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Symmetrical Bis(acetylido)ruthenium(II) Complexes

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Symmetrical, mononuclear bis(acetylido)ruthenium(II) complexes were prepared by the reaction of [*trans*-$RuMe_2$-$(dmpe)_2$] [dmpe = 1,2-bis(dimethylphosphanyl)ethane] with terminal alkynes. The complexes were characterised by multinuclear NMR spectroscopy and X-ray crystallography. In some cases, the complexes catalyse the head-to-head dimerisation of terminal alkynes to yield organic butenynes. The regiochemistry of this dimerisation depends on the solvent used; methanol results in the isolation of (*Z*)-butenynes, whereas toluene gives predominantly (*E*) isomers.

Introduction

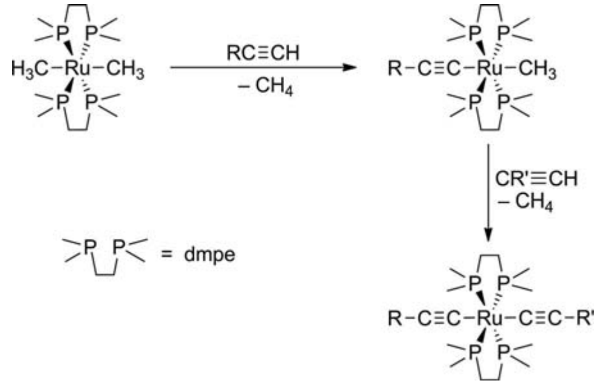
As a consequence of the potential applications of rigid-rod (σ-alkynyl)transition-metal complexes as nonlinear optical,[1] electronic communication (molecular wire),[1f,2] luminescent[3] or liquid-crystalline materials,[4] complexes of this type have been an active area of research in recent years.[5] All of these potential applications depend on the extended rigid linear structures, inherent stability and π-electron configuration[5b] of the σ-alkynyl complexes.

Until recently, most (σ-alkynyl)transition-metal complexes have been synthesised either by the reaction of an alkali-metal alkynide or an alkaline earth-metal alkynide RC≡CM (M = Li, Na, Mg, etc.) with a transition metal halide $L_nMX_{n'}$ (X = Cl, Br, I) or by the reaction of a terminal alkyne with a transition-metal complex.[2c,5b]

Touchard et al.[3a] have developed an effective method for the preparation of ruthenium acetylide complexes by deprotonation of a vinylidene complex – a reaction pioneered by Dixneuf and co-workers.[6]

Some time ago, we reported a relatively clean synthesis of ruthenium acetylide complexes, [*trans*-$Ru(C{\equiv}CR)_2$-$(depe)_2$] [depe = 1,2-bis(diethylphosphanyl)ethane], by the reaction of [*trans*-$RuCl_2(depe)_2$] with terminal alkynes in the presence of NaOMe in methanol.[7] Attempts to prepare analogous dmpe complexes by using the same technique were unsuccessful, and until now, Ru(dmpe) acetylide complexes have been traditionally prepared by the reaction of [$RuH_2(dmpe)_2$] with terminal alkynes. This latter approach is less appealing, as the hydrogen byproduct of the reaction can hydrogenate the terminal alkynes, resulting in contamination of the desired alkynyl complexes with alkenyl complexes. Symmetrical ruthenium bis(acetylide) complexes bearing dmpe or 16-TMC (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) coligands have also been prepared by the reaction of $Ru(dmpe)_2Cl_2$ or [Ru(16-TMC)Cl_2]Cl with terminal alkynes in the presence of sodium methoxide and zinc amalgam.[8] The role of the zinc amalgam is not obvious; however, no reaction occurs in its absence. The reaction possibly proceeds by reduction of the Ru^{II} centre, which then undergoes reaction with the terminal alkyne.

We have recently reported the development of a route to mono- and bis(acetylido) complexes of ruthenium(II),[9] by the reaction of terminal acetylenes with alkylruthenium compounds (Scheme 1). The synthesis of a range of dinuclear and trinuclear acetylido-bridged ruthenium complexes has now been demonstrated by using this route.[10] We report here the synthesis of symmetrically substituted, mono-



Scheme 1.

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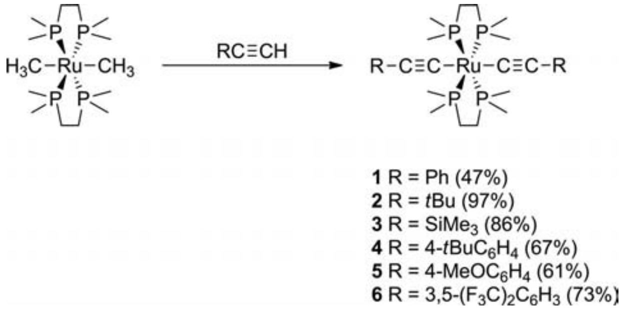
nuclear bis(acetylido)ruthenium complexes in high yields by the metathesis reaction of alkylruthenium(II) complexes with terminal alkynes.

Results and Discussion

Ruthenium Bis(acetylides)

In benzene solution, the reaction between [*trans*-$RuMe_2(dmpe)_2$] and phenylacetylene or *tert*-butylacetylene occurs very slowly, even with heating or UV irradiation, and typically requires several days to reach completion. The addition of a small quantity of methanol[10] to a benzene or toluene solution of the starting materials resulted in complete reaction at room temperature within several hours, and the products were isolated in excellent yield and purity. Neat methanol can also be employed as solvent.

A range of symmetrical bis(acetylide) complexes, [*trans*-$Ru(C{\equiv}CR)_2(dmpe)_2$] [R = Ph (**1**), *t*Bu (**2**), Me_3Si (**3**), 4-$tBuC_6H_4$ (**4**), 4-$MeOC_6H_4$ (**5**) and 3,5-$(F_3C)_2C_6H_3$ (**6**); Scheme 2, yields in parentheses], was prepared. The methanol-promoted reaction was found to be necessary for the clean formation of complexes **4**–**6** (vide infra), whereas **1**–**3** could be successfully synthesised in the presence or absence of methanol, albeit with longer reaction times in the latter case.



Scheme 2.

The complexes were characterised by multinuclear NMR and IR spectroscopy, mass spectrometry and, in some cases, by X-ray crystallography. Complexes **1** and **2** have previously been prepared by the addition of the appropriate terminal alkyne to [$RuH_2(dmpe)_2$][7] and the reaction of [*trans*-$RuCl_2(dmpe)_2$] with phenylacetylene in the presence of Zn/Hg amalgam (complex **1** only),[2f] although characterisation of **2** was limited to ^{31}P and ^{1}H NMR spectroscopy. Complexes **3**–**6** have not been previously reported.

The $^{31}P\{^{1}H\}$ NMR spectra of all the complexes appear as a single resonance at $\delta \approx 40$ ppm, confirming the mutually *trans*-axial positions of the acetylido ligands. The chemical shift of the ^{31}P resonance varies slightly depending on the acetylide substitution. The ^{1}H NMR spectra display resonances typical of symmetrically substituted [*trans*-$RuX_2(dmpe)_2$] complexes.[7,9,11] The ^{1}H NMR spectrum of **3**, for example, consists of two broad singlet resonances corresponding to the CH_3 and CH_2 protons of the phosphane ligand, which are observed at $\delta = 1.39$ and 1.37 ppm, respectively. Additionally, the $Si(CH_3)_3$ protons are evident as a singlet resonance at $\delta = 0.25$ ppm.

The $^{13}C\{^{1}H\}$ NMR spectrum of **3**, and the symmetrical bis(acetylides) in general, are relatively uncomplicated. The spectrum of **3** displays two phosphorus-coupled quintets at $\delta = 15.4$ ($^{2}J_{PC} = 7.4$ Hz) and 30.1 ppm ($^{2}J_{PC} = 13.3$ Hz) due to the CH_3 and CH_2 carbon atoms of the phosphane ligand, respectively, and two acetylide carbon resonances: a singlet at $\delta = 110.9$ and a phosphorus-coupled quintet at $\delta = 155.5$ ppm ($^{2}J_{PC} = 14.2$ Hz) due to the $RuC{\equiv}\mathit{C}$ and $Ru\mathit{C}{\equiv}C$ carbon atoms, respectively. Finally, the $SiMe_3$ carbon atoms appear as a singlet resonance at $\delta = 2.45$ ppm.

The ^{13}C NMR shifts for the acetylene carbon atoms appear in Table 1, and – with the exception of **2** – the signal of the ruthenium-bound acetylene carbon atom appears at significantly lower field than that of the β-acetylene carbon atom. For comparison, Table 1 also contains selected NMR spectroscopic data for previously reported metal acetylide complexes. The signals of the acetylene carbon atoms of all of the bis(acetylido)iron complexes are shifted significantly downfield compared to the shifts of their ruthenium analogues. Additionally, there is only a slight change between the ^{13}C chemical shifts of the acetylene carbon atoms between analogous depe and dmpe complexes.

Table 1. $^{31}P\{^{1}H\}$ and selected $^{13}C\{^{1}H\}$ NMR shifts [ppm] of a variety of symmetrical bis(acetylido)iron(II) and -ruthenium(II) complexes.[a]

Complex	δ_P	δ_C	
		$M\mathit{C}{\equiv}CR$	$MC{\equiv}\mathit{C}R$
1	40.8	131.4	111.3
2	40.6	103.2	113.7
3	38.7	155.5	110.9
4[b]	40.6	127.2	108.5
5[b]	40.8	125.6	108.6
6[b]	39.5	143.5	109.3
[*trans*-$Ru(C{\equiv}CPh)_2(depe)_2$][7]	51.3	130.6	112.8
[*trans*-$Ru(C{\equiv}CtBu)_2(depe)_2$][7]	52.3	104.6	115.8
[*trans*-$Ru(C{\equiv}CC_6H_4\text{-}4\text{-}C{\equiv}CH)_2(depe)_2$][7]	52.3	136.9	113.7
[*trans*-$Fe(C{\equiv}CPh)_2(dmpe)_2$][12]	68.6	140.0	117.1
[*trans*-$Fe(C{\equiv}CtBu)_2(dmpe)_2$][12]	69.4	121.9	111.9
[*trans*-$Fe(C{\equiv}CSiMe_3)_2(dmpe)_2$][13]	66.2	165.7	118.8
[*trans*-$Ru(C{\equiv}CC_6H_4\text{-}4\text{-}C{\equiv}CH)_2(dmpe)_2$][12]	67.9	147.2	117.7

[a] NMR spectrum recorded in $[D_6]$benzene unless otherwise stated. [b] $[D_8]$thf.

The IR spectroscopic data for the ruthenium bis(acetylide) complexes **1**–**6** is summarised in Table 2, which also contains data for related complexes found in the literature. In general, the stretching frequency decreases as dmpe ligands are replaced by depe ligands and when Ru^{II} is replaced by Fe^{II}. This may reflect the slightly stronger metal–carbon bonding in Fe^{II} bis(acetylide) complexes relative to their Ru^{II} analogues resulting in a weaker C≡C bond and a lower C≡C stretching frequency; depe is also a sterically more demanding ligand than dmpe resulting in weakening of the metal–phosphorus bond and a corresponding strengthening of the metal–acetylide bond.

Table 2. IR C≡C stretching frequencies [cm^{-1}] for symmetrical bis(acetylido)ruthenium(II) and bis(acetylido)iron(II) complexes.

Complex	C≡C
1	2051
2	2070
3	1984
4	2049
5	2057
6	2044
[*trans*-Ru(C≡CPh)$_2$(depe)$_2$][7]	2043
[*trans*-Ru(C≡C*t*Bu)$_2$(depe)$_2$][7]	2062
[*trans*-Ru(C≡CC$_6$H$_4$-4-C≡CH)$_2$(depe)$_2$]	2049
[*trans*-Fe(C≡C*t*Bu)$_2$(dmpe)$_2$][12]	2059
[*trans*-Fe(C≡CPh)$_2$(dmpe)$_2$][12]	2037
[*trans*-Fe(C≡CSiMe$_3$)$_2$(dmpe)$_2$][13]	1972
[*trans*-Fe(C≡CC$_6$H$_4$-4-C≡CH)$_2$(dmpe)$_2$][12]	2037, 2016

Crystals of **2** and **3** suitable for X-ray diffraction were obtained by slow concentration of benzene solutions. Crystals of **4** were deposited from a saturated benzene solution.

The complexes **2**, **3** and **4** are isostructural (Figure 1, Table 3), and their X-ray structures confirm the expected octahedral geometry in which the acetylido ligands occupy mutually *trans* positions. The structures of **2** and **3** have a C_2 centre of inversion about the metal centre.

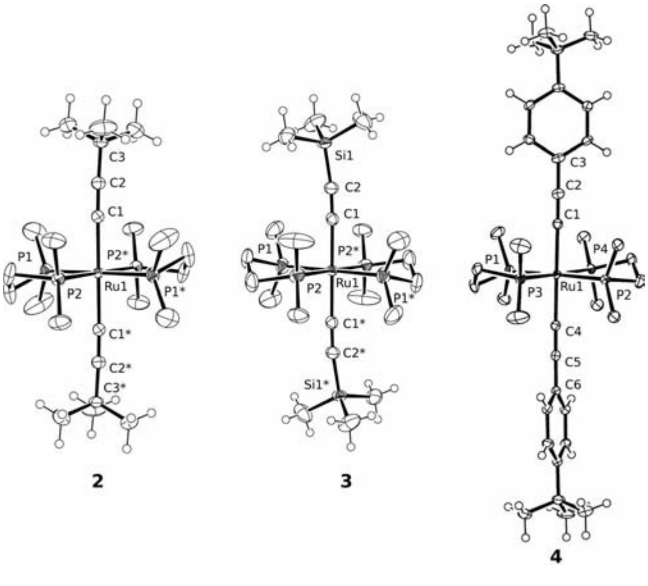


Figure 1. ORTEP plots of **2**, **3** and **4**. Thermal ellipsoids are shown at the 50% probability level, some hydrogen atoms have been omitted for clarity.

The Ru–C bond lengths at approximately 2.06 Å are identical (within experimental error) and compare well with those of previously reported bis(acetylido)ruthenium complexes.[7,8b,9,14] The C≡C bond lengths at approximately 1.22 Å are also consistent with those of previously reported complexes. There is a slight deviation from colinearity in the C≡C–Ru–C≡C acetylide backbones of **2** and **4**, with Ru(1)–C(1)–C(2) and C(1)–C(2)–C(3) angles of ca. 178 and ca. 177°, respectively, differing slightly from 180°. This distortion is even more pronounced in **3**, where the C(1)–C(2)–Si(1) bond angle of 172.0(2)° gives the complex a marked bend.

Table 3. Selected bond lengths [Å] and angles [°] for **2**, **3** and **4**.

Bond	2	3	4
Ru(1)–C(1)	2.067(2)	2.053(2)	2.057(3)
Ru(1)–C(4)			2.057(3)
C(1)–C(2)	1.214(4)	1.225(3)	1.223(4)
C(4)–C(5)			1.217(4)
C(2)–C(3)	1.476(3)	1.796(2)[a]	1.439(4)
C(5)–C(6)			1.440(4)
Ru(1)–P(1)	2.2989(7)	2.3072(6)	2.3058(8)
Ru(1)–P(2)	2.3030(7)	2.3020(6)	2.3061(8)
Ru(1)–P(3)			2.3093(8)
Ru(1)–P(4)			2.3173(8)
C(1)–Ru(1)–C(1)	180.00(12)	180.00(13)	
C(1)–Ru(1)–C(4)			179.20(11)
Ru(1)–C(1)–C(2)	178.4(2)	177.7(2)	178.1(3)
Ru(1)–C(4)–C(5)			176.4(2)
C(1)–C(2)–C(3)	177.4(3)	172.0(2)[b]	177.2(3)
C(4)–C(5)–C(6)			175.5(3)

[a] C(2)–Si(1) bond length. [b] C(1)–C(2)–Si(1) bond angle.

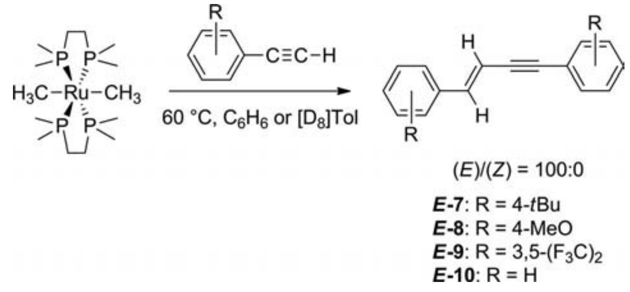
Alkyne Dimerisation

Head-to-head dimerisation of terminal alkynes is an attractive, atom-economical method of synthesising conjugated butenynes,[15] which are important as building blocks in organic synthesis and components of biologically active molecules.[16] Although many metal complexes, including early and late transition metals and lanthanides, are known to catalyse the dimerisation reaction of terminal alkynes,[17] in most cases a mixture of regio- and stereoisomeric butenynes is obtained. To date there have been few reported examples of highly selective catalysis.[16b]

A small number of ruthenium-based complexes have proven valuable catalysts for the formation of specific butenynes.[18] For example, Rappert and Yamamoto[19] reported the catalytic dimerisation of phenylacetylene to (*Z*)-1,4-diphenyl-1-buten-3-yne using [*cis*-RuH(NH$_3$)(PMe$_3$)$_4$]-[PF$_6$].

In the absence of methanol, heating of (4-*tert*-butylphenyl)acetylene with 8 mol-% of [*trans*-Ru(CH$_3$)$_2$(dmpe)$_2$] at 60 °C in benzene solution afforded (*E*)-1,4-bis(4-*tert*-butylphenyl)-1-buten-3-yne (*E*-**7**) (Scheme 3; Table 5, Run 1), which precipitated from solution. Identical reactions involving (4-methoxyphenyl)acetylene and [3,5-bis(trifluoromethyl)phenyl]acetylene gave (*E*)-1,4-bis(4-methoxyphenyl)-1-buten-3-yne (*E*-**8**) and (*E*)-1,4-bis[3,5-bis(trifluoromethyl)-phenyl]-1-buten-3-yne (*E*-**9**), respectively (Table 5, Runs 2 and 3). The butenynes produced crystallised directly from the reaction mixture or were isolated by evaporation of the solvent followed by recrystallisation from pentane.

Similarly, the reaction of [*trans*-RuMe$_2$(dmpe)$_2$] with 20 equiv. of PhCCH in [D$_8$]toluene at 60 °C for 16 h (Table 5, Run 4) resulted in the formation of the known compound[20] (*E*)-1,4-diphenyl-1-buten-3-yne (*E*-**10**) in 64% yield (based on phenylacetylene). In all cases, the phos-



Scheme 3.

phorus-containing species present after the reaction were mixtures of the mono- and bis(acetylido) complexes, [*trans*-RuMe(C≡CR)(dmpe)$_2$][9] and [*trans*-Ru(C≡CR)$_2$(dmpe)$_2$].

The ^{1}H NMR spectra of the organic butenynes show two vinyl proton resonances with a $^3J_{HH}$ coupling of ca. 16 Hz, characteristic of a disubstituted double bond with (*E*) stereochemistry.[21] For example, *E*-**8** exhibits doublet resonances at δ = 7.45 and 7.03 ppm with 16.4 Hz coupling.

The ^{13}C{^{1}H} NMR spectrum of *E*-**9** shows two F$_3$*C* carbon resonances as ^{19}F-coupled quartets at δ = 124.0 and 124.3 ppm with $^1J_{CF}$ = 272 Hz. The two F$_3$C*C* carbon atoms are observed as almost coincident quartets, with a smaller $^2J_{CF}$ = 33 Hz coupling at δ = 132.8 ppm, and there are $^3J_{CF}$ couplings of 4 Hz to the Ar*C*H atoms.

Crystals of *E*-**7** and *E*-**9** suitable for X-ray diffraction were obtained by recrystallisation of the compounds from pentane. Crystals of *E*-**8** were grown by slow concentration of toluene solutions. ORTEP plots of *E*-**7**, *E*-**8** and *E*-**9** are shown in Figure 2, and selected bond lengths and angles given in Table 4. The crystal structures confirm the (*E*) stereochemistry about the double bonds. The structures of *E*-**8** and *E*-**9** are disordered over two positions around the alkene and alkyne bridging units.

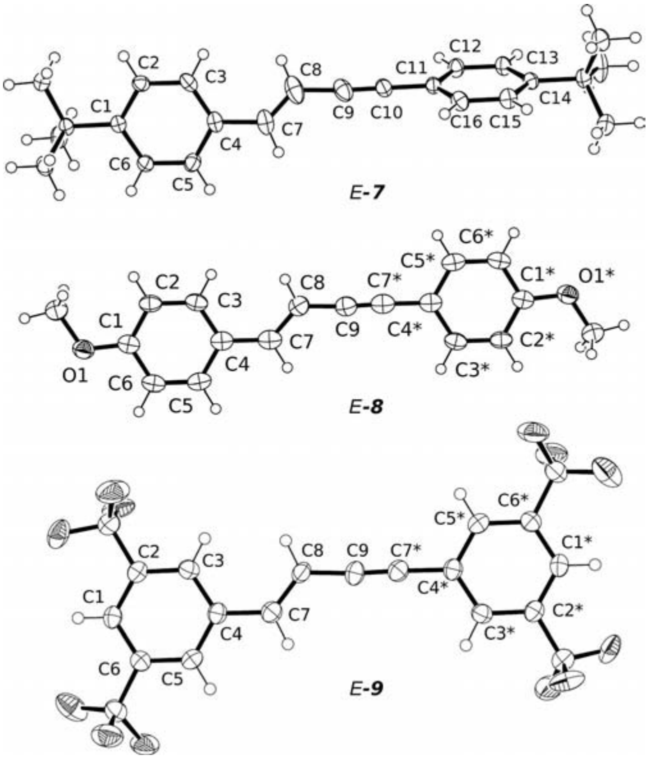
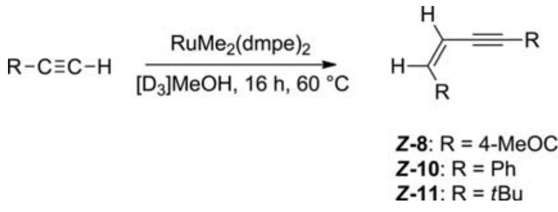


Figure 2. ORTEP plots of *E*-**7**, *E*-**8** and *E*-**9**. Thermal ellipsoids are shown at the 50% probability level; only one component of the disorder is shown in *E*-**8** and *E*-**9**.

Table 4. Selected bond lengths [Å] and angles [°] for *E*-**7**, *E*-**8** and *E*-**9**.

	E-**7**	*E*-**8**	*E*-**9**
C(10)–C(11)	1.442(2)	1.443(2)	1.454(3)
C(9)–C(10)	1.187(3)	1.107(3)	1.155(5)
C(8)–C(9)	1.421(3)	1.414(4)	1.427(6)
C(7)–C(8)	1.267(3)	1.376(3)	1.328(5)
C(4)–C(7)	1.472(2)	1.443(2)	1.454(3)
C(9)–C(10)–C(11)	178.3(2)	176.9(2)	178.1(3)
C(8)–C(9)–C(10)	175.0(2)	175.6(4)	175.9(5)
C(7)–C(8)–C(9)	131.4(2)	128.7(3)	126.0(5)
C(4)–C(7)–C(8)	131.6(2)	130.21(19)	128.2(3)

The known butenynes *Z*-**8**,[22] *Z*-**10**[22] and *Z*-**11**[23] were the exclusive dimerisation products resulting from the reaction of the respective terminal alkynes with [*trans*-RuMe$_2$(dmpe)$_2$] (5 mol-%) in neat [D$_3$]MeOH at 60 °C over 16 h (Scheme 4; Table 5, Runs 5–8). The use of [D$_4$]MeOD as solvent in place of [D$_3$]MeOH resulted in the formation of a mixture of D$_0$, D$_1$ and D$_2$ isotopologues of the (*Z*)-butenyne product.



Scheme 4.

When the reactions are monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy, it can be seen that, initially, there is rapid formation of [*trans*-Ru(C≡CR)$_2$(dmpe)$_2$], and the bis(acetylido) complexes may be isolated at this stage if required. With continued heating, the terminal alkyne is consumed completely, and the predominant phosphorus-containing species displays ^{31}P{^{1}H} and ^{1}H NMR resonances consistent with butenynylruthenium complexes.[24] Organometallic η^1- and/or η^3-butenynyl complexes are often observed as intermediates in alkyne dimerisation reactions, and their presence here is entirely consistent with the proposed literature mechanism of the dimerisation reaction.[25]

Attempts to dimerise [3,5-bis(trifluoromethyl)phenyl]acetylene in [D$_3$]MeOH were unsuccessful (Table 5, Run 8). This failure may be attributed to the insolubility of [*trans*-Ru[C≡CC$_6$H$_3$-3,5-(CF$_3$)$_2$]$_2$(dmpe)$_2$], which precipitates from the reaction medium immediately after addition of the terminal alkyne to [*trans*-RuMe$_2$(dmpe)$_2$].[26]

The choice of solvent clearly has a strong influence on the geometry of the final butenyne compound obtained in this reaction. Different mechanisms have been suggested for the formation of (*E*)- and (*Z*)-butenynes from terminal al-

Table 5. Dimerisation of terminal alkynes by *trans*-$RuMe_2(dmpe)_2$.

Run	Substrate	Catalyst loading[a] [mol-%]	Solvent	Time[b] [h]	(*E*)/(*Z*)[c]	Conversion[c] [%]	Yield[d] [%]
1	4-*t*BuC_6H_4CCH	8	C_6H_6	16	>99:1	47	37
2	4-$MeOC_6H_4CCH$	8	C_6H_6	16	>99:1	43	40
3	3,5-$(F_3C)_2C_6H_3CCH$	4	C_6H_6	100	>99:1	77	59
4	PhCCH	5	[D_8]toluene	16	96:4	35	26
5	4-$MeOC_6H_4CCH$	5	[D_3]MeOH	16	1:>99	>99	97
6	PhCCH	5	[D_3]MeOH	16	1:>99	>99	78
7	*t*BuCCH	5	[D_3]MeOH	16	1:>99	>99	81
8	3,5-$(F_3C)_2C_6H_3CCH$	5	[D_3]MeOH	16	n. a.	trace	0

[a] Catalyst loading = (mol catalyst/mol substrate) × 100. [b] Reactions carried out at 60 °C. [c] Determined by NMR spectroscopy. [d] Isolated yield.

kynes;[27] formation of the (*Z*) isomer occurs by intramolecular addition of an alkynyl ligand onto the α-carbon atom of a metal-bound vinylidene ligand.[18a,28] Conversely, (*E*) isomers result from the insertion of a π-bound alkyne into an alkynyl–metal bond.[27] The use of methanol as a solvent appears to favour the formation of a vinylidene complex as the intermediate and the (*Z*) isomer as the product.

Conclusions

The reaction between terminal acetylenes and dimethylruthenium complexes was used as a viable alternative approach to synthesise a range of bis(acetylido)ruthenium complexes. The effectiveness of this route has been demonstrated, and a number of new symmetrically substituted bis(acetylido)ruthenium complexes were isolated and characterised. The bis(acetylido)ruthenium complexes also serve as catalysts for the head-to-head dimerisation of terminal acetylenes to butenynes and, depending on the reaction solvent, the stereochemistry of the butenyne products can be controlled to give predominately either (*E*) or (*Z*) isomers.

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. Methanol, toluene, and benzene were dried and degassed by heating with standard drying agents under dry nitrogen and were freshly distilled prior to use. NMR spectra were recorded with Bruker Avance III 600 (operating at 600.13, 150.9 and 242.9 MHz for ^1H, ^{13}C and ^{31}P, respectively), Bruker DMX500 (operating at 500.13, 125.92, and 202.45 MHz for ^1H, ^{13}C and ^{31}P, respectively), Bruker AVANCE DRX400 (operating at 400.13, 125.76, and 161.98 MHz for ^1H, ^{13}C and ^{31}P, respectively) or Bruker DPX300 (operating at 300.13 and 121.49 MHz for ^1H and ^{31}P, respectively) spectrometers at 300 K unless otherwise stated. ^1H and ^{13}C NMR spectra were referenced to residual solvent resonances, whereas ^{31}P NMR spectra were referenced to external neat trimethyl phosphite (δ = 140.85 ppm). IR spectra were recorded with a Shimadzu 8400 series FTIR spectrometer. Where indicated, mass spectra were recorded by electrospray ionization (ESI) with a Finnigan LCQ mass spectrometer. The complex [*trans*-$RuMe_2(dmpe)_2$] was prepared as described.[9] Terminal alkynes were purchased from Aldrich and used as received.

[*trans*-Ru(C≡CPh)$_2$(dmpe)$_2$] (1): Phenylacetylene (0.50 mL, 4.5 mmol) was added to a solution of [*trans*-$Ru(CH_3)_2(dmpe)_2$] (0.35 g, 0.81 mmol) in benzene (2 mL). The solution was heated under nitrogen at 60 °C for 2 d. The volatile components were removed under reduced pressure, and the residue was recrystallised from benzene to give **1** as a yellow crystalline solid (0.23 g, 47%). The NMR spectra are identical to reported data.[29] $C_{28}H_{42}P_4Ru$ (603.596): calcd. C 55.72, H 7.01; found C 55.55, H 7.09. IR (KBr): $\tilde{\nu}_{max}$ = 2051 [ν(C≡C)] cm^{-1}.

[*trans*-Ru(C≡C*t*Bu)$_2$(dmpe)$_2$] (2):[7] *tert*-Butylacetylene (0.50 mL, 4.0 mmol) was added to a solution of [*trans*-$Ru(CH_3)_2(dmpe)_2$] (0.26 g, 0.60 mmol) in benzene (0.5 mL). The solution was heated under nitrogen at 60 °C for 14 d. The solvent was removed under reduced pressure to give **2** as a white solid (0.33 g, 97%). Crystals suitable for X-ray diffraction were obtained from a benzene solution. $^{31}P\{^1H\}$ NMR (121.51 MHz, [D_6]benzene): δ = 40.64 (s) ppm. $^1H\{^{31}P\}$ NMR (300.13 MHz, [D_6]benzene): δ = 1.45 (s, 24 H, PCH_3), 1.42 (s, 8 H, PCH_2), 1.32 (s, 18 H, CCH_3) ppm. $^{13}C\{^1H,^{31}P\}$ (161.98 MHz, [D_6]benzene): δ = 113.7 (RuC≡*C*), 103.2 (Ru*C*≡C), 33.8 (*C*CH$_3$), 30.4 (P*C*H$_2$), 29.8 (C*C*H$_3$), 15.6 (P*C*H$_3$) ppm. $C_{24}H_{50}P_4Ru$ (563.62): calcd. C 51.14, H 8.94; found C 51.26, H 9.03. ESI-MS: *m*/*z* (%) = 565 [M + H]$^+$ (20), 523 (70), 494 (100), 441 (30), 401 [M – (C≡C*t*Bu)$_2$]$^+$ (15). HRMS (ESI$^+$, MeOH): calcd. for [M + 1] 565.1979; found 565.1988. IR (KBr): $\tilde{\nu}_{max}$ = 2070 [ν(C≡C)] cm^{-1}.

[*trans*-Ru(C≡CSiMe$_3$)$_2$(dmpe)$_2$] (3): (Trimethylsilyl)acetylene (0.50 mL, 3.5 mmol) was added to a solution of [*trans*-$Ru(CH_3)_2(dmpe)_2$] (0.22 g, 0.51 mmol) in benzene (0.5 mL). The solution was heated under nitrogen at 60 °C for 14 d. The solvent was removed under reduced pressure and the residue washed with ice-cold pentane (2 mL) to give **3** (0.26 g, 86%) as a white solid, which required no further purification. $^{31}P\{^1H\}$ NMR (121.51 MHz, [D_6]benzene): δ = 38.72 (s) ppm. $^1H\{^{31}P\}$ NMR (300.13 MHz, [D_6]benzene): δ = 1.39 (s, 24 H, PCH_3), 1.37 (s, 8 H, PCH_2), 0.25 (s, 18 H, $SiCH_3$) ppm. $^{13}C\{^1H,^{31}P\}$ (100.61 MHz, [D_6]benzene): δ = 155.5 (Ru*C*≡C), 110.9 (RuC≡*C*), 30.1 (P*C*H$_2$), 15.4 (P*C*H$_3$), 2.45 (Si*C*H$_3$) ppm. $C_{22}H_{50}P_4RuSi_2$ (595.78): calcd. C 44.35, H 8.46; found C 44.63, H 8.72. ESI-MS: *m*/*z* (%) = 597 [M + H]$^+$ (100), 539 (30), 524 (15), 441 (30), 401 [M – (C≡CSiMe$_3$)$_2$]$^+$ (10). HRMS (ESI$^+$, MeOH): calcd. for [M + 1] 597.15174; found 597.15153. IR (KBr): $\tilde{\nu}_{max}$ = 1984 [ν(C≡C)] cm^{-1}.

[*trans*-Ru(C≡CC$_6$H$_4$-4-*t*Bu)$_2$(dmpe)$_2$] (4): (4-*tert*-Butylphenyl)acetylene (0.50 mL, 2.77 mmol) was added to a solution of [*trans*-$Ru(CH_3)_2(dmpe)_2$] (0.058 g, 0.134 mmol) in toluene (3 mL). Methanol (1 mL) was added, and the solution was stirred at room temperature for 45 min. The volatile compounds were removed under reduced pressure, and the residue was washed with hexane (2 ×

2 mL). The compound was dried in vacuo to give **4** as a pale yellow powder. Yield: 0.064 g (67%). $^{31}P\{^1H\}$ NMR (202 MHz, $[D_8]$thf): δ = 40.6 ppm. ^1H NMR (500 MHz, $[D_8]$thf): δ = 7.01 (AA′ of AA′XX′, 4 H, Ar*H*), 6.88 (XX′ of AA′XX′, 4 H, Ar*H*), 1.71 (m, 8 H, PCH_2), 1.59 (br. s, 24 H, PCH_3), 1.23 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $[D_8]$thf): δ = 144.3 [s, Ar*C*C(CH$_3$)$_3$], 129.4 (s, Ar*C*H), 128.6 (s, ≡C*C*), 127.2 (p, $^2J_{CP}$ = 15.2 Hz, Ru*C*≡C), 123.9 (s, Ar*C*H), 108.5 (br. s, RuC≡*C*), 33.7 [s, *C*(CH$_3$)$_3$], 30.8 [s, C(*C*H$_3$)$_3$], 30.0 (m, P*C*H$_2$), 15.0 (m, P*C*H$_3$) ppm. $C_{36}H_{58}P_4Ru$ (715.804): calcd. C 60.45, H 8.17; found C 60.22, H 8.26. IR (Fluorolube): $\tilde{\nu}_{max}$ = 2049 [ν(C≡C)] cm^{-1}.

[*trans*-Ru(C≡CC$_6$H$_4$-4-OMe)$_2$(dmpe)$_2$] (5): (4-Methoxyphenyl)acetylene (1 mL, 7.7 mmol) was added to a solution of [*trans*-Ru(CH$_3$)$_2$(dmpe)$_2$] (0.1615 g, 0.374 mmol) in methanol (10 mL). The solution was stirred at room temperature for 90 min, during which time a yellow solid precipitated. The volatile compounds were removed under reduced pressure, and the residue was washed with pentane (2 × 2 mL). The compound was dried in vacuo to give **5** as a pale yellow powder. Yield: 0.152 g (61%). $^{31}P\{^1H\}$ NMR (161 MHz, $[D_8]$thf): δ = 40.8 ppm. ^1H NMR (400 MHz, $[D_8]$thf): δ = 6.86 (AA′ of AA′XX′, 4 H, Ar*H*), 6.55 (XX′ of AA′XX′, 4 H, Ar*H*), 3.63 (s, 6 H, OC*H*$_3$), 1.69 (m, 8 H, PC*H*$_2$), 1.57 (br. s, 24 H, PC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $[D_8]$thf): δ = 156.7 (s, *C*OCH$_3$), 131.5 (s, Ar*C*H), 125.6 (m, Ru*C*≡C), 125.5 (s, Ar*C*$_{ipso}$), 113.9 (s, Ar*C*H), 108.6 (br. s, RuC≡*C*), 55.4 (s, O*C*H$_3$), 31.0 (m, P*C*H$_2$), 16.1 (m, P*C*H$_3$) ppm. $C_{30}H_{46}O_2P_4Ru$ (663.659): calcd. C 54.29, H 6.99; found C 54.58, H 7.26. IR (Fluorolube): $\tilde{\nu}_{max}$ = 2057 [ν(C≡C)] cm^{-1}.

[*trans*-Ru[C≡CC$_6$H$_3$-3,5-(CF$_3$)$_2$]$_2$(dmpe)$_2$] (6): [3,5-Bis(trifluoromethyl)phenyl]acetylene (200 µL, 1.13 mmol) was added to a solution of [*trans*-RuMe$_2$(dmpe)$_2$] (0.0945 g, 0.219 mmol) in MeOH (15 mL). The solution was stirred at room temperature for 4 h, then concentrated under reduced pressure to ca. 3 mL. The supernatant was decanted and the yellow residue dried in vacuo to give *cis*-**6** as a pale yellow powder. Yield: 0.141 g (73%). $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_8]$thf): δ = 40.2 (apparent t, splitting = 22.7 Hz), 30.0 (apparent t, splitting = 22.7 Hz) ppm. This compound was taken up in $[D_8]$thf and irradiated with a mercury-vapour lamp for 18 h. The solvent was removed under reduced pressure, and the residue was crystallised from toluene to yield **6** as a pale yellow powder. $^{31}P\{^1H\}$ NMR (242.93 MHz, $[D_8]$thf): δ = 39.5 (s) ppm. ^1H NMR (600.13 MHz, $[D_8]$thf): δ = 7.41 (s, 2 H, *p*-Ar*H*), 7.38 (s, 4 H, *o*-Ar*H*), 1.78 (m, 8 H, PC*H*$_2$), 1.60 (s, 24 H, PC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $[D_8]$thf): δ = 143.5 (p, $^2J_{CP}$ = 15.1 Hz, Ru*C*), 133.8 (s, *ipso-C*), 132.0 (q, $^2J_{CF}$ = 32.1 Hz, *C*CF$_3$), 130.3 (br. s, *o*-Ar*C*), 125.0 (q, $^1J_{CF}$ = 269.7, *C*F$_3$), 115.7 (sept, $^3J_{CF}$ = 3.8 Hz, *p*-Ar*C*), 109.3 (s, RuC≡*C*), 30.9 (p, $^1J_{CP}$ = 13.4 Hz, P*C*H$_2$), 16.0 (m, P*C*H$_3$) ppm. $C_{32}H_{38}F_{12}P_4Ru$ (875.604): calcd. C 43.89, H 4.37; found C 44.18, H 4.66. IR (Fluorolube): $\tilde{\nu}_{max}$ = 2044 [ν(C≡C)] cm^{-1}.

(*E*)-1,4-Bis(4-*tert*-butylphenyl)-1-buten-3-yne (*E*-7): (4-*tert*-Butylphenyl)acetylene (1 mL, 5.5 mmol) was added to a solution of [*trans*-Ru(CH$_3$)$_2$(dmpe)$_2$] (0.20 g, 0.46 mmol) in benzene (2 mL). The reaction mixture was heated under nitrogen at 60 °C for 16 h. The mixture was allowed to cool, and the volatile components were removed under reduced pressure. The residue was redissolved in pentane from which colourless crystals of *E*-**7** precipitated (0.32 g, 37%), which were isolated by filtration. ^1H NMR (400.13 MHz, $[D_6]$benzene): δ = 7.99 (AA′ of AA′XX′, 2 H, Ar*H*C≡C), 7.49 (AA′ of AA′XX′, 2 H, Ar*H*C=C), 7.34 (XX′ of AA′XX′, 2 H, Ar*H*C≡C), 7.17 (XX′ of AA′XX′, 2 H, Ar*H*C=C), 6.52 (d, $^3J_{HH}$ = 11.7 Hz, 1 H, ArC*H*=CH), 5.85 (d, $^3J_{HH}$ = 11.7 Hz, 1 H, ArCH=C*H*C≡C), 1.27 [s, 9 H, C(C*H*$_3$)$_3$], 1.18 [s, 9 H, C(C*H*$_3$)$_3$] ppm. Spectroscopic properties are identical to those reported by Eisen and co-workers.[30]

(*E*)-1,4-Bis[3,5-bis(trifluoromethyl)phenyl]-1-buten-3-yne (*E*-8): 1-Ethynyl-3,5-bis(trifluoromethyl)benzene (1.0 mL, 5.6 mmol) was added to a solution of [*trans*-Ru(CH$_3$)$_2$(dmpe)$_2$] (0.10 g, 0.23 mmol) in benzene (2 mL). The reaction mixture was heated under nitrogen at 60 °C for 16 h and allowed to cool. Colourless crystals formed, which were isolated by filtration and washed with pentane to give *E*-**8** (0.53 g, 40%). ^1H NMR (300.13 MHz, $[D_6]$acetone): δ = 8.26 (s, 2 H, Ar*H*C≡C), 8.12 (s, 2 H, Ar*H*C=C), 8.08 (s, 1 H, Ar*H*C≡C), 8.00 (s, 1 H, Ar*H*C=C), 7.45 (d, $^3J_{HH}$ = 16.4 Hz, 1 H, ArC*H*=CH), 7.03 (d, $^3J_{HH}$ = 16.4 Hz, 1 H, ArCH=C*H*C≡C) ppm. $^{13}C\{^1H\}$ NMR (75.49 MHz, $[D_6]$acetone): δ = 141.1 (Ar*C*), 139.4 (Ar*C*), 132.8 (q, $^2J_{CF}$ = 33 Hz, *C*CF$_3$), 132.8 (q, $^2J_{CF}$ = 33 Hz, *C*CF$_3$), 132.5 (d, $^3J_{CF}$ = 4 Hz, Ar*C*H), 127.8 (d, $^3J_{CF}$ = 4 Hz, Ar*C*H), 126.4 (s, C≡C*C*=C), 124.3 (q, $^1J_{CF}$ = 272 Hz, *C*F$_3$), 124.0 (q, $^1J_{CF}$ = 272 Hz, *C*F$_3$), 122.9 (q, $^3J_{CF}$ = 4 Hz, Ar*C*H), 122.8 (q, $^3J_{CF}$ = 4 Hz, Ar*C*H), 112.4 (s, C≡CC=*C*), 92.2 (s, C≡*C*C=C), 90.6 (s, *C*≡CC=C) ppm. $C_{20}H_8F_{12}$ (476.264): calcd. C 50.44, H 1.69; found C 50.40, H 1.81.

(*E*)-1,4-Bis(4-methoxyphenyl)-1-buten-3-yne (*E*-9): (4-Methoxyphenyl)acetylene (1.50 mL, 11.6 mmol) was added to a solution of [*trans*-Ru(CH$_3$)$_2$(dmpe)$_2$] (0.40 g, 0.93 mmol) in benzene (2 mL). The reaction mixture was heated under nitrogen at 60 °C for 16 h and allowed to cool. Colourless crystals precipitated, and these were isolated by filtration and washed with pentane to afford the head-to-head dimer *E*-**9** (0.9 g, 59%). ^1H NMR (300.13 MHz, $[D_6]$benzene): δ = 7.49 (AA′ of AA′XX′, 2 H, Ar*H*), 7.07 (AA′ of AA′XX′, 2 H, Ar*H*), 7.05 (d, $^3J_{HH}$ = 16.7 Hz, 1 H, C*H*=CH), 6.61 (m, XX′ of AA′XX′, 4 H, Ar*H*), 6.30 (d, $^3J_{HH}$ = 16.7 Hz, 1 H, CH=C*H*), 3.22 (s, 3 H, OC*H*$_3$), 3.17 (s, 3 H, OC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.49 MHz, $[D_6]$benzene): δ = 160.2 (Ar*C*OMe), 160.1 (Ar*C*OMe), 140.6 (Ar*C*), 138.0 (Ar*C*), 133.2 (Ar*C*H), 130.7 (Ar*C*H), 130.3 (C≡C*C*=C), 114.5 (Ar*C*H), 114.1 (Ar*C*H), 105.6 (C≡CC=*C*), 96.1 (C≡*C*C=C), 88.3 (*C*≡CC=C), 54.7 (O*C*H$_3$), 54.6 (O*C*H$_3$) ppm. $C_{18}H_{16}O_2$ (264.324): calcd. C 81.79, H 6.10; found C 81.80, H 6.34. Spectroscopic properties are identical to those reported by Bassetti and co-workers.[31]

General Procedure for the Dimerisation of Terminal Alkynes

In $[D_3]$MeOH: $[D_3]$MeOH (ca 0.7 mL) was vacuum-transferred onto solid [*trans*-RuMe$_2$(dmpe)$_2$] (ca. 0.02 g). The mixture was thawed and the terminal alkyne added through a syringe. The mixture was heated to 60 °C and monitored periodically by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After the desired time, CDCl$_3$ was added and the mixture washed with water. The organic layer was separated, dried with MgSO$_4$ and subjected to NMR spectroscopic analysis. The organic product was isolated from the CDCl$_3$ solution.

In $[D_8]$Toluene: $[D_8]$Toluene (ca. 0.7 mL) was vacuum-transferred onto solid [*trans*-RuMe$_2$(dmpe)$_2$] (ca. 0.02 g). The mixture was thawed and the terminal alkyne added through a syringe. The mixture was heated to 60 °C for the desired time with periodic monitoring by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

X-ray Structure Determinations: Single crystals of **2**, **3** and *E*-**8** were attached, with Exxon Paratone N, to a short 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 kappa APEXII area detector diffractometer employing graphite-monochromated Mo-K_α radiation generated from a fine-focus sealed tube was used for the data

Table 6. Crystallographic data for **2**, **3**, **4**, *E*-**7**, *E*-**8** and *E*-**9**.

	2	**3**	**4**	*E*-**7**	*E*-**8**	*E*-**9**
Empirical formula	$C_{24}H_{50}P_4Ru$	$C_{22}H_{50}P_4RuSi_2$	$C_{36}H_{58}P_4Ru$	$C_{24}H_{28}$	$C_{18}H_{16}O_2$	$C_{10}H_{20}F_6$
Formula mass	563.59	595.75	715.77	316.46	264.31	254.26
Crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
a [Å]	9.0968(5)	9.3483(6)	13.8356(10)	12.707(4)	7.8575(8)	4.9195(14)
b [Å]	9.4867(5)	9.9106(7)	20.9962(14)	9.931(3)	8.6286(9)	23.257(6)
c [Å]	9.8880(6)	10.1310(7)	14.4248(10)	15.273(5)	11.7457(13)	8.262(2)
α [°]	74.721(2)	70.680(3)	90	90	102.281(5)	90
β [°]	70.786(2)	64.586(3)	112.461(2)	94.440(17)	99.895(5)	102.097(8)
γ [°]	71.702(2)	72.539(3)	90	90	108.734(4)	90
V [Å^3]	752.73(7)	786.16(9)	3872.5(5)	1921.5(11)	711.65(13)	924.2(4)
T [K]	150(2)	150(2)	296(2)	123(2)	150(2)	173(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Z	1	1	4	4	2	4
No. of reflections measured	6431	11125	33663	44290	10251	3638
No. of independent reflections	2627	2750	8526	4203	2500	1937
R_{int}	0.0538	0.0277	0.0568	0.0474	0.0422	0.0265
Final R_1 value [$I > 2\sigma(I)$]	0.0319	0.0253	0.0441	0.0609	0.0373	0.0473
Final $wR(F^2)$ value [$I > 2\sigma(I)$]	0.0859	0.0620	0.0894	0.1609	0.0966	0.0972
Final R_1 value (all data)	0.0329	0.0295	0.0650	0.0759	0.0442	0.0927
Final $wR(F^2)$ value (all data)	0.0869	0.0656	0.0978	0.1748	0.1024	0.1133

collection. Data were collected at 150(2) K. The data integration and reduction were undertaken with APEX2,[32] and subsequent computations were carried out with the X-Seed[33] graphical user interface. The structures were solved by direct methods with SHELXS-97[34] and extended and refined with SHELXL-97.[34] 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. Single crystals of **4**, *E*-**7** and *E*-**9** were mounted on glass fibres. Data were collected with a Bruker Nonius X8Apex2 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 123(2) (**4**) or 100(2) K (*E*-**7**) or with a Bruker SMART-CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 173(2) K (*E*-**9**). The structures were solved by direct methods and full-matrix least-squares refinements by using the SHELXTL-97 program package.[34] Hydrogen atoms were placed at calculated positions, and all non-hydrogen atoms were refined anisotropically. All calculations were performed by using the crystallographic and structure refinement data summarised in Table 6. CCDC-800005 (for **2**), -800006 (for **3**), -800007 (for **4**), -800008 (for *E*-**7**), -800009 (for *E*-**8**) and -800010 (for *E*-**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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