trans-Bis[1,2-bis(diphenylphosphino)-ethane-κ^2P,P']bis[4-(trimethylsilyl)-buta-1,3-diynyl]ruthenium(II) and *trans*-bis[1,2-bis(diphenylphosphino)-ethane-κ^2P,P']bis(buta-1,3-diynyl)-ruthenium(II)

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The crystal structures of the title compounds, [Ru(C$_7$H$_9$Si)$_2$(C$_{26}$H$_{24}$P$_2$)$_2$] and [Ru(C$_4$H)$_2$(C$_{26}$H$_{24}$P$_2$)$_2$], are described. The metal centre in both complexes has an octahedral coordination geometry, with mutually *trans* buta-1,3-diynyl ligands forming pseudo-linear ruthenium-centred polyyne chains.

Comment

There is currently widespread interest in extended pseudo-one-dimensional molecules that have the potential to act as 'molecular wires' in future nanoscale electronic/photonic devices (Joachim *et al.*, 2000; Tour *et al.*, 2001). Various organotransition metal complexes have received attention in this context (Ward, 1995), but those that arguably show the greatest promise contain linear polyyne chains that bridge metal centres (Bunz, 1996; Paul & Lapinte, 1998; Low & Bruce, 2001). Until very recently, all of the work on such complexes involved end-capped (generally binuclear) species, which have no potential for extension beyond their metallic terminii. However, several systems in which structural extensions may be possible have now been reported (Wong *et al.*, 2000; Fernández *et al.*, 2001; Xu & Ren, 2001).

The connection of multiple *trans*-{Ru^{II}(P–P)$_2$}$^{2+}$ (P–P is a chelating diphosphine ligand) centres *via* polyyne chains is an appealing strategy for the stepwise construction of novel wire-like multinuclear complexes. Attractive features of such compounds include visible transparency, reversible redox behaviour and good stability. The complex *trans*-Ru^{II}(C$_4$H)$_2$-

(dppe)$_2$, [dppe is 1,2-bis(diphenylphosphino)ethane], (II), is an ideal foundation for such syntheses, but was unknown until very recently (Rigaut *et al.*, 2003). We report here the X-ray crystal structure of (II) and of its bis-trimethylsilylated precursor, (I).

(I) R = SiMe$_3$
(II) R = H
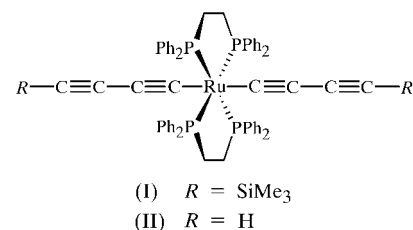
The molecular structures of complexes (I) and (II) are as indicated by ^{1}H NMR spectroscopy, with *trans*-octahedral coordination geometries (Figs. 1 and 2). The geometric parameters (Tables 1 and 2) of the *trans*-{Ru^{II}(P–P)$_2$}$^{2+}$ units are unremarkable, and those of the C$_4$—Ru—C$_4$ chains are very similar to the values found previously in the related complexes *trans,trans*-Ru^{II}(C$_4$R)$_2$(CO)$_2$(PEt$_3$)$_2$ (R = H or SiMe$_3$; Sun *et al.*, 1992). The bond distances are consistent with Ru—C≡C—C≡C structures, and the C≡C bonds remote from the Ru^{II} centres show a slight lengthening of ∼0.02 Å on repla-
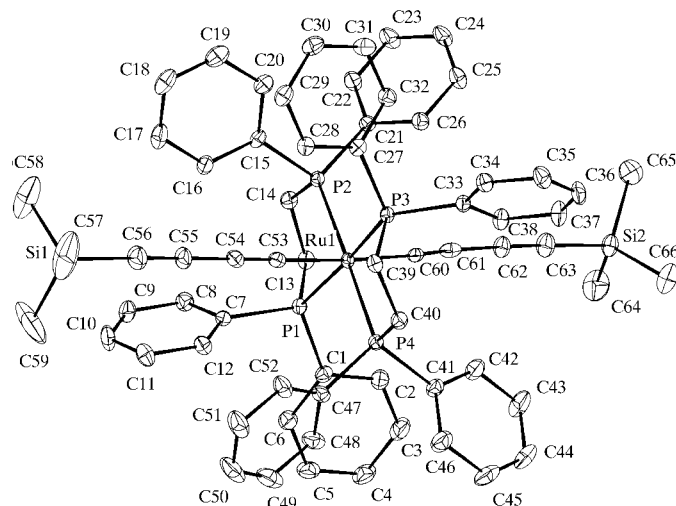

Figure 1
A view of the molecule of complex (I), with H atoms omitted and displacement ellipsoids shown at the 35% probability level.

cement of H atoms with SiMe$_3$ groups. Importantly, the Ru^{II}bis(buta-1,3-diynyl) chains are relatively linear. The largest distortion from linearity is the C60—C61—C62 angle of 170.7 (13)° in (I), and the C53—Ru1—C60 angle in this complex is 174.2 (4)°. Complex (II) is hence an attractive starting point for the preparation of linear multinuclear complexes that may be synthesized by the deprotonation and coordination of the C-atom terminii to further *trans*-{Ru^{II}(P–P)$_2$}$^{2+}$ or other suitable metal centres.
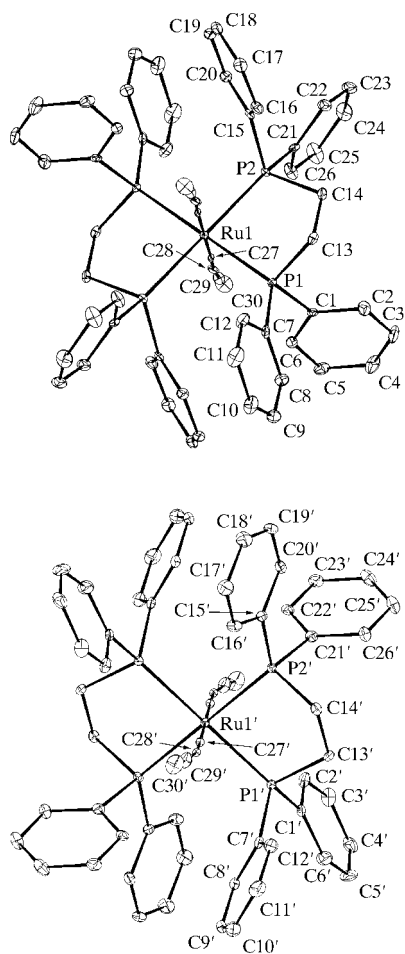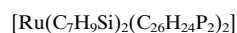
metal-organic compounds

Figure 2
Views of the two independent molecules of complex (II), with H atoms omitted and displacement ellipsoids shown at the 35% probability level.

Experimental

Although complexes (I) and (II) were unknown when their structures were solved, their syntheses and characterization have recently been reported by other workers (Rigaut *et al.*, 2003). We used essentially identical synthetic and characterization techniques to those now published, and obtained (I) and (II) as pale-yellow air-stable solids. Crystals of (I) and (II) suitable for single-crystal X-ray diffraction measurements were obtained by slow diffusion of acetone vapour into solutions in dichloromethane at 277 K.

Compound (I)

Crystal data

$[Ru(C_7H_9Si)_2(C_{26}H_{24}P_2)_2]$	$Z = 2$
$M_r = 1140.32$	$D_x = 1.247$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.677$ (3) Å	Cell parameters from 42 685
$b = 16.058$ (3) Å	reflections
$c = 16.085$ (3) Å	$\theta = 2.9–27.5°$
$\alpha = 110.32$ (3)°	$\mu = 0.44$ mm^{-1}
$\beta = 93.16$ (3)°	$T = 150$ (2) K
$\gamma = 96.36$ (3)°	Block, yellow
$V = 3036.3$ (13) Å^3	$0.20 \times 0.08 \times 0.05$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	9761 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.096$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SORTAV*; Blessing, 1995)	$h = -16 \rightarrow 16$
$T_{min} = 0.767$, $T_{max} = 0.986$	$k = -20 \rightarrow 20$
42 685 measured reflections	$l = -20 \rightarrow 20$
13 576 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2]$
$wR(F^2) = 0.122$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.059$
13 576 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
665 parameters	$\Delta\rho_{min} = -0.81$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C53—C54	1.179 (17)	C61—C62	1.444 (18)
C53—Ru1	2.041 (13)	C62—C63	1.221 (17)
C54—C55	1.395 (18)	P1—Ru1	2.352 (3)
C55—C56	1.217 (19)	P2—Ru1	2.356 (3)
C60—C61	1.099 (17)	P3—Ru1	2.362 (3)
C60—Ru1	2.095 (14)	P4—Ru1	2.373 (3)
C54—C53—Ru1	177.3 (11)	C60—C61—C62	170.7 (13)
C53—C54—C55	175.3 (14)	C63—C62—C61	178.9 (15)
C56—C55—C54	177.8 (15)	C53—Ru1—C60	174.2 (4)
C61—C60—Ru1	177.0 (11)		

Compound (II)

Crystal data

$[Ru(C_4H)_2(C_{26}H_{24}P_2)_2]$	$D_x = 1.396$ Mg m^{-3}
$M_r = 995.95$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 19 034
$a = 11.9017$ (2) Å	reflections
$b = 13.2669$ (3) Å	$\theta = 2.9–27.5°$
$c = 17.1934$ (4) Å	$\mu = 0.51$ mm^{-1}
$\alpha = 79.416$ (1)°	$T = 120$ (2) K
$\beta = 76.195$ (1)°	Plate, colourless
$\gamma = 64.499$ (2)°	$0.15 \times 0.10 \times 0.06$ mm
$V = 2369.38$ (9) Å^3	
$Z = 2$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	4873 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.073$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SORTAV*; Blessing, 1995)	$h = -14 \rightarrow 14$
$T_{min} = 0.780$, $T_{max} = 0.872$	$k = -15 \rightarrow 15$
26 880 measured reflections	$l = -20 \rightarrow 20$
7995 independent reflections	

Table 2
Selected geometric parameters (Å, °) for (II).

Ru1—C27	2.050 (4)	C27—C28	1.198 (5)
Ru1—P2	2.3581 (9)	C28—C29	1.396 (6)
Ru1—P1	2.3793 (9)	C29—C30	1.193 (6)
C27—Ru1—C27^i	180	C27—C28—C29	171.6 (4)
C28—C27—Ru1	178.4 (3)	C30—C29—C28	175.9 (5)

Symmetry code: (i) $-x, -y, -z$.

Refinement

Refinement on F^2

$R(F) = 0.038$

$wR(F^2) = 0.091$

$S = 0.94$

7995 reflections

589 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.018$

$\Delta\rho_{max} = 0.60$ e Å^{-3}
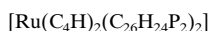
$\Delta\rho_{min} = -0.54$ e Å^{-3}

The SiMe$_3$ groups in (I) exhibit rotational thermal disorder, which it was not possible to model in separate, fractionally occupied, positions. As a result, the atomic displacement parameters were constrained to approximate isotropic thermal behaviour. The structure of (II) was initially solved and refined in a smaller cell containing one half molecule in the asymmetric unit. However, this approach resulted in unreasonable displacement ellipsoids. On examination of the diffraction pattern, extra weak reflections were noticed and the structure was then refined in a larger cell, giving two half molecules in the asymmetric unit with much more reasonable ellipsoids. 378 reflections are missing from the data set of (II) as a result of the data collection strategy being calculated for the initially determined smaller cell rather than for the subsequently found larger cell.

For compound (I), data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*. For compound (II), data collection: *COLLECT*; cell refinement: *DENZO*. For both compounds, data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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