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# Preparation, structures and some reactions of novel diynyl complexes of iron and ruthenium

Michael I. Bruce,<sup>*a*</sup> Benjamin G. Ellis,<sup>*a,b*</sup> Maryka Gaudio,<sup>*a*</sup> Claude Lapinte,<sup>*b*</sup> Giovanni Melino,<sup>*a*</sup> Frédéric Paul,<sup>*a,b*</sup> Brian W. Skelton,<sup>*c*</sup> Mark E. Smith,<sup>*a,b*</sup> Loic Toupet<sup>*d*</sup> and Allan H. White<sup>*c*</sup>

<sup>a</sup> Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005

<sup>b</sup> Organométalliques et Catalyse: Chimie et Electrochimie Moléculaire, UMR CNRS 6509,

Institut de Chimie de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

<sup>c</sup> Department of Chemistry, University of Western Australia, Crawley, Western Australia 6009

<sup>d</sup> Groupe Matière Condensée et Matériaux, UMR CNRS 6626, Université de Rennes 1, 35042 Rennes Cedex, France

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Reactions between HC=CC=CSiMe<sub>3</sub> and several ruthenium halide precursors have given the complexes Ru(C=CC=CSiMe<sub>3</sub>)(L<sub>2</sub>)Cp' [Cp' = Cp, L = CO (1), PPh<sub>3</sub> (2); Cp' = Cp\*, L<sub>2</sub> = dppe (3)]. Proto-desilylation of 2 and 3 have given unsubstituted buta-1,3-diyn-1-yl complexes Ru(C=CC=CH)(L<sub>2</sub>)Cp' [Cp' = Cp, L = PPh<sub>3</sub> (5); Cp' = Cp\*, L<sub>2</sub> = dppe (6)]. Replacement of H in 5 or 6 with Au(PR<sub>3</sub>) groups was achieved in reactions with AuCl(PR<sub>3</sub>) in the presence of KN(SiMe<sub>3</sub>)<sub>2</sub> to give Ru(C=CC=CAu(PR<sub>3</sub>))(L<sub>2</sub>)Cp' [Cp' = Cp, L = PPh<sub>3</sub>, R = Ph (7); Cp' = Cp\*, L<sub>2</sub> = dppe, R = Ph (8), tol (9)]. The asymmetrically end-capped {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C=CC=C{Ru(dppe)Cp\*} (10) was obtained from Ru(C=CC=CH)(dppe)Cp\* and RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp. Single-crystal X-ray structural determinations of 1–3 and 6–9 are reported, with a comparative determination of the structure of Fe(C=CC=CSiMe<sub>3</sub>)(dppe)Cp\* (4), and those of a fifth polymorph of {Ru(PPh<sub>3</sub>)<sub>2</sub>Cp}<sub>2</sub>( $\mu$ -C=CC=C) (12), and {Ru(dppe)Cp}<sub>2</sub>( $\mu$ -C=CC=C) (13).

## Introduction

The study of diynyl complexes of the Group 8 metals continues to provide novel chemistry,<sup>1,2</sup> while complexes containing C<sub>4</sub> chains end-capped by M(PP)Cp' [M = Fe, Ru, Os; PP = (PPh<sub>3</sub>)<sub>2</sub>, dppe, dppm; Cp' = Cp,  $Cp^*$ ] have been shown to undergo a variety of redox processes which suggest that electronic communication between the two metal centres occurs rather efficiently by way of the carbon chain.<sup>3-9</sup> A variety of precursors of these complexes has been made, including compounds containing M-C<sub>4</sub>R [R = H, SiMe<sub>3</sub>, Au(PR'<sub>3</sub>)] fragments. While the syntheses and spectroscopic properties of several of these have been reported earlier, we have recently been able to obtain crystalline samples which have been suitable for successful single-crystal X-ray structural characterisations. This paper describes and compares several of these structures and includes previously unreported synthetic procedures and spectroscopic data.

### Results

#### Syntheses

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The chemistry described below is summarised in Scheme 1 and details follow for the individual syntheses and characterisations.

(a) Ru(C=CC=CSiMe<sub>3</sub>)(L)<sub>2</sub>Cp' [Cp' = Cp, L = CO (1), PPh<sub>3</sub> (2); Cp' = Cp\*, L<sub>2</sub> = dppe (3)]. The copper(1)-catalysed coupling between RuBr(CO)<sub>2</sub>Cp and HC=CC=CSiMe<sub>3</sub> in thf/NEt<sub>3</sub> gave Ru(C=CC=CSiMe<sub>3</sub>)(CO)<sub>2</sub>Cp (1) in good yield. Reactions between RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp or RuCl(dppe)Cp\* and HC=CC= CSiMe<sub>3</sub> in a mixed thf/NEt<sub>3</sub> solvent in the presence of Na[BPh<sub>4</sub>] gave orange-brown Ru(C=CC=CSiMe<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cp (2) in 94% yield, or bright yellow Ru(C=CC=CSiMe<sub>3</sub>)(dppe)Cp\* (3) in 79% yield. For 2 and 3, thf was used to dissolve the RuCl-(PPh<sub>3</sub>)<sub>2</sub>Cp or RuCl(dppe)Cp\* precursors and heating was required to facilitate cleavage of the Ru–Cl bond, which is stronger than the Fe–Cl bond.<sup>6c,10</sup> No reaction was observed after stirring at r.t. for 24 h, but after stirring at 50 °C for 16 h the desired product 2 was obtained in almost quantitative yield.



The IR spectra are characterised by the presence of three  $\nu(C=C)$  bands between 2181 and 1990 cm<sup>-1</sup>, as found previously for Fe(C=CC=CSiMe<sub>3</sub>)(dppe)Cp\* (4), and ascribed to Fermi coupling of one of the modes with another oscillator, such as the SiMe<sub>3</sub> group.<sup>6c,11</sup> For 1, two  $\nu(CO)$  bands are observed at 2056 and 2002 cm<sup>-1</sup>. The NMR spectra of 1–3 (Table 1) contain

Table 1 Spectroscopic data

Complex [X]	(C - C) I = -1					$\delta_{\rm H} \left( J({\rm HP})/{\rm Hz} \right)$				
	$v(C=C)/cm^{-1}$	$v(C\equiv C)/cm^{-1}$		$\delta_{\mathbf{P}}$		Cp' CH <sub>2</sub>		Ph		
$1^a$ [SiMe <sub>3</sub> ]	2181m, 2128n	n, 2114 (sh)	_		0.12	5.41	_	_		
2 [SiMe <sub>2</sub> ]	2166m, 2103s	. 1997m	50.7		0.26	4.30	_	6.92-7.58		
3 <sup>b</sup> [SiMe <sub>1</sub> ]	2171w. 2095m	n. 1990w	81.3		0.23	1.53 (1.8)	1.78, 2.49	6.89-7.86		
5 (H)	2107s. 1970 (b	or)	51.0		1.42	4.29	_	7.06-7.42		
6° [H]	2109w. 1971w	,	81.3		1.44	1.55	1.79. 2.54	7.09-7.87		
$7 [Au(PPh_2)]$	2116s. 2073m	. 1982w	42.5 (	PAu), 50.0 (dppe)	_	4.28	_	7.08-7.59		
$8^{d}$ [Au(PPh_{2})]	2119m, 2072n	n. 1981w	42.5 (	PAu). 80.8 (dppe)	_	1.52	2.15. 2.77	7.04-7.76		
$9^{e}$ [Au{P(tol) <sub>2</sub> }]	2124m, 2073n	n. 1987m	51.5 (	PAu). 82.0 (dppe)	_	1.56	2.19, 2.81	7.08-7.79		
10	1966m	,	51.4 (	PPh <sub>2</sub> ), 86.1 (dppe)	_	4.42, 4.77	2.18, 3.02	6.83-8.16		
11	1965m		51.5 (	PPh <sub>2</sub> ), 82.0 (dppe)	_	1.73 (Cp*), 4.32 (Cp)	2.03, 2.92	7.00-8.09		
13	1970m		86.7 (dppe)		_	4.60	2.01, 2.35	7.03–7.71		
	$\delta_{\rm C} \left( J({\rm CP})/{\rm Hz} \right)$									
Complex [X]	$\overline{C_{a}}$	$C_{\beta}$	$\mathbf{C}_{\gamma}$	$C_{\delta}$	Х	Ср	Р	h		
$1^a$ [SiMe <sub>3</sub> ]	92.55	90.84	84.23	72.74	0.01	87.84	_			
2 [SiMe <sub>3</sub> ]	120.67 (24)	96.29	94.37	67.22	0.93	85.59	12	25.55-138.90		
$3^{b}$ [SiMe <sub>3</sub> ]	120.06	115.84	96.59	66.94	1.13	10.12, 93.40 (2.1)	12	29.16-138.88		
5 [H]	116.51 (24)	94.34	73.87	51.54	_	85.59	12	25.59-138.63		
6° [H]	124.90 (24)	91.73	75.33	52.47	_	10.77, 93.29	12	27.50-138.99		
7 [Au(PPh <sub>3</sub> )]	_	_	_	_	_	87.8	12	29.4–141.2		
$8^{d}$ [Au(PPh_3)]	118.65 (23)	92.20	94.61	110.00 (75)	_	10.26, 93.29	12	27.51-139.13		
$9^{e}$ [Au{P(tol) <sub>3</sub> }]	118.12 (24)	92.32	94.57	111.40 (128)	_	10.16, 93.28	12	27.47-142.11		
10 <sup>f</sup> .	_	_	_	-	_	82.06 [Ru(dppe)], 85.57 [Ru(PPh <sub>2</sub> ) <sub>2</sub> ]		28.17-139.86		
11 <sup>g</sup>	_	_	_	_	_	10.71, 93.05 (Cp*), 85.94 (Cp)		27.36-140.02		
13 <sup>h</sup>	_	_	_	_	_	82.23	12	27.21-143.06		

resonances which are characteristic of the ligand groups present. For 1, the CO singlet is at  $\delta_{\rm C}$  195.90. Four resonances in the <sup>13</sup>C NMR spectra of each compound could be assigned to the carbons of the C<sub>4</sub> chain. For 1, C<sub>a-δ</sub> are found at  $\delta_{\rm C}$  92.55, 90.84, 84.23 and 72.74, respectively. For 2 and 3, the presence of the tertiary phosphine ligands results in a downfield shift, so that C<sub>a-δ</sub> are now observed at  $\delta_{\rm C}$  120.67 (2) and 120.06 (3), 96.29 and 115.84, 94.37 and 96.59, and 67.22 and 66.94, respectively, those for C<sub>a</sub> showing triplet coupling to the <sup>31</sup>P nuclei. The <sup>31</sup>P NMR spectra of 2 and 3 contain singlets at  $\delta_{\rm P}$  50.7 and 81.3 for the PPh<sub>3</sub> and dppe ligands, respectively. The electrospray mass spectra of all compounds contained M<sup>+</sup> ions, in some cases accompanied by adduct ions formed by addition of MeOH solvent.

(b)  $Ru(C \equiv CC \equiv CH)(L)_2 Cp' [Cp' = Cp, L = PPh_3 (5); Cp' =$  $Cp^*$ ,  $L_2 = dppe$  (6)]. Proto-desilvation of 2 and 3 with [NBu<sub>4</sub>]F in wet thf<sup>12</sup> gave the versatile precursors Ru(C=CC=CH)-(PPh<sub>3</sub>)<sub>2</sub>Cp (5) and Ru(C=CC=CH)(dppe)Cp\* (6) in 74 and 96% yields, respectively. The former is a mustard-yellow solid, while 6 forms air-stable but moisture-sensitive yellow crystals. In their IR spectra  $v(\equiv CH)$  bands at 3298 and 3299, and two  $v(C\equiv C)$ bands at 2107 and 1970, or 2109 and 1971 cm<sup>-1</sup>, are also present. In addition to the resonances for the Ru(L)<sub>2</sub>Cp' fragments, the <sup>1</sup>H NMR spectra contained singlet resonances for the =CH protons at  $\delta_{\rm H}$  1.42 and 1.44. The four carbons of the chain ( $C_{a-\delta}$ ) resonated at  $\delta_{C}$  116.51 (5) and 124.90 (6), 94.34 and 91.73, 73.87 and 75.33, and 51.54 and 52.47, respectively, with  $C_{\alpha}$  giving triplets [both <sup>2</sup>J(CP) 24 Hz]. These were assigned by comparison with similar complexes<sup>6-8</sup> and it is notable that the chemical shifts are not as strongly affected by the different phosphines as found for 2 and 3. Singlets in the <sup>31</sup>P NMR spectrum at  $\delta_{\mathbf{P}}$  51.0 or 81.3 were assigned to the tertiary phosphine ligands.

(c)  $Ru{C=CC=CAu(PR_3)}(L)_2Cp'$  [ $Cp' = Cp, L = PPh_3, R = Ph$  (7);  $Cp' = Cp^*, L_2 = dppe, R = Ph$  (8), tol (9)]. Replacement

of the  $\equiv$ CH proton with the isolobal Au(PR<sub>3</sub>) (R = Ph, tol) group could be effected by addition of AuCl(PR<sub>3</sub>) to solutions of **5** or **6** in thf, followed by addition of an equivalent of KN(SiMe<sub>3</sub>)<sub>2</sub> in toluene. The reactions proceeded readily at r.t. to give Ru{C $\equiv$ CC $\equiv$ C[Au(PR<sub>3</sub>)]}(PP)Cp' [PP = (PPh<sub>3</sub>)<sub>2</sub>, Cp' = Cp, R = Ph (7); PP = dppe, Cp' = Cp\*, R = Ph (8), tol (9)]. The new ruthenium–gold complexes were characterised spectroscopically, only the IR  $\nu$ (C $\equiv$ C) spectra, consisting of three bands between 2124 and 1981 cm<sup>-1</sup>, being notable. Alternatively, the reaction between **3** and AuCl(PPh<sub>3</sub>) in methanol, in the presence of NaOMe, afforded **8** directly in almost quantitative yield. The solid state structures of **7–9** are described below.

(d) {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C=CC=C{Ru(dppe)Cp'} [Cp' = Cp (10), Cp\* (11)]. With the new butadiynyl-ruthenium complexes synthesised it was now possible to synthesise new asymmetric Ru-C<sub>4</sub>-Ru complexes. Accordingly, the complexes {Cp(Ph<sub>3</sub>P)<sub>2</sub>-Ru}C=CC=C{Ru(dppe)Cp'} [Cp' = Cp (10), Cp\* (11)] were made by reaction of 2 with a single equivalent of RuCl-(dppe)Cp' in the presence of KF and dbu (Scheme 2). Alternatively, the reaction between 6 and an equivalent amount of RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp in CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub> in the presence of dbu gave 11 in 35% yield. The yellow products could be crystallised from CHCl<sub>3</sub>/MeOH. The IR  $\nu$ (C=C) bands are at *ca*. 1965 cm<sup>-1</sup>,



while the <sup>31</sup>P NMR spectra contained two equal intensity resonances at  $\delta_P ca$ . 86 and 51 (for **10**) and *ca*. 82 and *ca*. 51 ppm (for **11**), assigned to the dppe and PPh<sub>3</sub> phosphine ligands, respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra contained all expected resonances except for those of the carbon chain, which were not observed as a result of the poor solubility of the complexes.

# Molecular structures

In the course of this work, the molecular structures of 1-4 and 6-9 were confirmed by single-crystal X-ray structure determinations. Plots of single molecules are shown in Figs. 1-4 and significant bond parameters are collected in Table 2. Common features, such as the pseudo-octahedral geometry about the iron or ruthenium atoms are in accord with a myriad of related structures to be found in the Cambridge Crystallographic Data Base.13 For the compounds reported here, Fe-P and average Fe-C(Cp\*) distances are 2.1801, 2.1875(9) and 2.125 Å, with corresponding Ru-P and Ru-C(Cp\*) distances in the ranges 2.286(4)-2.2975(4) (PPh<sub>3</sub>), 2.256-2.279(1) (dppe) and 2.23(1)-2.26(2) Å. Angles subtended by the two P atoms [Fe; 84.59(3); Ru: 81.84-83.93(4)°] and by the pair of P, C atoms [Fe: 84.67, 87.70(9)°; Ru: 84.01-88.40(4)°] are consistent with the pseudooctahedral arrangement of ligands and the restricted bite angle of chelating dppe. Complexes containing the unidentate PPh<sub>3</sub> ligand have larger P-Ru-P [99.9, 101.01(2)°] and P-Ru-C [86.62–91.1(4)°] angles. Of some interest is a comparison of the bite angles of the two ligands in the Ru(LL) fragments [LL = (CO)<sub>2</sub>, (PPh<sub>3</sub>)<sub>2</sub>, dppe]. While this may also be affected by replacement of Cp in the first two by Cp\* in the third, the sums of angles about the Ru atoms are 268.6 [(CO)<sub>2</sub>], 274.8 and 279.6 [(PPh<sub>3</sub>)<sub>2</sub>], 256.9 [Fe(dppe)] and between 253.1 and 255.8° [Ru(dppe)].



**Fig. 1** (a) Molecular projection of  $Ru(C \equiv CC \equiv CSiMe_3)(CO)_2Cp$  (1) down the Cp(centroid)–R line (molecule 1; molecules 2, 3 are similar). (b) Unit cell contents, projected down *a*.





 $\begin{array}{lll} \mbox{Fig. 2} & \mbox{Molecular projections of (a) } Ru(C\equiv CC\equiv CSiMe_3)(PPh_3)_2Cp~(2); \\ (b) & \mbox{Fe}(C\equiv CC\equiv CSiMe_3)(dppe)Cp^*~(4); & (c) & \mbox{Ru}(C\equiv CC\equiv CSiMe_3)-(dppe)Cp^*~(3). \end{array}$ 

The focus of interest in the present study is the diynyl ligand. Complexes 1-4 allow a comparison of changes wrought by different metals and associated ligands, although it has to be said that these are not major. The Fe-C [1.875(3) Å] and Ru-C bonds [1.983(2)-2.015(4) Å] reflect the difference in atomic radii, as also seen with the M-P distances (above). The diynyl nature of the carbon chain is shown by the short-long-short CC bond sequences [1.217-1.231(2), 1.36-1.380(2) and 1.205–1.222(3) Å], which are comparable with those in similar complexes<sup>6-8</sup> and in buta-1,3-diyne itself [1.2176(14), 1.384(2) Å].<sup>14</sup> Of interest here are the differences found for the butadiynyl complex 6, in which the C≡C bonds are shorter [at 1.186, 1.193(5) Å] and the central C-C bond longer [at 1.387(5) Å]. Angles at individual carbons C(1-4) are close to linear [range 169.9-179.7°], with cumulative bend angles of between 7.2 and 26.4°. In these eight complexes, the average angles at C(1-4) are 174.3, 174.8, 178.3, 175.9°, respectively, atom C(3) consistently



Fig. 3 Molecular projection of Ru(C=CC=CH)(dppe)Cp\* (6).

being the least affected by surrounding ligands attached to the metal centre(s). As can be seen from the plots, the overall bending results in a displacement of the terminal carbon such that the  $M \cdots C(4)$  distances are significantly less than the respective sums of the interatomic distances.

We have also obtained a further polymorph of the symmetrical binuclear complex {Ru(PPh<sub>3</sub>)<sub>2</sub>Cp}<sub>2</sub>(µ-C=CC=C) (12). On previous occasions<sup>15</sup> we have described solid-state structures of 12 which differ in solvation and in the conformation of the Cp groups (either *cis* or *trans* across the C<sub>4</sub> chain). The new modification reported here is the penta-thf solvate which has the trans conformation. Finally, the molecular structure of  $\{Ru(dppe)Cp\}_2(\mu-C\equiv CC\equiv C)$  (13), obtained by ligand substitution of 12 with dppe in refluxing toluene, confirms the expected molecular geometry, with the two Cp rings being oriented mutually cis. Other structural parameters for the Ru fragment are similar to those reported for RuCl(dppe)Cp<sup>16</sup> and do not merit further comment. Fig. 5 contains plots of 12 and 13. As shown in Table 3, all six structures have virtually identical bond parameters, although the torsion angles C(0)-Ru(1)  $\cdots$  C<sub>4</sub>  $\cdots$  Ru(1')-C(0') [C(0,0') are the centroids of the Cp rings] vary from  $-28.2^{\circ}$  (*cis*) to  $180^{\circ}$  (*trans*). Separations of the two Ru atoms are 7.795(1) (12) and 7.741(2) Å (13), some 0.02 and 0.12 Å, respectively, shorter than the sums of the interatomic distances.

#### Electrochemistry

We have measured the cyclic voltammograms for most of these complexes under similar conditions (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 V s<sup>-1</sup>, 25 °C, 0.1 M  $[NBu_4]PF_6$  and the observed redox potentials are listed in Tables 4 and 5. A single irreversible oxidation process at 0.43 V (vs. SCE) is found for 3, which does not become reversible at higher scan rates. The ruthenium complex 2 also shows a single irreversible oxidation processes at +0.58 V, whereas the iron analogue 4 gives one reversible event at +0.00 V. The latter complex is thermodynamically easier to oxidise by 0.43 V (it is more electron releasing) than its ruthenium congener. In contrast, there is no change in the redox potential when SiMe<sub>3</sub> in 4 is replaced by H, but there is a significant decrease in the chemical reversibility of the process  $(i_a/i_c = 0.48)$ , suggesting that the SiMe<sub>3</sub> group acts as a protecting group. For 5, an irreversible one-electron oxidation was observed at +0.52 V, showing that the butadiynyl complex is easier to oxidise than the trimethylsilyl-protected derivative by ca. 0.06 V.



**Fig. 4** Molecular projections of (a)  $Ru{C=CC=CAu(PPh_3)}(PPh_3)_2Cp$ (7); (b)  $Ru{C=CC=CAu(PPh_3)}(dppe)Cp^*$  (8); (c)  $Ru{C=CC=CAu-[P(tol)_3]}(dppe)Cp^*$  (9).

As previously discussed, <sup>6c,8c</sup> oxidation of M(C=CH)(dppe)-Cp\* with [FeCp<sub>2</sub>][PF<sub>6</sub>] gives the bis(vinylidenes) [{Cp\*-(dppe)M}=C=CHCH=C={M(dppe)Cp\*}][PF<sub>6</sub>]<sub>2</sub> (M = Fe, Ru, Os).<sup>6c,8c,9</sup> It is possible that the first oxidation wave in the CV of both **5** and **6** corresponds to the formation of a similar product. This agrees with the non-reversibility of both the oxidation waves. Replacement of H by the isolobal Au(PR<sub>3</sub>) group renders the resulting complexes easier to oxidise by between 140 and 290 mV; not surprisingly, use of Au{P(tol)<sub>3</sub>} in **9** further facilitates oxidation,  $E_1$  being 70 mV below that of **8**, but does not improve the chemical reversibility.

Comparison of the (admittedly limited) ranges found for  $E_1$  within groups of related complexes is consistent with the ease of oxidation being

 $Fe(dppe)Cp^* > Ru(dppe)Cp^* > Ru(dppe)Cp \ge Ru(PPh_3)_2Cp$ 

*i.e.*, consistent with the increase in electron donor power of the Cp\* and dppe ligands over Cp and PPh<sub>3</sub>. This is also supported by a comparison of the corresponding chloro complexes (Table 4), which exhibit a similar trend in their oxidation potentials.

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$\begin{array}{l} Ru - P(1) \\ Ru - P(2) \\ Ru - C(cp) \\ (av.) \\ Ru - C(1) \\ C(1) - C(2) \\ C(2) - C(3) \\ C(3) - C(4) \\ C(4) - Si \end{array}$	1.895, 1.881, 1.6 1.888, 1.885, 1.8 2.235–2.260(3), 2.243(9); 2.243( 2.010, 2.015, 2.0 1.216, 1.215, 1.2 1.384, 1.382, 1.3 1.207, 1.213, 1.2 1.841, 1.831, 1.8	887(4) 882(4) 2.234–2.252(3), 2.23 10), 2.241(7), 2.246(3) 113(3) 220(4) 373(5) 214(5) 334(4)	7–2.260(3) 10)	2.2980(5) 2.2975(4) 2.225-2.256(2) 2.242(12) 1.988(2) 1.225(2) 1.375(2) 1.213(3) 1.824(2)	2.2610(3) 2.2775(4) 2.233–2.275(2) 2.258(15) 1.983(2) 1.231(2) 1.371(2) 1.222(3) 1.822(2)	$\begin{array}{c} 2.1793(3)\\ 2.1876(9)\\ 2.102-2\\ 2.125(1)\\ 1.875(3)\\ 1.226(4)\\ 1.374(4)\\ 1.220(4)\\ 1.821(3)\end{array}$	$\begin{array}{cccc} 0 & 2.279(1) \\ 2.256(1) \\ .142(3) & 2.216-2.281 \\ 7 & 2.250(27) \\ 2.015(4) \\ 1.186(5) \\ 1.387(6) \\ 1.193(6) \end{array}$
$\begin{array}{l} P(1)-Ru-P(2)\\ P(1)-Ru-C(1)\\ P(2)-Ru-C(1)\\ Ru-C(1)-C(2)\\ C(1)-C(2)-C(3)\\ C(2)-C(3)-C(4)\\ C(3)-C(4)-Si\\ \Sigma(bend)\ Ru\ \cdots\ Si \end{array}$	92.1, 91.1, 91.7( 87.9, 88.3, 89.0( 90.6, 86.9, 88.2( 177.3, 178.3, 17 177.8, 178.1, 17 178.6, 178.9, 17 177.7, 178.1, 17 8.6, 6.6, 6.5	2) 1) 7.9(3) 7.1(4) 9.1(4) 9.4(4)	] ] ] ]	101.01(2) 87.15(5) 86.62(5) 179.6(1) 171.1(2) 178.0(2) 174.6(2) 16.7	81.84(1) 85.30(4) 88.40(4) 173.8(1) 176.7(1) 178.9(1) - 13.5	84.61(2 84.69(9 87.71(9 176.0(3) 175.6(3) 179.7(4) 175.2(3) 16.8	8) 83.43(4) 9) 84.2(1) 9) 85.5(1) 173.1(4) 172.7(5) 177.4(5) 16.8 [to C(4)
Complex	7	8	9	12		13	3
Ru–P(1) Ru–P(2) Ru–C(cp) (av.) Ru–C(1) C(1)–C(2) C(2)–C(3) C(3)–C(4) C(4)–X Au–P	2.286(4) 2.297(4) 2.23–2.24(2) 2.236(5) 1.99(1) 1.22(2) 1.36(2) 1.19(2) 1.99(1) [Au] 2.253(4)	2.2616(9) 2.2777(9) 2.220–2.284(3) 2.252(25) 1.992(3) 1.221(5) 1.378(5) 1.205(5) 1.992(3) [Au] 2.2666(8)	2.2571(4) 2.2778(4) 2.230–2.273( 2.255(16) 1.995(2) 1.225(2) 1.380(2) 1.211(2) 1.988(2) [Au] 2.2677(5)	2.280(1) 2.289(1) 2.227-2 2.236(7) 1.995(5) 1.231(6) 1.377(6) 1.219(6) 1.989(4) -	, 2.291(1) <sup><i>a</i></sup> , 2.285(1) <sup><i>a</i></sup> ,238(6), 2.217–2.242 , 2.229(12) <sup><i>a</i></sup> [Ru(2)]	(6) <sup><i>a</i></sup> 2. 2. 2. 2. 1. 1. 1. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2.	228(3), 2.246(3) <sup><i>a</i></sup> 256(3), 2.258(3) <sup><i>a</i></sup> 23–2.25(1), 2.223–2.26 243(9), 2.242(13) <sup><i>a</i></sup> 016(7) 22(1) 40(1) 22(1) 007(8) [Ru(2)]
$\begin{array}{l} P(1)-Ru-P(2)\\ P(1)-Ru-C(1)\\ P(2)-Ru-C(1)\\ Ru-C(1)-C(2)\\ C(1)-C(2)-C(3)\\ C(2)-C(3)-C(4)\\ C(3)-C(4)-X\\ C(4)-Au-P\\ \Sigma \ (bend) \ Ru \ \cdots \ C \end{array}$	99.9(1) 91.1(4) 88.6(4) 169.9(12) 176(1) 175(1) 172(1) [Au] 173.7(4) 28.1	83.62(3) 85.6(1) 86.6(1) 172.2(3) 174.0(4) 179.0(3) 176.5(3) [Au] 177.3(1) 18.3	82.77(1) 84.01(5) 87.50(4) 172.1(1) 175.7(2) 179.6(2) 175.9(2) [Au] 178.32(5) 16.7	103.25(5 86.7(1) 82.1(1) 175.5(4) 177.3(5) 176.2(6) 174.5(5) -	5), 103.10(5) <sup>d</sup> , 86.3(1) <sup>d</sup> , 82.5(1) <sup>d</sup> [Ru(2)]		$\begin{array}{l} 32.0(1), 82.3(1)^{d} \\ 35.0(3), 84.3(3)^{d} \\ 31.2(3), 81.5(3)^{d} \\ 77.1(9) \\ 76(1) \\ 72(1) \\ 71.4(9) \end{array}$

1 <sup>*a,b*</sup>

Complex

Table 2 Selected bond distances (Å) and angles (°) for some alkynyl and diynyl ruthenium complexes

2

3

**4**<sup>c</sup>

Table 3       Dimensions (A, $^{\circ}$ ) of the Ru–C <sub>4</sub> –Ru chain in complexes 12 and 13								
Complex	Ru(1)–C(1)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–Ru(2)	$\operatorname{Ru}(1) \cdots \operatorname{Ru}(2)$	Torsion angle	Ref.
12	2.01(3)	1.24(4)	1.32(3)	1.24(4)	2.01(3)	7.768(4)	-30.6 (cis)	15 <i>a</i>
12.0.8MeOH	2.00(1)	1.22(1)	1.39(1)	1.22(1)	2.00(1)	7.782(1)	-32.3 (cis)	15b
12·2thf	2.00(1)	1.20(2)	1.38(2)	1.25(2)	2.01(1)	7.774(1)	-28.2 (cis)	15b
12·2thf	2.001(3)	1.218(5)	1.369(5)	1.218(5)	2.001(3)	7.805(2)	180 (trans)	15 <i>a</i>
12.5thf	1.995(4)	1.231(6)	1.377(6)	1.219(6)	1.989(4)	7.7946(8)	-178.2 (trans)	This work
13	2.016(7)	1.22(1)	1.40(1)	1.22(1)	2.007(8)	7.741(2)	-39.4 ( <i>cis</i> )	This work

We have described elsewhere the electrochemistry of the binuclear complexes 12 and  $\{Ru(dppe)Cp^*\}_2(\mu-C\equiv CC\equiv C)$  (14).<sup>8</sup> The present results with 13 (Table 5) show that replacement of two PPh<sub>3</sub> ligands by dppe has little effect on the various oxidation potentials of these complexes, values for the mixed compound 10 lying between the values for 12 and 13. Replacement of Cp by Cp\* has a more pronounced effect, with values for the mixed derivative 11 again lying between those of 12 and 14. The magnitude of the comproportionation constant,  $K_{\rm C}$ (which is the equilibrium constant for reaction (1)),

$$\mathbf{ML}_n + [\mathbf{ML}_n]^{2+} \leftrightarrows 2[\mathbf{ML}_n]^+ \tag{1}$$

has been used as an indicator of the degree of electron delocalisation in the molecule. For complexes 10–15, values for  $K_{\rm C}$  are high, between 10<sup>10</sup> and 10<sup>12</sup>. The extent of electronic communication between the end-groups is related to the amount of delocalisation, in the limit the HOMOs extending over the M-C<sub>4</sub>-M bridge. While the present range of complexes is limited, some dependency of  $K_{\rm C}$  on the ligands surrounding the metal centre is found,  $K_{\rm C}$  increasing from the lowest value in 13 (Ru/Cp/dppe), through to 10 and 12 (Ru/Cp/PPh<sub>3</sub> or dppe), 11 (Ru/Cp/PPh<sub>3</sub> + Cp\*/dppe) and 14 (Ru/Cp\*/dppe) to 15 (the Fe analogue of 14). The  $K_{\rm C}$  values roughly correlate to the  $E_1$  values and are consistent with increased delocalisation occurring with the better donor ligands.

## Discussion

This paper describes the syntheses of several ruthenium complexes containing trimethylsilylbuta-1,3-diynyl groups and the proto-desilylation of some of them to give synthetically useful

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butadiynyl complexes by reactions which are very similar to those employed for the analogous iron compounds. Careful control of the reaction conditions in the syntheses of the diynyl



Fig. 5 Molecular projections of (a)  $\{Ru(PPh_3)_2Cp\}_2(\mu-C\equiv CC\equiv C)$  (12); (b)  $\{Ru(dppe)Cp\}_2(\mu-C\equiv CC\equiv C)$  (13).

Table 4 Electrochemical data for mononuclear complexes

Complex	$E_1(0/1+)/V$
RuCl(PPh <sub>3</sub> ) <sub>2</sub> Cp	0.595
RuCl(dppe)Cp	0.47
RuCl(PPh <sub>3</sub> ) <sub>2</sub> Cp*	0.385
RuCl(dppe)Cp*	0.28
FeCl(dppe)Cp*	$-0.22^{a}$
$Ru(C \equiv CC \equiv CSiMe_3)(PPh_3)_2Cp 2$	0.58 <sup>b</sup>
Ru(C=CC=CSiMe <sub>3</sub> )(dppe)Cp* 3	0.43 <sup><i>b</i></sup>
Fe(C=CC=CSiMe <sub>3</sub> )(dppe)Cp* 4	0.00
Ru(C=CC=CH)(PPh <sub>3</sub> ) <sub>2</sub> Cp 5	0.52 <sup>b</sup>
Ru(C=CC=CH)(dppe)Cp* 6	$0.44^{b}$
Fe(C=CC=CH)(dppe)Cp*	0.00 <sup>c</sup>
$Ru\{C \equiv CC \equiv CAu(PPh_3)\})(PPh_3)_2Cp 7$	0.38 <sup>b</sup>
$Ru\{C \equiv CC \equiv CAu(PPh_3)\})(dppe)Cp*8$	0.15 <sup>b</sup>
$Ru{C=CC=CAu[P(tol)_3]})(dppe)Cp*9$	$0.08^{b}$

<sup>*a*</sup> Ref. 2. <sup>*b*</sup> Peak potential for irreversible process. <sup>*c*</sup> Partially reversible  $(i_a i_e = 0.48)$ .

 Table 5
 Electrochemical data for binuclear complexes

complexes 1–4, achieved by using Na[BPh<sub>4</sub>] in a mixed thf/NEt<sub>3</sub> solvent, avoids formation of the butatrienylidene and subsequent unwanted reactions. The use of Na[BPh<sub>4</sub>] or K[PF<sub>6</sub>] to facilitate the ionisation of the Cl has much precedent.<sup>6</sup> Facile replacement of the =CH proton by Au(PR<sub>3</sub>) (R = Ph, tol) is also demonstrated. Single-crystal X-ray structure determinations confirm their characterisation by spectroscopic methods (IR, NMR, mass).

Both 2 and 4 show three v(C=C) bands which possibly result from the coupling of one of the normal modes with another oscillator such as the SiMe<sub>3</sub> moiety.<sup>11</sup> The v(C=C) frequencies decrease when the SiMe<sub>3</sub> moiety is replaced by H suggesting an increase in electron density on the carbon chain.

The C<sub>4</sub> chains are essentially linear, although deviations at individual carbon atoms (range 0.3–10.1°; least deviation is found for C<sub> $\gamma$ </sub>) sum up to between 6.5 and 28.1°. This feature is commonly found in unsaturated C<sub>n</sub> chains and can be ascribed to a low bending force constant or facile distortion within the crystal lattice as a result of interactions with adjacent molecules.<sup>17</sup> As commented by these authors, no one feature correlates well with observed distortions of the C<sub>n</sub> chain in molecules of this type.

These complexes are synthetically useful intermediates, subsequent reactions affording a variety of diyndiyl and related complexes. The present study has extended this range to include Au(PR<sub>3</sub>) derivatives. The isolobality of H with Au(PR<sub>3</sub>) is reflected in gross similarities between the gold complexes and the unsubstituted diynyl precursors. Further examples of complexes containing C<sub>4</sub> chains end-capped by the same or different ruthenium-phosphine fragments have also been obtained.

# Conclusions

Reliable, high-yield syntheses of several ruthenium complexes containing diynyl ligands attached to Ru(PP)Cp' centres have been developed. Further demonstration of their synthetic utility is provided by the preparation of gold-containing derivatives Ru{C=CC=C[Au(PR\_3)]}(PP)Cp' and several further examples of complexes {Ru(PR\_3)\_2Cp'}\_2( $\mu$ -C=CC=C) [Cp' = Cp, Cp\*; (PR\_3)\_2 = (PPh\_3)\_2, dppe; not all combinations]. Their spectroscopic properties are discussed and the structural characterisation of ten of the complexes is reported. Of interest is their electrochemical behaviour, which confirm expectations that the presence of strongly electron donating ligands in otherwise closely similar complexes results in a decrease in the oxidation potentials.

# Experimental

## General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

## Instrumentation

IR spectra were obtained on a Bruker IFS28 FT–IR spectrometer. Spectra in  $\rm CH_2Cl_2$  were obtained using a 0.5 mm

Complex	$E_1(0/1+)$	$E_2(1+/2+)$	$\Delta E_{1/2}$	$K_{\rm C}(0/1+/2+)$	$E_3(2+/3+)$	<i>E</i> <sub>4</sub> (3+/4+)
$\frac{\{Ru(PPh_{3})_{2}Cp\}(\mu-C=CC=C)\{Ru(dppe)Cp\} 10 \\ \{Ru(PPh_{3})_{2}Cp\}(\mu-C=CC=C)\{Ru(dppe)Cp\} 11 \\ \{Ru(PPh_{3})_{2}Cp\}_{2}(\mu-C=CC=C) 12 \\ \{Ru(dppe)_{2}Cp\}_{2}(\mu-C=CC=C) 13 \\ \{Ru(dppe)_{2}Cp\}_{2}(\mu-C=CC=C) 14 \\ \{Fe(dppe)_{2}Cp\}_{2}(\mu-C=CC=C) 15 \end{cases}$	$-0.22 \\ -0.33 \\ -0.23 \\ -0.24 \\ -0.43 \\ -0.68$	0.42 0.34 0.41 0.35 0.22 0.04	0.64 0.67 0.64 0.59 0.65 0.72	$\begin{array}{c} 6.53 \times 10^{10} \\ 2.09 \times 10^{11} \\ 6.53 \times 10^{10} \\ 9.34 \times 10^{9} \\ 9.64 \times 10^{10} \\ 1.47 \times 10^{12} \end{array}$	1.07 1.03 1.03 1.08 1.04 0.95	$1.52^{a}$ $1.56^{a}$ $1.68^{a}$ $1.44^{a}$ $1.51^{b}$

<sup>*a*</sup> Peak potential for irreversible process. <sup>*b*</sup> Partially reversible  $(i_a/i_c = 0.7)$ .

path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on Bruker AM300WB or ACP300 (1H at 300.13 MHz, 13C at 75.47 MHz, 31P at 121.503 MHz) instruments. Samples were dissolved in CDCl<sub>3</sub>, unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C NMR spectra and external H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR spectra. ES mass spectra: VG Platform 2 or Finnigan LCQ instruments were used, solutions in MeOH being directly infused into the instrument. Chemical aids to ionisation were used as required.<sup>18</sup> Cyclic voltammograms were recorded using a PAR model 263 apparatus, with ferrocene as internal calibrant ( $[FeCp_2]/[FeCp_2]^+ = +0.46$  V). Elemental analyses were performed at the Centre pour Microanalyses du CNRS, Vernaison, France, and CMAS, Melbourne, Australia.

#### Reagents

Na[BPh<sub>4</sub>] (Aldrich), and [NBu<sub>4</sub>]F (Aldrich) were used as received. The compounds RuBr(CO)<sub>2</sub>Cp,<sup>19</sup> RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp,<sup>20</sup> RuCl(dppe)Cp,<sup>21</sup> FeCl(dppe)Cp<sup>\*,22</sup> RuCl(dppe)Cp<sup>\*,8c</sup> {Ru-(PPh<sub>3</sub>)<sub>2</sub>Cp}<sub>2</sub>( $\mu$ -C<sub>4</sub>),<sup>8b</sup> [FeCp<sub>2</sub>]PF<sub>6</sub><sup>23</sup> and HC=CC=CSiMe<sub>3</sub><sup>24</sup> were prepared using the cited methods.

(a) Ru(C=CC=CSiMe<sub>3</sub>)(CO)<sub>2</sub>Cp (1). CuI (25 mg, 0.13 mmol) was added to a solution of RuBr(CO)<sub>2</sub>Cp (400 mg, 1.32 mmol) in thf/NEt<sub>3</sub> (1/2, 40 ml), followed immediately by HC=CC=CSiMe<sub>3</sub> (430 mg, 3.50 mmol). The solution was stirred in the dark for 45 min, filtered and the solvent was removed. Column chromatography (basic alumina), eluting with Et<sub>2</sub>O/pentane (1/1) gave an orange–yellow band which afforded pale yellow Ru(C=CC=CSiMe<sub>3</sub>)(CO)<sub>2</sub>Cp (1) (325 mg, 72%) (crystals from CHCl<sub>3</sub>/hexane). Anal. Found: C, 50.90; H, 4.02. Calc. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>RuSi·CHCl<sub>3</sub>: C, 51.66; H, 4.01%; *M*, 344. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 2056vs, 2002vs cm<sup>-1</sup>. <sup>13</sup>C NMR:  $\delta$  195.50 (s, CO). ES-mass spectrum (MS) (MeOH, *m/z*): 344, M<sup>+</sup>; 316, [M – CO]<sup>+</sup>.

(b)  $\operatorname{Ru}(C \equiv CC \equiv CSiMe_3)(PPh_3)_2Cp$  (2). A Schlenk flask was charged with  $\operatorname{RuCl}(PPh_3)_2Cp$  (2.0 g, 2.76 mmol),  $\operatorname{NaBPh_4}$  (1.04 g, 3.00 mmol) and thf/NEt<sub>3</sub> (1/1, 60 mL) at r.t. and  $\operatorname{HC} \equiv CC \equiv CSiMe_3$  (0.70 g, 5.70 mmol) in thf (5 mL) was added. The orange suspension was then warmed to 50 °C and stirred for 16 h. The solvent was then removed and the residue extracted with  $\operatorname{Et_2O}$  (3 × 15 mL) and filtered into another Schlenk tube. The  $\operatorname{Et_2O}$  was then removed and the resulting orange–brown solid was dried *in vacuo* to give Ru-(C \equiv CC \equiv CSiMe\_3)(PPh\_3)\_2Cp (2) (2.11 g, 94%). Anal. Found: C, 70.71; H, 5.31. Calc. for  $C_{48}H_{44}P_2RuSi:$  C, 71.00; H, 5.46%; *M*, 812.

(c)  $\operatorname{Ru}(C=CC=CSiMe_3)(\operatorname{dppe})Cp^*$  (3). To a suspension of RuCl(dppe)Cp<sup>\*</sup> (2000 mg, 2.98 mmol) and Na[BPh\_4] (1025 mg, 2.98 mmol) in thf/NEt<sub>3</sub> 1/1 (80 ml) was added HC=CC=CSiMe\_3 (1090 mg, 8.94 mmol). The suspension was allowed to stir at 50 °C in a sealed flask for 48 h. The orange suspension was then evaporated to dryness and a bright yellow complex could be extracted with hexane and filtered *via* cannula into another Schlenk flask. Extraction was continued until the hexane extracts were no longer coloured. The yellow solution was then concentrated to approximately 10 ml giving a bright yellow crystalline solid that was collected and dried on a sintered glass funnel to give Ru(C=CC=CSiMe\_3)(dppe)Cp (3) (1600 mg, 79%). Anal. Found: C, 68.12; H, 6.72. Calc. for C<sub>35</sub>H<sub>40</sub>P\_2Ru: C, 68.32; H, 6.39%; *M*, 756. ES-MS: 757, [M + H]<sup>+</sup>; 717, [Cp<sup>\*</sup>-(dppe)RuC\_3(OMe)CH\_2]<sup>+</sup>; 635, [Ru(dppe)Cp<sup>\*</sup>]<sup>+</sup>.

(d)  $Ru(C=CC=CH)(PPh_3)_2Cp$  (5). A Schlenk flask was charged with 2 (1.0 g, 1.23 mmol) and thf (40 mL). [NBu<sub>4</sub>]F (0.62 mL, 0.62 mmol of a 1.0 M solution in thf) was added and

the resulting dark red-brown solution stirred at r.t. for 24 h. The solvent was then removed *in vacuo*. Washing with cold MeCN (2 × 10 mL) and Et<sub>2</sub>O (2 × 10 mL) and drying under oil-pump vacuum gave mustard yellow Ru(C=CC=CH)-(PPh<sub>3</sub>)<sub>2</sub>Cp (**5**) (670 mg, 74%). Anal. Found: C, 73.11; H, 5.06. Calc. for C<sub>45</sub>H<sub>36</sub>P<sub>2</sub>Ru: C, 73.06; H, 4.90%. *M*, 740. IR (Nujol):  $\nu$ (=CH) 3298m cm<sup>-1</sup>.

(e) Ru(C=CC=CH)(dppe)Cp\* (6). To a solution of 3 (2000 mg, 2.65 mmol) in thf (30 ml) was added [NBu<sub>4</sub>]F (0.4 ml of a 1.0 M solution in thf). The solution was stirred at r.t. for 24 h. The solution was then evaporated to dryness and a bright yellow complex could be extracted with hot hexane and filtered *via* canula into another Schlenk flask. Extraction was continued until the hexane extracts were no longer coloured. The yellow solution was then concentrated to approximately 10 ml giving a bright yellow crystalline solid that was collected and dried on a sintered glass funnel to give Ru(C=CC=CH)(dppe)Cp (5) (1750 mg, 96%). Anal. Found: C, 69.97; H, 5.63. Calc. for  $C_{35}H_{40}P_2Ru: C, 70.26; H, 5.89\%; M, 684. IR (Nujol): v(=CH) 3299 cm<sup>-1</sup>. ES-MS: 684, M<sup>+</sup>; 635, [Ru(dppe)Cp<sup>+</sup>]<sup>+</sup>.$ 

(f) Ru{C=CC=C[Au(PPh<sub>3</sub>)]}(PPh<sub>3</sub>)<sub>2</sub>Cp (7). To a solution of 5 (200 mg, 0.27 mmol) and AuCl(PPh<sub>3</sub>) (134 mg, 0.27 mmol) in thf (30 ml) was added K[N(SiMe<sub>3</sub>)<sub>2</sub>] (2 ml of 0.5 M solution in toluene, 1.0 mmol). The mixture was stirred at r.t. for 4 h, after which time volatiles were removed. The residue was dissolved in the minimum amount of dichloromethane and the solution was filtered through cotton wool into stirred hexane (150 ml). The resulting yellow–brown precipitate was filtered off, washed with pentane (25 ml) and air dried to give Ru{C=CC=C[Au(PPh<sub>3</sub>)]}-(PPh<sub>3</sub>)<sub>2</sub>Cp (7) (300 mg, 93%). Anal. Found: C, 64.01; H, 4.61. Calc. for C<sub>66</sub>H<sub>56</sub>AuP<sub>3</sub>Ru: C, 63.92; H, 4.55%; *M*, 1198. IR (Nujol):  $\nu$ (C=C) 2116s, 2073m, 1982w cm<sup>-1</sup>. ES-MS: 1920, [M + Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; 1657, [M + Au(PPh<sub>3</sub>)]<sup>+</sup>; 1198, M<sup>+</sup>; 983, [Au(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>.

(g)  $Ru{C=CC=C[Au(PPh_3)]}(dppe)Cp^*$  (8). Method A. A Schlenk flask was charged with 6 (200 mg, 0.29 mmol) and AuCl(PPh<sub>3</sub>) (146 mg, 0.29 mmol) and the solids were dried under vacuum, after which thf (10 ml) was added followed by addition of KN(SiMe<sub>3</sub>)<sub>2</sub> (1.16 ml of a 0.5 M solution in toluene, 0.58 mmol). The yellow solution was left to stir at room temperature for 4 h. The solution was evaporated to dryness on the rotary evaporator and the solid was extracted in a minimum of CH<sub>2</sub>Cl<sub>2</sub> and filtered followed by evaporation of the solvent. To the oily residue was added acetone (5 ml) and crystallisation began immediately. The flask was left in the freezer for 1 h, and then the bright yellow crystals were collected and washed with a further portion of acetone (5 ml) to give Ru{C=CC=C[Au-(PPh<sub>3</sub>)]}(dppe)Cp\* (8) (231 mg, 69%). Anal. Found: C, 61.02; H, 4.71. Calc. for C<sub>58</sub>H<sub>54</sub>AuP<sub>3</sub>Ru: C, 61.00; H, 4.77%; M, 1142. IR (Nujol): v(C≡C) 2119m, 2072m, 1981w cm<sup>-1</sup>. ES–MS: 1601,  $[M + AuPPh_3]^+; 1142, M^+; 721, [Au(PPh_3)_2]^+.$ 

Method B. To a solution of NaOMe [from Na (50 mg) in MeOH (5 ml) was added AuCl(PPh<sub>3</sub>) (90 mg, 0.18 mmol) followed directly by **6** (136 mg, 0.18 mmol). The suspension was stirred for 1 h before being cooled to 0 °C in an ice bath. The bright yellow product was collected, washed with cold MeOH (2 × 5 ml) and hexane (2 × 10 ml) and dried to give **8** (202 mg, 98%).

(h) Ru{C=CC=C[AuP(tol)\_3]}(dppe)Cp\* (9). As for (g), method A, above, 6 (200 mg, 0.29 mmol) and AuCl{P(tol)\_3} (158 mg, 0.29 mmol) in thf (10 ml) were treated with an 0.5 M solution of KN(SiMe\_3)<sub>2</sub> (1.16 ml of an 0.5 M solution in toluene, 0.58 mmol). The CH<sub>2</sub>Cl<sub>2</sub> extract was filtered into rapidly stirred hexane to precipitate Ru{C=CC=C[AuP(tol)\_3]}-(dppe)Cp\* (9) as a bright yellow solid (260 mg, 76%). Anal. Found: C, 61.74; H, 5.04. Calc. for C<sub>61</sub>H<sub>60</sub>AuP<sub>3</sub>Ru: C, 61.88; H,

Formula $C_{14}H_{14}O_2RuSi$ $C_{53}H_{56}P_2RuSi$ $C_{43}H_{48}P_2RuSi$ $C_{43}H_{48}FeP_2Si \cdot C_7H_8$ $C_{40}H_{40}P_2R$ M         343.20         884.14         755.96         802.83         683.71	1 2
M 343 20 884 14 755 96 802 83 683 71	•
M 545.20 004.14 755.70 002.05 005.71	2
Crystal system Triclinic Monoclinic Monoclinic Triclinic Monoclini	
Space group $P\bar{I}$ $P_{2_1/c}$ $P_{2_1/n}$ $P\bar{I}$ $P_{2_1/c}$	
<i>a</i> /Å 6.6958(6) 11.1851(8) 15.6527(8) 10.4576(6) 10.344(1)	
<i>b</i> /Å 16.119(1) 17.171(1) 13.9997(7) 14.5424(6) 22.719(2)	
c/Å 21.291(2) 24.241(2) 18.9093(9) 15.4074(6) 14.810(2)	
<i>al</i> <sup>o</sup> 82.120(2) 70.850(2)	
$\beta \beta^{\circ}$ 88.887(2) 95.572(2) 110.977(1) 76.356(2) 109.681(2)	
y/° 89.629(2) 78.567(2)	
V/Å <sup>3</sup> 2276 4634 3869 2132 3277	
$D/g \text{ cm}^{-3}$ 150, 126, 129, 125, 137,	
$\frac{1}{10000000000000000000000000000000000$	
Crystal size/mm $0.45 \times 0.20 \times 0.09$ $0.25 \times 0.12 \times 0.07$ $0.38 \times 0.35 \times 0.16$ $0.28 \times 0.21 \times 0.14$ $0.15 \times 0.12$	$\times 0.06$
$(T_{1}^{2})_{1} = 0.73$ 0.88 0.88 0.88 - 0.83	
$2 \mu \beta^{\circ}$ 68 75 75 54 68	
$\frac{2\sigma_{\text{max}'}}{N}$ 06 7 80261 27563 58204	
$M_{\text{tot}} = 5770 + 5007 + 5007 + 50021 + 27505 + 5224 + 5007 + 50021 + 5002$	n
$N_{\rm (Aint)} = 17402(0.050) = 24505(0.041) = 20514(0.040) = 9770(10a) = 15597(0.17) = 10597(0.17) $	•)
$N_0$ 1577 14015 14141 7404 0750 P 0.048 0.041 0.032 0.050 0.054	
R 0.046 0.041 0.052 0.059 0.054 0	
Compound 7 8 9 12 13	
Formula $C_{63}H_{50}AuP_3Ru = C_{58}H_{54}AuP_3Ru \cdot 2CH_2Cl_2 = C_{61}H_{60}AuP_3Ru \cdot 0.125CH_2Cl_2 = C_{86}H_{70}P_4Ru_2 \cdot 5C_4H_8O = C_{66}H_{58}P_4Ru_2 \cdot 5C_4H_8O = C_{66}H_{66}H_8O = C_{66}H_{66}H_8O = C_{66}H_{66}H_8O = C_{66}H_{66}H_8O = C_{66}H_{66}H_8O = C_{66}H_8O = C_$	.l <sub>2</sub>
M 1198.05 1311.89 1194.73 1790.08 1177.23	
Crystal system Monoclinic Monoclinic Monoclinic Monoclinic Monoclinic	2
Space group $P2_1/c$ $P2_1/n$ $P2_1/n$ $P2_1/c$ $P2_1$	
<i>a</i> /Å 8.884(6) 17.414(2) 17.3282(7) 15.673(2) 9.434(2)	
<i>b</i> /Å 31.781(4) 17.739(2) 12.8802(5) 20.344(3) 18.936(4)	
c/Å 20.480(3) 17.806(2) 23.0007(7) 22.802(2) 15.324(4)	
$\beta^{\prime}$ 98.529(2) 91.051(3) 96.423(1) 100.819(2) 106.405(4)	
V/Å <sup>3</sup> 5718 5499 5257 9247 2626	
Z 4 4 4 2	
$D_{\rm c}/{\rm g}{\rm cm}^{-3}$ 1.39, 1.58, 1.50, 1.28, 1.48,	
$\mu/\text{mm}^{-1}$ 2.95 3.26 3.22 4.5 0.74	
Crystal size/mm $0.21 \times 0.14 \times 0.05$ $0.22 \times 0.18 \times 0.15$ $0.20 \times 0.18 \times 0.14$ $0.70 \times 0.35 \times 0.25$ $0.14 \times 0.112$	$\times 0.10$
$T_{\text{min}}^{*}$ 0.79 0.87 0.82 0.69 0.63	
$2\theta_{max}/^{\circ}$ 50 75 75 58 50	
N <sub>tor</sub> 53241 115669 108768 91349 26467	
$N(R_{er})$ 10090 (0.10) 28997 (0.062) 27598 (0.033) 23308 (0.074) 4763 (0.06	5)
N 7035 17913 20068 13098 4186	,
R 0.089 0.041 0.027 0.061 0.048	
<i>R</i> <sub>w</sub> 0.122 0.043 0.027 0.062 0.055	

Table 6 Crystal data and refinement details

5.11%; *M*, 1184. IR (Nujol):  $\nu$ (C=C) 2124m, 2073m, 1987w cm<sup>-1</sup> ES–MS: 1990, [M + Au{P(tol)}]<sub>2</sub><sup>+</sup>; 1184, M<sup>+</sup>.

(i) {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C=CC=C{Ru(dppe)Cp} (10). To a solution containing 2 (200 mg, 0.246 mmol), RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp (138 mg, 0.230 mmol) and KF (16 mg, 0.275 mmol) in MeOH (30 ml) was added dbu (90 mg, 0.59 mmol). The resulting orange–brown suspension was heated at reflux point for 16 h, after which time an olive-green precipitate had formed. This was filtered off, washed with hexane and dried in air. Recrystallisation (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave yellow {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C=CC=C{Ru(dppe)Cp} (10) (130 mg, 42%). Anal. Found: C, 66.40; H, 4.53. Calc. for C<sub>76</sub>H<sub>64</sub>P<sub>4</sub>Ru<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 66.33; H, 4.83%; *M*, 1303.

(j) {**C**p(**Ph**<sub>3</sub>**P**)<sub>2</sub>**Ru**}**C**=**C**{**Ru**(**d**ppe)**C**p\*} (11). *Method A.* As in (i) above, **2** (100 mg, 0.123 mmol), RuCl(dppe)**C**p\* (83 mg, 0.123 mmol) and KF (9 mg, 0.155 mmol) in MeOH (15 ml) was treated with dbu (45 mg, 0.30 mmol), to give yellow {**C**p(**Ph**<sub>3</sub>**P**)<sub>2</sub>**Ru**}**C**=**CC**=**C**{**Ru**(dppe)**C**p\*} (11) (76 mg, 45%). Anal. Found: C, 70.74; H, 5.46. Calc. for C<sub>81</sub>H<sub>74</sub>P<sub>4</sub>**Ru**<sub>2</sub>: C, 70.83; H, 5.43%; *M*, 1375. ES-MS: 1375, M<sup>+</sup>; 1112, [M – Ph]<sup>+</sup>.

*Method B*. A Schlenk flask was charged with  $RuCl(PPh_3)_2Cp$  (106 mg, 0.14 mmol),  $Na[BPh_4]$  (48 mg, 0.14 mmol) and **6** (100 mg, 0.14 mmol). A degassed solution of dbu (90 mg, 0.59

mmol) in CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub> (2/3, 50 ml) was added *via* cannula and the solution was heated at reflux point overnight. The solvent was removed and the residue was extracted in hot hexane until no further yellow fractions could be extracted. Removal of solvent and recrystallisation (acetone) gave {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}-C=CC=C{Ru(dppe)Cp\*} (11) as an orange solid (68 mg, 35%).

(k) {Ru(dppe)Cp}<sub>2</sub>( $\mu$ -C=CC=C) (13). A toluene solution (120 ml) containing {Ru(PPh<sub>3</sub>)<sub>2</sub>Cp}<sub>2</sub>( $\mu$ -C=CC=C) (1.0 g, 0.69 mmol) and dppe (580 mg, 1.46 mmol) was heated at reflux point for 3 d, after which time the colour had deepened to orange–red. Evaporation of solvent and trituration of the residue with hot hexane (3 × 25 ml) left bright orange {Ru(dppe)Cp}<sub>2</sub>-( $\mu$ -C=CC=C) (13) (705 mg, 86%). Anal. Found: C, 67.29; H, 4.94. Calc. for C<sub>66</sub>H<sub>58</sub>P<sub>4</sub>Ru<sub>2</sub>: C, 67.34; H, 4.97%; *M*, 1177.

#### Structure determinations

Crystal data are provided in Table 6. For all except **4**, full spheres of diffraction data to the indicated limits were measured at *ca*. 153 K using a Bruker AXS CCD area-detector instrument.  $N_{\text{tot}}$  reflections were merged to N unique ( $R_{\text{int}}$  quoted) after "empirical"/multiscan absorption correction (proprietary software),  $N_{o}$  with  $F > 4\sigma(F)$  being used in the full matrix least squares refinement. All data were measured using monochromatic Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å. Anisotropic

Data acquisition and refinement for **4** were carried out at Rennes using a Nonius Kappa CCD diffractometer (Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å), T = 293 K. The structure was solved using SHELX97,<sup>26</sup> SIR-92 and the MOLEN package.<sup>27</sup>

Pertinent results are given in the Figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and Tables.

CCDC reference numbers 223445–223453 (1–3, 6–9, 12, 13) and 224446 (4).

See http://www.rsc.org/suppdata/dt/b3/b316297b/ for crystallographic data in CIF or other electronic format.

#### Variata

**2**, **3**:  $(x, y, z, U_{iso})_{H}$  were refined (solvent excepted).

**4**: The toluene solvent molecule was modelled as disordered over two sites, occupancies set at 0.7 and complement after trial refinement. Some difficulties with the refinement have resulted in a larger than usual (shift/error)<sub>max</sub>.

7: Weak and limited data would support anisotropic displacement parameter form refinement for Ru, Au, P only.

**8**: The  $CH_2Cl_2$  solvent molecules were each modelled as disordered in concert over two sets of sites, occupancies refining to 0.611(1) and complement.

**9**: The CH<sub>2</sub>Cl<sub>2</sub> solvent molecule was modelled as disordered, site occupancy set at 0.25 after trial refinement.

12: The thf solvent molecules were refined with constrained geometries; T = 300 K.

13: Friedel data were initially retained distinct,  $x_{abs}$  refining to a value not significantly different from 0.5, whereupon they were merged.

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