 to 3.71 (1 H). Finally, the resonances of the $HB(pz)_3$ and $P(C_6H_{11})_3$ ligands are in the expected ranges.

Catalytic dimerization of terminal acetylenes

Reaction of complex **2b** with an excess of HC≡CPh in toluene at reflux for 20 h results in the formation (about 50% conversion) of the head-to-head dimers (*E*)-1,4-diphenylbut-1-en-3-yne (**I**) and the *Z* isomer (**II**) in 67 and 33% yields, respectively (Table 1). The selectivity is found to vary with the alkyne substituent as follows. For R = CO_2Et the reaction is selective giving predominantly the head-to-head dimer **I** and only small amounts of the 1,3,5-tricarboxylic acid ester **III**, while for R = $SiMe_3$ the regioselectivity is reversed with no **I** but 100% of **II**. For R = Bu^n, no coupling reaction took place at all.

Table 1 Conversion and product distribution of the catalytic dimerization of terminal alkynes



		Product (%)			
Catalyst	R	I	II	III	% Conversion
2b	Ph	67	33		50
2a	CO_2Et	91		9	44
2b	$SiMe_3$		100		47
2a	Bu^n				0

The mechanism of the catalytic dimerization of terminal alkynes can only be speculated upon at present. From our preceding paper it is reasonable to suggest that the reaction is initiated by the neutral vinylidene complex [Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(=C=CHR)] formed as an intermediate with subsequent HCl elimination affording a 16e alkynyl catalyst.[2] Neutral vinylidene complexes have been shown recently to undergo 1,3-HCl eliminations upon treatment with base to give 16e alkynyl intermediates which could be trapped in the presence of potential ligands such as CO, pyridine or MeCN.[11] Similar intermediates have been suggested to be involved in the coupling reaction of terminal acetylenes catalysed by [Ru{$HB(pz)_3$}$(PPh_3)_2$Cl] and [Ru(η^5-C_5Me_5)$(PR_3)H_3$] (R = Ph, Me or C_6H_{11}).[2,12]

Experimental

General information

All reactions were performed under an inert atmosphere of purified argon using Schlenk techniques. All chemicals were standard reagent grade used without further purification. The solvents were purified according to standard procedures. The deuteriated solvents (Aldrich) were dried over 4 Å molecular sieves. The complex [Ru{$HB(pz)_3$}(cod)Cl] was prepared according to the literature.[5] 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%). Microanalyses were by Microanalytical Laboratories, University of Vienna.

Syntheses

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(OEt)] 2a. A solution of complex **1** (465 mg, 1.02 mmol) in dmf (8 cm^3) was treated with $P(C_6H_{11})_3$ (285 mg, 1.02 mmol) and the mixture heated under reflux for 2 h. After removal of the solvent, ethanol was added and air was admitted to the solution, whereupon an immediate change from yellow to dark red occurred. After 15 min a red precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 445 mg (65%) (Found: C, 51.25; H, 7.3; N, 12.25. $C_{29}H_{48}BClN_6OPRu$ requires C, 51.6; H, 7.15; N, 12.45%).

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(OMe)] 2b. This complex was synthesized analogously to **2a** using methanol instead of ethanol as the solvent. Yield: 49% (Found: C, 50.75; H, 7.1; N, 12.6. $C_{28}H_{46}BClN_6OPRu$ requires C, 50.9; H, 7.0; N, 12.7%). $\mu_{eff} = 1.83\mu_B$ (295 K).

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(MeCN)] 3. A solution of complex **2a** (70 mg, 0.104 mmol) in benzene (5 cm^3) was treated with MeCN (0.1 cm^3, 1.91 mmol) and the mixture stirred at 70 °C for 5 h. After removal of the solvent the residue was redissolved in acetone and the product precipitated by addition of diethyl ether and light petroleum (b.p. 40–70 °C). It was collected on a glass frit, washed with light petroleum and dried under vacuum. Yield: 51 mg (73%) (Found: C, 52.1; H, 7.05; N, 14.25. $C_{29}H_{46}BClN_7PRu$ requires C, 51.9; H, 6.9; N, 14.6%). NMR (C_6D_6, 20 °C): δ_H 8.30 (m, 2 H), 7.71 (d, 2 H, J = 2.5), 7.63 (d, 1 H, J = 1.6), 7.57 (d, 1 H, J = 2.5 Hz), 6.15–6.00 (m, 3 H), 2.57 (m, 3 H), 2.10–1.60 (m, 30 H) and 1.53 (s, 3 H, CH_3CN); δ_P 38.5.

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(py)] 4. A solution of complex **2a** (70 mg, 0.104 mmol) in CH_2Cl_2 (5 cm^3) was treated with pyridine (py) (0.1 cm^3, 1.24 mmol) and stirred at room temperature for 12 h. After removal of the solvent the residue was redissolved in CH_2Cl_2 and the product precipitated by addition of diethyl ether and light petroleum. It was collected on a glass frit, washed with light petroleum and dried under vacuum. Yield: 60 mg (81%) (Found: C, 54.05; H, 7.05; N, 13.6. $C_{32}H_{48}BClN_7PRu$ requires C, 54.2; H, 6.8; N, 13.85%). NMR ($CDCl_3$, 20 °C): δ_H 9.7 (br s, 2 H, py), 8.07 (s, 1 H), 7.85 (s, 1 H), 7.52 (s, 1 H), 7.49 (m, 1 H, py), 7.21 (s, 1 H), 6.98 (s, 1 H), 6.90 (br s, 2 H, py), 6.24 (s, 1 H), 6.19 (s, 1 H), 6.04 (s, 1 H) and 2.23–1.05 (m, 33 H); δ_C 148.4, 146.8, 142.3, 137.3, 136.2, 134.5, 134.4, 128.9, 128.5, 128.1, 123.4, 36.4 (br s), 30.0 (br s), 28.9 and 27.08; δ_P 34.5.

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(CO)] 5. A solution of complex **2a** (70 mg, 0.104 mmol) in CH_2Cl_2 (5 cm^3) was purged with CO for 5 min and then stirred for 48 h. After removal of the solvent the residue was redissolved in CH_2Cl_2 and the product precipitated by addition of diethyl ether and light petroleum. It was collected on a glass-frit, washed with light petroleum and dried under vacuum. Yield: 52 mg (76%) (Found: C, 50.95; H, 6.65; N, 12.55. $C_{28}H_{43}BClN_6OPRu$ requires C, 51.1; H, 6.6; N, 12.75%). NMR ($CDCl_3$, 20 °C): δ_H 8.11 (s, 1 H), 7.89 (s, 1 H), 7.77 (s, 1 H), 7.72 (s, 1 H), 7.49 (s, 1 H), 7.42 (s, 1 H), 7.26 (s, 1 H), 6.27 (s, 1 H), 6.19 (s, 1 H), 6.13 (s, 1 H), 2.45–2.10 (m, 3 H), 1.93–1.45 (m, 21 H) and 1.42–1.0 (m, 9 H); δ_C 205.9 (d, J = 14.5), 146.4, 144.8, 143.1, 137.1, 136.6, 134.5, 106.9, 106.0, 105.7, 34.8 (d, J = 19.3), 29.6, 29.4 and 28.1 (d, J = 9.6 Hz); δ_P 35.3.

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl{$P(OMe)_3$}] 6. This complex was prepared analogously to **4** using $P(OMe)_3$ instead of pyridine. Yield: 84% (Found: C, 47.6; H, 7.1; N, 10.85. $C_{30}H_{52}BClN_6O_3P_2Ru$ requires C, 47.8; H, 6.95; N, 11.15%). NMR ($CDCl_3$, 20 °C): δ_H 8.14 (d, 1 H, J = 1.7), 7.92 (d, 1 H, J = 2.1), 7.84 (d, 1 H, J = 2.1), 7.71 (d, 1 H, J = 2.44), 7.68 (s, 1 H), 7.49 (d, 1 H, J = 2.44), 6.21 (m, 1 H), 6.05 (m, 2 H), 3.39 (d, 9 H, J = 10.1), 2.46 (m, 3 H) and 1.93–1.05 (m, 30 H); δ_C 150.1, 145.5 (d, J = 3.8), 145.2, 137.8, 135.4 (d, J = 2.9), 134.7, 106.3 (d, J = 3.8), 105.7 (d, J = 1.9), 104.9, 52.3 (d, J = 7.2), 38.0 (m), 29.6 (br s), 29.1 (d, J = 8.6) and 27.3; δ_P 146.9 (d, J = 50.9) and 28.7 (d, J = 50.9 Hz).

[Ru{$HB(pz)_3$}{$P(C_6H_{11})_3$}Cl(PMe_3)] 7. This complex was prepared analogously to **4** using PMe_3 instead of pyridine. Yield: 59% (Found: C, 52.85; H, 7.55; N, 11.75. $C_{30}H_{52}BClN_6P_2Ru$ requires C, 51.05; H, 7.4; N, 11.9%). NMR ($CDCl_3$, 20 °C): δ_H 8.02 (d, 1 H, J = 1.9), 7.81 (d, 1 H, J = 1.9), 7.68 (br s, 1 H), 7.65 (d, 1 H, J = 2.6), 7.50 (d, 1 H, J = 2.2), 7.19 (s, 1 H), 6.17 (m, 1 H), 6.05 (m, 2 H), 2.28 (m, 3 H), 2.0–1.0 (m, 30 H) and

1.33 (d, 9 H, J = 6.3); δ_P 33.4 (d, J = 31.1) and 6.2 (d, J = 31.1 Hz).

[Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(=C=CHPh)] 8. A 5 mm NMR tube was charged with a solution of complex **2a** (20 mg, 0.0296 mmol) in $CDCl_3$ (0.5 cm^3) and was capped with a septum. The compound HC≡CPh (10 μl, 0.089 mmol) was added by syringe and the sample was transferred to a NMR probe. Proton and ^{31}P-{^{1}H} NMR spectra were immediately recorded showing the slow but quantitative formation of **8**. All attempts to isolate this complex failed. NMR ($CDCl_3$, 20 °C): δ_H 8.25 (d, 1 H, J = 2.2), 7.83 (d, 2 H, J = 2.2), 7.78 (d, 1 H, J = 2.6), 7.41 (d, 1 H, J = 1.7), 7.3 (d, 1 H, J = 1.7), 7.14 (m, 3 H), 6.94 (m, 2 H), 6.35 (m, 1 H), 6.23 (m, 1 H), 6.02 (m, 1 H), 5.01 (d, 1 H, J = 3.5 Hz), 2.37 (m, 3 H) and 2.0–0.7 (m, 30 H); δ_P 30.3.

[Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(=C=CHCO$_2$Et)] 9. This complex was prepared analogously to **4** using HC≡CCO$_2$Et instead of pyridine. Yield: 79% (Found: C, 52.6; H, 7.0; N, 11.35. $C_{32}H_{49}BClN_6O_2PRu$ requires C, 52.8; H, 6.8; N, 11.55%). NMR (C_6D_6, 20 °C): δ_H 8.48 (d, 1 H, J = 2.2), 8.18 (d, 1 H, J = 2.2), 8.04 (d, 1 H, J = 2.2), 7.62 (d, 1 H, J = 2.2), 7.50 (d, 1 H, J = 2.5), 7.27 (s, 1 H), 6.10 (m, 1 H), 5.95 (m, 1 H), 5.81 (m, 1 H), 5.18 (d, 1 H, J = 3.6), 4.07 (q, 1 H, J = 7.1), 4.06 (q, 1 H, J = 7.0), 2.62 (m, 3 H), 2.1–1.1 (m, 30 H) and 1.0 (t, 3 H, J = 7.1 Hz); δ_P 29.5.

[Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(=C=CHBu^n)] 10. This complex was prepared analogously to **4** using hex-1-yne instead of pyridine. Yield: 87% (Found: C, 55.45; H, 7.2; N, 12.15. $C_{33}H_{53}BClN_6PRu$ requires C, 55.65; H, 7.5; N, 11.8%). NMR ($CDCl_3$, 20 °C): δ_H 8.14 (d, 1 H, J = 2.1), 7.79 (d, 1 H, J = 2.5), 7.76 (d, 1 H, J = 2.9), 7.69 (d, 1 H, J = 2.9), 7.43 (d, 1 H, J = 2.9), 7.41 (d, 1 H, J = 2.9), 6.27 (m, 1 H), 6.15 (m, 1 H), 6.06 (m, 1 H), 4.06 (dt, 1 H, J = 3.6, 8.0), 2.37 (dt, 1 H, J = 13.8, J = 8.0), 2.25–2.05 (m, 3 H), 2.0–1.4 (m, 21 H), 1.4–1.0 (m, 14 H) and 0.95–0.65 (m, 4 H); δ_C 361.0 (d, J = 16.9), 146.4, 145.1, 143.3, 137.5, 136.6, 134.5, 108.6, 106.6, 106.2, 105.8, 35.7, 35.4, 35.0, 29.8 (d, J = 7.2), 28.5 (d, J = 8.8 Hz), 27.0, 22.7, 18.4 and 14.4; δ_P 33.9.

[Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(=C=CHSiMe$_3$)] 11. This complex was prepared analogously to **4** using HC≡CSiMe$_3$ instead of pyridine. Yield: 76% (Found: C, 52.65; H, 7.4; N, 11.4. $C_{32}H_{53}BClN_6PRuSi$ requires C, 52.8; H, 7.35; N, 11.5%). NMR ($CDCl_3$, 20 °C): δ_H 8.10 (d, 1 H, J = 2.0), 8.0 (d, 1 H, J = 2.0), 7.72 (d, 1 H, J = 2.0), 7.70 (d, 1 H, J = 2.8), 7.67 (d, 1 H, J = 2.4), 7.43 (d, 1 H, J = 2.4), 6.22 (m, 1 H), 6.18 (m, 1 H), 6.08 (m, 1 H), 3.71 (d, 1 H, J = 3.6), 2.0–1.0 (m, 33 H) and −0.27 (s, 9 H); δ_C 340.2 (d, J = 15.3), 146.6, 144.6, 143.4, 137.3, 136.7, 134.7, 106.6, 106.0, 105.9, 94.9, 35.5 (d, J = 19.5), 29.9, 28.5 (d, J = 10.2 Hz), 27.1 and 1.2; δ_P 33.9.

[Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl{=C(OMe)Me}] 12. A solution of complex **11** (68 mg, 0.093 mmol) in MeOH (5 cm^3) was stirred at room temperature for 15 h. The product was obtained on addition of diethyl ether and light petroleum. Yield: 53 mg (83%) (Found: C, 52.25; H, 7.3; N, 12.05. $C_{30}H_{49}BClN_6OPRu$ requires C, 52.35; H, 7.2; N, 12.2%). NMR ($CDCl_3$, 20 °C): δ_H 8.21 (d, 1 H, J = 2.1), 7.73 (d, 1 H, J = 2.4), 7.71 (d, 1 H, J = 2.4), 7.53 (d, 1 H, J = 2.7), 7.25 (d, 1 H, J = 1.7), 6.88 (d, 1 H, J = 2.4), 6.25 (m, 1 H), 6.10 (m, 1 H), 6.03 (m, 1 H), 4.07 (s, 3 H), 2.51 (s, 3 H) and 2.1–0.7 (m, 33 H); δ_C 318.2 (d, J = 13.7), 146.3, 145.9, 142.7, 137.0, 135.4, 134.4, 106.4, 106.1, 105.8, 59.7, 40.2, 35.4 (d, J = 14.5), 29.8, 28.8 (d, J = 7.2 Hz) and 27.7; δ_P 40.1.

Catalytic dimerization of HC≡CR (R = Ph, CO$_2$Et, Bu^n or SiMe$_3$)

In a typical procedure, the alkyne (0.3 mmol) was added to a suspension of either complex **2a** or **2b** (2 mol %) in toluene (5 cm^3) and the sealed Schlenk tube was heated in an oil-bath for 20 h at 111 °C. After that time the reaction mixture was evaporated to dryness under vacuum and the coupling products were extracted with hexane. The solvent was again removed under vacuum affording isomeric mixtures of coupling products. The product distribution was determined by ^{1}H NMR spectroscopy.

Table 2 Crystallographic data for [Ru{HB(pz)$_3$}{P(C$_6$H$_{11}$)$_3$}Cl(OMe)] **2b**

Formula	$C_{28}H_{46}BClN_6OPRu$
M	661.01
Crystal size/mm	0.32 × 0.25 × 0.21
Space group	$P\bar{1}$
Crystal system	Triclinic
a/Å	9.638(1)
b/Å	10.715(1)
c/Å	16.335(1)
α/°	108.17(1)
β/°	92.37(1)
γ/°	103.83(1)
U/Å^3	1 544.1(1)
F(000)	690
Z	2
D_c/g cm^{-3}	1.422
T/K	297
μ(Mo-Kα)/mm^{-1}	0.678
θ_{max}/°	30.5
hkl Index ranges	−13 to 11, −10 to 15, −23 to 23
No. reflections measured	13 407
No. unique reflections	9290
No. reflections $F > 4\sigma(F)$	9289
No. parameters	350
$R(F)[F > 4\sigma(F)]$	0.038
(all data)	0.063
$wR(F^2)$ (all data)	0.105
Minimum, maximum Fourier-difference peaks/e Å^{-3}	−0.69, 0.53

$R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.27P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Crystallography

Crystal data and experimental details are given in Table 2. X-Ray data for complex **2b** were collected on a Siemens Smart CCD area-detector diffractometer, with 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 were used. Corrections for Lorentz-polarization effects, crystal decay, and absorption (SADABS)[13] were applied. The structures were solved by direct methods.[14] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[15] The structures were refined against F^2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/504.

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