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Bis(acetylide) complexes of ruthenium

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Complexes of the form $[Ru(C{\equiv}CR')_2(L{-}L)_2]$ [L–L = $R_2PCH_2CH_2PR_2$; R = Me (dmpe) or Et (depe); R′ = Bu^t, Ph, 4-$HC{\equiv}CC_6H_4$, 4-$MeOC_6H_4$ or 3,5-$(F_3C)_2C_6H_3$] were prepared by reaction of $[RuCl_2(L{-}L)_2]$ or $[RuH_2(L{-}L)_2]$ with terminal acetylenes in methanol solution. The spectroscopic data indicate that the acetylide groups adopt a *trans* stereochemistry across the metal centre. The crystal structure of $[Ru(C{\equiv}CPh)_2(dmpe)_2]$ was determined.

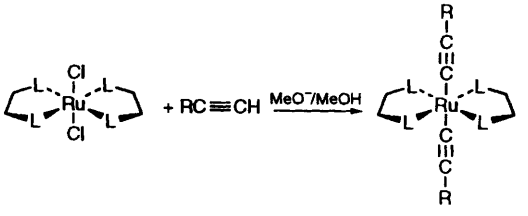
Metal acetylide complexes were first isolated in the 1950s and since that time many alkynyl transition-metal complexes (and metal clusters) with a range of co-ordination modes have been reported.[1] Acetylide complexes have been used as the π component of cycloaddition reactions[2] and transition-metal acetylides have been implicated as intermediates in the catalytic dimerisation of terminal acetylenes.[3] The increasing significance of simple transition-metal acetylides reflects the growing interest in elongated, rigid metal complexes as components of new non-linear optical materials,[4,5] liquid crystals[6] or organometallic conductors.[7] The versatility of materials formed from organometallic subunits is enhanced by the possibility that their properties can, in principle, be 'tuned' by adjusting the ligand set attached to the metals or by varying the metal itself.

Acetylide complexes of transition metals have been synthesised by substitution of existing ligands by acetylides, or acetylide derivatives,[8,9] by deprotonation of vinylidene species,[10] by insertion of a co-ordinatively unsaturated metal centre into the C–H bond of a terminal acetylene,[11] by addition of a co-ordinatively unsaturated metal centre to the electrophilic alkynyl(phenyl)iodonium cation in a co-ordinating solvent,[12] or by the reaction of alkynylstannanes with metal halides.[4] We have previously demonstrated[9] that iron bis(acetylide) complexes can be synthesised by reaction of $[FeH_2(L{-}L)_2]$ [L–L = $R_2PCH_2CH_2PR_2$; R = Me (dmpe) or Et (depe)] with terminal acetylenes in alcohol solution. We now report general synthetic routes to ruthenium bis(acetylide) complexes $[Ru(C{\equiv}CR)_2(L{-}L)_2]$ from $[RuCl_2(L{-}L)_2]$ or $[RuH_2(L{-}L)_2]$ [L–L = dmpe or depe; R = Bu^t, Ph, 4-$HC{\equiv}CC_6H_4$, 4-$MeOC_6H_4$ or 3,5-$(F_3C)_2C_6H_3$], details of their spectroscopic characteristics and an X-ray crystallographic study of $[Ru(C{\equiv}CPh)_2(dmpe)_2]$.

Results and Discussion

Synthesis of ruthenium bis(acetylide) complexes

The complex $[RuCl_2(depe)_2]$ **1a** reacts with terminal acetylenes in methanol solution, in the presence of sodium methoxide, to give high yields of the bis(acetylide) complexes $[Ru(C{\equiv}CR)_2(depe)_2]$ [R = Ph **2a**, 4-$MeOC_6H_4$ **3a**, 4-$HC{\equiv}CC_6H_4$ **4a**, Bu^t **5a** or 3,5-$(F_3C)_2C_6H_3$ **6a**] as powders which precipitate from solution (Scheme 1). The complexes are air stable and may be kept indefinitely as dry powders. The corresponding ruthenium complexes with dmpe instead of depe ligands *do not* form by direct reaction of the appropriate acetylene with $[RuCl_2(dmpe)_2]$ **1b** under the conditions used to synthesise $[Ru(C{\equiv}CR)_2(depe)_2]$. The complexes $[Ru(C{\equiv}CR)_2(dmpe)_2]$ were formed from $[RuH_2(dmpe)_2]$ by reaction with a terminal alkyne in alcohol solution. The complex $[RuH_2(dmpe)_2]$ (as a mixture of *cis* and *trans* isomers) was obtained by reduction of a tetrahydrofuran (thf) solution of $[RuCl_2(dmpe)_2]$ with sodium and propan-2-ol.[13] The complexes $[Ru(C{\equiv}CR)_2(dmpe)_2]$ (R = Ph **2b** or Bu^t **5b**) formed when a methanol solution of the terminal acetylene was added to a methanol solution of $[RuH_2(dmpe)_2]$; $[Ru(C{\equiv}CPh)_2(depe)_2]$ was also formed by an analogous route from $[RuH_2(depe)_2]$ and had identical properties to the compound synthesised directly from $[RuCl_2(depe)_2]$ (Scheme 2).



Scheme 1

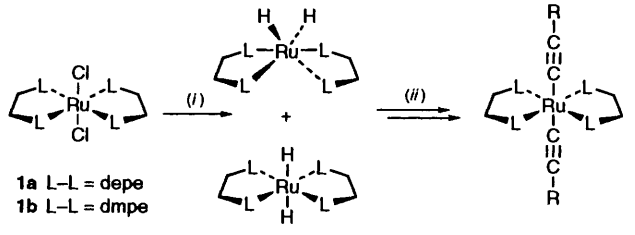
Mixed acetylide complexes of ruthenium

Ruthenium complexes $[Ru(C{\equiv}CR^1)(C{\equiv}CR^2)(depe)_2]$ containing two different acetylide units were assembled by reaction of a mixture of two different terminal acetylenes with $[RuCl_2(depe)_2]$ **1a**. By adjusting the relative amounts of the component acetylenes in the reaction mixture it was possible to obtain the mixed acetylide complex as the major component of the product mixture. When a 1:1 mixture of phenylacetylene and 4-methoxyphenylacetylene was treated with **1a** the symmetrically substituted complexes $[Ru(C{\equiv}CPh)_2(depe)_2]$ **2a** and $[Ru(C{\equiv}CC_6H_4OMe\text{-}4)_2(depe)_2]$ **3a** were formed as well as the unsymmetrically substituted bis(acetylide) $[Ru(C{\equiv}CPh)(C{\equiv}CC_6H_4OMe\text{-}4)(depe)_2]$ **7a** in a ratio **2a**:**7a**:**3a** = 17:70:13 (Fig. 1). The identity of the symmetrical bis(acetylides) was confirmed by doping an NMR sample with authentic complexes **2a** and **3a** and the spectroscopic properties of **7a** are as expected for the unsymmetrical bis(acetylide) complex. When the ratio of phenylacetylene to 4-methoxyphenylacetylene in the starting reaction mixture was changed to 1:5 the product ratio was 0:33:66 for **2a**:**7a**:**3a** and when the starting ratio was 5:1 the product ratio was 55:45:0.

Table 1 Carbon-13 NMR chemical shifts of the acetylenic carbon atoms in uncomplexed acetylenes and σ-bound iron and ruthenium acetylides[a]

	HC≡CR		[Ru(C≡CR)$_2$(depe)$_2$]		[Fe(C≡CR)$_2$(dmpe)$_2$]		[Fe(C≡CR)$_2$(depe)$_2$]	
R	HC≡	≡CR	MC≡	≡CR	MC≡	≡CR	MC≡	≡CR
Ph[b]	78.5	84.6	130.6	112.8	140.0[c]	117.1[c]	139.7[c]	118.7[c]
4-MeOC$_6$H$_4$	76.4[d,e]	84.3[d,e]	127.3	110.6	133.0[e]	119.4[e]	134.5[e]	115.0[e]
4-HC≡CC$_6$H$_4$	80.0[d]	84.2[d]	136.9[f]	113.7/117.2[f]	146.9[c,g]	117.7/117.9[c,g]	146.7[e,h]	116.9/119.6[e,h]
Me	60.0[i]	65.0[i]	—	—	112.8[c]	104.7[c]	—	—
Bu^t	69.3[d]	94.3[d]	104.6	115.8	111.9[c]	121.9[c]	111.7[e]	122.4[e]
3,5-(F$_3$C)$_2$C$_6$H$_3$	81.3[d]	81.3[d]	142.2[d]	111.0[d]	—	—	—	—

[a] Solvent: C_6D_6 at 300 K. [b] [Ru(C≡CPh)$_2$(dmpe)$_2$] in [$^2H_8$] thf: δ 131.4 (RuC≡) and 111.3 (≡CPh). [c] From ref. 9; some values have been reassigned. [d] Solvent: $CDCl_3$. [e] Ref. 14. [f] HC≡C group: HC≡ at δ 78.0, ≡CR at δ 85.8. [g] HC≡C group: HC≡ at δ 79.1, ≡CR at δ 86.6. [h] HC≡C group: HC≡ at δ 78.1, ≡CR at δ 85.8. [i] Solvent: CD_3OD.



Scheme 2 (*i*) Na, Pr^{i}OH; (*ii*) RC≡CH, MeOH

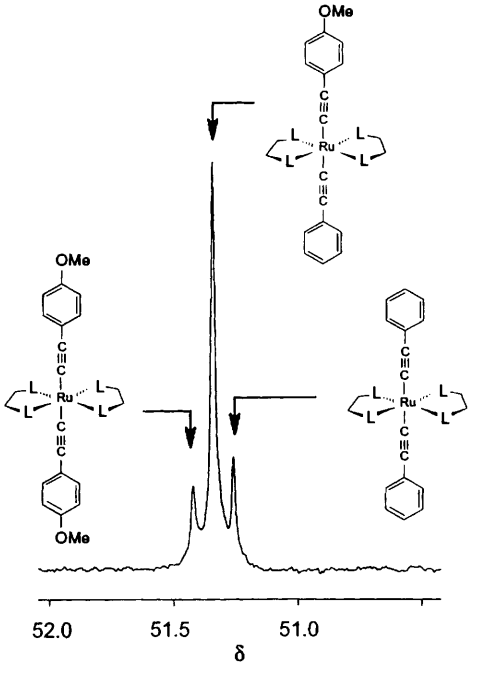


Fig. 1 Phosphorus-31 NMR spectrum (162 MHz, thf solution) of the product mixture obtained when a 1:1 mixture of PhC≡CH and 4-MeOC$_6$H$_4$C≡CH reacts with [RuCl$_2$(depe)$_2$] **1a** in methanol solution

The fact that a degree of control can be exercised over the distribution of products when more than one terminal acetylene competes for complex **1a** means that non-symmetrical mixed bis(acetylide)complexes [Ru(C≡CR^1)(C≡CR^2)(depe)$_2$] containing two different acetylides can be assembled by this approach. Mixed bis(acetylides) are useful in assembling metal systems with non-zero dipole moments and for studying systems where there is a well defined electronic gradient across the metal centre.

Spectroscopic properties of ruthenium bis(acetylide) complexes

The [Ru(C≡CR)$_2$(L–L)$_2$] complexes which have been synthesised are all diamagnetic and display a single sharp singlet resonance in the ^{31}P-{^{1}H} NMR spectrum associated with the RuP_4 donor set. The ^{31}P resonances appear characteristically in the region δ 51–53 for the complexes with depe ligands and in the range δ 40–41 for those with dmpe ligands. In solution all of the complexes so far examined have a geometry where the acetylide ligands adopt positions *trans* to each other across the metal centre and there is no evidence in the NMR spectra for the presence of a *cis* stereoisomer.

In the ^{13}C NMR spectra both carbon atoms of the acetylide unit experience a downfield shift on complexation with ruthenium (Table 1). The terminal acetylenic carbon experiences a shift of up to 61 ppm on binding to Ru and the β acetylenic carbon experiences a less pronounced shift (25–30 ppm). The resonance of the metal-bound carbon of the complex occurs downfield of the acetylide β-carbon in all cases except for complexes of *tert*-butylacetylene. The resonance of the β-acetylenic carbon (δ 115.8) in [Ru(C≡CBu^t)$_2$(depe)$_2$] appears downfield of the metal-bound acetylenic carbon (δ 104.6) and this is a result of the substantial deshielding effect of the *tert*-butyl group on the acetylenic carbon to which it is bound.

For all [Ru(C≡CR)$_2$(L–L)$_2$] complexes the ^{13}C-{^{1}H} resonance of the metal-bound acetylenic carbon atoms appear as quintets ($^2J_{PC} \approx 15$ Hz) with splitting due to coupling to the four equivalent ^{31}P nuclei of the ligands. In the depe complexes, [Ru(C≡CR)$_2$(depe)$_2$], the methylene protons of the ethyl groups attached to the phosphine ligand, (CH$_3$CH$_2$)$_2$PCH$_2$-CH$_2$P(CH$_2$CH$_3$)$_2$, are diastereotropic and appear as a multiplet consisting of two overlapping doublets of quartets in the ^{1}H-{^{31}P} NMR spectrum.

The infrared spectra of all acetylide complexes studied display an absorption near 2050 cm^{-1} assigned to the stretching frequency of the C≡C bond and this represents a shift to lower frequency of between 40 and 70 wavenumbers compared to the unbound terminal acetylene. The colour of the complexes ranges from near white for [Ru(C≡CBu^t)$_2$(depe)$_2$] to orange-brown for the more highly conjugated [Ru(C≡CC$_6$H$_4$C≡CH-4)$_2$(depe)$_2$].

Crystal structure of [Ru(C≡CPh)$_2$(dmpe)$_2$] 2b

Crystals of [Ru(C≡CPh)$_2$(dmpe)$_2$] suitable for the X-ray study were grown by slow evaporation of the solvent from a thf solution of the complex. Important bond distances and angles are given in Table 2. The structure (Fig. 2) shows that the seven atoms of the C–C≡C–Ru–C≡C–C grouping are essentially collinear. The ruthenium atom is co-ordinated in the equatorial plane by two bidentate phosphine ligands and in the axial positions by acetylide ligands. The ligand bridges are disordered, C(9a, 9b′) and can be resolved into two sites, with occupancies of the components refining to values not differing significantly from 0.5; maximum difference-map residuals (1.8 e Å^{-3}) occur in the vicinity of the disorder, being less than 0.6 e Å^{-3} elsewhere. The molecule has a non-crystallographic pseudo-inversion centre and the disordered components are

Table 2 Ruthenium–ligand distances, r/Å and important core bond angles X–Ru–Y/° in $[Ru(C{\equiv}CPh)_2(dmpe)_2]$ **2b**

	r	P(1b)	C(1a)	P(1a′)	P(1b′)	C(1b)
P(1a)	2.306(2)	95.88(7)	92.1(1)	84.54(7)	179.13(6)	88.2(1)
P(1b)	2.298(2)		89.9(2)	179.24(7)	84.61(7)	90.6(2)
C(1a)	2.042(5)			89.4(2)	88.6(1)	179.4(2)
P(1a′)	2.304(2)				94.99(7)	90.1(2)
P(1b′)	2.301(2)					91.0(1)
C(1b)	2.044(5)					

Table 3 Comparison of bond lengths (Å) for phenylacetylide complexes of iron and ruthenium

Complex	M–P	M–C	C≡C	C–C(Ph)
$[Ru(C{\equiv}CPh)_2(dppe)_2]$[a]	2.356(2)–2.363(2)	2.061(5) 2.064(5)	1.194(7) 1.207(7)	1.449(8) 1.434(7)
$[Ru(C{\equiv}CPh)_2(dmpe)_2]$	2.298(2)–2.306(2)	2.042(5)–2.044(5)	1.226(7)–1.221(6)	1.424(7)–1.437(6)
$[Fe(C{\equiv}CPh)_2(dmpe)_2]$[b]	2.191(3) 2.180(5)	1.925(6)	1.209(9)	1.438(9)

[a] Ref. 15. [b] Ref. 9(*a*).

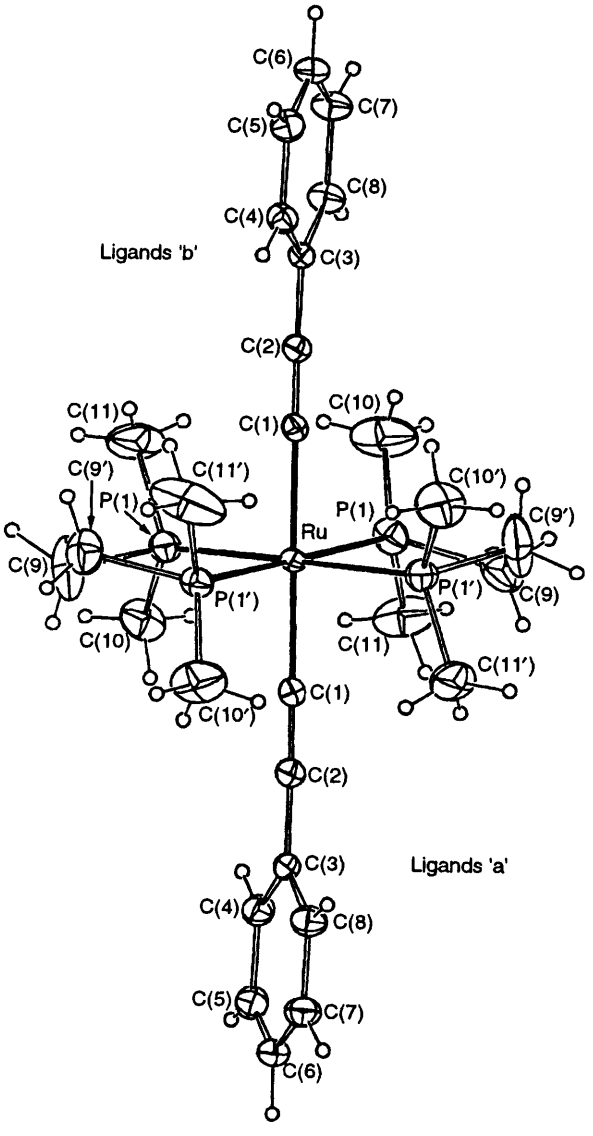


Fig. 2 Molecular projection of $[Ru(C{\equiv}CPh)_2(dmpe)_2]$ **2b**. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å. Only one component of each of the disordered $(CH_2)_2$ groups is shown

disposed in conformity. The ruthenium environment exhibits significant changes with respect to its dppe congener.

The metal–carbon bonds in complex **2b** [2.042(5), 2.044(5) Å] are significantly longer than in the corresponding iron analogue [1.925(6) Å][9a] but shorter than those in $[Ru(C{\equiv}CPh)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) [2.064(5), 2.061(5) Å].[15] Similarly, the C≡C bond of the acetylide ligand is longer in **2b** than in $[Fe(C{\equiv}CPh)_2(dmpe)_2]$ which may suggest a greater degree of M→π* donation than in the iron analogue (Table 3).

Conclusion

Bis(acetylide) complexes of ruthenium of general formula $[Ru(C{\equiv}CR')_2(L{-}L)_2]$ [L–L = $R_2PCH_2CH_2PR_2$; R = Me (dmpe) or Et (depe); R′ = Bu^t, Ph, 4-HC≡CC_6H_4, 4-MeO-C_6H_4 or 3,5-$(F_3C)_2C_6H_3$] have been prepared from $[RuCl_2(L{-}L)_2]$ (L–L = depe) or $[RuH_2(L{-}L)_2]$ (L–L = depe or dmpe) in good yield. They are stable solids and were characterised spectroscopically. In all of the complexes examined the stereochemistry is such that the acetylide groups are mutually *trans*. An X-ray crystallographic study of $[Ru(C{\equiv}CPh)_2(dmpe)_2]$ indicates the seven atoms in the central C–C≡C–Ru–C≡C–C core are essentially collinear. Ruthenium complexes $[Ru(C{\equiv}CR^1)(C{\equiv}CR^2)(depe)_2]$ with different acetylide groups were synthesised by reaction of a mixture of terminal acetylenes with $[RuCl_2(depe)_2]$.

Experimental

General

All reactions and manipulations involving $[RuH_2(L{-}L)_2]$ complexes were performed under nitrogen in standard Schlenk apparatus. Tetrahydrofuran was distilled from sodium–benzophenone under nitrogen prior to use. Methanol was dried by distillation from magnesium methoxide.[16] Deuteriated solvents were obtained from Merck and Aldrich and used as received. Proton (400.1), ^{31}P (162.0) and ^{13}C (100.6 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer, in the solvents indicated, ^{31}P referenced to external $P(OMe)_3$ taken as δ 140.85, ^1H and ^{13}C to solvent residuals. The UV/VIS spectra were recorded on a Hitachi 150-20 spectrophotometer with thf as solvent. Infrared spectra on a Perkin-Elmer 1600 FTIR spectrometer with samples in Nujol mull and electron impact (EI) mass spectra using an AEIMS30 mass spectrometer. Microanalyses were performed by the University of New South Wales Analytical Chemistry Laboratories and the National

Analytical Laboratories. Nitrogen (>99.5%) was obtained from Commonwealth Industrial Gases (C.I.G.) and used as received. Phenyl- and *tert*-butyl-acetylene were obtained from Aldrich and distilled before use. 1,4-Diethynylbenzene,[17] 4-methoxyphenylacetylene[18] and 3,5-bis(trifluoromethyl)phenylacetylene[19] were synthesised following literature procedures.

Preparations

***trans*-[RuCl$_2$(depe)$_2$] 1a.**[20] A solution of depe (2.6 g, 12.6 mmol) in dry acetone (5 cm^3) was added to a suspension of [RuCl$_2$(PPh$_3$)$_3$] (5.0 g, 5.2 mmol)[21] in dry acetone (100 cm^3). The solution was refluxed for 3 h, cooled to room temperature, filtered and the solvent removed under vacuum to give a yellow residue. This was washed with hexane (2 × 10 cm^3) and dried under vacuum to give *trans*-[RuCl$_2$(depe)$_2$] **1a** as a bright yellow, crystalline solid (2.26 g, 74%), m.p. 230 °C (decomp., lit.,[20] 241–242 °C) (Found: C, 41.6; H, 8.2. $C_{20}H_{48}Cl_2P_4Ru$ requires C, 41.10; H, 8.30%). NMR (C_6D_6): ^{31}P-{^{1}H}, δ 48.0; ^{1}H-{^{31}P}, δ 1.28 (24 H, m, CH_3), 1.88 (8 H, s, CH_2), 2.00 (8 H, m, C*H*HCH$_3$) and 2.56 (8 H, m, CH*H*CH$_3$); ^{13}C-{^{1}H, ^{31}P}, δ 9.9 (CH_3), 18.0 (CH_2) and 21.4 (CH_2).

***trans*-[RuCl$_2$(dmpe)$_2$] 1b.**[20] This complex was prepared by a method analogous to that used for [RuCl$_2$(depe)$_2$] and employed [RuCl$_2$(PPh$_3$)$_3$] (3.6 g, 3.8 mmol)[21] to give [RuCl$_2$(dmpe)$_2$] (1.5 g, 87%) as a pale yellow solid. NMR (C_6D_6): ^{31}P-{^{1}H}, δ 38.7; ^{13}C-{^{1}H, ^{31}P}, δ 12.7 (CH_3) and 29.3 (CH_2).

***trans*-[Ru(C≡CPh)$_2$(depe)$_2$] 2a.** Phenylacetylene (200 mg, 1.96 mmol) was added to a solution of [RuCl$_2$(depe)$_2$] **1a** (64.4 mg, 0.11 mmol) in dry methanol (8 cm^3). The solution was stirred for 5 min before sodium (*ca.* 60 mg) was added and the solution refluxed under N_2 for 40 min. It was cooled to room temperature and the resulting solid filtered off to yield *trans*-[Ru(C≡CPh)$_2$(depe)$_2$] **2a** as an off-white powder (76.9 mg, 98%), decomposed without melting at >290 °C (Found: C, 60.7; H, 8.2. $C_{36}H_{58}P_4Ru$ requires C, 60.40; H, 8.15%); $\tilde{\nu}_{max}$(Nujol) 2043 cm^{-1} (C≡C), λ_{max}(thf) 214 (log ε 4.55), 243 (4.26) and 334 nm (4.65). NMR (C_6D_6): ^{31}P-{^{1}H}, δ 51.3; ^{1}H-{^{31}P}, δ 1.58 (24 H, m, CH_3), 2.05 (8 H, s, CH_2), 2.31 (8 H, m, C*H*HCH$_3$), 2.81 (8 H, m, CH*H*CH$_3$), 7.40 (2 H, m, CH), 7.62 (4 H, m, CH) and 7.84 (4 H, m, CH); ^{13}C-{^{1}H, ^{31}P}, δ 9.8 (CH_2CH_3), 21.7 (CH_2CH_3), 22.7 (CH_2), 112.8 (RuC≡*C*), 123.6 (CH), 128.6 (CH), 130.6 (Ru*C*≡C), 131.1 (CH) and 132.7 (C).

***trans*-[Ru(C≡CPh)$_2$(dmpe)$_2$] 2b.** Sodium (200 mg) was added to a solution of [RuCl$_2$(dmpe)$_2$] **1b** (80 mg, 0.17 mmol) in propan-2-ol–thf (10:90 v/v, 20 cm^3) and the mixture was stirred for 3 h. The residue was extracted exhaustively with pentane and the pentane extracts evaporated to dryness to give [RuH$_2$(dmpe)$_2$] (purity >98% according to ^{31}P NMR spectroscopy) and this was used without further purification in subsequent reactions. The residue was dissolved in methanol (10 cm^3), phenylacetylene (1 cm^3) was added and the solution was refluxed for 3 h. The volume was reduced to *ca.* 5 cm^3 and the mixture was centrifuged. The solid precipitate was washed with methanol (2 × 2 cm^3) and dried under vacuum to give *trans*-[Ru(C≡CPh)$_2$(dmpe)$_2$] **2b** as a cream coloured solid (58 mg, 59%), decomposed without melting at >300 °C. NMR ([$^2H_8$]thf): ^{31}P-{^{1}H}, δ 40.8; ^{1}H-{^{31}P}, δ 2.08 (24 H, m, CH_3), 2.21 (8 H, br s, CH_2) and 7.43 (10 H, m, CH); ^{13}C-{^{1}H, ^{31}P}, δ 17.3 (CH_3), 32.3 (CH_2), 111.3 (RuC≡*C*), 124.1 (CH), 129.5 (CH), 131.4 (Ru*C*≡C), 132.1 (CH) and 133.7 (C). Mass spectrum: m/z = 604 (M^+) and 402.

***trans*-[Ru(C≡CC$_6$H$_4$OMe-4)$_2$(depe)$_2$] 3a.** 4-Methoxyphenylacetylene (200 mg, 1.52 mmol) was added to a solution of [RuCl$_2$(depe)$_2$] **1a** (67 mg, 0.11 mmol) in dry methanol (10 cm^3) followed by sodium (*ca.* 80 mg) and the solution was refluxed under N_2 for 2 h. The mixture was stirred for 65 h before the precipitated solid was filtered off. Complex **3a** was obtained as a cream coloured powder (69.2 mg, 78%), decomposed on melting at 310–320 °C (Found: C, 58.9; H, 8.1. $C_{38}H_{62}O_2P_4Ru$ requires C, 58.85; H, 8.05%); $\tilde{\nu}_{max}$(Nujol) 2056 cm^{-1} (C≡C); λ_{max}(thf) 210 (log ε 4.66), 237 (3.33) and 322 nm (4.63). NMR: ^{31}P-{^{1}H} (CD_2Cl_2), δ 51.3; ^{1}H-{^{31}P} (CD_2Cl_2), δ 1.17 (24 H, m, CH_3), 1.72 (8 H, s, CH_2), 1.90 (8 H, m, C*H*HCH$_3$), 2.27 (8 H, m, CH*H*CH$_3$), 3.68 (6 H, s, OCH_3), 6.60 (4 H, m, CH) and 6.89 (4 H, m, CH); ^{13}C-{^{1}H, ^{31}P} (C_6D_6), δ 9.7 (CH_2CH_3), 21.5 (CH_2CH_3), 22.6 (CH_2), 56.1 (OCH_3), 110.6 (RuC≡*C*), 114.5 (CH), 125.5 (C), 127.3 (Ru*C*≡C), 131.4 (CH) and 156.3 (CH_3OC).

***trans*-[Ru(C≡CC$_6$H$_4$C≡CH-4)$_2$(depe)$_2$] 4a.** 1,4-Diethynylbenzene (240 mg, 1.90 mmol) was added to a solution of [RuCl$_2$(depe)$_2$] **1a** (50.5 mg, 0.086 mmol) in dry methanol (7 cm^3). The solution was stirred for 5 min before sodium (*ca.* 60 mg) was added and the solution was refluxed under N_2 for 40 min. After cooling to room temperature, the solid was filtered off to give *trans*-[Ru(C≡CC$_6$H$_4$C≡CH-4)$_2$(depe)$_2$] **4a** as an orange-brown powder (46 mg, 71%), decomposed without melting at >300 °C; $\tilde{\nu}_{max}$(Nujol) 2049 cm^{-1} (C≡C). NMR (C_6D_6): ^{31}P-{^{1}H}, δ 52.3; ^{1}H-{^{31}P}, δ 1.26 (24 H, m, CH_3), 3.01 (2 H, s, CH), 1.71 (8 H, s, CH_2), 1.97 (8 H, m, C*H*HCH$_3$), 2.43 (8 H, m, CH*H*CH$_3$), 7.60 (4 H, d, J = 8.3, CH) and 7.87 (4 H, d, J = 8.3 Hz, CH); ^{13}C-{^{1}H, ^{31}P}, δ 9.8 (CH_2CH_3), 21.6 (CH_2CH_3), 22.6 (CH_2), 78.0 (C≡*C*H), 85.8 (*C*≡CH), 113.7, 117.2 (2C, RuC≡*C* and C), 130.9 (CH), 132.8 (C), 133.0 (CH) and 136.9 (Ru*C*≡C).

***trans*-[Ru(C≡CBu^t)$_2$(depe)$_2$] 5a.** *tert*-Butylacetylene (200 mg, 2.4 mmol) was added to a solution of [RuCl$_2$(depe)$_2$] **1a** (60.0 mg, 0.10 mmol) in dry methanol (8 cm^3). The solution was stirred for 5 min before sodium (*ca.* 60 mg) was added and the solution was refluxed under N_2 for 40 min. After cooling to room temperature, the solid was filtered off to give *trans*-[Ru(C≡CBu^t)$_2$(depe)$_2$] **5a** as a white powder (59.6 mg, 88%), decomposed without melting at >280 °C (Found: C, 56.6; H, 10.0. $C_{32}H_{66}P_4Ru$ requires C, 56.85; H, 9.85%); $\tilde{\nu}_{max}$(Nujol) 2063 cm^{-1} (C≡C); λ_{max}(thf) 216 nm (log ε 4.38). NMR (C_6D_6): ^{31}P-{^{1}H}, δ 52.3; ^{1}H-{^{31}P}, δ 1.37 (24 H, m, CH_3), 1.50 (18 H, s, CH_3), 1.78 (8 H, s, CH_2), 2.00 (8 H, m, C*H*HCH$_3$) and 2.59 (8 H, m, CH*H*CH$_3$); ^{13}C-{^{1}H, ^{31}P}, δ 9.9 (CH_2CH_3), 21.2 (CH_2CH_3), 22.3 (CH_2), 30.0 (C), 34.1 (CH_3), 104.6 (Ru*C*≡C) and 115.8 (RuC≡*C*). Mass spectrum: m/z = 676 (M^+) and 514.

***trans*-[Ru(C≡CBu^t)$_2$(dmpe)$_2$] 5b.** *tert*-Butylacetylene (*ca.* 0.05 cm^3) was added to a solution of [RuH$_2$(dmpe)$_2$] (*ca.* 10 mg)[13] in dry methanol (0.5 cm^3) and heated at 70 °C overnight. The complex *trans*-[Ru(C≡CBu^t)$_2$(dmpe)$_2$] **5b** formed as a white precipitate which was separated from the solution after the sample was centrifuged and liquid decanted. NMR ($C_6D_5CD_3$): ^{31}P-{^{1}H}, δ 40.0; ^{1}H-{^{31}P}, δ 1.34 (18 H, s, CH_3), 1.50 (24 H, s, PCH_3) and 1.51 (8 H, s, PCH_2).

***trans*-[Ru{C≡CC$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(depe)$_2$] 6a.** 3,5-Bis(trifluoromethyl)phenylacetylene (123 mg, 0.52 mmol) was added to a solution of [RuCl$_2$(depe)$_2$] **1a** (55 mg, 0.094 mmol) in dry methanol (10 cm^3) followed by sodium (*ca.* 50 mg) and the solution was refluxed under N_2 for 18 h. The mixture was cooled before the solid was filtered off to give *trans*-[Ru{C≡CC$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(depe)$_2$] **6a** as a pale yellow powder (67.8 mg, 73%), melted with decomposition at 260–265 °C; $\tilde{\nu}_{max}$(Nujol) 2029 cm^{-1} (C≡C). NMR ($CDCl_3$): ^{31}P-{^{1}H}, δ 50.5; ^{1}H-{^{31}P}, δ 1.21 (24 H, m, CH_3), 1.75 (8 H, s, CH_2), 1.90 (8 H, m, C*H*HCH$_3$), 2.24 (8 H, m, CH*H*CH$_3$), 7.29 (2 H, s CH) and 7.33 (1 H, s, CH); ^{13}C-{^{1}H, ^{31}P}, δ 9.6 (CH_2CH_3), 21.2 (CH_2CH_3), 22.3 (CH_2), 111.0 (RuC≡*C*), 115.7 (CH), 124.4

Table 4 Non-hydrogen positional parameters for [Ru(C≡CPh)$_2$(dmpe)$_2$] **2b**

Atom	*x*	*y*	*z*
Ru	0.249 04(3)	0.610 55(3)	0.261 98(2)
P(1a)	0.272 0(1)	0.454 1(1)	0.229 8(1)
P(1b)	0.241 5(1)	0.679 5(1)	0.149 53(8)
C(1a)	0.072 2(4)	0.598 3(3)	0.208 2(3)
C(2a)	−0.034 2(4)	0.593 1(4)	0.176 6(3)
C(3a)	−0.157 7(4)	0.591 5(3)	0.143 3(3)
C(4a)	−0.228 3(4)	0.571 8(4)	0.062 9(3)
C(5a)	−0.348 2(5)	0.575 5(4)	0.031 8(3)
C(6a)	−0.399 6(4)	0.597 1(4)	0.078 1(4)
C(7a)	−0.332 4(5)	0.615 0(4)	0.157 9(4)
C(8a)	−0.214 1(4)	0.612 4(4)	0.189 1(3)
C(9a)	0.245(3)	0.378(1)	0.300(1)
C(9ad)	0.342(3)	0.385(1)	0.320(1)
C(10a)	0.390 4(7)	0.422 2(6)	0.208 0(6)
C(11a)	0.153 4(7)	0.391 3(6)	0.151 5(6)
C(9a′)	0.291(1)	0.413 4(7)	0.374 5(7)
C(10a′)	0.363 0(7)	0.580 8(7)	0.470 8(4)
C(11a′)	0.124 9(6)	0.537 9(7)	0.387 7(5)
P(1a′)	0.254 3(1)	0.542 3(1)	0.374 33(9)
P(1b′)	0.228 7(1)	0.766 4(1)	0.295 80(1)
C(1b)	0.426 0(4)	0.623 2(3)	0.317 0(3)
C(2b)	0.531 8(4)	0.629 6(3)	0.350 3(3)
C(3b)	0.656 6(4)	0.634 2(3)	0.389 1(3)
C(4b)	0.716 1(4)	0.700 0(4)	0.449 6(3)
C(5b)	0.835 8(4)	0.702 7(4)	0.486 7(3)
C(6b)	0.899 0(4)	0.641 5(4)	0.465 3(3)
C(7b)	0.842 5(4)	0.576 2(4)	0.406 7(3)
C(8b)	0.723 9(4)	0.572 6(4)	0.369 1(3)
C(9b)	0.214 9(9)	0.808 7(6)	0.152 0(5)
C(10b)	0.127 7(6)	0.646 5(5)	0.053 4(3)
C(11b)	0.368 7(6)	0.678 9(9)	0.132 7(5)
C(9b′)	0.253(2)	0.852(1)	0.235(1)
C(9bd′)	0.172(2)	0.838(1)	0.201(1)
C(10b′)	0.107 4(6)	0.801 6(6)	0.313 3(5)
C(11b′)	0.346 7(7)	0.825 7(6)	0.376 9(7)

Site occupancy factors: C(9a) 0.48(2); C(9ad) 1–0.48(2); C(9b′) 0.52(2); C(9bd′) 1–0.52(2).

(CF_3, $^1J_{CF}$ = 272.9), 129.9 (CH), 131.7 (CCF_3, $^2J_{CF}$ = 32.5 Hz), 132.6 (C) and 142.2 (Ru*C*≡C).

***trans*-[Ru(C≡CPh)(C≡CC$_6$H$_4$OMe-4)(depe)$_2$] 7a.** Phenylacetylene (268 mg, 2.65 mmol) and 4-methoxyphenylacetylene (367 mg, 2.78 mmol) in methanol (10 cm^3) were added to a solution of [RuCl$_2$(depe)$_2$] **1a** (202 mg, 345 μmol) in methanol (10 cm^3) and sodium (*ca.* 80 mg) was added. The resulting yellow solution was refluxed for 5 h during which time a white precipitate formed. The reaction mixture was cooled, the solid filtered off, washed with methanol (5 cm^3) and dried under vacuum to give crude *trans*-[Ru(C≡CPh)(C≡CC$_6$H$_4$OMe-4)(depe)$_2$] **7a** (235 mg) as a white powder. The solid contained **7a** as the major product (> 70%) with the remainder being a mixture of *trans*-[Ru(C≡CC$_6$H$_4$OMe-4)$_2$(depe)$_2$] **3a** and *trans*-[Ru(C≡CPh)$_2$(depe)$_2$] **2a**. NMR ($CDCl_3$): ^{31}P-{^{1}H}, δ 51.3; ^{1}H-{^{31}P}, δ 1.1 (24 H, m, CH_3), 1.7 (8 H, s, CH_2), 1.9 (8 H, m, C*H*HCH$_3$), 2.3 (4 H, m, CH*H*CH$_3$), 2.4 (4 H, m, CH*H*CH$_3$), 3.7 (3 H, s, OCH_3), 6.6 (2 H, m, CH), 6.8 (1 H, m, CH), 6.9 (2 H, m, CH), 7.2 (2 H, m, CH) and 7.3 (2 H, m, CH); ^{13}C-{^{1}H, ^{31}P}, δ 9.3 (CH_2CH_3), 21.5 (2*C*H$_2$CH$_3$), 22.5 (CH_2), 55.4 (CH_3O), 111.2 (RuC≡*C*), 112.2 (Ru*C*≡C), 114.0 (CH), 122.6 (CH), 128.2 (CH), 130.6 (CH), 130.8 (Ru*C*≡C), 131.3 (CH), 133.8 (Ru*C*≡C), 156.7 (CH_3OC); one quaternary aromatic C not identified.

Crystallography

Crystal data for [Ru(C≡CPh)$_2$(dmpe)$_2$] 2b. $C_{28}H_{42}P_4Ru$, M = 603.65, monoclinic, space group $P2_1/c$, (C_{2h}^5, no. 14), a = 12.89(1), b = 13.857(5), c = 18.97(1) Å, β = 116.75(6)°, U = 3025 Å^3, Z = 4, D_c = 1.32 g cm^{-3}, $F(000)$ = 1256, μ(Mo-Kα) = 0.74 mm^{-1}, λ(Mo-Kα) = 0.7107$_3$ Å.

A unique room-temperature diffractometer data set ($T \approx$ 295 K; 2θ–θ scan mode, $2\theta_{max}$ = 50°, crystal dimensions 0.30 × 0.40 × 0.65 mm) yielded 5318 absorption-corrected reflections, 4212 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for C, P, Ru; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F_o|$ at convergence $[(\Delta/\sigma)_{max} < 0.05]$ were 0.045, 0.051 [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.004\sigma^4(I_{diff})$, n_v = 318]. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system implemented by S. R. Hall.[22] Final atom coordinates are given in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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