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Preliminary communication

Octahedral bis(acetylide) and bis(diacetylide) complexes of ruthenium(II) with linear  $C_2MC_2$  and  $C_4MC_4$  chains: the first X-ray structures of the all *trans* bis(acetylides)  $Ru(CO)_2(C\equiv CPh)_2(PEt_3)_2$  and  $Ru(CO)_2(C\equiv CH)_2(PEt_3)_2$

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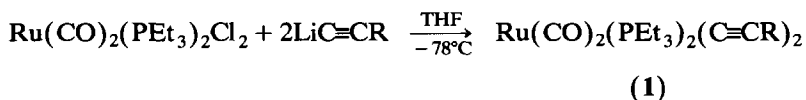
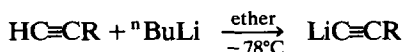
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**Abstract**

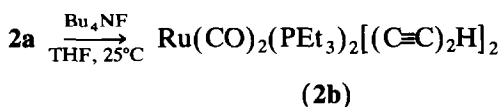
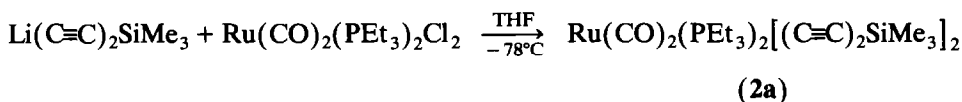
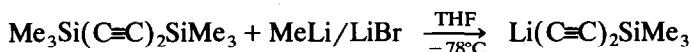
Bis(acetylides) and bis(diacetylides) of ruthenium(II), *trans*- $Ru(CO)_2(PEt_3)_2(C\equiv CR)_2$  (**1**) (**1a**, R = Ph; **1b**, R = <sup>t</sup>Bu; **1c**, R = SiMe<sub>3</sub>; **1d**, R = H) and *trans*- $Ru(CO)_2(PEt_3)_2(C\equiv C-C\equiv CR)_2$  (**2**) (**2a**, R = SiMe<sub>3</sub>; **2b**, R = H) have been synthesized and characterised. The first single crystal X-ray analyses of these all *trans*-acetylides have revealed linear  $C_2RuC_2$  chains in **1a** and **1d**.

There is great current interest in materials containing transition metal fragments linked into a linear array by acetylide or polyacetylide ligands [1,2]. With the possibility that extended  $\pi$ -interactions through a metal centre may lead to novel physical properties, attention has focussed particularly on the liquid crystalline [3] and non-linear optical behaviour [4] of polymers with square planar metals such as Ni<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup> in the backbone. More recently some examples of five and six-coordinate Rh<sup>III</sup> have been described [5] and the first rigid rod iron containing polyene polymers have been prepared [6]. In this communication we describe the synthesis and characterisation of a series of Ru<sup>II</sup> bis(acetylides) and bis(diacetylides) with all *trans* octahedral stereochemistry at the metal centre as models and precursors of linear polymers. X-ray structures of *trans*- $Ru(CO)_2(C\equiv CPh)_2(PEt_3)_2$  (**1a**) and the parent bis(acetylide) *trans*- $Ru(CO)_2(C\equiv CH)_2(PEt_3)_2$  (**1d**) have revealed linear  $C_2RuC_2$  chains perpendicular to planar  $Ru(CO)_2P_2$  cores.

Our approach to the synthesis of bis(acetylides) of ruthenium(II) was via the known chloro phosphine complex, *trans*- $Ru(CO)_2Cl_2(PEt_3)_2$  which is readily accessible directly from ruthenium trichloride via treatment with CO and PEt<sub>3</sub> in ethanol [7]. Reaction of *trans*- $Ru(CO)_2(PEt_3)_2Cl_2$  (0.76 g, 1.63 mmol) in THF (40 ml) with two equivalents of LiC≡CPh (from HC≡CPh and <sup>n</sup>BuLi) at 195 K for 2 h under a nitrogen atmosphere followed by warming to 293 K and chromatography on silica gel under N<sub>2</sub> (eluent CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>14</sub>, 1:1) gave, on cooling to 263 K,



(1a, R = Ph; 1b, R = <sup>t</sup>Bu; 1c, R = SiMe<sub>3</sub>; 1d, R = H)



Scheme 1

colourless crystals of **1a** (60%). Complexes **1b**, **1c** and **1d** were prepared similarly from  $\text{HC}\equiv\text{C}^t\text{Bu}$ ,  $\text{HC}\equiv\text{CSiMe}_3$  and  $\text{HC}\equiv\text{CH}$ , respectively. The diacetylide **2a** was synthesized via the acetylene  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  by treatment with  $\text{CH}_3\text{Li}/\text{LiBr}$  in THF while the parent bis(diacetylide) **2b** was readily obtained by the transformation of **2a** using tetrabutyl-ammonium fluoride in THF at room

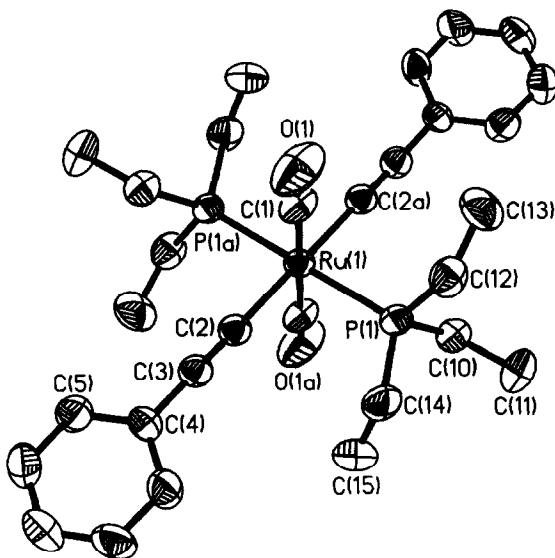


Fig. 1. A perspective view of the molecular structure of *trans*- $\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$  (**1a**) showing the atomic numbering. Bond lengths (Å) and angles (°) not mentioned in the text are: Ru(1)–P(1) 2.373(1), Ru(1)–C(1) 1.917(3), C(2)–C(3) 1.200(4), C(3)–C(4) 1.438(4); P(1)–Ru(1)–C(1) 90.1(1), P(1)–Ru(1)–C(2) 91.7(1), C(1)–Ru(1)–C(2) 89.5(1).

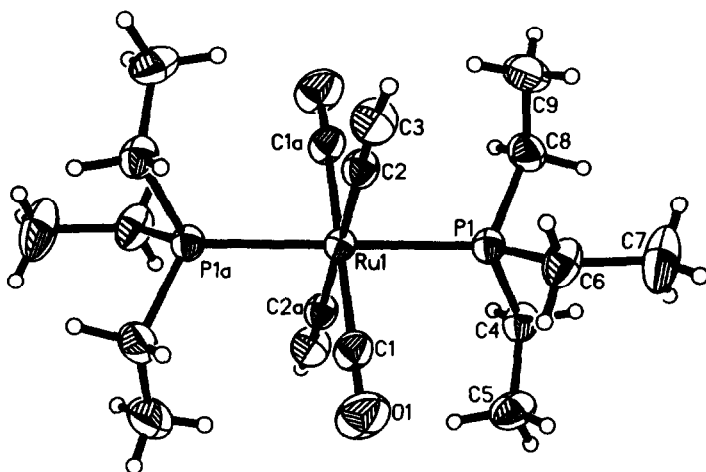


Fig. 2. A perspective view of the molecular structure of *trans*-Ru(CO)<sub>2</sub>(C≡CH)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> (**1d**) showing the atomic numbering. Bond lengths (Å) and angles (°) not mentioned in the text are: Ru(1)–P(1) 2.371(1), Ru(1)–C(1) 1.932(2), C(2)–C(3) 1.199(2); P(1)–Ru(1)–C(1) 88.4(1), P(1)–Ru(1)–C(2) 89.4(1), C(1)–Ru(1)–C(2) 89.4(1).

temperature (Scheme 1) \*. All of these acetylides are air sensitive in solution; solids can be handled in air for short periods but should be stored under N<sub>2</sub>.

The acetylide complexes **1a–1d** displayed a single  $\nu(\text{C}\equiv\text{C})$  band, one  $\nu(\text{CO})$  frequency and a single <sup>31</sup>P resonance indicative of an all *trans* configuration. For **2a** two different  $\nu(\text{C}\equiv\text{C})$  bands, corresponding to the free and metal coordinated alkynyl moieties, were observed. While only one  $\nu(\text{C}\equiv\text{C})$  band was present in

\* Selected spectroscopic data: **1a**, IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{C}\equiv\text{C})$  2093m;  $\nu(\text{CO})$  1987s cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  21.04 s. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  198.64 (t, CO, <sup>2</sup>J(P–C) = 13.5 Hz), 130.86 (s, C<sub>o</sub>), 129.72 (s, C<sub>i</sub>), 128.20 (s, C<sub>m</sub>), 124.62 (s, C<sub>p</sub>), 111.17 (s, C<sub>β</sub>), 104.94 (t, C<sub>α</sub>, <sup>2</sup>J(P–C) = 13.3 Hz), 19.08 (virtual triplet, CH<sub>2</sub>), 7.7 (s, CH<sub>3</sub>). Anal. Found: C, 60.52; H, 6.66; P, 10.57. C<sub>30</sub>H<sub>40</sub>O<sub>2</sub>P<sub>2</sub>Ru calcd.: C, 60.94; H, 6.77; P, 10.40%.

**1b**, IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{C}\equiv\text{C})$  2033m;  $\nu(\text{CO})$  1985s cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  18.18.

**1c**, IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{C}\equiv\text{C})$  2021m;  $\nu(\text{CO})$  1986s cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  19.86. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  198.12 (t, CO, <sup>2</sup>J(P–C) = 13.4 Hz), 128.4 (t, C<sub>α</sub>, <sup>2</sup>J(P–C) = 12.4 Hz), 116.1 (s, C<sub>β</sub>), 18.57 (virtual triplet, CH<sub>2</sub>), 7.67 (s, CH<sub>3</sub>), 1.34 (s, SiMe<sub>3</sub>). Anal. Found: C, 49.07; H, 8.12; P, 10.43. C<sub>24</sub>H<sub>48</sub>O<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>Ru calcd.: C, 49.04; H, 8.23; P, 10.54%.

**1d**, IR (CDCl<sub>3</sub>):  $\nu(\equiv\text{C}-\text{H})$  3271m,  $\nu(\text{CO})$  1987s,  $\nu(\text{C}\equiv\text{C})$  1944m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.05 (multiplet, 6H, CH<sub>2</sub>), 1.54 (t, 1H, ≡CH, <sup>4</sup>J(P–H) = 1.69 Hz), 1.19 (multiplet, 9H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  19.86. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  198.43 (t, CO, <sup>2</sup>J(P–C) = 13.4 Hz), 98.49 (t, C<sub>α</sub>, <sup>2</sup>J(P–C) = 13.0 Hz), 95.01 (s, C<sub>β</sub>), 18.55 (virtual triplet, CH<sub>2</sub>), 7.68 (s, CH<sub>3</sub>). Anal. Found: C, 48.50; H, 7.18; P, 14.12. C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>P<sub>2</sub>Ru calcd.: C, 48.75; H, 7.27; P, 13.97%.

**2a**, IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{C}\equiv\text{C})$  2165m, 2121m;  $\nu(\text{CO})$  2002s cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  20.10.

**2b**, IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  2002s,  $\nu(\text{C}\equiv\text{C})$  2137m,  $\nu(\equiv\text{C}-\text{H})$  3302m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.00 (multiplet, 6H, CH<sub>2</sub>), 1.45 (t, 1H, CH, <sup>9</sup>J(P–H) = 0.8 Hz), 1.19 (multiplet, 9H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  20.04. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  196.32 (t, CO, <sup>2</sup>J(P–C) = 12.2 Hz), 101.31 (t, C<sub>1</sub>, <sup>2</sup>J(P–C) = 12.0 Hz), 91.70 (s, C<sub>2</sub>), 72.13 (s, C<sub>3</sub>), 54.46 (s, C<sub>4</sub>), 18.80 (virtual triplet, CH<sub>2</sub>), 7.60 (s, CH<sub>3</sub>). Proton coupled <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  196.37 (t, CO, <sup>2</sup>J(P–C) = 12.4 Hz), 101.31 (t, C<sub>1</sub>, <sup>2</sup>J(P–C) = 13.7 Hz), 91.70 (s, C<sub>2</sub>), 72.13 (d, C<sub>3</sub>, <sup>2</sup>J(H–C) = 50.80 Hz), 54.46 (d, C<sub>4</sub>, <sup>1</sup>J(H–C) = 252.0 Hz), 18.80 (virtual triplet of triplets, CH<sub>2</sub>, <sup>1</sup>J(H–C) = 127.8 Hz), 7.60 (quartet, CH<sub>3</sub>, <sup>1</sup>J(H–C) = 127.8 Hz).

compound **2b**, the terminal  $\nu(\text{C}\equiv\text{C})$  band may be obscured by  $\nu(\text{CO})$ . The parent acetylide and diacetylide exhibited sharp, medium intensity  $\nu(\text{C}\equiv\text{H})$  bands at 3271 and 3320  $\text{cm}^{-1}$ , respectively, and the related protons have unusually upfield resonances at 1.54 and 1.45 ppm. Similar observations were reported for cyclopentadienyl iron diacetylide compounds [8]. The acetylene carbon atoms in complex **2b** were assigned on the basis of C–H coupling constants obtained from a proton-coupled  $^{13}\text{C}$  NMR spectrum ( $\text{C}_1$  is bound to Ru), and an unusual upfield shift was found for terminal carbon ( $\text{C}_4$ ) at 54.46 ppm. The large  $^1\text{J}(\text{H}\text{--}\text{C})$  coupling constant of 252 Hz for  $\text{C}_4$  is consistent with  $\text{C}_{sp}$  hybridisation of this carbon atom. Complexes **2a** and **2b** are the first bis(diacetylides) of ruthenium(II) to be synthesized. The only previous reports of octahedral ruthenium(II) bis(acetylides) were the unsymmetrical *cis*  $\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})_2(\text{P}^i\text{Pr}_3)_2$  and *cis, trans*  $\text{Ru}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{P}^i\text{Pr}_3)$  prepared indirectly from  $\text{Ru}^{\text{II}}$  (hydrido)(borohydride) complexes [9]. The molecular structures of complexes **1a** and **1d** were determined by single crystal X-ray diffraction and are illustrated in Figs. 1 and 2\*. The ruthenium atoms in the all *trans* individual molecules sit on crystallographic centres of symmetry and are octahedrally coordinated by two acetylides, two carbonyl groups and two triethylphosphines. The largest deviations from octahedral symmetry at the metal atoms are the angles  $\text{P}(1)\text{--}\text{Ru}(1)\text{--}\text{C}(2)$  of  $91.7(1)^\circ$  in **1a** and  $\text{P}(1)\text{--}\text{Ru}(1)\text{--}\text{C}(1)$  of  $91.6(1)^\circ$  in **1d**. The most significant feature of the structures is the five-atom chain  $\text{C}(3)\text{--}\text{C}(2)\text{--}\text{Ru}(1)\text{--}\text{C}(2a)\text{--}\text{C}(3a)$ . The  $\text{Ru}(1)\text{--}\text{C}(2)\text{--}\text{C}(3)$  angles ( $177.1(3)$  in **1a** and  $179.8(1)^\circ$  in **1d**) indicate that there is little deviation from linearity. For metal linked acetylides such as **1a** and **1d**, interest has focussed on the nature of the metal-acetylide bonding and the possibility of electronic communication along the chain. Although the presence of two strong  $\pi$ -acid CO ligands in **1a**–**1d**, **2a**, **2b** might be expected to inhibit metal ( $d\pi$ )/ $\text{C}\equiv\text{CR}(p\pi^*)$  interaction, the  $\text{Ru}(1)\text{--}\text{C}(2)$  bond length of 2.074(3) and 2.078(1) Å in **1a** and **1d** are significantly shorter than the  $\text{Ru}\text{--}\text{C}_\alpha\text{Ph}$  distance in  $\text{Ru}(\text{CO})[\text{C}_6\text{H}_3\text{MeC}(\text{O})\text{C}_6\text{H}_4\text{Me}](\text{C}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2$  (2.120(5) Å) where the ruthenium atom is also six-coordinate [10]. In the monoacetylide complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2$  where the ruthenium atom is electron rich by virtue of the presence of three donor ligands and the absence of a strong  $\pi$ -acid the  $\text{Ru}\text{--}\text{C}_\alpha$  distance is 2.016(3) Å [11]. If the covalent radius of ruthenium is taken as one half of the standard  $\text{Ru}\text{--}\text{Ru}$  distance in  $\text{Ru}_3(\text{CO})_{12}$  (2.854 Å) [12] and the  $\text{C}_{sp}$  radius of carbon as 0.70 Å [13], the expected length of an  $\text{Ru}\text{--}\text{C}(\text{acetylide})$  single bond is 2.127 Å. This suggests that in **1a** and **1d** the  $\text{Ru}\text{--}\text{acetylide}$  bonds have at best only a small amount of  $\pi$ -character, a conclusion

\* Crystal data: **1a**, colourless prism from  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ ,  $\text{C}_{30}\text{H}_{40}\text{O}_2\text{P}_2\text{Ru}$ ,  $M = 595.6$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.9954(5)$ ,  $b = 9.5310(7)$ ,  $c = 10.1869(12)$  Å,  $\alpha = 89.240(8)$ ,  $\beta = 83.247(7)$ ,  $\gamma = 77.484(5)^\circ$ ,  $Z = 1$ ,  $V = 752.51(11)$  Å<sup>3</sup>,  $d = 1.314$  Mg  $\cdot$  m<sup>-3</sup>,  $\mu(\text{Mo}\text{--}\text{K}_\alpha) = 6.37$  cm<sup>-1</sup>,  $F(000) = 310$ . The structure was solved and refined on the basis of 1876 observed reflections for which  $F \geq 6.0\sigma(F)$ , measured by  $\omega$  scans in the  $2\theta$  range  $3.5\text{--}56.0^\circ$  at 295 K on a Siemens R3 m/v automatic diffractometer using  $\text{Mo}\text{--}\text{K}_\alpha$  radiation. Refinement by full matrix least squares methods, with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic lead to  $R$  and  $R_w$  values of 0.020 and 0.019, respectively. **1b**, orange-brown needle prisms from  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_{18}\text{H}_{32}\text{O}_2\text{P}_2\text{Ru}$ ,  $M = 443.5$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.391(1)$ ,  $b = 10.039(1)$ ,  $c = 10.464(1)$  Å,  $\beta = 94.72(1)^\circ$ ,  $Z = 2$ ,  $V = 1087.8(23)$  Å<sup>3</sup>,  $d = 1.354$  Mg  $\cdot$  M<sup>-3</sup>,  $\mu(\text{Mo}\text{--}\text{K}_\alpha) = 8.6$  cm<sup>-1</sup>,  $F(000) = 460$ . The structure was solved and refined on the basis of 2830 observed reflections for which  $F \geq 6.0\sigma(F)$ , measured by  $\omega$  scans in the  $2\theta$  range  $4.0\text{--}60.0^\circ$  at 200 K. Final  $R$  and  $R_w$  values are 0.023 and 0.035.

reinforced by the length of the Ru–C(1)(CO) bonds (1.917(3) and 1.932(2) Å in **1a** and **1d**).

The synthesis and characterisation of **1a–1d** and **2a, 2b** together with the X-ray structural data for **1a** and **1d** suggest that *trans* bisacetylides of Ru<sup>II</sup> may serve as useful starting materials for the design of rod-like polymers with long range conjugation along the chain. We are currently pursuing the generation of oligomers and polymers based on the structural units established for **1a** and **1d**.

*Supplementary material available.* Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, H-atom coordinates, structure determination summaries (16 pages) and listings of structure factors (26 pages) of **1a** and **1d** are available from the authors.

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