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Communication

An unusual Cu_2Ru_2 cluster containing a tetrameric phenylethynyl ligand

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Abstract

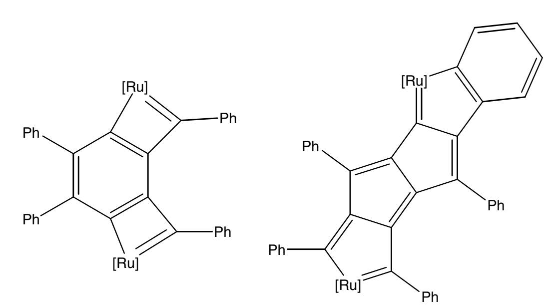
The reaction between $RuCl(PPh_3)_2Cp^*$ and $\{Cu(CCPh)\}_n$ in refluxing benzene afforded $Ru_2Cu_2(C_2Ph)_5H_2(Cl)(PPh_3)Cp^*_2$, which contains an unusual tetramer of the phenylethynyl group which interacts with an Ru...Cu...Cu...Ru chain. The second Ru atom is part of a ruthenocenyl moiety which interacts weakly with the second Cu atom, and bears a vinylidene which bridges an Ru–Cu vector. The structure of a second modification of $Ru(C{\equiv}CPh)(CO)(PPh_3)Cp^*$ is also reported.

Keywords: Copper; Ruthenium; Cluster; Phenylethynyl; XRD structure

1. Introduction

Continuing interest in the oligomerisation of alkynes on transition metal centres prompts us to report an unusual tetramerisation of a phenylethynyl moiety on a mixed ruthenium–copper cluster. Tetramerisation of alkynes is not unusual, the most well-known example being the Ni-catalysed conversion of ethyne to cyclooctatetraene discovered by Reppe [1], whose mechanism continues to be of interest [2]. Other examples include the Pd-catalysed conversion of arylalkynes to dihydropentalenes [3], the conversion of 2-propynol to 2,5-dimethyl-2,5-bis(2-propynoxy)-1,4-dioxane catalysed by $[Pt(CO)_4](Sb_2F_{11})_2$ [4] and the formation of linear tetramers of diarylalkynes over a $CrCl_3/ZrCl_2Cp_2$ catalyst [5]. Complexes containing alkyne tetramers include the η^5-cyclohexadienyl $RuCp\{\eta^5\text{-}C_6[C(CO_2Me){:}CH(CO_2Me)](CO_2Me)_6\}$ [from $C_2(CO_2Me)_2$ and $RuCl(PPh_3)_2Cp$] [6], cyclopentadienylvinylcarbene complexes [from $W(CO)_3(NCMe)_3$ or $W(CO)(\eta\text{-}PhC_2Ph)_3$ and C_2Ph_2] [7] and hydropentalenyl complexes $Rh(cod)(\eta^5\text{-}C_8H_3R_4)$ [from bulky terminal alkynes $HC{\equiv}CR$ ($R = Bu^t$, $SiMe_3$) and $\{RhCl(cod)\}_2$] [8].

The present example arose out of a re-examination of reactions of Group 11 alkynyls, free from other donor ligands, with $RuCl(PPh_3)_2Cp$ and related complexes [9]. These compounds are known to dissociate a PPh_3 ligand easily, thus allowing access to coordinatively unsaturated intermediates. Previously, we reported on the reaction between $RuCl(PPh_3)_2Cp$ and $\{AgCCPh\}_n$, which afforded $\{Ru(PPh_3)Cp\}_2(\mu\text{-}C_8Ph_4)$ **1** and $\{Ru(PPh_3)Cp\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}$ **2** containing four and five phenylethynyl residues, respectively [10]. We considered it would be of interest, therefore, to investigate the analogous reactions of complexes containing the more bulky and electron-rich Cp^* ligand.



(1) (2)
[Ru] = Ru(PPh3)Cp

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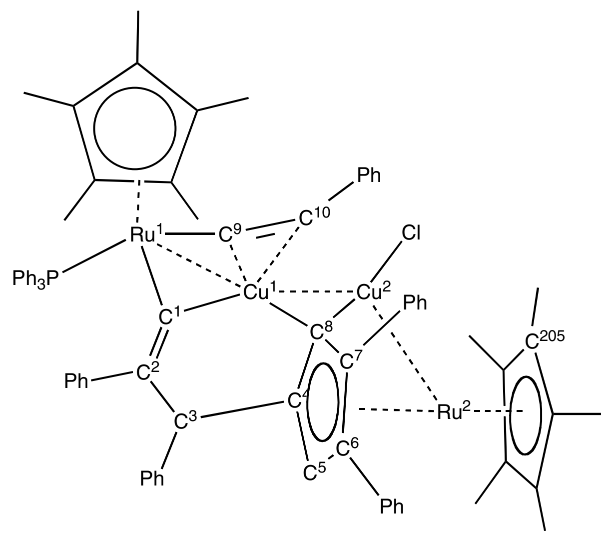
2. Results and discussion

The reaction between $RuCl(PPh_3)_2Cp^*$ and $\{CuCCPh\}_n$ was carried out in refluxing benzene for several hours, after which time a dark brown solution containing a dark green precipitate was obtained. Filtration and work-up of the filtrate by preparative t.l.c. afforded two fractions containing (a) an orange-red tetranuclear complex **3** (Scheme 1) and (b) pale yellow $Ru(C{\equiv}CPh)(CO)(PPh_3)Cp^*$, obtained as a previously undescribed polymorph (see Section 3).

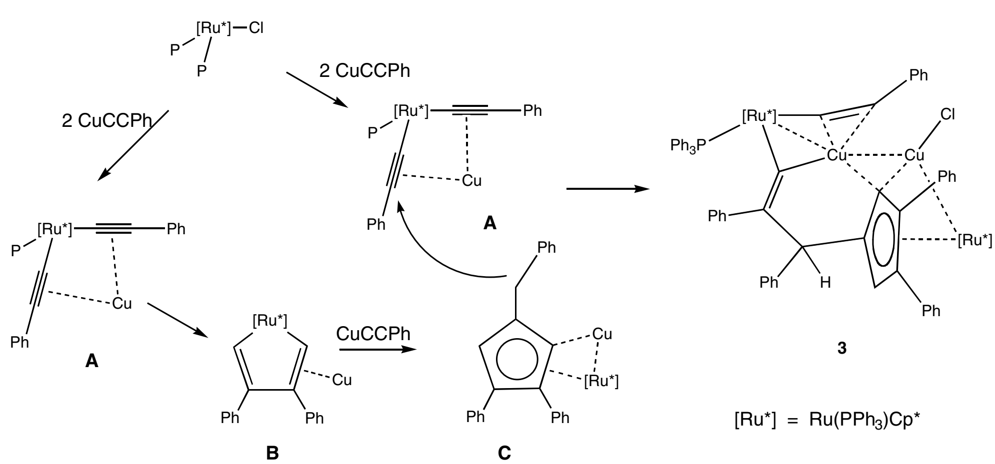


(3)

Although elemental analyses, ES-MS and other spectroscopic data of **3** are in accord with the subsequently determined molecular structure by XRD, the nature of this intriguing complex was not fully revealed until the latter was complete. For example, the IR spectrum contained a weak $\nu(C{\equiv}C)$ band at 2014 cm^{-1}, while other absorptions were not characteristic (see Section 3). The ^1H NMR spectrum contained two equal intensity resonances at δ 1.26 and 1.47, assigned to two inequivalent Cp^* groups. Two other resonances at δ 2.65 and 3.88, each corresponding to one H, were not immediately assignable. The aromatic region contained a 40H multiplet, indicating the presence of eight Ph groups. Only one resonance was present at δ 50.9 in the ^{31}P NMR spectrum and was assigned to one PPh_3 ligand. The ES-MS from a solution in MeOH containing MeCN contained ions at m/z 1411 and 1370, assigned to $[M+n\text{MeCN}-Cl]^+$ ($n = 1$, 0), respectively. These data were interpreted in terms of a tetranuclear complex formulated as $Ru_2Cu_2(C_2Ph)_5H_2(Cl)(PPh_3)Cp^*_2$ ($M = 1404$).

A single-crystal XRD study revealed the structure shown in Fig. 1; relevant dimensions are given in the caption. An Ru–Cu–Cu–Ru chain [Ru(1)–Cu(1) 2.5771(3), Cu(1)–Cu(2) 2.5069(4), Cu(2)–Ru(2) 2.8050(3) Å] supports conventional Cp^* (one per Ru), PPh_3 [on Ru(1)] and Cl [on Cu(1)] ligands, together with a $C{\equiv}CPh$ group which bridges the Ru(1)Cu(1) vector [Ru(1)–C(9) 2.004(2), Cu(1)–C(9, 10) 1.998(2), 2.405(2) Å] by an $\eta^1{:}\eta^2$ interaction. The asymmetry of this interaction suggests that it is not very strong and this is borne out by the small distortion from linearity of the $RuC{\equiv}CPh$ group [Ru(1)–C(9)–C(10) 173.2(2)°, C(9)–C(10)–C(91) 163.2(2)°]. In these systems, the bond distances and angles are within the limits found for other, simpler, complexes containing them. Of note, however, is the significant difference in average Ru–C(cp) distances for the rings attached to Ru(1) and Ru(2) [2.27(3), 2.19(3) Å, respectively], quite unsymmetrically in both cases.

It is the remaining $C_8H_2Ph_4$ ligand, formed from four C_2Ph groups with addition of two H atoms (presumably from solvent), which is unprecedented. Atoms C(4)–C(8) form a five-membered planar ring, bearing Ph groups on C(6) and C(7), an H atom on C(5) and a CHPhCPhC chain on C(4). The C_5 ring forms a ruthenocene derivative (again somewhat unsymmetrical) with the $Ru(2)Cp^*$ fragment [Ru(2)–C(4–8) 2.179(3)–2.264(2) Å, av. 2.21(3) Å, i.e., about 0.06 Å closer than found for the Ru(1)–Cp^* interac-



Scheme 1.

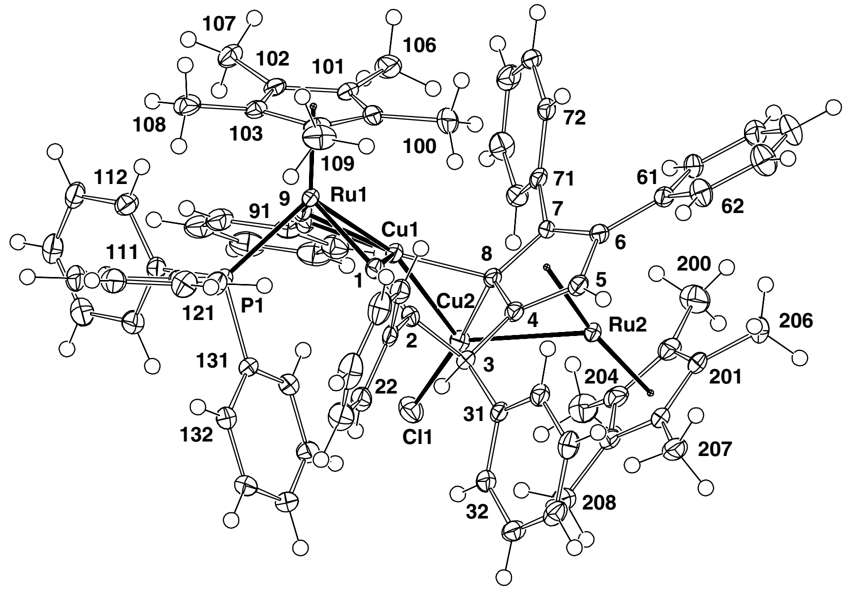
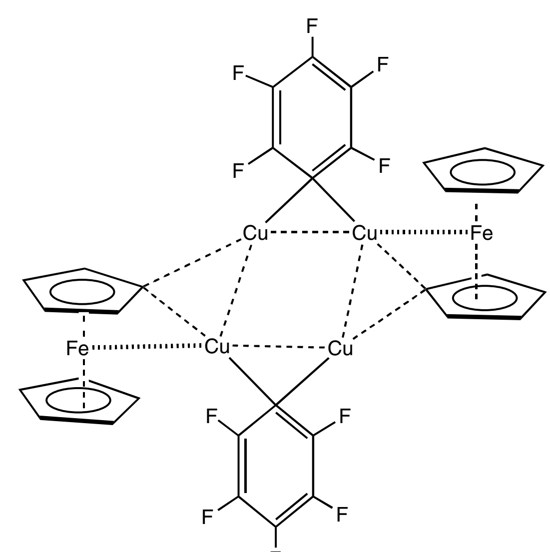


Fig. 1. Projection of a molecule of $Ru_2Cu_2(C_2Ph)\{C_5H_2Ph_2(CHPhCPh{=}C)\}(Cl)(PPh_3)Cp^*_2$ **3**. Selected bond parameters: Ru(1)–Cu(1) 2.5771(3), Cu(1)–Cu(2) 2.5069(4), Cu(2)–Ru(2) 2.8050(3), Ru(1)–P(1) 2.3237(6), Cu(2)–Cl 2.1419(6), Ru(1)–C(cp) 2.238–2.309(2) [av. 2.27(3)], Ru(2)–C(cp) 2.163–2.232(4) [av. 2.19(3)], Ru(1)–C(1) 1.925(2), Ru(1)–C(9) 2.004(2), Cu(1)–C(1) 2.137(2), Cu(1)–C(9, 10) 1.998(2), 2.405(2), Cu(1, 2)–C(8) 1.992(2), 1.949(2), Ru(2)–C(4–8) 2.219(2), 2.179(2), 2.183(2), 2.213(2), 2.264(2) [av. 2.21(3)], C(1)–C(2) 1.329(3), C(2)–C(3) 1.564(3), C(3)–C(4) 1.519(3), C(4)–C(5, 8) 1.420(3), 1.441(3), C(5)–C(6) 1.450(3), C(6)–C(7) 1.438(3), C(7)–C(8) 1.466(3), C(9)–C(10) 1.224(3), C(10)–C(91) 1.441(3) Å; Ru(1)–Cu(1)–Cu(2) 161.73(1), Cu(1)–Cu(2)–Ru(2) 104.50(1), P(1)–Ru(1)–Cu(1) 101.80(2), P(1)–Ru(1)–C(1, 9) 89.13(6), 83.67(3), C(1)–Ru(1)–C(9) 99.73(9), Ru(1)–C(9)–C(10) 173.2(2), C(9)–C(10)–C(91) 163.2(2), Ru(1)–C(1)–Cu(1) 78.56(8), Ru(1)–C(1)–C(2) 163.6(2), C(1)–C(2)–C(3) 122.4(2), C(2)–C(3)–C(4) 108.1(2), Cu(1)–C(8)–Cu(2) 79.00(8)°. The angles within the C(4–8) ring are: 109.4, 108.6, 107.1, 108.8, 106.2(2) (Σ 540.1°).

tion]. The C–C distances range between 1.420(3) and 1.466(3) Å [⟨⟩ 1.44(3) Å], with intra-ring angles at C(4–8) between 106.2(2)° and 109.4(2)° (Σ 540.1°) the extremes being found at C(4) and C(8), the latter no doubt reflecting its interaction with Cu(2). Atom C(8) is also further away from Ru(2) [2.264(2) Å] and asymmetrically bridges the Cu(1)–Cu(2) vector [Cu(1, 2)–C(8) 1.992(2), 1.949(2) Å] in a manner similar to that found in $Cu_4(\mu\text{-}C_6F_5)_2(\mu\text{-Fc})_2$ **4**, obtained from a reaction between $\{Cu(C_6F_5)\}_4$ and $FcSnMe_3$ [11]; the related reaction with $RcSnMe_3$ similarly gives a complex with a Cu–Ru interaction [12]. As with similar complexes, the M–M interaction is probably best considered as an Ru → Cu donor interaction, enhanced by tilting of the C_5 rings [tilt angles: 14.0(1) for **3**, 10.7° for **4**]. For **4**, the C–Cu distances are 1.971(5), 1.969(5) Å. In both compounds, the bridging C_5 ligand brings the Cu atom within bonding distance of Ru (for **3**) or Fe (for **4**) [Cu(2)–Ru(2) 2.8050(3), Cu(1)–Fe(1) 2.7011(9) Å; cf. also Cu(1)–Ru(1) 2.5771(3) Å in **3**, 2.633(1) Å in $[Rc'(quin)_2Cu]BF_4$ [$Rc' = Ru(\eta\text{-}C_5H_4)_2$, quin = 8-quinolinyl [13]]. These separations are somewhat longer than the respective sums of covalent radii (Cu–Ru 2.60, Cu–Fe 2.53 Å).

Atom C(4) carries a CHPhCPh=C group as a vinylidene [C(1)–C(2) 1.329(3) Å] which bridges Cu(1)–Ru(1) [Cu(1)–C(1) 2.137(2), Ru(1)–C(1) 1.925(2) Å]. The latter distance is considerably longer, and C(1)–C(2) shorter, than those found in $[Ru({=}C{=}CHPh)(PMe_3)_2Cp]^+$ [Ru–C(1) 1.845(7), C(1)–C(2) 1.313(10) Å] [14] and suggest that there is significantly reduced back-bonding to the vinylidene ligand in **3**. The closest precedent is the complex $[\{Cp(dppf)Ru\}_2\{\mu\text{-}C_4[Cu(NCMe)]_2\}](ClO_4)(SbF_6)$, in which the Cu–Ru separation is 2.95, with Ru–C 2.006, Cu–C 1.945, 2.119, and CC 1.31 Å (av. values) [15].



(4)

The electron counts for the two Ru atoms are precise, whereas for Cu(1) and Cu(2), the ligands contribute a total of 10 electrons, if the Ru(2)–Cu(2) interaction is considered to be a donor bond.

The relatively low yield of **3** precludes any more than speculation on its possible mode of formation. Ready exchange of phenylethynyl for chloride, followed by coordination of Cu to the Ru–C≡CPh fragment, has been reported earlier [9] and the lability of the ligands on an RuL_2Cp^* centre resulting from steric interactions is well-known. The isolation of the carbonyl complex $Ru(C{\equiv}CPh)(CO)(PPh_3)Cp^*$ suggests that interaction of an ethynyl-ruthenium intermediate with adventitious water (to give a hydroxyvinylidene and hence carbonyl and benzaldehyde) or oxygen (or both) has occurred. Consequently, it is reasonable to suggest that interaction of $RuCl(PPh_3)_2Cp^*$ with $\{CuCCPh\}_n$ initially gives $Ru(C{\equiv}CPh)(PPh_3)_2Cp^*$, which interacts further with a second CuCCPh moiety to give the bis-alkynyl complex $Ru(C{\equiv}CPh)_2(PPh_3)Cp^*$ **A** (Scheme 1), possibly retaining an interaction with Cu. Intramolecular coupling to give ruthenacyclopentadiene **B**, followed by insertion of a third phenylethynyl group to give a ruthenacyclohexadiene **C**, has some precedent in the recently proposed mechanism for formation of a binuclear substituted cyclopentadienyl-osmium complex, which incorporates six phenylethynyl groups [16], although in the present case, insertion into an Ru–C bond, followed by displacement and ring-closure to the η-cyclopentadienyl ligand shown in **C**, occurs. The formation of Ru complexes containing bulky Cp ligands formed directly from solvated $RuCl_3$ and $HC{\equiv}CBu^t$ has also been described recently [17]. This could be followed by attack of a second molecule of **A** at C_β of one of the phenylethynyl groups to give the substituted vinylidene, again interacting with one of the two Cu atoms present in **3**. The second Cu atom retains one of the Cl ligands displaced by phenylethynyl, the second possibly being trapped together with the displaced PPh_3 ligand(s) as a $CuCl(PPh_3)$ complex.

3. Experimental

General experimental details have been described elsewhere [18]. The complexes $RuCl(PPh_3)_2Cp^*$ [19] and $\{Cu(CCPh)\}_n$ [20] were obtained as previously described.

A mixture of $RuCl(PPh_3)_2Cp^*$ (108 mg, 0.136 mmol) and $\{Cu(CCPh)\}_n$ (112.2 mg, 0.68 mmol) was heated in refluxing benzene (20 ml) for 4.5 h. the liquid turning dark brown, with some precipitate present. This was filtered off to give a dark green solid (not further characterised), while the filtrate was evaporated and separated by preparative t.l.c. (silica gel, acetone–hexane, 1/4). A broad yellow band ($R_f = 0$, 45) contained $Ru(C{\equiv}CPh)(CO)(PPh_3)Cp^*$ (34 mg, 14%), obtained as pale yellow crystals of a previously unidentified polymorph (from CH_2Cl_2/hexane), identified by XRD (see below). The second orange band ($R_f = 0.29$) afforded orange-red crystals of **3** (8.1 mg, 8.5%). Anal. Calc. for $C_{78}H_{72}ClCu_2PRu_2$: C, 66.66; H, 5.17; M, 1406. Found: C, 66.70; H, 5.12%. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2014w; other bands at 1720m, 1673w, 1600s, 1483m, 1451m, 1378m, 1178w, 1094m, 1071m. ^1H NMR (d_6-acetone): δ 1.26 [s(br), 15H, Cp*], 1.47 [s(br), 15H, Cp*], 2.65 (s, 1H), 3.88 (s, 1H), 6.88–7.75 (m, 40H, Ph). ^{31}P NMR (d_6-acetone): δ 50.9 [s(br), PPh_3]. ES-MS (positive ion mode, MeOH + MeCN, m/z): 1411 $[M+MeCN-Cl]^+$; 1370 $[M-Cl]^+$. Crystals for the X-ray study were obtained from acetone.

3.1. Structure determinations

Full spheres of diffraction data were measured at ca 100 K using a 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 considered "observed". All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.7107$ Å^3. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ following a riding model. Neutral atom complex scattering factors were used; computation used the SHELXL97 program system [21]. Pertinent results are given below and in the figure (which shows non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in the caption thereto.

3 $Ru_2Cu_2(C_2Ph)\{C_5H_2Ph_2(CHPhCPh{=}C)\}(Cl)(PPh_3)Cp^*_2 \cdot 2.5Me_2CO \cdot 0.5H_2O \equiv C_{78}H_{72}ClCu_2PRu_2 \cdot 2.5C_3H_6O \cdot 0.5H_2O$, $M_W = 1559.29$. Monoclinic, space group $P2_1/c$, $a = 15.4970(5)$ Å, $b = 16.4088(9)$ Å, $c = 28.1825(6)$ Å, $\beta = 94.418(2)°$, $V = 7145$ Å^3, $Z = 4$. $2\theta_{max} = 63$. $D_c = 1.44_8$ g cm^{-3}, $\mu = 1.11$ mm^{-1}, 'T'$_{min/max} = 0.96$. Crystal $0.25 \times 0.18 \times 0.16$ mm. $N_{tot} = 75496$, $N = 22735$ ($R_{int} = 0.028$), $N_o = 15123$, $R_1 = 0.037$, $wR_2 = 0.096$.

The recorded polymorph of $Ru(C{\equiv}CPh)(CO)(PPh_3)Cp^*$ [22] is monoclinic, $P2_1/n$, $Z = 4$ (as also is the present), $a = 8.7254(2)$ Å, $b = 17.8548(2)$ Å, $c = 19.5265(5)$ Å, $\beta = 98.9732(3)°$, $V = 3005$ Å^3 (223 K). For the present form ($C_{37}H_{35}OPRu$, $M = 627.7$), $a = 10.5262(7)$ Å, $b = 10.7300(10)$ Å, $c = 26.921(3)$ Å, $\beta = 98.495(7)°$, $V = 3007$ Å^3 (100 K), $D_c = 1.38_6$ g cm^{-3}, $\mu_{Mo} = 0.60$ mm^{-1}; specimen: $0.33 \times 0.12 \times 0.11$ mm; 'T'$_{min/max} = 0.93$. $2\theta_{max} = 68°$; $N_{tot} = 58518$, $N = 11681$ ($R_{int} = 0.031$), $N_o = 8839$; $R_1 = 0.032$, $wR_2 = 0.081$. In the present [cf. previous] Ru–P, C(O), C are 2.3113(4) [2.3144(10)], 1.852(2) [1.850(4)], 2.020(2) [2.030(5)] Å.

4. Supplementary material

CCDC 656852 and 656898 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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