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Cluster-containing carbon-rich molecules: Reactions of ruthenium cluster carbonyls with $\{Au(PR_3)\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ (R = Ph, tol)

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Abstract

Complexes containing C_4 ligands attached to one or two $AuRu_3$ clusters by conventional σ, 2π interactions have been obtained from reactions between $(R_3P)AuC{\equiv}CC{\equiv}CAu(PR_3)$ (R = Ph, tol) or $Au(C{\equiv}CC{\equiv}CH)\{P(tol)_3\}$ and either $Ru_3(CO)_{12}$, $Ru_3(CO)_{10}(NCMe)_2$ or $Ru_3(\mu\text{-dppm})(CO)_{10}$. The X-ray determined structures of $\{(R_3P)AuRu_3(CO)_9\}_2(\mu_3,\eta^2{:}\mu_3,\eta^2\text{-}C_2C_2)$ [R = Ph (**1**) (three solvates), tol (**2**)], $AuRu_3\{\mu_3,\eta^2\text{-}C_2C{\equiv}CAu(PPh_3)\}(CO)_9(PPh_3)$ (**3**) and $\{(Ph_3P)AuRu_3(\mu\text{-dppm})(CO)_7\}(\mu_3,\eta^2{:}\mu_3,\eta^2\text{-}C_2C_2)\{Ru_3(\mu\text{-H})(\mu\text{-dppm})(CO)_7\}$ (**4**) are reported.

Keywords: Carbon-rich; Cluster; Gold; Ruthenium; X-ray

1. Introduction

Current interest in metal complexes containing all-carbon ligands such as carbon chains, C_n, has largely concentrated on derivatives having mononuclear metal–ligand end-groups [1]. In contrast, related systems having metal cluster capping groups remain rare, although they might be considered especially relevant to studies involving electron (or hole) transport along the carbon chains. Useful cluster capping groups include substituted cluster methylidynes formally derived from $HC\{M_xL_y\}$, such as those with $M_xL_y = M_3(\mu\text{-H})_3(CO)_9$ (M = Ru, Os) [2], $Co_3(CO)_9$ [3], or $M_3Cp'_3$ (M = Co, Rh, Ir; Cp′ = Cp, Cp*) [4], and $M_3(\mu\text{-dppm})_3$ (M = Cu, Ag) [5,6], the latter containing a $-C{\equiv}C\{M_3L_3\}$ cap. In these examples, the terminal carbon atom of the chain is attached to all three metal atoms by between one and three σ-type bonds, the detailed electronic structures having been explored by DFT methods [7].

There are fewer examples of complexes in which the C_n chain is attached by two of the carbon atoms. The addition of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ to $Ru_3(CO)_{10}(NCMe)_2$ afforded the alkyne cluster $Ru_3\{\mu_3,\eta^2\text{-}HC_2\text{-}C{\equiv}C[W(CO)_3Cp]\}(CO)_{10}$ which on heating converted to the hydrido-alkynyl complex $Ru_3(\mu\text{-H})\text{-}\{\mu_3,\eta^2\text{-}C_2C{\equiv}C[W(CO)_3Cp]\}(CO)_9$; the dppm-substituted analogue of the latter was also described [8]. Oxidative addition of $Re\{(C{\equiv}C)_mC{\equiv}CH\}(NO)\text{-}(PPh_3)Cp^*$ (m = 1–3) to $Os_3(CO)_{10}(NCMe)_2$ gave firstly $Os_3(\mu\text{-H})\{\mu,\eta^1\text{-}C{\equiv}C(C{\equiv}C)_m[Re(NO)(PPh_3)Cp^*]\}(CO)_{10}$ which, in the cases of m = 1 or 2, is thermally decarbonylated to $Os_3(\mu\text{-H})\{\mu_3,\eta^2\text{-}C_2(C{\equiv}C)_m[Re(NO)(PPh_3)\text{-}Cp^*]\}(CO)_9$ [9]. Reactions of $\{Cp(OC)_3W\}C{\equiv}CC{\equiv}C\{M(CO)\text{-}(PPh_3)_2\}$ (M = Rh, Ir) with $Fe_2(CO)_9$ proceeded stepwise to give $Fe_2M\{\mu_3,\eta^2\text{-}C_2C{\equiv}C[W(CO)_3Cp]\}\text{-}(CO)_7(PPh_3)$ and $\{Cp(OC)_8Fe_2W\}(\mu_3,\eta^2{:}\mu_3,\eta^2\text{-}C_2C_2)\text{-}\{Fe_2M(CO)_7(PPh_3)\}$ [10].

Perhaps the earliest example of a bis-cluster complex is the dianion $[\{Fe_3(CO)_9\}_2(\mu_3,\eta^2{:}\mu_3,\eta^2\text{-}C_2C_2)]^{2-}$, which

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was obtained from the reaction between the ketenylidene cluster $[Fe_3(\mu_3,\eta^2\text{-CCO})(CO)_9]^-$ with an excess of triflic anhydride [11], or of $[Fe_3\{\mu_3,\eta^2\text{-}C_2[Fe(CO)_2\text{-}Cp]\}(CO)_9]^{2-}$ with $[Mn(CO)_3(NCMe)_3]^+$ [12]. The C_4 ligand in this complex has been described in terms of a metallated butadiene, the C–C distances of 1.306(7) and 1.42(1) Å, and an internal angle of 148.0(6)°, being cited as support for this interpretation. Considering the two carbon atoms, their bonding is closely related to that of an alkynyl group, such as those found in $M_3(\mu\text{-H})(\mu_3,\eta^2\text{-}C_2R)(CO)_9$ (M = Fe, Ru, Os), of which several examples have been structurally characterised [13]. The well-known isolobal relationship between H and $Au(PR_3)$ [14] led to the isolation and characterisation of several related gold-containing Ru_3 and Os_3 clusters, the first example being $AuRu_3(\mu_3,\eta^2\text{-}C_2Bu^t)(CO)_9\text{-}(PPh_3)$ [15] obtained from $Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-}C_2Bu^t)(CO)_9$ by deprotonation with NaH or K-Selectride [16], followed by reaction of the resulting monoanion with $AuCl(PPh_3)$. The same complex was also described by Salter [17]. Other ruthenium complexes were prepared by addition of $Au(C_2Ph)(PR_3)$ (R = Ph, tol) to $Ru_3(\mu\text{-dppm})(CO)_{10}$ [18]. Oxidative addition of Au(C≡CPh)-(PR_2Ph) (R = Me, Ph) to $Os_3(CO)_{10}(NCMe)_2$ afforded $AuOs_3(\mu,\eta^2\text{-}C_2Ph)(CO)_{10}(PR_2Ph)$ which on heating undergoes decarbonylation to form the μ_3,η^2-alkynyl complex $AuOs_3(\mu_3,\eta^2\text{-}C_2Ph)(CO)_9(PR_2Ph)$ [19]. The isostructural ethynylferrocene derivatives $AuM_3(\mu_3,\eta^2\text{-}C_2Fc)(CO)_9(PPh_3)$ (M = Ru, Os) have also been described [20].

The H/$Au(PR_3)$ analogy, coupled with experimental difficulties working with the potentially explosive buta-1,3-diyne itself, prompted us to examine the reactions of digold derivatives of buta-1,3-diyne, $\{Au(PR_3)\}_2$(μ-C≡CC≡C) (R = Ph, tol) [21,22] with ruthenium carbonyl clusters as a route to further examples of this type of complex. Our results are described below.

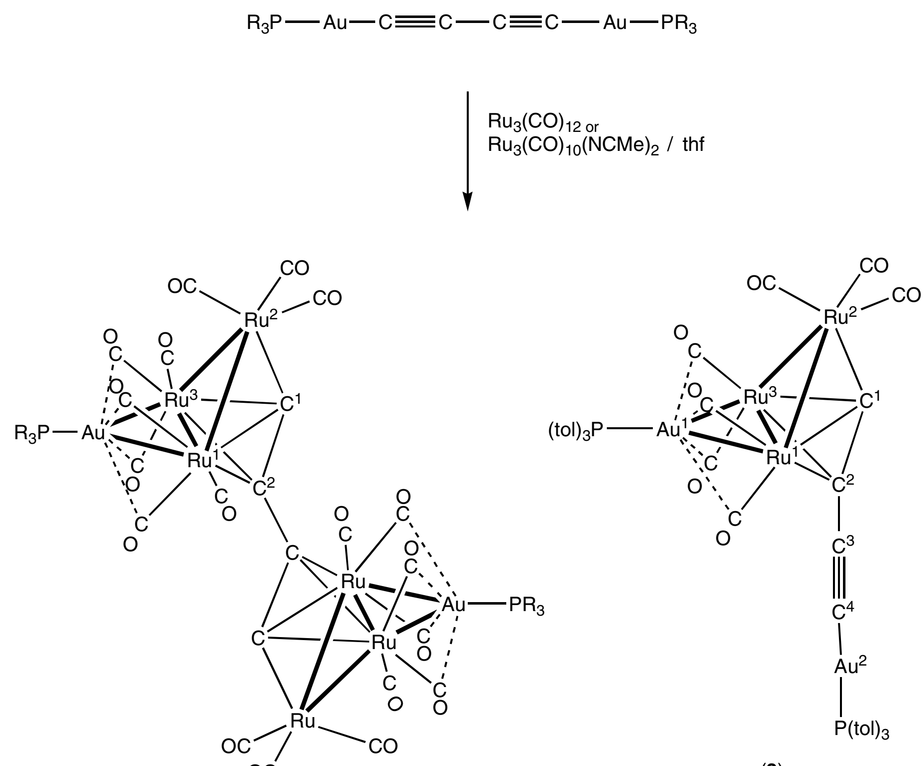
2. Results and discussion

The thermal reaction between $Ru_3(CO)_{12}$ and $\{Au(PPh_3)\}_2$(μ-C≡CC≡C) in refluxing thf was accompanied by a considerable amount of decomposition, but work-up and thin-layer chromatographic separation of the products afforded bright yellow $\{AuRu_3\text{-}(CO)_9(PPh_3)\}_2(\mu_3,\eta^2\text{:}\mu_3,\eta^2\text{-}C_2C_2)$ (**1**; Scheme 1) in 42% yield. Surprisingly, the r.t. reaction carried out with $Ru_3(CO)_{10}(NCMe)_2$ gave only a 12% yield of the same complex. The analogous P(tol)$_3$ complex (**2**) precipitated from a similar reaction between $\{Au[P(tol)_3]\}_2$(μ-C≡CC≡C) and $Ru_3(CO)_{12}$ in 38% yield. However, when the reaction was interrupted when the precipitate started to form (about 1 h), the solution was found to contain a different product, identified as the mono-cluster complex $AuRu_3\{\mu_3,\eta^2\text{-}C_2C{\equiv}CAu[P(tol)_3]\}(CO)_9\text{-}\{P(tol)_3\}$ (**3**). The reaction between Au(C≡CC≡CH)-$\{P(tol)_3\}$ and $Ru_3(\mu\text{-dppm})(CO)_{10}$, also carried out in refluxing thf, gave orange $\{Ru_3(\mu\text{-H})(\mu\text{-dppm})(CO)_7\}\text{-}(\mu_3,\eta^2\text{:}\mu_3,\eta^2\text{-}C_2C_2)\{AuRu_3(\mu\text{-dppm})(CO)_7[P(tol)_3]\}$ (**4**; Scheme 2).

The various complexes have been characterised by elemental analyses, spectroscopically, and by single-crystal X-ray structural determinations. The IR spectra of all complexes contain strong to medium intensity bands in the ν(CO) region, which may also include ν(CC) bands from the C_4 fragment, although these could not be assigned separately. The ^1H NMR spectra contain resonances in the aromatic region for the PR_3 substituents and, for **1**, at δ 2.09 and 2.38 for the Me groups of the two different P(tol)$_3$ ligands. In **2**, this resonance occurs at δ 2.36, suggesting that the lower frequency signal in **3** arises from the Au{P(tol)$_3$} group which remains attached to the C_4 chain. In **4**, the dppm CH_2 groups give a broad resonance at δ 3.91-4.37. Limited solubilities precluded detection of any of the C_4 resonances in the ^{13}C NMR spectra. The ^{31}P NMR spectra contain signals at δ 61.6 (**1**), 59.9 (**2**), 40.0 and 59.5 [**3**, for C≡CAu{P(tol)$_3$} and Ru_3Au{P(tol)$_3$, respectively], and for **4**, at δ 24.2 and 31.8 [doublets for Ru_3(dppm)], 28.1 (double doublet), 32.3 and 58.9 [P(tol)$_3$]. The electrospray mass spectra (ES-MS) were not very informative, that for **1** containing ions formed by loss of $Au(PPh_3)$ and CO groups or of [H + Au{P(tol)$_3$}] and CO for **3**. Only in the case of **4** was M^+ found at *m/z* 2319, accompanied by $[M + Na]^+$ at *m/z* 2342 in the presence of NaOMe; the latter solution also gave $[M - 2H]^-$.

2.1. Molecular structures

Plots of single molecules of **1**, **2**, **3** and **4** are given in Figs. 1–4, respectively, and selected structural data are collected in Table 1. Three separate samples of **1** were examined, each of which proved to contain a pair of dichloromethane, chloroform or benzene solvate molecules, all well-defined in cavities disposed about the crystallographic inversion centres (see Fig. 1(b)). The molecular structures of the complex in each crystal were identical within experimental uncertainty and the discussion below cites values for the CH_2Cl_2 solvate. All complexes contain several structural features in common, which are conveniently discussed together, citing ranges of values for the pertinent bond lengths or angles. The structures are based upon an approximately equilateral Ru_3 core, the Ru(1)–Ru(3) edge of which is bridged by an $Au(PR_3)$ (R = Ph or tol) group. The C_2 fragment of the alkynyl is attached to the Ru_3 core by one σ-type and two π-type bonds, the former involving Ru(2), which is not attached to the $Au(PR_3)$ group. The Ru(2)–C(1)–C(2)–C(2′ or 3) group is bent at C(1) and



(**3**)

R = Ph (**1**), tol (**2**)

Scheme 1.

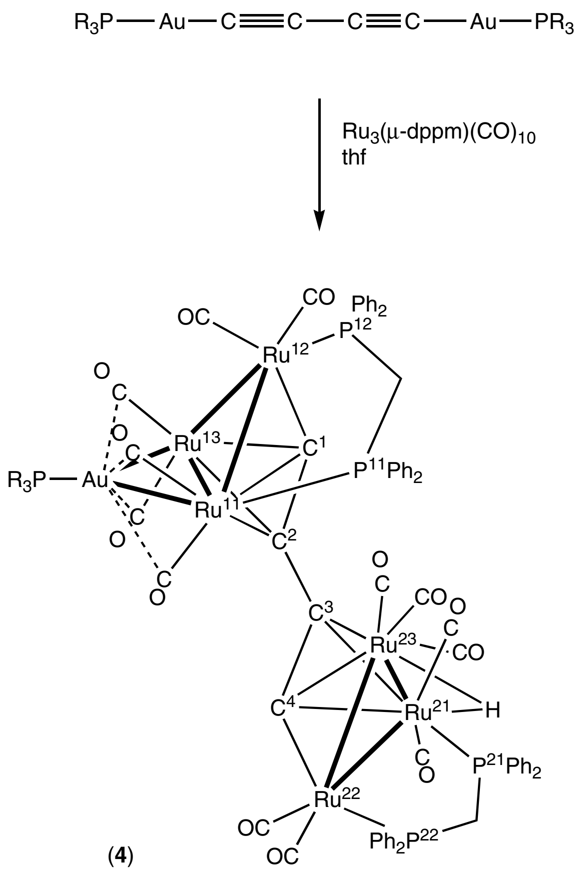
C(2) resulting in a *transoid* conformation, and attached to the second C_2 fragment by a single C(2)–C(2′ or 3) bond. Complexes **1** and **2** differ only in the substituent on the gold-bonded phosphine ligand (Ph and tol, respectively). Complex **3** contains only one $AuRu_3$ cluster, C(2) now being attached to a —C≡CAuPPh$_3$ fragment. Atoms C(2)–C(3)–C(4)–Au(2)–P(2) are approximately linear, deviations of 1.2(5), 8.9(3), 4.2(1)° being found at C(3), C(4), Au(2), respectively.

The ranges of atom separations of each type exceed the e.s.d.s but nevertheless fall within the values previously found for complexes of this type [15–20]. Thus, the Au–Ru distances fall in the range 2.7465(3)–2.7977(5) Å, with Au–P separations of between 2.2842(9) and 2.2974(7) Å. Values for Ru(1)–Ru(3) (bridged by Au) are between 2.8208(4) and 2.8307(4) Å (for **1**, **2** and **3**), while the non-bridged Ru(1,3)–Ru(2) separations are somewhat shorter at 2.7981(4)–2.8264(3) Å. In **4**, Ru(n_1)–Ru(n_2), bridged by the dppm ligands, are 2.780, 2.829(2) Å, with values between 2.787 and 2.818(2) Å for the non-bridged Ru–Ru bonds.

Attachment of the alkynyl group is via one σ and two π bonds. The Ru(2)–C(1) bond is the shortest, at between 1.937 and 1.962(5) Å for **1**, **2** and **3**; the longer π bonds are Ru(1,3)–C(1) 2.178–2.205(2) Å and Ru(1,3)–C(2) between 2.210(6) and 2.255(4) Å. Coordination of the C(1)–C(2) fragment to the cluster results in elongation of this bond to between 1.309(4) and 1.329(4) Å. The Ru(2)–C(1)–C(2) and C(1)–C(2)–C(2′ or 3) angles range between 151.5(3) and 153.6(3)° and between 144.3(3) and 149.4(4)°, respectively.

Ligation at Au is completed by the two phosphine ligands [Au(1,2)–P(1,2) range 2.2842(9)–2.305 Å] and at Ru by the nine terminal CO ligands. Of interest is the close approach of C(12, 13, 32, 33) to Au(1) [2.776(4) to 2.986(4) Å]. However, the relevant Ru–C–O angles fall in the range 170.7(6)–178.0(3)°, indicating a negligible bonding interaction of these CO ligands with the Au centres.

Complex **4** contains one triangular Ru_3 cluster and one $AuRu_3$ butterfly cluster, metal–metal bond distances closely resembling those found in the other complexes described above. A hydride ligand bridges Ru(1′)–Ru(3′), as indicated in the ^{1}H NMR spectrum by the doublet resonance at δ −18.43 [J(HP) 35.7 Hz]. Both clusters contain a dppm ligand bridging one of the Ru–Ru bonds, which as a consequence are shortened to 2.780, 2.787(2) Å. In **4**, the ≡C—H and ≡C—Au(PPh$_3$) bonds have each oxidatively added to an Ru_3 cluster, thereby allowing an internal comparison of the effects resulting from bridging the Ru(1)–Ru(3) bond by H or Au(PPh$_3$). However, with the exception of the Au–CO interactions mentioned above, all geometric parameters are similar. These bonds are 2.818(2) and



Scheme 2.

2.806(2) Å, respectively, and show a net shortening when compared with the other Ru–Ru bonds present in the cluster. The Au{P(tol)$_3$} fragment appears to be subject to a curious disorder fully described in Section 3.

In each case, the C_2Ru_3 cluster is attached either to a second such cluster or to an unaltered gold-alkynyl group. The C(2)–C(2′ or 3) bond lies between 1.396(7) and 1.425(4) Å, considerably longer than the complexed C≡C triple bonds and resembling, as previously noted, the central bond of a buta-1,3-diene fragment. For **3**, this value is 1.396(7) Å, while within the uncomplexed —C≡C—Au(PPh$_3$) group, the C(3)–C(4) triple bond is 1.208(7) Å and C(4)–Au(2) is 1.989(5) Å (cf. values of 1.390(6), 1.196(6) and 1.996(5) Å, respectively, found in {(tol)$_3$P}AuC≡CC≡CAu{P(tol)$_3$} [22]).

The chemistry described above is consistent with the digold complex {Au(PR$_3$)}$_2$(μ-C≡CC≡C) oxidatively adding to the Ru_3 clusters in two steps with sequential cleavage of the Au–C(sp) bonds. In the case of Au(C≡CC≡CH){P(tol)$_3$}, the isolation of the hydrido cluster **4** suggests that cleavage of the H–C(sp) and Au–C(sp) bonds proceeds with similar facility. These reactions are seen to be efficient sources of complexes in which cluster moieties are attached to a C_4 chain by interaction in a σ,2π fashion with the two carbon atoms of each C_2 fragment. Such bonding is likely to result in electronic interactions between the capping groups which differ from those already established in complexes such as {Co$_3$(CO)$_9$}$_2$(μ$_3$,η^2:μ$_3$,η^2-C$_2$C$_2$) [23,24]. Further studies of these and related materials will be reported elsewhere.

3. Experimental

3.1. General experimental conditions

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

3.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_2 were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz). Samples were dissolved in $CDCl_3$ and contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. ES mass spectra: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [25]. Elemental analyses were performed by CMAS, Belmont, Australia.

3.3. Reagents

The compounds {Au(PR$_3$)}$_2$(μ-C≡CC≡C) (R = Ph, tol) [21,22], Au(C≡CC≡CH){P(tol)$_3$} [26], Ru$_3$(CO)$_{12}$ [27] and Ru$_3$(CO)$_{10}$(NCMe)$_2$ [28] were made by the cited methods.

3.4. Reactions of {Au(PPh$_3$)}$_2$(μ-C≡CC≡C)

(a) *Ru$_3$(CO)$_{12}$*. A mixture of Ru$_3$(CO)$_{12}$ (100 mg, 0.16 mmol) and {Au(PPh$_3$)}$_2$(μ-C≡CC≡C) (75.6 mg, 0.08 mmol) in thf (30 ml) was heated at reflux point until all Ru$_3$(CO)$_{12}$ had reacted (2 h). Considerable decomposition occurred during this time. Removal of solvent under vacuum and extraction of the residue with CH_2Cl_2 was followed by preparative t.l.c. (SiO$_2$; dichloromethane/hexane 1/2). A bright yellow band (R_f 0.5) contained {AuRu$_3$(CO)$_9$(PPh$_3$)}$_2$(μ$_3$,η^2:μ$_3$,η^2-C$_2$C$_2$) (**1**) (67.9 mg, 42%), obtained as yellow crystals (CHCl$_3$). Anal. Found: C, 33.68; H, 1.50. Calcd. (C$_{58}$H$_{30}$Au$_2$O$_{18}$P$_2$Ru$_6$): C, 33.54; H, 1.46%; *M*, 2078.

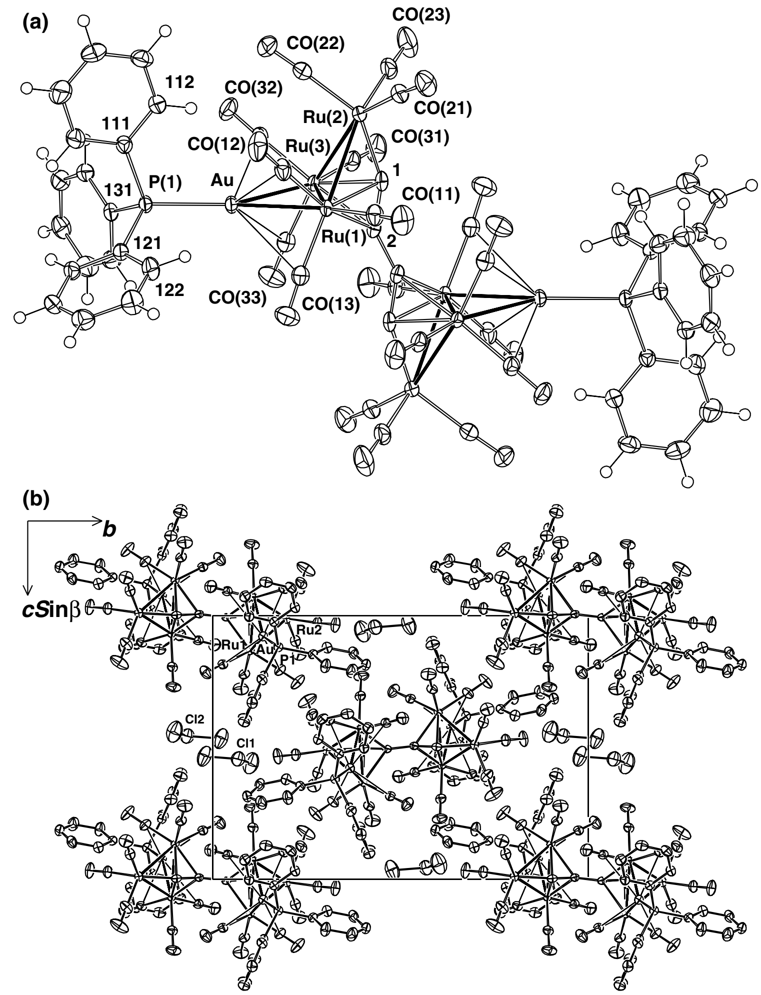


Fig. 1. (a) Molecular projection of centrosymmetric **1** (CH_2Cl_2 solvate). (b) Unit cell contents projected down *a*, showing the solvent disposition.

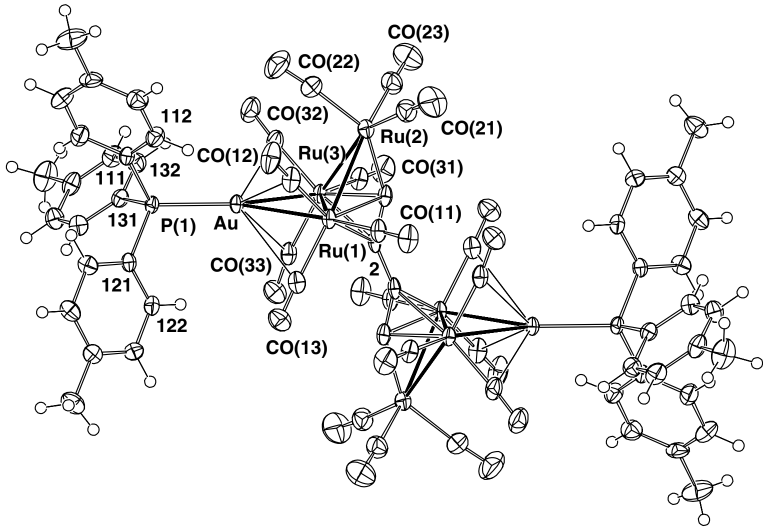


Fig. 2. Molecular projection of centrosymmetric **2**.

IR (cyclohexane): ν(CO) 2063 m, 2047 vs, 2036 m, 2000 m, 1990 m, 1978 vw, 1963 w cm^{-1}. ^1H NMR: δ 7.26–7.48 (m, Ph). ^{31}P NMR: δ 61.64 (s, PPh_3). ES-MS (positive ion, MeOH + NaOMe, *m*/*z*): 1535, $[M - Au(PPh_3) - 3CO]^+$; 1451, $[M - Au(PPh_3) - 6CO]^+$.

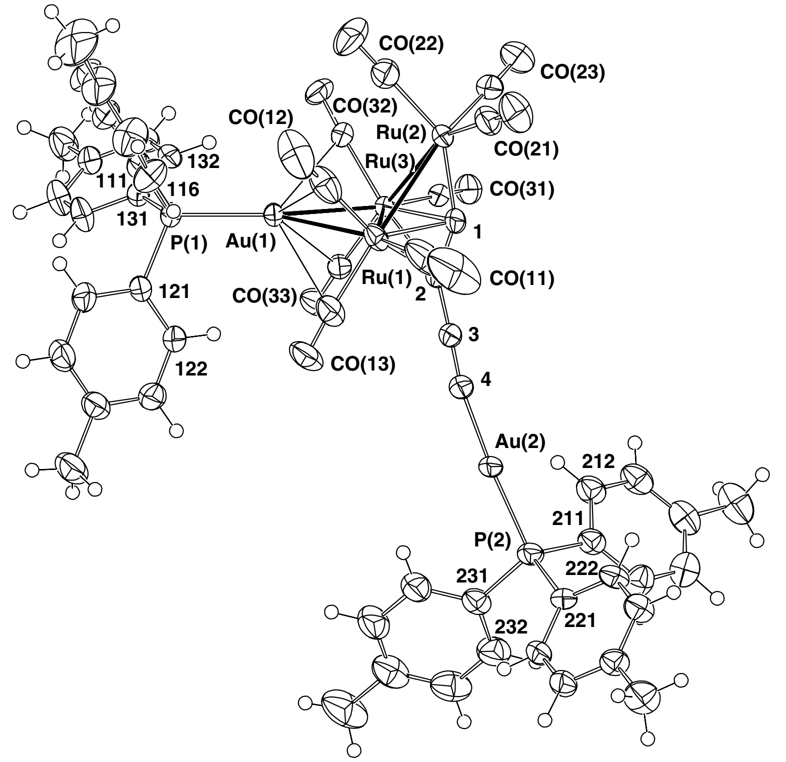


Fig. 3. Molecular projection of **3**.

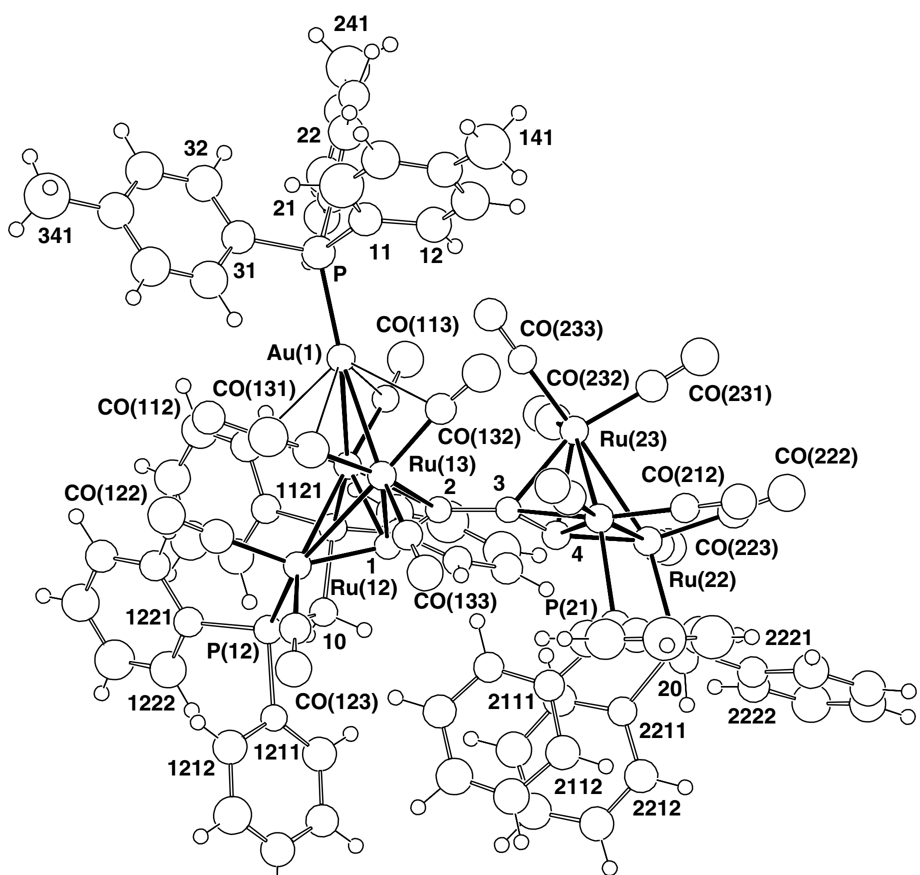


Fig. 4. Molecular projection of **4** (major component).

Table 1
Selected bond parameters

Complex	**1**·$2CH_2Cl_2$	**1**·$2C_6H_6$	**1**·$2CHCl_3$	**2**	**3**[a]	**4** (part 1)[b]
Bond distances (Å)						
Au–Ru(1)	2.7611(2)	2.7536(3)	2.7500(3)	2.7977(5)	2.7693(4)	2.776(2)
Au–Ru(3)	2.7767(2)	2.7465(3)	2.7773(3)	2.7596(5)	2.7524(3)	2.786(2)
Ru(1)–Ru(2)	2.8264(3)	2.8002(4)	2.8116(4)	2.7981(8)	2.8100(5)	2.829(2)
Ru(1)–Ru(3)	2.8238(3)	2.8307(4)	2.8273(4)	2.8267(7)	2.8208(4)	2.818(2)
Ru(2)–Ru(3)	2.8193(3)	2.8108(4)	2.8201(4)	2.8018(7)	2.8081(5)	2.787(2)
Au–P(1)	2.2974(7)	2.2842(9)	2.2934(9)	2.305(1)	2.289(1)	2.285(5)
Ru(1)–C(1)	2.187(2)	2.207(3)	2.188(3)	2.199(6)	2.196(3)	2.17(2)
Ru(1)–C(2)	2.226(2)	2.215(3)	2.213(3)	2.218(5)	2.238(4)	2.28(2)
Ru(2)–C(1)	1.944(3)	1.937(3)	1.953(3)	1.954(6)	1.962(5)	1.98(2)
Ru(3)–C(1)	2.205(2)	2.196(3)	2.198(3)	2.178(6)	2.189(4)	2.17(2)
Ru(3)–C(2)	2.223(2)	2.223(3)	2.227(3)	2.210(6)	2.255(4)	2.27(2)
Au–CO(12)	2.786(3)	2.825(4)	2.792(4)	2.897(7)	2.834(5)	2.84(2)
Au–CO(13)	2.928(3)	2.922(4)	2.928(4)	2.999(7)	2.915(4)	2.93(2)
Au–CO(32)	2.776(3)	2.823(4)	2.804(4)	2.828(9)	2.894(3)	2.90(2)
Au–CO(33)	3.031(3)	2.871(4)	2.986(4)	2.920(6)	2.884(3)	2.79(2)
C(1)–C(2)	1.315(4)	1.329(4)	1.309(5)	1.313(9)	1.314(7)	1.31(3)
C(2)–C(2′)	1.416(3)	1.425(4)	1.424(5)	1.431(8)	1.396(7)	1.47(3)
Bond angles (°)						
Ru(2)–C(1)–C(2)	153.2(2)	151.5(3)	152.6(3)	151.7(5)	153.6(3)	157(1)
C(1)–C(2)–C(2′)	144.6(2)	145.1(3)	144.3(3)	144.9(5)	149.4(4) [C(3)]	145(2) [C(3)]
Ru(1)–C(12)–O(12)	177.9(2)	178.4(3)	177.6(3)	175.1(7)	177.3(5)	179(2)
Ru(1)–C(13)–O(13)	177.0(2)	176.0(4)	174.2(3)	177.5(6)	176.4(4)	174(1)
Ru(3)–C(32)–O(32)	178.0(3)	178.3(3)	177.7(3)	174.8(7)	175.9(3)	175(2)
Ru(3)–C(33)–O(33)	176.4(3)	176.9(3)	177.6(3)	170.7(6)	176.1(3)	173(2)

[a] In **3**, Au(1)–P(1), Au(2)–P(2) are 2.289(1), 2.268(1); Au(2)–C(4) 1.989(5), C(3)–C(4) 1.208(7) Å; C(2)–C(3)–C(4) 178.8(5), Au(2)–C(4)–C(3) 170.1(3), C(4)–Au(2)–P(2) 175.8(1)°.

[b] In **4**, Ru(21)–Ru(22, 23), Ru(22)–Ru(23) are 2.780(3), 2.806(2), 2.791(2), Ru(mn)–P(mn) (mn = 11, 12, 21, 22) 2.327(5), 2.296(5), 2.325(5), 2.290(5), Ru(21)–C(3,4), Ru(22)–C(4), Ru(23)–C(3,4) 2.31(2), 2.22(2), 1.98(2), 2.26(2), 2.20(2) Å; C(3)–C(4) 1.30(3); C(2)–C(3)–C(4) 147(2), C(3)–C(4)–Ru(2) 154(1), P(*n*1)–C(*n*0)–P(*n*2) (*n* = 1,2) 115(1), 112(1)°.

(b) *$Ru_3(CO)_{10}(NCMe)_2$*. A solution of $Ru_3(CO)_{10}(NCMe)_2$ [prepared from $Ru_3(CO)_{12}$ (66 mg, 0.1 mmol) and TMNO (19 mg, 0.25 mmol) in CH_2Cl_2/MeCN (100/20 ml)] was treated with $\{Au(PPh_3)\}_2$(μ-C≡CC≡C) (100 mg, 0.1 mmol) at 0°C. The mixture was warmed to r.t. and stirred for a further 3 h, after which the colour had changed to brown. Work-up as described in (a) above afforded **1** (26.3 mg, 12%) as the only product isolated.

3.5. Reactions of $\{Au[P(tol)_3]\}_2$(μ-C≡CC≡C)

(a) A bright yellow precipitate had separated after heating a mixture of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and $\{Au[P(tol)_3]\}_2$(μ-C≡CC≡C) (84 mg, 0.08 mmol) in refluxing thf (20 ml). After cooling to r.t., the solid was filtered off, washed with cold thf and hexane and further purified by preparative t.l.c. (SiO_2; acetone–hexane 3/7). The yellow band (R_f 0.39) contained $\{AuRu_3(CO)_9[P(tol)_3]\}_2(\mu_3,\eta^2:\mu_3,\eta^2\text{-}C_2C_2)$ (**2**) (66.4 mg, 38%), obtained as yellow crystals ($CHCl_3$). Anal. Found: C, 35.52; H, 1.84. Calcd. ($C_{64}H_{42}Au_2O_{18}P_2Ru_6$): C, 35.56; H, 1.95%. IR (cyclohexane): ν(CO) 2063 m, 2045 m, 2035 vs, 1999 m, 1990 m, 1982 m, 1974 (sh), 1959 (sh) cm^{-1}. ^1H NMR: δ 2.27 (s, 18H, Me), 7.12–7.31 (m, 24H, C_6H_4). ^{31}P NMR: δ 59.88 [s, $P(tol)_3$].

(b) A similar reaction, using $Ru_3(CO)_{12}$ (0.08 mmol) and $\{Au[P(tol)_3]\}_2$(μ-C≡CC≡C) (84 mg, 0.08 mmol) in refluxing thf (15 ml) for 1 h, gave a yellow precipitate under a brown solution. The solid was filtered off to give $\{AuRu_3(CO)_9[P(tol)_3]\}_2(\mu_3,\eta^2:\mu_3,\eta^2\text{-}C_2C_2)$ (**2**) (11.8 mg, 10%), identical with the material prepared in (a). Evaporation of the filtrate, extraction of the residue with CH_2Cl_2 and purification by preparative t.l.c. (SiO_2; acetone–hexane 3/7) gave a bright yellow band (R_f 0.57) which afforded $AuRu_3\{\mu_3,\eta^2\text{-}C_2C{\equiv}CAu[P(tol)_3]\}(CO)_9\{P(tol)_3\}$ (**3**) (38.4 mg, 30.6%) as yellow crystals (from CH_2Cl_2/hexane). Anal. Found: C, 41.19; H, 2.70. Calcd. ($C_{55}H_{42}Au_2O_9P_2Ru_3$): C, 41.12; H, 2.62%; *M*, 1607. IR (cyclohexane): ν(CO) 2067 m, 2054 w, 2036 vs, 2032 (sh), 1993s, 1987 (sh), 1972 w, 1957 w cm^{-1}. ^1H NMR: δ 2.09, 2.38 (2 × s, 2 × 9H, Me), 7.11–7.42 (m, 24H, C_6H_4). ^{31}P NMR: δ 39.99 [s, C≡CAuP$(tol)_3$], 59.50 [$Ru_3AuP(tol)_3$]. ES-MS (negative ion, MeOH + NaOMe, *m/z*): 1105, $[M - H - AuP(tol)_3]^-$; 1077, 1049 $[M - H - P(tol)_3 - nCO]^-$ (*n* = 1, 2).

Table 2
Crystal data and refinement details

Compound	**1**·$2C_6H_6$	**1**·$2CHCl_3$	**1**·$2CH_2Cl_2$	**2**	**3**	**4**
Formula	$C_{58}H_{30}Au_2O_{18}P_2Ru_6 \cdot 2C_6H_6$	$C_{58}H_{30}Au_2O_{18}P_2Ru_6 \cdot 2CHCl_3$	$C_{58}H_{30}Au_2O_{18}P_2Ru_6 \cdot CH_2Cl_2$	$C_{64}H_{42}Au_2O_{18}P_2Ru_6 \cdot 2CHCl_3$	$C_{55}H_{42}Au_2O_9P_2Ru_3 \cdot 0.5CH_2Cl_2$	$C_{89}H_{66}AuO_{14}P_5Ru_6 \cdot 2C_6H_6$
MW	2233.4	2315.9	2247.0	2400.1	1648.5	2474.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a (Å)	13.2208(8)	12.8714(5)	12.9953(5)	9.4761(6)	12.2358(7)	12.866(2)
b (Å)	18.644(1)	19.2148(8)	19.3385(7)	13.0788(8)	16.1970(9)	19.494(3)
c (Å)	14.6527(9)	14.1929(6)	13.6390(5)	16.117(1)	16.8256(9)	19.995(3)
α (°)				98.691(2)	104.902(1)	79.104(4)
β (°)	97.941(2)	94.228(1)	96.218(1)	104.139(2)	99.765(1)	71.513(4)
γ (°)				90.594(2)	109.777(1)	85.620(4)
V (Å^3)	3577	3500	3407	1912	2909	4670
Z	2	2	2	1	2	2
D_c (g cm^{-3})	2.07_3	2.19_7	2.19_0	2.08_4	1.88_2	1.75_9
μ (mm^{-1})	5.4	5.8	5.9	5.3	5.9	2.7
Crystal size (mm)	0.12 × 0.10 × 0.09	0.32 × 0.10 × 0.07	0.14 × 0.13 × 0.12	0.24 × 0.09 × 0.07	0.28 × 0.24 × 0.13	0.10 × 0.09 × 0.08
$T_{min/max}$	0.66	0.65	0.81	0.55	0.59	0.61
$2\theta_{max}$ (°)	75	65	75	63	75	50
N_{tot}	74,809	73,269	70,808	41,008	60,064	43,664
N (R_{int})	18,696 (0.068)	12,377 (0.076)	17,942 (0.041)	12,216 (0.040)	29,914 (0.038)	16,231 (0.101)
N_o	11,422	8687	12,746	9608	17,871	8087
R	0.036	0.029	0.029	0.050	0.036	0.074
R_w (n_w)	0.030(2)	0.023 (0.5)	0.025 (1)	0.064 (20)	0.036 (3)	0.077 (6)

3.6. Reaction between Au(C≡CC≡CH){P(tol)$_3$} and Ru$_3$(μ-dppm)(CO)$_{10}$

A solution of Ru$_3$(μ-dppm)(CO)$_{10}$ (150 mg, 0.155 mmol) and Au(C≡CC≡CH){P(tol)$_3$} (42.6 mg, 0.078 mmol) in thf (20 ml) was heated at reflux point for 4 h, after which no ruthenium precursor was present (t.l.c.). Removal of solvent under vacuum and preparative t.l.c. (SiO_2; acetone–hexane 3/7) of a dichloromethane extract of the residue gave a major orange band (R_f 0.42) containing {Ru$_3$(μ-H)(μ-dppm)(CO)$_7$}(μ-C_2C_2)-{AuRu$_3$(μ-dppm)(CO)$_7$[P(tol)$_3$]} (**4**) (140.3 mg, 78%), obtained as orange crystals (CH_2Cl_2/hexane). Anal. Found: C, 45.93; H, 2.65. Calcd. ($C_{89}H_{66}AuO_{14}P_5Ru_6$): C, 46.12; H, 2.87%; *M*, 2319. IR (cyclohexane): ν(CO) 2063 m, 2036 vs, 2007 m, 1996 s, 1979 m, 1970 m, 1952 m (br), 1931 w (br) cm^{-1}. ^{1}H NMR: δ −18.43 [d, *J*(HP) 35.7 Hz, RuH], 2.36 (s, 9H, Me), 3.91–4.37 (m, 4H, CH_2), 6.74–7.78 (m, 52H, Ph + C_6H_4). ^{31}P NMR: δ 24.24 [d, *J*(PP) 56.9 Hz, P(4)], 28.14 [dd, *J*(PP) 39.0, 64.8 Hz, P(2)], 31.84 [d, *J*(PP) 64.8 Hz, P(3)], 32.34 [d, *J*(PP) 56.9 Hz, P(5)], 58.93 [d, *J*(PP) 39.0 Hz, P(1)]. ES-MS (positive ion, MeOH/CH_2Cl_2, *m/z*): 2319, M^+; 2342, $[M + Na]^+$; (negative ion, CH_2Cl_2/MeOH + NaOMe, *m/z*): 2317, $[M - 2H]^-$.

3.7. Structure determinations

Full spheres of diffraction data were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinements. All data were measured using monochromatic Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms $(x, y, z, U_{iso})_H$ included constrained at estimated values. Conventional residuals R, R_w on $|F|$ are quoted [weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [29]. 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 in Tables 1 and 2.

Variata **1**. Three determinations of the structure of **1** were carried out on crystals from different sources, obtained as different solvates, including one from a reaction in which a mixture of {Au[P(tol)$_3$]}$_2$(μ-C≡CC≡C) and Au(C≡CC≡CH){P(tol)$_3$} was inadvertently used. All solvent molecules refined as ordered, as also in the case of **2**.

3. Solvent residues were modelled in terms of a disordered CH_2Cl_2 molecule disposed about a crystallographic inversion centre.

4. A large residue disposed between Ru(21, 23) was modelled in terms of disordered Au [occupancies: 0.898(1) and complement], i.e., the Au{P(tol)$_3$} fragment is disordered between the pair of Ru$_3$ clusters. P, C components of the minor fragment were not located, the disorder impacting on the refinement of the major component (isotropic displacement parameter forms for C, O) and a fortiori, of the solvent, tentatively modelled in terms of C_6H_6.

3.8. Supplementary material

Full details of the structure determinations of **1** (three solvates) and **2**–**4** (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 261544–261549. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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