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Bis(acetylido) Complexes of Ruthenium(II) Bearing Monodentate Phosphane Ligands

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Terminal acetylenes react with *cis*-$RuMe_2(PMe_3)_4$ to form the bis(acetylido) complexes *cis*/*trans*-$Ru(C{\equiv}CR)_2(PMe_3)_4$ in good yield. The structures of *trans*-**2** (R = Ph), *cis*-**3** (R = *p*-C_6H_4-OMe), *trans*-**4** (R = *p*-C_6H_4-Me), *cis*-**6** (R = Me), *trans*-**7** (R = $SiMe_3$) and *cis*-**8** (R = H) were determined by X-ray crystallography.

Introduction

Transition-metal σ-acetylido complexes, particularly those with an oligomeric or polymeric structure, have become an increasingly important class of compounds in organometallic chemistry. Interest stems from the potential applications of these complexes in many areas of material science, notably in the fields of nonlinear optics,[1,2] luminescence,[3] liquid-crystalline materials,[4] and molecular electronics.[5–7] The metal acetylide fragment possesses a π-bonding system that facilitates electronic communication between the conjugated organic ligand and the metal centre, with the possibility of extended π-electron conjugation conceivably providing a mechanism for electronic communication between remote metal centres.[6,7] Additionally, the presence of transition metals in a polymer or oligomer backbone allows the electrochemical and spectroscopic properties to be tuned through changes in the metal ion and ancillary ligands.[7,8]

The reaction of terminal acetylenes with simple iron(II) and ruthenium(II) precursors e. g. $MH_2(dmpe)_2$ [M = Fe, Ru; dmpe = 1,2-bis(dimethylphosphanyl)ethane] is known[9,10] to yield symmetrical bis(acetylido) complexes, whereas the deprotonation of (vinylidene)ruthenium(II) complexes has emerged as a powerful and versatile route for the formation of both symmetrical and unsymmetrical bis(acetylido) complexes.[2,11] Other routes to transition-metal acetylido complexes include the reaction of alkynylstannanes with metal halides,[12] and the reaction of low-valent metals with terminal alkynes[13,14] or alkynyl(phenyl)iodonium reagents.[15]

The reaction of alkyl transition-metal complexes and terminal alkynes by a σ-bond metathesis with concomitant loss of methane has been used to prepare complexes of Rh^{I}[14,16] and Co^{I}.[17] We have previously reported the successful synthesis of unsymmetrically substituted iron(II) bis(acetylido) complexes by a σ-bond metathesis reaction between *trans*-$Fe(C{\equiv}CR)Me(dmpe)_2$ and a terminal alkyne,[18] and more recently have shown that the stepwise reaction of *trans*-$RuMe_2(dmpe)_2$ firstly with one acetylene then with another can lead to sequential reaction of the methyl groups, and this provides a synthetic approach to both symmetrical and unsymmetrical bis(acetylido) complexes in good yield.[19]

In this paper we examine the σ-bond metathesis reaction of *cis*-$RuMe_2(PMe_3)_4$ with terminal acetylenes as a clean and effective route to ruthenium bis(acetylides) $Ru(C{\equiv}CR)_2(PMe_3)_4$.

Results and Discussion

Acetylido complexes, $Ru(C{\equiv}CR)_2(PMe_3)_4$, were synthesised by the addition of a terminal acetylene to *cis*-$RuMe_2(PMe_3)_4$ (**1**), in thf or acetone at 40 °C (Scheme 1).

The reactions are complete within 2 h and, in general, afford a mixture of *cis* and *trans* isomers, from which either the *cis* isomer or the *trans* isomer may be recrystallised exclusively. In the ^1H NMR spectrum of the reaction mixture, methane can be observed (signal at $\delta = 0.15$ ppm) as a reaction byproduct, and this is consistent with the σ-bond metathesis mechanism for the formation of the metal acetylides. With the exception of **7**, the *cis* isomers tend to predominate in the crude reaction mixtures. Once isolated, the complexes are quite stable towards both air and moisture

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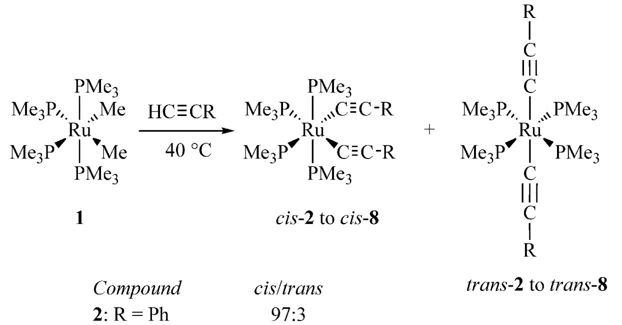
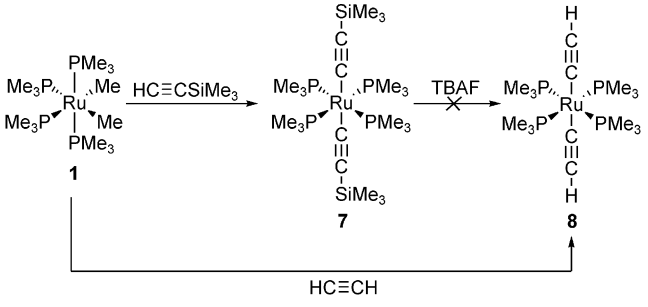


Compound	*cis/trans*
2: R = Ph	97:3
3: R = *p*-C_6H_4-OMe	91:9
4: R = *p*-C_6H_4-Me	72:28
5: R = CMe_3	82:18
6: R = Me	99:1
7: R = $SiMe_3$	7:93
8: R = H	94:6

Scheme 1.

and may be handled briefly without precautions; for prolonged storage, an inert gas is preferred.

Attempts to prepare the terminal acetylido complex $Ru(C{\equiv}CH)_2(PMe_3)_4$ by the deprotection of **7** with tetra-*n*-butylammonium fluoride in thf were unsuccessful. Increased stability of the carbon–silicon bond in complexes bearing trimethylsilylacetylide ligands has been observed for other ruthenium complexes,[6,20,21] and has been attributed to either steric protection of the silyl group[6,21–23] or an increase in the vinylidene character of the ligand brought about by the donor effects of the phosphane ligands.[6] Subsequently, *cis*/*trans*-$Ru(C{\equiv}CH)_2(PMe_3)_4$ (**8**) was successfully synthesised by direct reaction of acetylene with *cis*-$RuMe_2(PMe_3)_4$ (Scheme 2).



Scheme 2.

The complexes **3**, **6** and **8** were crystallised as their *cis* isomers, whereas the complexes **2**, **4** and **7** were crystallised as their *trans* isomers. ORTEP[24] depictions of the complexes are given in Figures 1 and 2, together with selected core bond lengths in Table 1.

The complexes all exhibit a distorted octahedral coordination environment. The *trans* complexes **2**, **4** and **7** exhibit a staggering of the phosphane ligands around the coordination plane, with *trans* P–Ru–P angles between 161.12(3) and 163.45(1)°. This arrangement, which allows for reduction in steric strain between the PMe_3 ligands, has been reported previously for *trans*-$Ru(N_3)_2(PMe_3)_4$.[25] Similarly, the *cis* complexes **3**, **6** and **8** show a significant narrowing of the *trans* P–Ru–P bond angles to approximately 161°, whereas the equatorial *cis* P–Ru–P bond angles are of the order of 97°. The Ru–P bond lengths (average 2.34 Å) are typical of other ruthenium(II) complexes bearing trialkylphosphane ligands,[25,26] and vary little upon changing the geometry

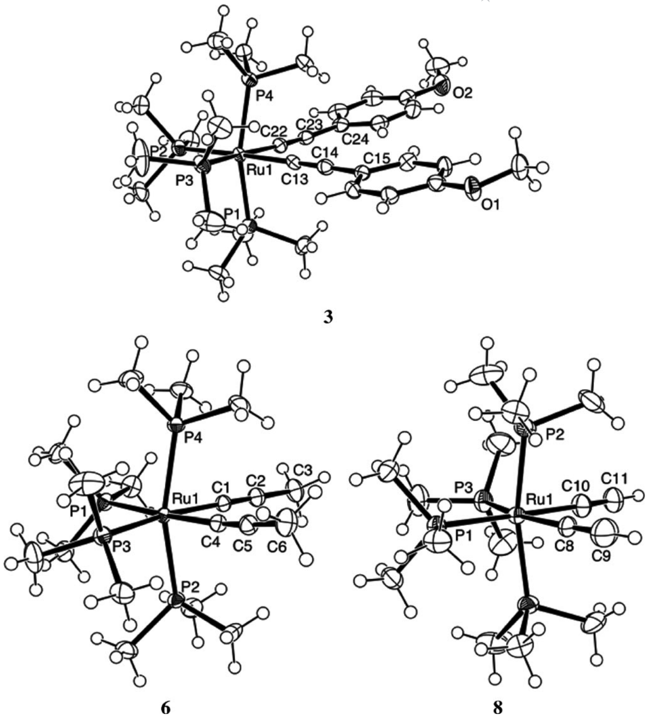


Figure 1. Crystal structures of *cis*-$Ru[C{\equiv}C(p\text{-}C_6H_4\text{-}OMe)]_2(PMe_3)_4$ (**3**), *cis*-$Ru(C{\equiv}CMe)_2(PMe_3)_4$ (**6**) and *cis*-$Ru(C{\equiv}CH)_2(PMe_3)_4$ (**8**). Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms have an arbitrary radius of 0.1 Å.

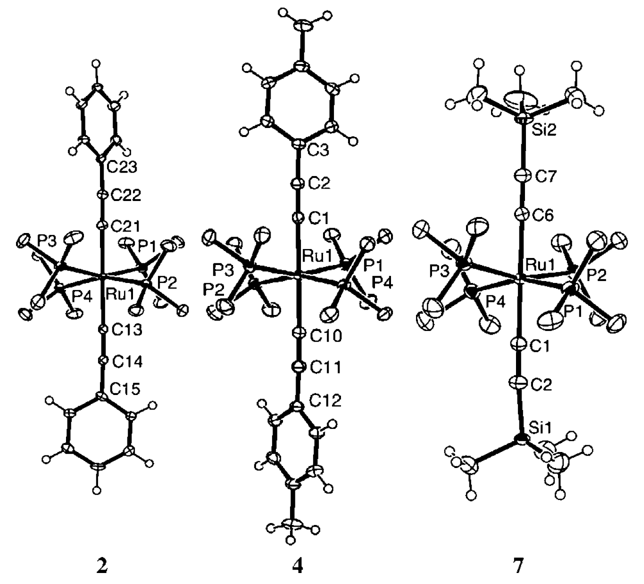


Figure 2. Crystal structures of *trans*-$Ru(C{\equiv}CPh)_2(PMe_3)_4$ (**2**), *trans*-$Ru[C{\equiv}C(p\text{-}C_6H_4\text{-}Me)]_2(PMe_3)_4$ (**4**) and *trans*-$Ru(C{\equiv}CSiMe_3)_2(PMe_3)_4$ (**7**). Hydrogen atoms on phosphane ligands have been removed for clarity. Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms have an arbitrary radius of 0.1 Å.

Table 1. Selected bond lengths [Å] and angles [°] for **2**–**4** and **6**–**8**.

	2	**3**	**4**	**6**	**7**	**8**
Ru–C	2.053(3) 2.061(3)	2.046(4) 2.060(3)	2.056(1) 2.061(1)	2.064(1) 2.070(2)	2.050(2) 2.052(2)	2.035(9) 2.086(8)
C≡C	1.219(4) 1.226(4)	1.205(5) 1.202(5)	1.220(2) 1.219(2)	1.205(2) 1.202(2)	1.221(2) 1.224(2)	1.21(2) 1.17(1)
Ru–P_{ax}	n/a	2.3531(9) 2.3421(9)	n/a	2.3601(5) 2.3302(5)	n/a	2.342(2)
Ru–P_{eq}	2.3297(9) 2.3333(8) 2.3461(9) 2.3521(8)	2.348(1) 2.365(1)	2.3230(4) 2.3347(4) 2.3427(4) 2.3448(4)	2.3405(5) 2.3423(4)	2.3340(4) 2.3343(4) 2.3345(4) 2.3359(4)	2.343(2) 2.339(3)
C–Ru–C	179.4(1)	87.3(1)	178.20(5)	89.00(6)	179.70(6)	86.4(3)
P_{ax}–Ru–P_{ax}	n/a	161.04(3)	n/a	162.70(2)	n/a	161.2(1)
P_{eq}–Ru–P_{eq}	161.12(3), 162.27(3)	97.38(4)	163.45(1), 162.20(1)	97.767(2)	162.84(2), 162.60(2)	98.21(8)

from *trans* to *cis*. The carbon–carbon triple bond lengths are also reasonably consistent, and the C≡C bond lengths are comparable to those previously reported for related acetylido complexes, *trans*-Ru(C≡CPh)$_2$(dppe)$_2$ [1.194(7) and 1.207(7) Å],[27] *trans*-Ru(CO)$_2$(PEt$_3$)$_2$(C≡CPh)$_2$ [1.200(4) Å][22] and *trans*-Ru(CO)$_2$(PEt$_3$)$_2$(C≡CSiMe$_3$)$_2$ [1.221(2) Å].[21]

The ruthenium–acetylide bond lengths in both the *cis* complexes **3**, **6**, and **8** and the *trans* complexes **2**, **4** and **7** are generally comparable to the bond lengths in related complexes, *trans*-Ru(CO)$_2$(C≡CPh)$_2$(PEt$_3$)$_2$ [2.074(3) Å],[22] *trans*-Ru(CO)$_2$(C≡CH)$_2$(PEt$_3$)$_2$ [2.078(1) Å][22] and *trans*-Ru(C≡CPh)$_2$(dmpe)$_2$ [2.042(5) and 2.044(5) Å],[10] although one Ru–C bond of complex **8** is considerably shortened at 2.035(9) Å.

The symmetric nature of the products in solution is confirmed by the ^{31}P{^{1}H} NMR spectra, which exhibit a singlet resonance for the *trans*-substituted products, and two triplets for the *cis*-substituted products. The PMe$_3$ resonances of the *cis* complexes all exhibit second-order behaviour in their ^{1}H NMR spectra, with one resonance typically appearing as a filled-in doublet.[28] The other PMe$_3$ resonance typically appears as a broadened triplet.

Ultraviolet irradiation of a [D$_6$]benzene solution of *cis*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (**6**) results in complete conversion to *trans*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ within 2 h, as evidenced by ^{31}P{^{1}H} NMR spectroscopy. Similarly, a sample of *cis*/*trans*-Ru[C≡C(*p*-C$_6$H$_4$-Me)]$_2$(PMe$_3$)$_4$ (**4**) containing 72% *cis* isomer underwent complete isomerisation to *trans* upon exposure to UV irradiation for 90 min, whereas irradiation of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (**7**) failed to yield any of the *cis* isomer. At room temperature, *trans*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (**6**) shows little tendency to revert back to the *cis* complex when left undisturbed in solution for several months (<4% could be observed by NMR after three months). Heating of a photochemically generated sample of *trans*-Ru(C≡CPh)$_2$(PMe$_3$)$_4$ (**2**) to 75 °C in [D$_8$]-toluene resulted in slow reconversion to the *cis* isomer, with a mixture containing approximately 78% *trans* and 22% *cis* obtained after about 12 h. Kinetic analysis of the thermal *trans*/*cis* isomerisation gives a $\Delta G^{\ddagger}$ value of 117.6 kJ mol^{-1} at 75 °C. Photoisomerisation of octahedral complexes, and the thermally reversible nature of this process, has been reported previously for ruthenium(II)[29] and other transition metals.[18,30]

DFT calculations show that the *trans* isomer of Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (**6**) is only about 7.6 kJ mol^{-1} more stable than the *cis* isomer (Figure 3). The calculated geometries compare well with those observed in the solid state, with both *cis* and *trans* isomers calculated to exhibit distortions from ideal octahedral geometries.

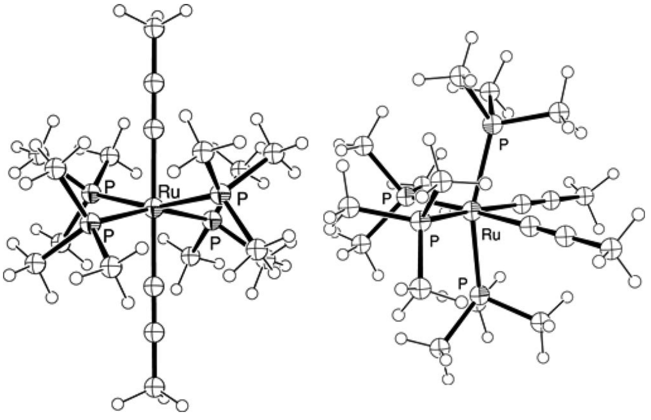


Figure 3. Calculated structures of *trans*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (left) and *cis*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (right).

In the stepwise reaction of *trans*-RuMe$_2$(dmpe)$_2$ with phenylacetylene to yield firstly *trans*-Ru(C≡CPh)Me(dmpe)$_2$ then *trans*-Ru(C≡CPh)$_2$(dmpe)$_2$,[19] the second metathesis reaction is clearly the rate-limiting step, and the intermediate (acetylido)(methyl) complex can be isolated. The reaction of *cis*-RuMe$_2$(PMe$_3$)$_4$ with terminal alkynes is significantly faster and yields only the doubly substituted product. No evidence for (acetylido)(methyl) complexes, *cis*/*trans*-Ru(C≡CR)Me(PMe$_3$)$_4$, was observed by ^{31}P{^{1}H} NMR spectroscopy at 40 °C or at room temperature.[31] In the case of complexes bearing PMe$_3$ ligands, substitution of the second methyl group is significantly faster than substitution of the first.

It is conceivable that the different reactivities of *cis*-RuMe$_2$(PMe$_3$)$_4$ and *trans*-RuMe$_2$(dmpe)$_2$ may arise from the inclusion of bidentate phosphanes in the latter, although the possibility that stereochemistry may be important can-not be easily ruled out. As *trans*-$RuMe_2(PMe_3)_4$ is a seemingly unknown compound,[32] we studied the reactivity of *cis*-$RuMe_2(dmpe)_2$ to determine what effect both chelation and stereochemistry have on the reactivity of dimethylruthenium starting materials.

An excess of phenylacetylene was added to the complex *cis*-$RuMe_2(dmpe)_2$. No reaction occurred after heating to 40 °C for 15 h. The substitution of monodentate phosphanes for chelating phosphanes does have a significant influence on the reactivity of the starting material. If the mechanism does involve the dissociation of a phosphane ligand prior to acetylide coordination and subsequent elimination of methane,[18] then this observation is not unexpected.

The failure of *cis*-$RuMe_2(dmpe)_2$ to undergo any reaction at 40 °C also contrasts with the behaviour of *trans*-$RuMe_2(dmpe)_2$. The stereochemistry of the complex, i.e. the relative disposition of the methyl groups, is a factor that also significantly influences the rate of reaction.

In the case of the *trans* complexes, substitution of one methyl group by an acetylide ligand may result in a "deactivation" of the remaining methyl group. In contrast, the inclusion of one acetylide group in the *cis* complex is less likely to alter the strength of the remaining metal–alkyl bond; thus, if there is sufficient energy present to overcome the energy barrier to the first metathesis step, the second step will also occur.

Conclusions

A method for the preparation of symmetrically substituted bis(acetylido)ruthenium(II) complexes has been developed, entailing a σ-bond metathesis reaction between *cis*-$RuMe_2(PMe_3)_4$ and a terminal acetylene. Several of the product complexes were isolated and crystallographically characterised and found to exhibit a significantly distorted octahedral coordination environment. Inclusion of monodentate phosphane ligands significantly enhances the rate of reaction with terminal acetylenes when compared to complexes bearing bidentate phosphanes. A change in geometry of the dimethylruthenium complex from *cis* to *trans* results in significantly different patterns of reactivity.

Experimental Section

General: All syntheses and manipulations involving air-sensitive compounds were carried out by using standard vacuum-line and Schlenk techniques under dry nitrogen or argon. Diethyl ether, tetrahydrofuran, petroleum ether, toluene and benzene were dried and degassed by refluxing in the presence of standard drying agents[33] under dry nitrogen, and were freshly distilled prior to use. All other solvents were dried according to standard methods. [D$_8$]thf and [D$_6$]benzene were dried with sodium benzophenone ketyl and vacuum-transferred into ampoules prior to use. NMR spectra were recorded with Bruker DMX600 (operating at 600.13, 150.92 and 242.95 MHz for ^{1}H, ^{13}C and ^{31}P, respectively), Bruker AVANCE DRX400 (operating at 400.13, 100.62 and 161.98 MHz for ^{1}H, ^{13}C and ^{31}P, respectively), Bruker DPX300 (operating at 300.13 and 121.49 MHz for ^{1}H and ^{31}P, respectively) or Bruker DPX200 (operating at 200.13 MHz for ^{1}H) instruments at 300 K, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances, whereas ^{31}P NMR spectra were referenced to external H_3PO_4. IR spectra were recorded with a Shimadzu 8400 series FTIR instrument. UV irradiation of metal complexes was performed by using an Oriel 300 W high-pressure mercury vapour lamp with the incident beam directed through a water-filled jacket to filter IR radiation. Complexes subject to irradiation were dissolved in [D$_6$]benzene (ca. 0.1 M solution) in thin-walled 5-mm NMR tubes fitted with concentric teflon valves. Terminal acetylenes were purchased from Aldrich and used as received. *cis*-$RuMe_2(PMe_3)_4$ (**1**) was prepared from *trans*-$RuCl_2(PMe_3)_4$[34] and Me_2Mg in thf. The NMR spectra of this complex corresponded with that reported in the literature.[35] *cis*-$RuMe_2(dmpe)_2$ was prepared according to a literature procedure.[36]

***cis/trans*-Ru(C≡CPh)$_2$(PMe$_3$)$_4$ (2):** Phenylacetylene (0.40 mL, 3.64 mmol) was added to a solution of *cis*-$RuMe_2(PMe_3)_4$ (**1**, 0.148 g, 0.340 mmol) in thf (10 mL). The mixture was warmed to 40 °C for 2 h, after which time the volatiles were removed in vacuo. The pale yellow product was washed with pentane and dried in vacuo. Yield: 0.155 g (75%). The product contained approximately 97% *cis*-$Ru(C{\equiv}CPh)_2(PMe_3)_4$ and 3% *trans*-$Ru(C{\equiv}CPh)_2(PMe_3)_4$. Characterisation data were consistent with that reported previously.[37,38] UV irradiation of a [D$_6$]benzene solution for 3 h followed by slow cooling gave crystals of *trans*-$Ru(C{\equiv}CPh)_2(PMe_3)_4$ suitable for X-ray diffraction.

***cis*-Ru[C≡C-(*p*-C$_6$H$_4$OMe)]$_2$(PMe$_3$)$_4$ (3):** Prepared as described for **2** from $RuMe_2(PMe_3)_4$ (0.154 g, 0.354 mmol) and (4-methoxyphenyl)acetylene (0.46 mL, 3.55 mmol). The crude product contained approximately 91% *cis*-Ru[C≡C(*p*-C_6H_4OMe)]$_2$(PMe_3)$_4$ and 9% *trans*-Ru[C≡C(*p*-C_6H_4OMe)]$_2$(PMe_3)$_4$. Yield: 0.175 g (74%). Crystals suitable for X-ray diffraction were obtained by layering a benzene solution of the complex with pentane. ^{1}H NMR (400 MHz, [D$_8$]thf): δ = 7.04 (AA′ of AA′XX′, 4 H, Ar*H*), 6.63 (XX′ of AA′XX′, 4 H, Ar*H*), 3.67 (s, 6 H, OC*H*$_3$), 1.60 [m, 18 H, P(C*H*$_3$)$_3$], 1.43 [m, 18 H, P(C*H*$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]thf): δ = –11.8 (t, $^2J_{PP}$ = 29.3 Hz), –15.4 (t, $^2J_{PP}$ = 29.3 Hz) ppm. ^{13}C{^{1}H,^{31}P} NMR (100 MHz, [D$_8$]thf): δ = 156.8, 131.4, 125.7, 125.1, 113.8, 107.3, 55.2, 23.2, 21.5 ppm. MS (ESI): *m/z* (%) = 593 (70) [M – PMe$_3$]$^+$, 517 (100) [M – 2 PMe$_3$]$^+$. IR (Fluorolube, NaCl cell): $\tilde{\nu}_{max}$ = 2075 (ν_{CC}) cm^{-1}. $C_{30}H_{50}O_2P_4Ru$ (667.69): calcd. C 53.97, H 7.55; found C 53.97, H 7.67.

***cis/trans*-Ru[C≡C(*p*-C$_6$H$_4$Me)]$_2$(PMe$_3$)$_4$ (4):** Prepared as described for **2** from *cis*-$RuMe_2(PMe_3)_4$ (0.199 g, 0.456 mmol) and *p*-ethynyltoluene (235 µL, 1.85 mmol). The product contained approximately 72% *cis*-Ru[C≡C(*p*-C_6H_4Me)]$_2$(PMe_3)$_4$ and 28% *trans*-Ru[C≡C(*p*-C_6H_4Me)]$_2$(PMe_3)$_4$. Yield: 0.146 g (52%). ***cis*-4:** ^{1}H NMR (500 MHz, [D$_8$]thf): δ = 7.02 (AA′ of AA′XX′, 4 H, Ar*H*), 6.86 (XX′ of AA′XX′, 4 H, Ar*H*), 2.22 (s, C-C*H*$_3$), 1.60 [m, 18 H, P(C*H*$_3$)$_3$], 1.44 [m, 18 H, P(C*H*$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene): δ = –11.72 (t, $^2J_{PP}$ = 29.1 Hz), –15.24 (t, $^2J_{PP}$ = 29.1 Hz) ppm. ^{13}C{^{1}H,^{31}P} NMR (125 MHz, [D$_8$]thf): δ = 132.5 (Ar*C*), 130.9 (Ar*C*H), 129.7 (Ar*C*), 129.09 (Ar*C*H), 119.8 (Ru*C*≡C), 108.3 (RuC≡*C*), 23.44 [P(*C*H$_3$)$_3$], 21.73 [P(*C*H$_3$)$_3$], 21.41 (*C*H$_3$) ppm. ***trans*-4:** ^{1}H NMR (500 MHz, [D$_8$]thf): δ = 6.97 (AA′ of AA′XX′, 4 H, Ar*H*), 6.85 (XX′ of AA′XX′, 4 H, Ar*H*), 2.21 (s, C-C*H*$_3$), 1.58 [s, P(C*H*$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene): δ = –7.02 (s) ppm. ^{13}C{^{1}H,^{31}P} NMR (125 MHz, [D$_8$]thf): δ = 132.4 (Ar*C*), 130.8 (Ar*C*H), 129.6 (Ar*C*), 129.1 (Ar*C*H), 120.0 (Ru*C*≡C), 108.7 (Ru-C≡*C*), 21.38 (*C*H$_3$), 20.42 [br., P(*C*H$_3$)$_3$] ppm. MS (ESI): *m/z* (%) = 637 (8) [M$^+$], 561 (100) [M – PMe$_3$]$^+$, 485 (18) [M – 2 PMe$_3$]$^+$. IR (KBr): $\tilde{\nu}_{max}$ = 2077 (ν_{CC}) cm^{-1}.

$C_{30}H_{50}P_4Ru$ (635.69): calcd. C 56.68, H 7.93; found C 56.55, H 7.88. Ultraviolet Irradiation of a [D$_6$]benzene solution for 90 min followed by slow concentration gave crystals suitable for X-ray diffraction.

***cis*/*trans*-Ru(C$\equiv$C*t*Bu)$_2$(PMe$_3$)$_4$ (5):** Prepared as described for **2** from RuMe$_2$(PMe$_3$)$_4$ (0.172 g, 0.394 mmol) and *tert*-butylacetylene (120 µL, 0.974 mmol) in acetone (4 mL). The crude product contained approximately 82% *cis*-Ru(C$\equiv$C*t*Bu)$_2$(PMe$_3$)$_4$ and 18% *trans*-Ru(C$\equiv$C*t*Bu)$_2$(PMe$_3$)$_4$. Concentration of the solution by half and cooling to –20 °C resulted in precipitation of needle-shaped white crystals. These were collected and dried in vacuo. Yield: 0.139 g (61%). ***cis*-5:** ^{1}H NMR (300 MHz, [D$_8$]thf): δ = 1.52 [m, 18 H, P(CH_3)$_3$], 1.35 [m, 18 H, P(CH_3)$_3$], 1.13 [s, 18 H, C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_8$]thf): δ = –8.70 (t, $^2J_{PP}$ = 30.0 Hz), –11.4 (t, $^2J_{PP}$ = 30.0 Hz) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene): δ = 111.9 (t, $^2J_{PC}$ = 12.1 Hz), 104.5 (dd, $^2J_{PC}$ = 88.2, 23.0 Hz), 33.3 [C(CH$_3$)$_3$], 30.0 [C(CH$_3$)$_3$], 23.3 [t, $^1J_{PC}$ = 9.6 Hz, P(CH$_3$)$_3$], 21.4 [t, $^1J_{PC}$ = 15.4 Hz, P(CH$_3$)$_3$] ppm. ***trans*-5:** ^{1}H NMR (300 MHz, [D$_8$]thf): δ = 1.49 [br. s, 36 H, P(CH_3)$_3$], 1.10 [s, 18 H, C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_8$]thf): δ = –3.41 (s) ppm. MS (ESI): *m*/*z* (%) = 493 (12) [M – PMe$_3$]$^+$, 417 (100) [M – 2 PMe$_3$]$^+$. IR (CCl$_4$, NaCl cell): $\tilde{\nu}_{max}$ = 2091 (ν_{CC}) cm^{-1}. $C_{24}H_{54}P_4Ru$ (567.66): calcd. C 50.78, H 9.59; found C 50.82, H 9.33.

***cis*-Ru(C$\equiv$CMe)$_2$(PMe$_3$)$_4$ (6):** Propyne was bubbled through a warm (40 °C) solution of RuMe$_2$(PMe$_3$)$_4$ (0.155 g, 0.355 mmol) in thf (20 mL) for 1 h. The mixture was filtered, and the volatiles were removed in vacuo to yield an off-white powder. The product contained >99% *cis*-Ru(C$\equiv$CMe)$_2$(PMe$_3$)$_4$. Yield: 0.117 g (68%). This was recrystallised from pentane to yield crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 2.11 (m, 6 H, CCH_3), 1.54 [m, 18 H, P(CH_3)$_3$], 1.16 [m, 18 H, P(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = –10.0 (t, $^2J_{PP}$ = 29.1 Hz), –13.8 (t, $^2J_{PP}$ = 29.1 Hz) ppm. ^{13}C{^{1}H,^{31}P} NMR (100 MHz, [D$_6$]benzene): δ = 106.0 (Ru$C$$\equiv$C), 97.3 (RuC$\equiv$$C$), 23.3 [P($CH_3$)$_3$], 21.6 [P($CH_3$)$_3$], 7.3 ($\equiv$C$CH_3$) ppm. MS (ESI): *m*/*z* (%) = 409.1 (100) [M – P(CH$_3$)$_3$]$^+$, 395.1 (45), 333.0 (23) [M – 2 P(CH$_3$)$_3$]$^+$. IR (Fluorolube, NaCl cell): $\tilde{\nu}_{max}$ = 2098 (ν_{CC}) cm^{-1}. $C_{18}H_{42}P_4Ru$ (483.50): calcd. C 44.71, H 8.76; found C 44.57, H 8.87. UV irradiation of a [D$_6$]benzene solution of this complex for 2 h resulted in complete conversion to *trans*-Ru(C$\equiv$CMe)$_2$(PMe$_3$)$_4$. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 2.11 (q, $^5J_{PH}$ = 1.9 Hz, 6 H, CCH$_3$), 1.45 [br. s, 36 H, P(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene): δ = –5.62 (s) ppm. Slow concentration of a benzene solution gave crystals suitable for X-ray diffraction.

***trans*-Ru(C$\equiv$CSiMe$_3$)$_2$(PMe$_3$)$_4$ (7):** Prepared as described for **2** from RuMe$_2$(PMe$_3$)$_4$ (0.406 g, 0.932 mmol) and (trimethylsilyl)acetylene (0.50 mL, 3.54 mmol) in acetone (4 mL). The product contained approximately 7% *cis*-Ru(C$\equiv$CSiMe$_3$)$_2$(PMe$_3$)$_4$ and 93% *trans*-Ru(C$\equiv$CSiMe$_3$)$_2$(PMe$_3$)$_4$. Yield: 0.328 g (59%). Crystals suitable for X-ray diffraction were grown by slow concentration of a benzene solution of the product. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 1.40 [s, 36 H, P(CH_3)$_3$], 0.32 [s, 18 H, Si(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = –8.4 (s) ppm. ^{13}C{^{1}H,^{31}P} NMR (100 MHz, [D$_6$]benzene): δ = 157.0 (Ru$C$$\equiv$C), 110.5 (RuC$\equiv$$C$), 19.5 [br., P($CH_3$)$_3$], 2.3 [Si($CH_3$)$_3$] ppm. IR (Fluorolube, NaCl cell): $\tilde{\nu}_{max}$ = 1985 (ν_{CC}) cm^{-1}. Spectroscopic characterisation was consistent with that previously reported.[37] Slow concentration of a benzene solution gave crystals suitable for X-ray diffraction.

***cis*-Ru(C$\equiv$CH)$_2$(PMe$_3$)$_4$ (8):** Prepared as described for **6** from RuMe$_2$(PMe$_3$)$_4$ (0.403 g, 0.925 mmol) and acetylene. The product contained approximately 94% *cis*-Ru(C$\equiv$CH)$_2$(PMe$_3$)$_4$ and 6% *trans*-Ru(C$\equiv$CH)$_2$(PMe$_3$)$_4$. The product was recrystallised from pentane to yield the *cis* isomer exclusively. Yield: 0.161 g (38%). ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 2.08 (m, 2 H, C$\equiv$CH), 1.56 [m, 18 H, P(CH_3)$_3$], 1.15 [m, 18 H, P(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (202 MHz, [D$_6$]benzene): δ = –12.3 (t, $^2J_{PP}$ = 29.4 Hz), –15.1 (t, $^2J_{PP}$ = 29.4 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene): δ = 118.5 (m, Ru$C$$\equiv$C), 92.3 (m, RuC$\equiv$$C$), 22.8 [m, P($CH_3$)$_3$], 21.2 [m, P($CH_3$)$_3$] ppm. $C_{16}H_{38}P_4Ru$ (455.44): calcd. C 42.19, H 8.41; found C 42.07, H 8.35.

Computational Details: Geometry optimisations were performed by using the B3LYP[39] density functional employing a general basis set consisting of LANL2DZ[40] and the associated effective core potential (ECP) on the metal atom, combined with the 6-31G(d)[41] basis set on the remaining atoms. Optimisations were

Table 2. Crystallographic and structure refinement data for **2**–**4**, and **6**–**8**.

	2	**3**	**4**	**6**	**7**	**8**
Empirical formula	$C_{28}H_{46}P_4Ru$	$C_{30}H_{50}O_2P_4Ru$	$C_{30}H_{50}P_4Ru$	$C_{18}H_{42}P_4Ru$	$C_{22}H_{54}P_4RuSi_2$	$C_{16}H_{38}P_4Ru$
Formula mass	607.60	667.65	635.65	483.47	599.78	455.41
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$Pna2_1$	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$Pmc2_1$
a [Å]	15.25780(10)	36.7671(3)	14.361(2)	9.940(2)	16.1250(10)	13.409(3)
b [Å]	10.58100(10)	13.1365(1)	13.801(2)	16.200(2)	10.5815(7)	8.8805(18)
c [Å]	18.7283(2)	13.9300(1)	17.596(3)	15.248(2)	20.9015(13)	18.601(4)
β [°]	92.4250(10)	90	110.195(2)	100.448(2)	111.577(1)	90
V [Å^3]	3020.84(5)	6728.06(9)	3273.1(9)	2414.6(7)	3316.4(4)	2215.0(8)
Z	4	8	4	4	4	4
T [K]	123(2)	123(2)	150(2)	150(2)	150(2)	173(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.336	1.318	1.290	1.330	1.201	1.366
μ(Mo-K_α) [mm^{-1}]	0.746	0.680	0.691	0.913	0.746	0.991
$2\theta_{max}$ [°]	56.40	55.00	56.60	56.70	56.66	54.28
Total number of reflections	40287	56700	32020	23850	32562	6954
Number of unique reflections	14649	12904	7884	5827	7992	3690
R [F, $I > 2\sigma(I)$]	0.0386	0.0365	0.0205	0.0199	0.0235	0.0529
Rw [F, $I > 2\sigma(I)$]	0.0557	0.0769	0.0577	0.0494	0.0639	0.1511
CCDC-	677063	677064	677065	677066	677067	677068

performed without symmetry constraints. For optimised geometries, harmonic vibrational frequencies were calculated to confirm the stationary points as minima. Zero-point vibrational energy (ZPVE) and thermodynamic corrections were obtained by using unscaled frequencies. Single-point energies were calculated at the B3LYP level of theory by using a LANL2DZ-augmented:6-311+G(2d,p) basis set (incorporating the LANL2 ECP and the large f-polarised valence basis set of Bauschlicher et al.[42] on Ru, and the 6-311+G(2d,p) basis set[43] on all atoms. All energies mentioned throughout the text refer to these final levels of theory and include unscaled enthalpy and ZPVE corrections calculated at the optimisation level of theory. All calculations were performed by using the Gaussian 03 suite of programs.[44]

X-ray Structure Determinations

Single crystals of **2–4** and **6–7** were attached, with Exxon Paratone N, to a short length of fibre supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. A Bruker CCD-1000 area detector diffractometer employing graphite monochromated Mo-K_α radiation generated from a fine-focus sealed tube was used for the data collection. Data were collected at 123(2) or 150(2) K. The data integration and reduction were undertaken with SAINT and XPREP,[45] and subsequent computations were carried out with the X-Seed[46] graphical user interface. A Gaussian absorption correction[45,47] was applied to the data. The structures were solved by direct methods with SHELXS-97[48] and extended and refined with SHELXL-97.[48] The non-hydrogen atoms in the asymmetric unit were modelled with anisotropic displacement parameters. A riding atom model with group displacement parameters was used for the hydrogen atoms.

A single crystal of complex **8** was mounted on a glass fibre. Data was collected with a Bruker SMART-CCD diffractometer equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 173(2) K. The structures were solved with direct methods and full-matrix least-squares refinements by using the SHELXTL-97 program package.[48] Hydrogen atoms were placed at calculated positions and all non-hydrogen atoms were refined anisotropically. All calculations were performed using the crystallographic and structure refinement data summarised in Table 2.

Supporting Information (see footnote on the first page of this article): Details of computational geometries and l2aug.Ru basis set.

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