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FULL PAPER

A new family of phosphido-bridged dinuclear ruthenium carbonyl complexes: synthesis of $[Ru_2(CO)_6\{\mu\text{-}P(\overline{C(CH)_3O})_2\}(\mu\text{-}\eta^1,\eta^2\text{-}\overline{C(CH)_3O})]$ and its reactivity towards terminal alkynes

Wai-Yeung Wong,* Fai-Lung Ting and Wai-Lim Lam

Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P.R. China. E-mail: rwywong@hkbu.edu.hk

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Thermal reaction of $[Ru_3(CO)_{12}]$ with tri(2-furyl)phosphine affords the dinuclear phosphido-bridged complex $[Ru_2(CO)_6\{\mu\text{-}P(\overline{C(CH)_3O})_2\}(\mu\text{-}\eta^1,\eta^2\text{-}\overline{C(CH)_3O})]$ **1a** in good yield *via* cleavage of Ru–Ru and P–C(furyl) bonds in the starting compounds and a small amount of the disubstitution product $[Ru_3(CO)_{10}\{P(\overline{C(CH)_3O})_3\}_2]$ **1b**. The X-ray structural analysis of **1a** shows that it contains a dissociated furyl fragment bonded to the Ru_2 unit in a $\mu\text{-}\eta^1,\eta^2$ coordination mode through one σ and one π bond. This represents the first structurally characterised example of such a furyl-bonded dinuclear organometallic complex. Complex **1a** readily reacts with two equivalents of terminal alkynes HC≡CR [R = Ph, *p*-C_6H_4Me, *p*-$C_6H_4NO_2$, $(C_4H_2S)C{\equiv}CH$ or $(C_4H_2S)_2C{\equiv}CH$] by an interesting head-to-tail ynyl coupling with a furan group to form a series of phosphido-bridged diruthenium compounds containing a novel furyl-substituted C_4 hydrocarbyl chain of stoichiometry $[Ru_2(CO)_4\{\mu\text{-}P(\overline{C(CH)_3O})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^2,\eta^3\text{-}RCC(H)C(R)C(H)\text{-}\overline{C(CH)_3O}\}]$ [R = Ph **2**, *p*-C_6H_4Me **3**, *p*-$C_6H_4NO_2$ **4**, $(C_4H_2S)C{\equiv}CH$ **5** or $(C_4H_2S)_2C{\equiv}CH$ **6**] in moderate to good yields, all of which have been characterised by spectroscopic and crystallographic methods. Assignments of the proton NMR spectra have been made with the aid of a 2-D ^1H–^1H COSY technique. On reaction with the thienyl-linked diyne ligands, only one free C≡CH group is involved in the coupling sequence while the other terminal alkyne functionality remains intact. All these new dinuclear complexes are electron precise with 34 cluster valence electrons.

Introduction

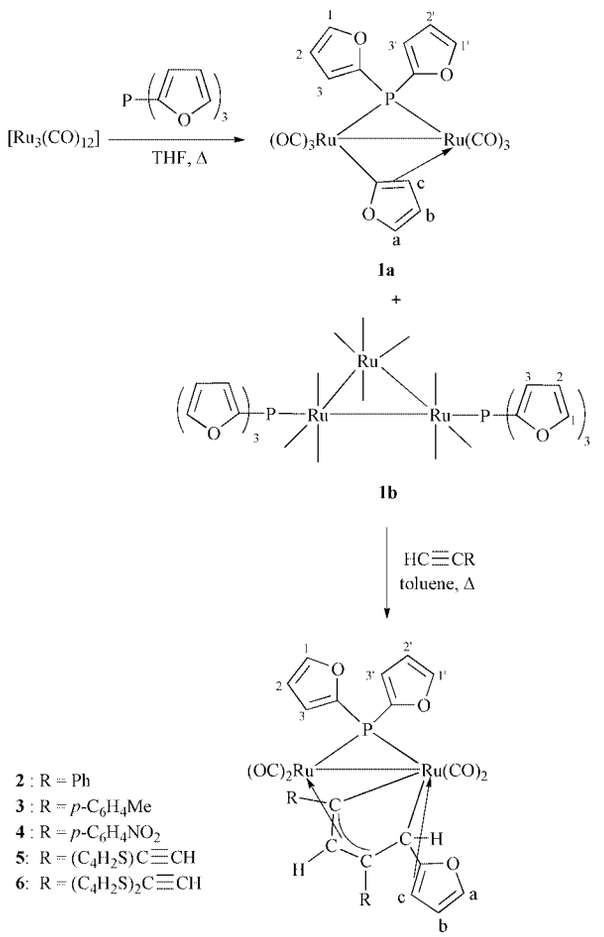
Reactions of triruthenium carbonyl clusters with alkyl-, aryl- and alkoxy-substituted phosphines L have been extensively studied in the past few decades, affording a vast range of substitution products $[Ru_3(CO)_{12-n}(L)_n]$ (n = 1–4).[1] More recently, considerable effort has been devoted to the reactivity studies of phosphine ligands with additional donor sites towards $[Ru_3(CO)_{12}]$ and other derivatives.[2–5] For instance, trinuclear ruthenium carbonyl clusters containing functionalised phosphine ligands such as $PPh_2(C_5H_4N)$,[3] $PPh_2(CH_2COPh)$[4] or $PPh_2(C_6H_4X\text{-}2)$ (X = NH_2, NCHPh, CHO)[5] have been shown to undergo cleavage of P–C bonds. Phosphine ligands containing sulfur donor substituents were also widely used in this context, with particular regard to phosphines bearing the 2-thienyl group.[6] It is well-documented that the coordination chemistry of thiophene is rather diverse and different types of bonding modes to metal atoms have been observed.[7] Oxidative addition reactions of thiophene can also play an important role, leading to 2-thienyl hydrido complexes by C–H bond scission or to ring opening with C–S bond cleavage to afford metallasulfacyclohexadiene systems.[7,8] The preparation of the cyclometallated compound $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2S)]$ has been reported by Deeming and co-workers, which, upon thermal treatment with $[Ru_3(CO)_{12}]$, yields the μ_4-thiophyne complex $[Ru_4(CO)_{11}(\mu_4\text{-}PPh)(\mu_4\text{-}C_4H_2S)]$ by elimination of benzene, and the μ_4-benzyne complex $[Ru_4(CO)_{11}(\mu_4\text{-}PPh)(\mu_4\text{-}C_6H_4)]$ by elimination of thiophene.[9] These compounds possess capping phosphorus donor ligands, inhibiting metal–metal bond cleavage. Likewise, the reaction between $[Ru_3(CO)_{12}]$ and tri(2-thienyl)phosphine has been studied and a donor-induced cluster degradation product $[Ru(CO)_3\{P(\overline{C(CH)_3S})_3\}_2]$ was isolated.[10] However, related chemical studies involving the furan group, an oxygen analogue of thiophene, remain virtually unexplored, even though the use of tri(2-furyl)phosphine as a ligand for transition metal-mediated synthesis has been exhaustively reviewed.[11]

On the other hand, the synthesis and catalytic behaviour of phosphido-bridged di- and poly-nuclear complexes continue to attract much attention.[12] The $\mu\text{-}PR_2$ (R = alkyl or aryl) group can act as a strongly bound yet flexible ligand which may help maintain the integrity of a metal cluster framework while allowing facile metal–metal bond cleavage and reformation during catalytic transformations. Complexes $[M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CR)]$ (M = iron triad; R = alkyl or aryl) have been widely studied as useful precursors for preparing polymetallic multisite-bound polycarbon materials *via* head-to-head or head-to-tail coupling of alkynyl ligands.[13] Such complexes of the type $[Ru_2(CO)_6(\mu\text{-}PPh_2)\text{-}\{\mu\text{-}\eta^1,\eta^2\text{-}CH(C_6H_4)C(Ph){=}CC{\equiv}CBu^t\}]$ and $[Ru_2(CO)_6(\mu\text{-}PPh_2)\text{-}\{\mu\text{-}\eta^1,\eta^2\text{-}C{=}C(Ph)C{=}C(Ph)(C_6H_4)CH\}]$ have been prepared.[14] In these reactions, the organometallic species promote alkyne oligomerisation and exert a template effect on the resulting organic moieties.[13–15] Bearing the above concepts in mind, we set out to develop the chemistry between ruthenium carbonyl clusters and the polyfunctional tri(2-furyl)phosphine ligand. Here we describe a convenient route to the novel dinuclear complex $[Ru_2(CO)_6\{\mu\text{-}P(\overline{C(CH)_3O})_2\}(\mu\text{-}\eta^1,\eta^2\text{-}\overline{C(CH)_3O})]$ **1a**. Subsequent reactions of **1a** with an excess of 1-alkynes result in an unprecedented head-to-tail ynyl coupling with a furan group to form a novel furyl-based four-carbon chain with an unusual $\mu\text{-}\eta^1,\eta^1,\eta^2,\eta^3$ coordination mode to the Ru centres.

Results and discussion

Reaction of $[Ru_3(CO)_{12}]$ with tri(2-furyl)phosphine

Treatment of $[Ru_3(CO)_{12}]$ with one molar equivalent of tri(2-furyl)phosphine in refluxing THF readily afforded a deep red solution, and subsequent work-up by preparative TLC on silica gave the oxidative addition dinuclear compound $[Ru_2(CO)_6\{\mu\text{-}P(\overline{C(CH)_3O})_2\}(\mu\text{-}\eta^1,\eta^2\text{-}\overline{C(CH)_3O})]$ **1a** as a pale yellow solid in 56% yield (Scheme 1). Complex **1a** was fully characterised by



Scheme 1

satisfactory elemental analysis, FAB mass spectrometry, IR and NMR spectroscopies, and the molecular structure of **1a** has been elucidated by single-crystal X-ray diffraction (*vide infra*). The formation of **1a** is in contrast to the products from the reaction of PPh_3[16] or diphenylpyridylphosphine[3] with $[Ru_3(CO)_{12}]$ and other Ru systems. Spectroscopic evidence indicated that a small amount of the disubstitution product $[Ru_3(CO)_{10}\{P(\overline{C(CH)_3O})_3\}_2]$ **1b** was also obtained in this reaction. Its mass spectrum reveals a single molecular ion peak along with fragmentation peaks corresponding to the loss of up to nine carbonyls and the IR data show close resemblance to those reported in other triruthenium bis(phosphine) clusters.[1,10]

The spectroscopic properties of **1a** are consistent with its dinuclear formulation. In the IR spectrum four ν(CO) bands due to the terminal carbonyls were observed in the region 2000–2090 cm^{-1} and no bridging carbonyl group was present. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1a** showed a very downfield singlet peak at δ 58.5, as compared to δ −75.8 for the free phosphine ligand. Complex **1a** displayed a FAB mass spectrum exhibiting a parent ion peak at *m*/*z* 602 and daughter ions due to successive loss of CO groups. The proton NMR signals arising from the furyl moieties were all apparent and integrated to a total of nine protons. It is possible to interpret the resonances of the

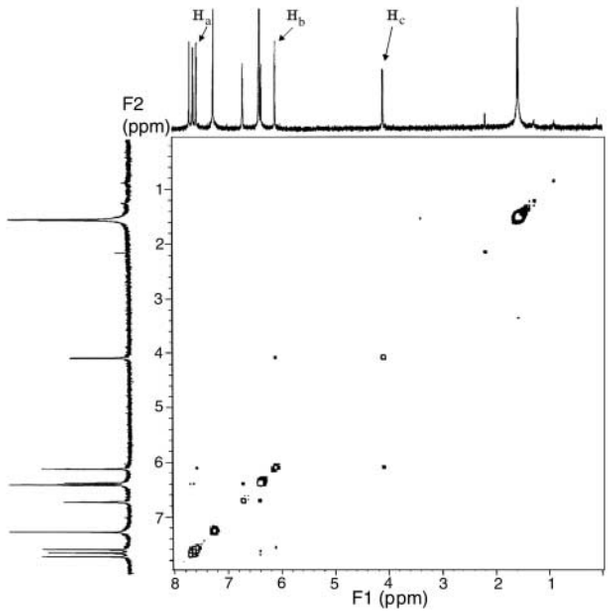


Fig. 1 2-D ^1H–^1H COSY spectrum of compound **1a** recorded in $CDCl_3$.

$\mu\text{-}\eta^1,\eta^2$-bound furyl ring with the aid of a 2-D ^1H–^1H COSY technique (Fig. 1). The presence of two cross peaks at δ 4.10 and 7.58 for the peak at δ 6.11 revealed that the proton at δ 6.11 is spin-coupled to those protons at δ 4.10 and 7.58 and is thus assigned to proton H_b (see Scheme 1 for the labelling system used). The protons at δ 7.58 and 4.10 are assigned to H_a and H_c, respectively, because of the close proximity of H_a to the electronegative oxygen atom. The proton H_c is also spin-coupled to the phosphorus atom of the μ-phosphido group. Inspection of the relative intensities of 1 : 1 : 1 of these three signals confirmed our assignment.

Reactions of complex 1a with HC≡CR [R = Ph, *p*-C_6H_4Me or *p*-$C_6H_4NO_2$]

Reactions of **1a** with two molar equivalents of terminal alkynes HC≡CR (R = Ph, *p*-C_6H_4Me, *p*-$C_6H_4NO_2$) proceeded smoothly in refluxing toluene, finally resulting in a dark reddish-brown/red solution. Novel phosphido-stabilised complexes $[Ru_2(CO)_4\{\mu\text{-}P(\overline{C(CH)_3O})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^2,\eta^3\text{-}RCC(H)C(R)C(H)\overline{C(CH)_3O}\}]$ (R = Ph **2**, *p*-C_6H_4Me **3** or *p*-$C_6H_4NO_2$ **4**) were isolated in moderate to good yields after TLC purification on silica gel and recrystallisation from their hexane–CH_2Cl_2 solutions. They were obtained as stable red crystalline solids and are soluble in common organic solvents. A few minor products remain unidentified in these reactions. The transformation of these products is shown in Scheme 1. When the experiment was carried out in the presence of one equivalent of the alkynes, identical reaction products were produced in each case. The formulae of these new diruthenium compounds were initially established by FAB mass spectrometry and the molecular ions correspond to products formed from the addition of two alkyne molecules to **1a** with the loss of two CO ligands. Their IR spectra indicated the presence of terminal carbonyl ligands only with absorption bands appearing within the region 1940–2050 cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR chemical shifts range from δ 75.8 to 82.0 for **2**–**4** and they follow the order **3** < **2** < **4**. This is in line with the electron-withdrawing tendency of the appended R groups *p*-C_6H_4Me < Ph < *p*-$C_6H_4NO_2$ in the resulting phosphido-bridged Ru_2 complexes which renders the metal core most electron-deficient in **4**. These $^{31}P\text{-}\{^1H\}$ NMR signals resonated further downfield than that of the precursor complex **1a**. In each case, the ^1H NMR spectrum in $CDCl_3$ comprised a complex series of multiplet resonances, some of which overlap.

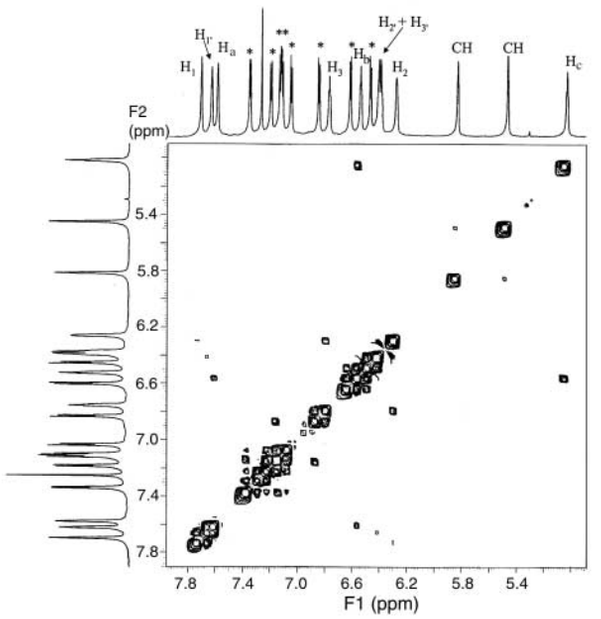


Fig. 2 2-D ^{1}H–^{1}H COSY spectrum of compound **6** recorded in $CDCl_3$. Peaks marked with asterisks correspond to bithienyl proton resonances.

The three furyl rings in **2**–**4** are predicted to give rise to a total of nine resonances which, from the integral trace of the spectrum, appears to be the case. The C_6H_4 and phenyl protons were easily identified in their respective spectra. For **3**, two strong methyl singlets were observed at δ 2.19 and 2.39. These alkyne-coupled compounds have also been analysed by 2-D ^{1}H–^{1}H COSY experiments, which allow us to locate the positions of protons H_a, H_b and H_c as well as the two protons on the C_4 hydrocarbyl chain. However, no attempt has been made to assign fully the actual positions of these ring systems.

Reactions of complex 1a with HC≡CR [R = $(C_4H_2S)C{\equiv}CH$ or $(C_4H_2S)_2C{\equiv}CH$]

Analogous to the previous reactions, the thermolysis of a toluene solution of **1a** in the presence of two equivalents of the thienyl-linked diyne ligands $HC{\equiv}C(C_4H_2S)_mC{\equiv}CH$ (m = 1 or 2)[17] led to a dark red-brown solution in each case which yielded a red band when the crude mixture was chromatographed on silica plates. Two new diruthenium compounds were isolated and identified as $[Ru_2(CO)_4\{\mu\text{-}P(\overline{C(CH)_3O})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^2,\eta^3\text{-}HC{\equiv}C(C_4H_2S)CC(H)C((C_4H_2S)C{\equiv}CH)C(H)\overline{C(CH)_3O}\}]$ (**5**) and $[Ru_2(CO)_4\{\mu\text{-}P(\overline{C(CH)_3O})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^2,\eta^3\text{-}HC{\equiv}C(C_4H_2S)_2CC(H)C((C_4H_2S)_2C{\equiv}CH)C(H)\overline{C(CH)_3O}\}]$ (**6**) in 30 and 38% yields (based on complex **1**), respectively (Scheme 1). From the FAB mass spectral data (m/z = 810 **5**, 975 **6**), coupled with the similar ν(CO) IR pattern as for **2**–**4**, it is very likely that identical coupling products as for the mono-alkyne ligands were produced. The ^{31}P-{^{1}H} NMR spectra of **5** and **6** show a rather similar resonance at around δ 78.0, in common with the chemical shifts mentioned above for **2**–**4** and consistent with the retention of a phosphido bridge. The ^{1}H NMR data for **5** and **6** were also in agreement with their solid-state structures. Their ^{1}H NMR spectra incorporate a manifold series of multiplets in close proximity integrating for 17 (for **5**) and 21 protons (for **6**). A more conclusive assignment was achieved by performing the ^{1}H–^{1}H COSY experiments (Fig. 2). In each case, resonances caused by the furyl protons H_a, H_b and H_c were successfully assigned from the connectivity pattern of the cross peaks within a given spin system. The free acetylenic protons of both compounds showed up as two singlets in the range δ 3.2–3.4 and the two distinct protons on the C_4 fragment as two sharp peaks at about δ 5.4 and 5.8. The observation of four and eight resonances in **5** and **6**, respectively, due to the two thienyl and bithienyl rings is a manifestation of the chemical non-equivalence of these ligands in the resulting alkyne-coordinated complexes.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1a**

	Molecule 1	Molecule 2	Molecule 3
Ru(1)–Ru(2)	2.7735(3)	2.7796(3)	2.7752(3)
Ru(2)–P(1)	2.3214(7)	2.3208(7)	2.3310(7)
Ru(1)–C(30)	2.426(3)	2.426(3)	2.451(3)
C(27)–C(30)	1.395(4)	1.400(4)	1.401(4)
Ru(1)–P(1)	2.3374(7)	2.3415(7)	2.3437(7)
Ru(1)–C(27)	2.350(3)	2.355(3)	2.354(2)
Ru(2)–C(27)	2.085(3)	2.076(3)	2.074(3)
Ru(1)–Ru(2)–P(1)	53.73(2)	53.75(2)	53.79(2)
Ru(1)–C(27)–Ru(2)	77.16(8)	77.42(9)	77.35(8)
C(27)–Ru(1)–C(30)	33.9(1)	34.0(1)	33.82(9)
Ru(2)–C(27)–C(30)	134.5(2)	134.4(2)	135.7(2)
Ru(2)–Ru(1)–C(30)	76.21(7)	75.96(7)	76.01(7)
Ru(2)–Ru(1)–P(1)	53.20(2)	53.06(2)	53.37(2)
Ru(1)–C(27)–C(30)	76.0(2)	75.8(2)	76.9(2)
Ru(1)–C(30)–C(29)	120.7(2)	120.5(2)	121.9(2)
Ru(2)–Ru(1)–C(27)	47.14(7)	46.81(7)	46.81(6)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Ru(1)–Ru(2)	2.8006(6)	Ru(1)–P(1)	2.315(1)
Ru(2)–P(1)	2.271(1)	Ru(1)–C(5)	2.264(4)
Ru(1)–C(6)	2.422(5)	Ru(1)–C(15)	2.418(5)
Ru(1)–C(18)	2.146(5)	Ru(2)–C(16)	2.185(5)
Ru(2)–C(17)	2.221(5)	Ru(2)–C(18)	2.244(5)
C(5)–C(6)	1.387(7)	C(15)–C(16)	1.474(7)
C(16)–C(17)	1.434(6)	C(17)–C(18)	1.414(7)
Ru(1)–Ru(2)–P(1)	53.08(4)	Ru(2)–Ru(1)–P(1)	51.64(4)
Ru(1)–C(5)–C(6)	79.1(3)	C(5)–Ru(1)–C(6)	34.2(2)
Ru(1)–C(15)–C(16)	109.1(3)	Ru(1)–C(18)–Ru(2)	79.3(2)
Ru(2)–Ru(1)–C(18)	51.9(1)	C(16)–Ru(2)–C(17)	38.0(2)
C(17)–Ru(2)–C(18)	36.9(2)	C(15)–C(16)–C(17)	114.5(4)
C(16)–C(17)–C(18)	120.4(5)		

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Ru(1)–Ru(2)	2.7991(5)	Ru(1)–P(1)	2.303(1)
Ru(2)–P(1)	2.258(1)	Ru(1)–C(5)	2.269(4)
Ru(1)–C(6)	2.397(4)	Ru(1)–C(16)	2.404(4)
Ru(1)–C(19)	2.172(4)	Ru(2)–C(17)	2.212(4)
Ru(2)–C(18)	2.231(4)	Ru(2)–C(19)	2.191(4)
C(5)–C(6)	1.381(6)	C(16)–C(17)	1.466(6)
C(17)–C(18)	1.420(6)	C(18)–C(19)	1.417(5)
Ru(1)–Ru(2)–P(1)	52.88(3)	Ru(2)–Ru(1)–P(1)	51.42(3)
Ru(1)–C(5)–C(6)	78.0(2)	C(5)–Ru(1)–C(6)	34.3(1)
Ru(1)–C(16)–C(17)	108.8(3)	Ru(1)–C(19)–Ru(2)	79.8(1)
Ru(2)–Ru(1)–C(19)	50.39(9)	C(17)–Ru(2)–C(18)	37.3(1)
C(18)–Ru(2)–C(19)	37.4(1)	C(16)–C(17)–C(18)	115.7(3)
C(17)–C(18)–C(19)	120.3(3)		

Molecular structures of compounds 1a and 2–6

In order to establish the molecular geometries and in particular to obtain precise details on the nature of metal–ligand bonding and the regioselectivity of alkyne coordination, crystal structure analyses of **1a** and **2**–**6** were undertaken. Selected bond parameters are presented in Tables 1–6. An X-ray structure determination on **1a** confirmed a $(OC)_3Ru{-}Ru(CO)_3$ skeleton spanned by a difurylphosphido group and by a furyl group through a σ,η^2-vinyl type bridge. The lattice contains three independent but structurally similar molecules in the asymmetric unit, the geometry of one molecule being quoted as representative (Fig. 3). The average Ru–Ru bond length is 2.7761(3) Å, which is comparable to that observed in $[Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}C{-}C{\equiv}CBu^t)]$ [2.769(1) Å][18] but

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**

Ru(1)–Ru(2)	2.7885(3)	Ru(1)–P(1)	2.3109(7)
Ru(2)–P(1)	2.2831(7)	Ru(1)–C(5)	2.267(3)
Ru(1)–C(6)	2.438(3)	Ru(1)–C(15)	2.382(3)
Ru(1)–C(18)	2.144(3)	Ru(2)–C(16)	2.189(3)
Ru(2)–C(17)	2.239(3)	Ru(2)–C(18)	2.235(3)
C(5)–C(6)	1.391(5)	C(15)–C(16)	1.474(4)
C(16)–C(17)	1.431(4)	C(17)–C(18)	1.411(4)
Ru(1)–Ru(2)–P(1)	53.08(2)	Ru(2)–Ru(1)–P(1)	52.18(2)
Ru(1)–C(5)–C(6)	79.7(2)	C(5)–Ru(1)–C(6)	34.2(1)
Ru(1)–C(15)–C(16)	108.8(2)	Ru(1)–C(18)–Ru(2)	79.07(9)
Ru(2)–Ru(1)–C(18)	51.92(7)	C(16)–Ru(2)–C(17)	37.7(1)
C(17)–Ru(2)–C(18)	36.8(1)	C(15)–C(16)–C(17)	116.2(2)
C(16)–C(17)–C(18)	118.7(2)		

Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

Ru(1)–Ru(2)	2.7825(3)	Ru(1)–P(1)	2.3152(5)
Ru(2)–P(1)	2.2711(5)	Ru(1)–C(5)	2.281(2)
Ru(1)–C(6)	2.450(2)	Ru(1)–C(15)	2.414 (2)
Ru(1)–C(18)	2.170(2)	Ru(2)–C(16)	2.172(2)
Ru(2)–C(17)	2.233(2)	Ru(2)–C(18)	2.250(2)
C(5)–C(6)	1.386(3)	C(9)–C(10)	1.171(3)
C(23)–C(24)	1.173(4)	C(15)–C(16)	1.458(3)
C(16)–C(17)	1.431(3)	C(17)–C(18)	1.415(3)
Ru(1)–Ru(2)–P(1)	53.37(1)	Ru(2)–Ru(1)–P(1)	51.93(1)
Ru(1)–C(5)–C(6)	79.8(1)	C(5)–Ru(1)–C(6)	33.84(8)
Ru(1)–C(15)–C(16)	108.3(1)	Ru(1)–C(18)–Ru(2)	78.02(6)
Ru(2)–Ru(1)–C(18)	52.27(5)	C(16)–Ru(2)–C(17)	37.87(7)
C(17)–Ru(2)–C(18)	36.79(7)	C(9)–C(10)–C(11)	178.2(3)
C(15)–C(16)–C(17)	116.7(2)	C(16)–C(17)–C(18)	119.7(2)
C(22)–C(23)–C(24)	178.7(3)		

Table 6 Selected bond lengths (Å) and angles (°) for complex **6**

Ru(1)–Ru(2)	2.7863(6)	Ru(1)–P(1)	2.318(2)
Ru(2)–P(1)	2.267(2)	Ru(1)–C(5)	2.273(6)
Ru(1)–C(6)	2.448(6)	Ru(1)–C(19)	2.398(7)
Ru(1)–C(22)	2.169(6)	Ru(2)–C(20)	2.185(6)
Ru(2)–C(21)	2.236(6)	Ru(2)–C(22)	2.251(6)
C(5)–C(6)	1.40(1)	C(17)–C(18)	1.18(1)
C(19)–C(20)	1.442(9)	C(20)–C(21)	1.426(9)
C(21)–C(22)	1.403(8)	C(31)–C(32)	1.14(1)
Ru(1)–Ru(2)–P(1)	53.42(4)	Ru(2)–Ru(1)–P(1)	51.73(4)
Ru(1)–C(5)–C(6)	79.8(4)	C(5)–Ru(1)–C(6)	34.1(3)
Ru(1)–C(19)–C(20)	109.5(5)	Ru(1)–C(22)–Ru(2)	78.1(2)
Ru(2)–Ru(1)–C(22)	52.2(2)	C(20)–Ru(2)–C(21)	37.6(2)
C(21)–Ru(2)–C(22)	36.4(2)	C(16)–C(17)–C(18)	179(1)
C(19)–C(20)–C(21)	115.6(5)	C(20)–C(21)–C(22)	120.8(6)
C(30)–C(31)–C(32)	176(1)		

is slightly shorter than that in $[Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C(C{\equiv}CBu^t){=}C{=}CPh_2)]$ [2.825(1) Å][14] and other $Ru_2(\mu\text{-}PR_2)$ systems.[19] The formation of **1a** involves cleavage of Ru–Ru and P–C(furyl) bonds in the starting species. This type of P–C bond activation is believed to be triggered by ruthenium carbonyl fragments.[3a,20] The molecular structure of **1a** revealed that all the furyl rings are essentially planar and the dissociated furyl fragment is bonded to the Ru_2 unit in a $\mu\text{-}\eta^1,\eta^2$ fashion, formally *via* a σ and a π bond. The furyl moiety is σ bonded to one Ru atom [av. Ru–C 2.078(3) Å] and π bonded to the next Ru atom [av. Ru–C 2.394(3) Å]. To the best of our knowledge, this type of furyl coordination to a bimetallic framework is unprecedented in the literature but such a σ,η^2 bonding mode is typical of a substituted bridging vinyl ligand.[21] Also, although there are numerous reports of structural data on diphenylphosphido diruthenium complexes,[18,19] the furyl-substituted counterparts remain uncommon. The coordination sphere of the molecule is completed by six terminal CO ligands which agree with the IR spectral data. The phosphido moiety bridges the Ru–Ru edge symmetrically [av. Ru–P 2.3326(7) Å]. The

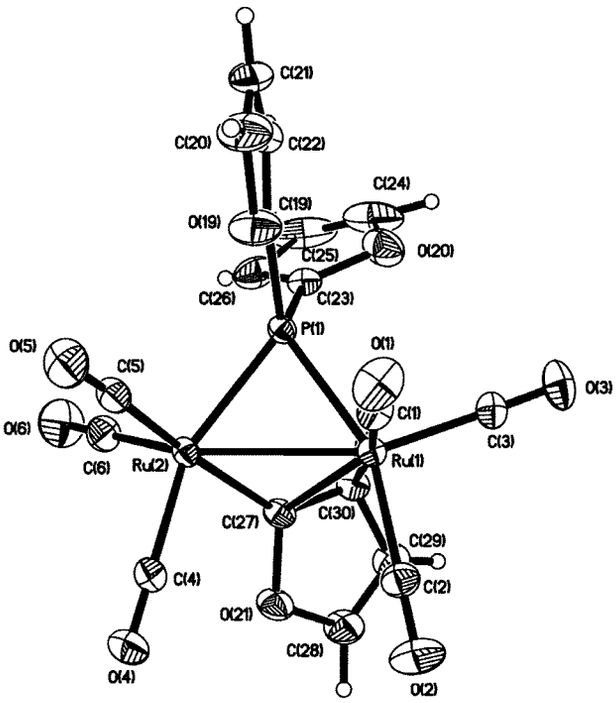


Fig. 3 A perspective drawing of compound **1a**.

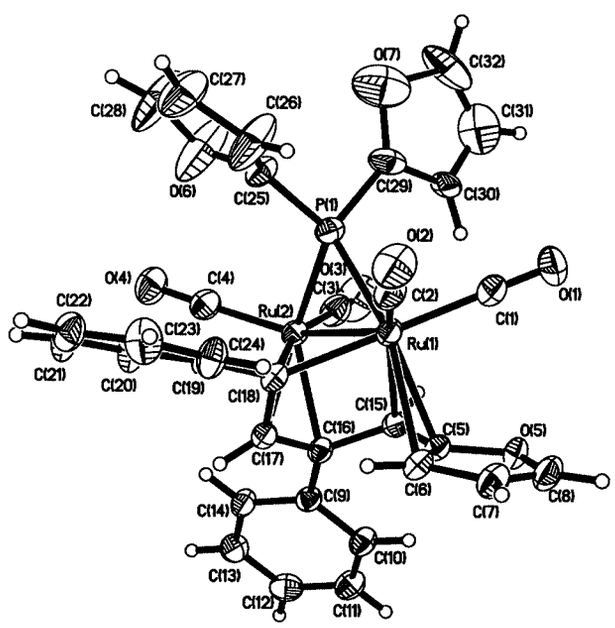


Fig. 4 A perspective drawing of compound **2**.

$\mu\text{-}\eta^1,\eta^2$-furyl ligand acts as a three-electron donor and thus **1a** is electron precise with 34 cluster valence electrons (CVE), in accord with the EAN rule.

Perspective views of the molecular structures of **2**–**4** are illustrated in Figs. 4–6, and the overall geometry is similar among each of them except for the presence of a different substituent at the *para* position of the C_6H_4 moiety. The μ-phosphido Ru_2 framework is retained in the products upon alkyne coupling reactions and the Ru–Ru distances lie within the narrow range 2.7885(3)–2.8006(6) Å. All carbonyls are terminally bound to each Ru atom. The $P(furyl)_2$ bridge is asymmetrically bonded to Ru(1) and Ru(2) [Ru(1)–P(1) 2.303(1)–2.315(1) Å, Ru(2)–P(1) 2.258(1)–2.2831(7) Å] with *ca.* Δ(Ru–P) = 0.028–0.045 Å. Each structure shows that head-to-tail coupling of two alkyne molecules with the furyl group in **1a** and insertion of a C_4 fragment into the Ru–C(furyl) bond occur, followed by the loss of two coordinated carbonyls. In each case, a salient structural

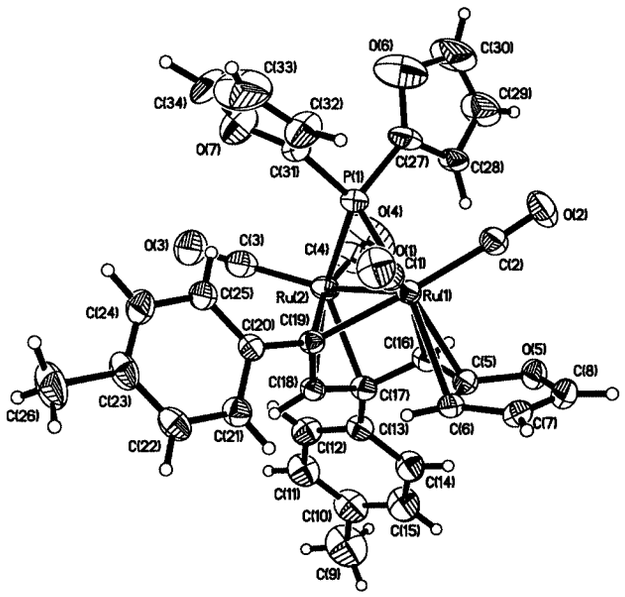


Fig. 5 A perspective drawing of compound **3**.

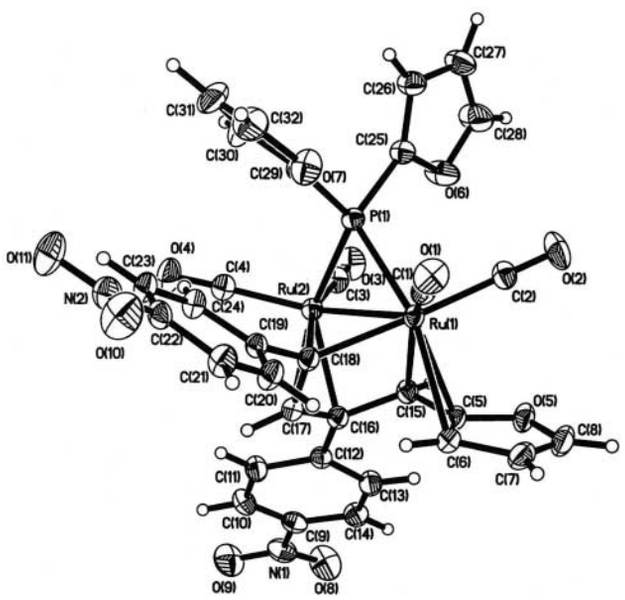


Fig. 6 A perspective drawing of compound **4**.

feature is the generation of a novel furyl-bonded C_4 hydrocarbyl fragment RCC(H)C(R)C(H)$\overline{C(CH)_3O}$ with an intriguing μ-$\eta^1,\eta^1,\eta^2,\eta^3$ coordination mode. The coordination environment at each metal atom is completed by two terminally bound CO groups. The formation of **2**–**4** is accompanied by the rupture of one Ru–C(furyl) bond in **1a**. The resulting organic fragment of each complex is coordinated to the Ru atoms *via* a π, a π-allyl and two σ bonds, and donates seven electrons to the metal core to achieve the 34 CVE required for a bimetallic framework. The furyl ring forms a π bond to Ru(1) with average Ru(1)–C(5) and Ru(1)–C(6) distances of 2.267(4) and 2.419(5) Å, respectively. The allyl moiety is σ bonded to Ru(1) [Ru–C 2.144(3)–2.172(4) Å] and coordinated in an η^3 fashion to Ru(2) [Ru–C 2.185(5)–2.244(5) Å]. The distances within the η^3-allyl system range from 1.411(4) to 1.434(6) Å in **2**–**4**. The Ru(1) centre also forms a σ bond with C(15) in **2** and **4** [2.418(5) **2**, 2.382(3) Å **4**] and with C(16) in **3** [2.404(4) Å]. Hence, the dimerised C_4 chain together with Ru(1) forms a five-membered ruthenacycle ring. The two protons on the C_4 hydrocarbyl fragment were located readily from the Fourier map in each structure solution. The nearest intermolecular contact arises

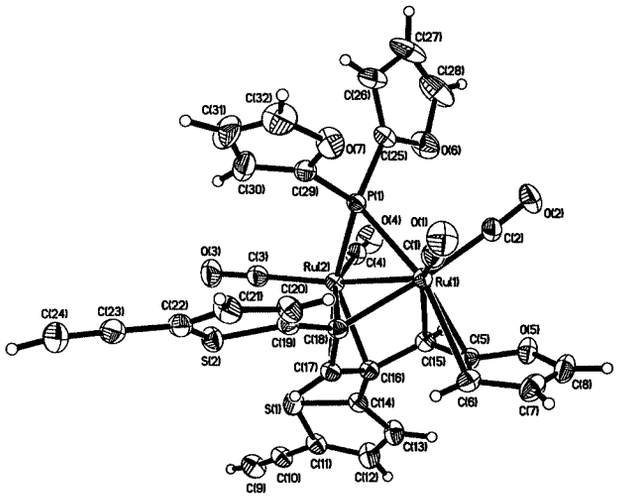


Fig. 7 A perspective drawing of compound **5**.

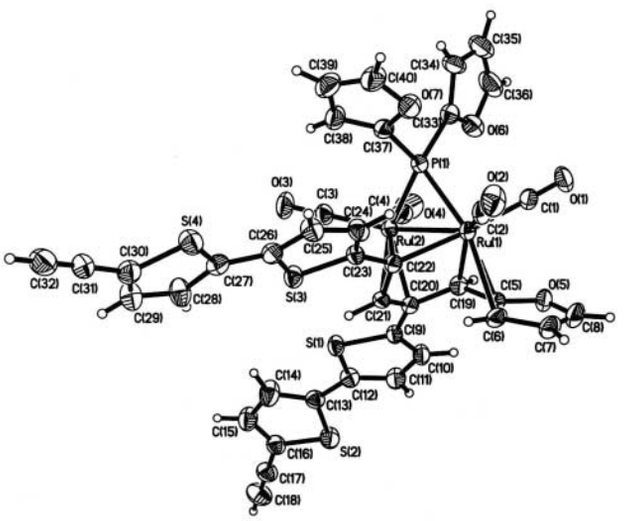


Fig. 8 A perspective drawing of compound **6**.

from O(6) · · · H(31) (2.499 Å) in **2**, O(4) · · · H(34) (2.125 Å) in **3** and O(1) · · · H(26) (2.508 Å) in **4**.

The molecular structures of **5** and **6** are depicted in Figs. 7 and 8, respectively, and the asymmetric unit of **6** consists of **6**·$CHCl_3$. The basic geometry of the central metal core of **5** and **6** is closely related to those found in **2**–**4**, each containing a $Ru_2(CO)_4(\mu\text{-}PR_2)$ (R = furyl) entity with a furyl-substituted C_4 hydrocarbyl chain bound to it in a μ-$\eta^1,\eta^1,\eta^2,\eta^3$ manner. With the μ-phosphido bridge and the hydrocarbyl group as a three-electron and a seven-electron donor, respectively, each structure is electron precise (34 CVE) with a single Ru–Ru bond. The Ru(1)–Ru(2) distances are quite typical at 2.7825(3) (**5**) and 2.7863(6) Å (**6**) whereas the metal–metal bond is asymmetrically bridged by the phosphido P atom [av. Ru(1)–P(1) 2.317(2), Ru(2)–P(1) 2.269(2) Å] in each compound. Similar bonding features were encountered for the C_4 fragment, in which C(16), C(17) and C(18) participate in a π-allyl interaction to Ru(2) in **5** and C(20), C(21) and C(22) to Ru(2) in **6** (Tables 5 and 6). The C(5)–C(6) edge is π-bound to Ru(1). The Ru(1)–C(18) and Ru(1)–C(22) distances are, respectively, 2.170(2) and 2.169(6) Å for **5** and **6**, characteristic of a Ru–C σ bond.[18,19] A striking observation in the structures of **5** and **6** is the presence of a pendant acetylenic group at each end and the average uncoordinated alkyne C≡C bond distances of 1.172(4) (**5**) and 1.16(1) Å (**6**) lie in the normal range for free alkynes.[17a,22] The alkynyl bond angles in **5** and in **6** [176(1)–179(1)°] are all close to linearity. In both structures, all the thienyl rings are nearly planar. For **6**, the two thiophene groups within each bithienyl

fragment display a *trans* conformation for the sulfur atoms to minimise steric repulsions between their lone pairs. The dihedral angle between the S(1)- and S(2)-thienyl rings is *ca.* 13.1° and the corresponding angle between the S(3)- and S(4)-thienyl planes is 4.9°.[17a,23] There is no apparent short intermolecular interaction between the planar rings in both **5** and **6**. The closest intermolecular contact is due to O(2)···H(12) (2.566 Å) in **5** and O(2)···H(8) (2.510 Å) in **6**.

Concluding remarks

A novel phosphido-stabilised dinuclear ruthenium complex containing a μ-η¹,η²-furyl group **1a** was prepared by the facile oxidative addition of a 2-furyl phosphine to $[Ru_3(CO)_{12}]$ which can provide a convenient access to a series of μ-phosphido dinuclear species, while the triangular Ru–P–Ru skeleton remains intact. In this reaction, the facility for tri(2-furyl)-phosphine to act as sources of furyl and phosphide (PR_2) fragments on transition metal centres has been demonstrated. The reactions of **1a** towards monoynes and diynes have been studied in detail, generating a range of new alkyne-coupling compounds with the entire bridging ligands bonded *via* σ/π/π-allyl networks. The isolation of compounds **2**–**6** opens up another interesting example of the potential of phosphido-bridged dinuclear complexes in alkyne oligomerisation and functionalisation of the coordinated furyl moiety. Indeed, insertion of an incipient four-carbon chain into a metal–carbon(furyl) bond is, to our knowledge, unknown and no structures exhibiting this coordination mode in dinuclear complexes have been reported previously. Attempts will be made to investigate the coordination ability of the free alkyne functionality in complexes **5** and **6** towards various organic and organometallic fragments. In addition, further studies of the chemical reactivity and catalytic behaviour of **1a** are currently in progress in our laboratory.

Experimental

General

All reactions were conducted under an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents for preparative work were dried and distilled before use. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The syntheses of the ligands *p*-HC≡C$C_6H_4NO_2$,[24] 2,5-diethynylthiophene[17a] and 5,5′-diethynyl-2,2′-bithiophene[17a] were carried out as reported previously. Infrared spectra were recorded as CH_2Cl_2 solutions on a Perkin-Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in $CDCl_3$ on a JEOL EX270 or a Varian INOVA 400 MHz FT-NMR spectrometer, with ^{1}H NMR chemical shifts quoted relative to $SiMe_4$ and ^{31}P chemical shifts relative to an 85% H_3PO_4 external standard. The labelling system for ^{1}H NMR assignments is shown in Scheme 1. Fast atom bombardment (FAB) mass spectra were recorded in *m*-nitrobenzyl alcohol matrices on a Finnigan-SSQ 710 spectrometer. Separation of products was accomplished by preparative TLC plates coated with silica (Merck, Kieselgel 60).

Syntheses

Compounds 1a and 1b. A mixture of $[Ru_3(CO)_{12}]$ (50 mg, 0.078 mmol) and tri(2-furyl)phosphine (18 mg, 0.078 mmol) in THF (25 cm³) was heated under reflux for 1 h. The solution gradually changed from orange to deep red. The solvent was then removed *in vacuo* and the residue redissolved in CH_2Cl_2 for TLC separation on silica using hexane–CH_2Cl_2 (9 : 1, v/v) as eluent. The pale-yellow band (R_f = 0.45) afforded product **1a** as a pale-yellow solid in 56% yield (26 mg) after recrystallisation from a hexane–CH_2Cl_2 solution. The disubstitution product $[Ru_3(CO)_{10}\{P(\overline{C(CH)_3O})_3\}_2]$ **1b** was also isolated from the deep red band (R_f = 0.10) with a yield of 10% (8 mg). **1a**: IR (CH_2Cl_2): *ν*(CO) 2084vs, 2054vs, 2016vs and 2001vs cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.70 (s, 1H, H_1), 7.64 (s, 1H, $H_{1'}$), 7.58 (d, 1H, J_{ab} = 1.8 Hz, H_a), 6.72 (m, 1H, $H_{3'}$), 6.39 (m, 3H, H_2, $H_{2'}$ and H_3), 6.11 (virtual t, 1H, H_b) and 4.10 (m, 1H, H_c). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 58.51. FAB MS: *m*/*z* 602 (M^+). Calc. for $C_{18}H_9O_9PRu_2$: C, 35.89; H, 1.51. Found: C, 35.65; H, 1.38%. **1b**: IR (CH_2Cl_2): *ν*(CO) 2082w, 2061s, 2030vs, 2002vs and 1980sh cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.70 (m, 6H, H_1), 6.62 (m, 6H, H_3) and 6.47 (m, 6H, H_2). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* −14.62. FAB MS: *m*/*z* 1048 (M^+). Calc. for $C_{34}H_{18}O_{16}P_2Ru_3$: C, 38.98; H, 1.73. Found: C, 38.69; H, 1.55%.

Compound 2. To a solution of **1a** (50 mg, 0.083 mmol) in toluene (20 cm³) was added a slight excess of HC≡CPh (21 mg, 0.208 mmol). The reaction mixture was heated to reflux at 110 °C for 8 h during which time the solution turned deep reddish-brown. Excess solvent was then removed under reduced pressure. The residue was dissolved in the minimum amount of CH_2Cl_2 and subjected to TLC using hexane–CH_2Cl_2 (3 : 1, v/v) as eluent to afford a red band (R_f = 0.35) identified as **2** (29 mg, 46%). Trace amounts of other products were also observed in the preparation but remained unidentified. IR (CH_2Cl_2): *ν*(CO) 2035s, 2009vs, 1978s and 1948s cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.85 (m, 2H, Ph), 7.60 (m, 1H, H_1), 7.56 (m, 1H, H_a), 7.52 (m, 1H, $H_{1'}$), 7.41 (m, 2H, Ph), 7.30 (m, 2H, Ph), 6.94 (m, 2H, Ph), 6.87 (m, 2H, Ph), 6.73 (m, 1H, $H_{3'}$), 6.57 (m, 1H, H_b), 6.35 (m, 1H, H_2), 6.32 (m, 1H, H_3), 6.19 (m, 1H, $H_{2'}$), 5.44 (m, 1H, CH), 5.38 (m, 1H, CH) and 5.05 (m, 1H, H_c). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 76.00. FAB MS: *m*/*z* 750 (M^+). Calc. for $C_{32}H_{21}O_7PRu_2$: C, 51.20; H, 2.82. Found: C, 51.02; H, 2.65%.

Compound 3. Using the same procedure as above, the title compound was obtained in 53% yield from *p*-HC≡CC_6H_4Me and isolated as a red solid (R_f = 0.40, hexane–CH_2Cl_2, 3 : 1, v/v). IR (CH_2Cl_2): *ν*(CO) 2033s, 2007vs, 1977m and 1946m cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.73 (d, 2H, *J* = 8.0 Hz, C_6H_4), 7.60 (m, 1H, H_1), 7.55 (m, 2H, H_a + $H_{1'}$), 7.21 (d, 2H, *J* = 8.0 Hz, C_6H_4), 6.74 (m, 4H, C_6H_4), 6.72 (m, 1H, $H_{3'}$), 6.55 (m, 1H, H_b), 6.34 (m, 1H, H_2), 6.31 (m, 1H, H_3), 6.19 (m, 1H, $H_{2'}$), 5.42 (m, 1H, CH), 5.34 (m, 1H, CH), 5.01 (m, 1H, H_c), 2.39 (s, 3H, Me) and 2.19 (s, 3H, Me). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 75.77. FAB MS: *m*/*z* 779 (M^+). Calc. for $C_{34}H_{25}O_7PRu_2$: C, 52.44; H, 3.24. Found: C, 52.36; H, 3.18%.

Compound 4. This compound was prepared as described above for **2** from **1a** (50 mg, 0.083 mmol) and *p*-HC≡C$C_6H_4NO_2$ (31 mg, 0.208 mmol). The residue was purified by preparative TLC on silica using hexane–CH_2Cl_2 (1 : 1, v/v) as eluent to yield crude product **4** from the major orange-red band (R_f = 0.32). Recrystallisation from the same solvents led to red crystals of **4** with an isolated yield of 40% (28 mg). IR (CH_2Cl_2): *ν*(CO) 2042m, 2018vs, 1987m and 1960m cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 8.28 (d, 2H, *J* = 8.8 Hz, C_6H_4), 7.95 (d, 2H, *J* = 8.8 Hz, C_6H_4), 7.82 (d, 2H, *J* = 8.4 Hz, C_6H_4), 7.65 (s, 2H, H_a + H_1), 7.61 (s, 1H, $H_{1'}$), 6.90 (d, 2H, *J* = 8.4 Hz, C_6H_4), 6.62 (s, 1H, H_b), 6.39–6.35 (m, 4H, H_2, $H_{2'}$, H_3 and $H_{3'}$), 5.58 (s, 1H, CH), 5.43 (s, 1H, CH) and 5.10 (s, 1H, H_c). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 81.99. FAB MS: *m*/*z* 840 (M^+). Calc. for $C_{32}H_{19}N_2O_{11}PRu_2$: C, 45.72; H, 2.28; N, 3.33. Found: C, 45.52; H, 2.25; N, 3.01%.

Compound 5. This red solid was obtained in 30% yield (20 mg) by reacting **1a** (50 mg, 0.083 mmol) with freshly prepared 2,5-diethynylthiophene (27.5 mg, 0.208 mmol) in refluxing toluene for 3 h followed by the usual TLC work-up (R_f = 0.44, hexane–CH_2Cl_2, 3 : 1, v/v). IR (CH_2Cl_2): *ν*(≡CH) 3300m, *ν*(CO) 2040s, 2016vs, 1984s and 1958s cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.70 (s, 1H, H_1), 7.62 (s, 1H, $H_{1'}$), 7.57 (s, 1H, H_a), 7.28 (d, 1H,

Table 7 Summary of crystal structure data for complexes **1a**, **2**–**5** and **6**·$CHCl_3$

	1a	**2**	**3**	**4**	**5**	**6**·$CHCl_3$
Empirical formula	$C_{18}H_9O_9PRu_2$	$C_{32}H_{21}O_7PRu_2$	$C_{34}H_{25}O_7PRu_2$	$C_{32}H_{19}N_2O_{11}PRu_2$	$C_{32}H_{17}O_7PRu_2S_2$	$C_{41}H_{22}Cl_3O_7PRu_2S_4$
Formula weight	602.36	750.60	778.65	840.60	810.69	1094.29
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
a/Å	8.2392(4)	16.021(1)	14.047(1)	9.2527(7)	13.5711(9)	11.7185(8)
b/Å	17.7814(9)	10.9923(8)	15.817(1)	13.770(1)	17.204(1)	13.4100(9)
c/Å	22.116(1)	17.088(1)	14.700(1)	13.792(1)	13.5664(9)	15.208(1)
α/°	103.065(1)			86.827(1)		109.347(1)
β/°	91.590(1)	99.169(2)	90.372(1)	71.179(1)	90.806(1)	102.311(1)
γ/°	91.399(1)			74.829(1)		98.329(1)
U/Å^3	3153.4(3)	2971.0(4)	3265.8(4)	1604.5(2)	3167.1(4)	2142.0(3)
Z	6	4	4	2	4	2
μ(Mo-Kα)/mm^{-1}	1.559	1.117	1.020	1.055	1.182	1.173
Reflections collected	18438	17394	18418	9282	18216	12805
Unique reflections	13413	6720	7282	6757	7079	9260
R_{int}	0.0150	0.0557	0.0162	0.0164	0.0168	0.0211
$R1$, $wR2$ $[I > 2.0\sigma(I)]$[a]	0.0250, 0.0636	0.0419, 0.0996	0.0416, 0.1143	0.0323, 0.0872	0.0211, 0.0550	0.0615, 0.1641

[a] $R1 = \Sigma\|\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

J = 4.0 Hz, thienyl), 7.20 (d, 1H, J = 4.0 Hz, thienyl), 6.75 (m, 1H, H_3), 6.70 (d, 1H, J = 4.0 Hz, thienyl), 6.52 (m, 1H, H_b), 6.39 (m, 3H, thienyl + $H_{2'}$ + $H_{3'}$), 6.33 (m, 1H, H_2), 5.78 (m, 1H, CH), 5.40 (s, 1H, CH), 5.00 (m, 1H, H_c), 3.41 (s, 1H, C≡CH) and 3.26 (s, 1H, C≡CH). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 78.02. FAB MS: m/z 810 (M^+). Calc. for $C_{32}H_{17}O_7PRu_2S_2$: C, 47.41; H, 2.11. Found: C, 47.22; H, 2.20%.

Compound 6. A similar synthetic procedure as for complex **5** was employed using 5,5′-diethynyl-2,2′-bithiophene (44.5 mg, 0.208 mmol) to produce red crystalline **6** in 38% yield (31 mg) after TLC purification (R_f = 0.39, hexane–CH_2Cl_2, 2 : 1, v/v) and recrystallisation. IR (CH_2Cl_2): ν(≡CH) 3300m, ν(CO) 2039m, 2014vs, 1984m and 1956m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.70 (s, 1H, H_1), 7.63 (s, 1H, $H_{1'}$), 7.58 (s, 1H, H_a), 7.35 (d, 1H, J = 4.0 Hz, thienyl), 7.19 (d, 1H, J = 4.0 Hz, thienyl), 7.13 (d, 1H, J = 4.0 Hz, thienyl), 7.11 (d, 1H, J = 4.0 Hz, thienyl), 7.04 (d, 1H, J = 4.0 Hz, thienyl), 6.84 (d, 1H, J = 4.0 Hz, thienyl), 6.77 (m, 1H, H_3), 6.61 (d, 1H, J = 4.0 Hz, thienyl), 6.54 (m, 1H, H_b), 6.46 (d, 1H, J = 4.0 Hz, thienyl), 6.39 (m, 2H, $H_{2'}$ + $H_{3'}$), 6.27 (m, 1H, H_2), 5.83 (m, 1H, CH), 5.46 (s, 1H, CH), 5.03 (m, 1H, H_c), 3.42 (s, 1H, C≡CH) and 3.39 (s, 1H, C≡CH). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 77.65. FAB MS: m/z 975 (M^+). Calc. for $C_{40}H_{21}O_7PRu_2S_4$: C, 49.28; H, 2.17. Found: C, 49.08; H, 2.10%.

Crystallography

Pale yellow crystals of **1a** and red crystals of **2**–**5** and **6**·$CHCl_3$ suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in hexane–CH_2Cl_2 (for **1a** and **2**–**5**) and hexane–$CHCl_3$ (for **6**) at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS SMART 1000 CCD area-detector. The collected frames were processed with the software SAINT[25] and an absorption correction was applied (SADABS)[26] to the collected reflections.

The structures of these molecules were solved by direct methods (SHELXTL)[27] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **6**, the $CHCl_3$ solvate was assigned with isotropic displacement parameters. Hydrogen atoms in these structures were either generated from Fourier maps or placed in their idealised positions and allowed to ride on the respective carbon atoms. Crystal data and other experimental details are summarised in Table 7.

CCDC reference numbers 149996 and 168830–168834.

See http://www.rsc.org/suppdata/dt/b1/b104625j/ for crystallographic data in CIF or other electronic format.

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