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Saturated and unsaturated tetraruthenium clusters containing sterically demanding dicyclohexylphosphido ligands: synthesis and structure of $[H_4Ru_4(CO)_8(PCy_2)_4]$ and $[H_5Ru_4(CO)_8(PCy_2)_3]$ †

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The thermal reaction of the dinuclear complex $[Ru_2(CO)_4(O_2CH)_2(PCy_2H)_2]$ with molecular hydrogen in cyclohexane afforded the tetranuclear clusters $[H_4Ru_4(CO)_8(PCy_2)_4]$ (64e) and $[H_5Ru_4(CO)_8(PCy_2)_3]$ (62e), both of which have a square-planar arrangement of the metal framework.

Tetranuclear ruthenium clusters, mainly accessible by pyrolytic methods, have been obtained from unsystematic synthetic routes.[1] Most of these Ru_4 clusters adopt tetrahedral or butterfly geometries, but there are a small number of compounds which form square-planar clusters.[2,3] We reported in 1994 the assembly of the square-planar clusters $[Ru_4(CO)_8(PCy_2)_4]$ and $[Ru_4(CO)_8(PCy)_2(PCy_2)_2]$ by condensation of the dinuclear clusters $[Ru_2(CO)_4(O_2CH)_2(PCy_2H)_2]$ or $[Ru_2(CO)_6(PCy)_2]$.[4] In a recent paper, Frediani *et al.* described the thermal behaviour of the dinuclear complex $[Ru_2(CO)_4(O_2CMe)_2(PPh_3)_2]$ towards molecular hydrogen which gives rise to the formation of the tetranuclear clusters $[Ru_4(CO)_8(PPh)_2(PPh_2)_2]$ and $[H_4Ru_4(CO)_7(PPh)(PPh_2)_2(PPh_3)]$, along with the trinuclear cluster $[H_2Ru_3(CO)_8(PPh)(PPh_3)]$.[5] This prompted us to report our own findings on the hydrogenation of the dinuclear dicyclohexylphosphine complexes $[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]$ (R = H or Me) to give, with fusion of two Ru_2 units, the tetranuclear square-planar hydrido clusters $[H_4Ru_4(CO)_8(PCy_2)_4]$ and $[H_5Ru_4(CO)_8(PCy_2)_3]$.

Results and Discussion

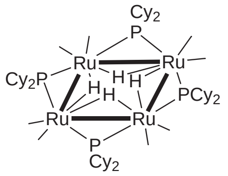
The reaction of the dinuclear ruthenium carboxylato complexes $[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]$ (R = H **1a**, R = Me **1b**) in cyclohexane with molecular hydrogen (60 bar) at 160 °C yields the two tetranuclear clusters $[H_4Ru_4(CO)_8(PCy_2)_4]$ **2** and $[H_5Ru_4(CO)_8(PCy_2)_3]$ **3** [equations (1) and (2)], resulting from the

$$\underset{\mathbf{1}}{2[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]} + 2\,H_2 \longrightarrow \underset{\mathbf{2}}{[H_4Ru_4(CO)_8(PCy_2)_4]} + 4\,RCO_2H \quad (1)$$

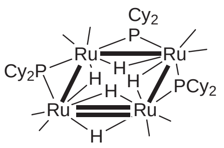
$$\underset{\mathbf{1}}{2[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]} + 3\,H_2 \longrightarrow \underset{\mathbf{3}}{[H_5Ru_4(CO)_8(PCy_2)_3]} + 4\,RCO_2H + PCy_2H \quad (2)$$

condensation of two Ru_2P_2 units to give a Ru_4P_4 core. If the reaction is performed at 120 °C, only complex **3** is obtained. On the other hand, prolonged reaction (14 h) at 160 °C also gives, along with **2** and **3**, the known violet cluster $[Ru_4(CO)_8(PCy)_2(PCy_2)_2]$ as a side-product.[3] Complexes **2** and **3** can be separated by thin-layer chromatography; they are obtained as yellow crystals from dichloromethane–methanol (**2**) and as red crystals from dichloromethane–hexane (**3**), respectively.

The tetrahydrido cluster **2**, formed in the reaction of **1** with H_2, is identical with one of the minor products formed in the pyrolysis of **1** in the absence of molecular hydrogen to give mainly $[Ru_4(CO)_8(PCy)_2(PCy_2)_2]$ and $[Ru_4(CO)_8(PCy_2)_4]$. For this product (**2**) we had proposed the formula $[HRu_3(CO)_7(PCy_2)_3]$ on the basis of the spectroscopic and analytical data.[4] This compound now turns out, by a single-crystal structure analysis (see below), not to be trinuclear but tetranuclear, the microanalytical data being the same within the error limits. The true compound $[HRu_3(CO)_7(PCy_2)_3]$ had been reported in the past by Keister and co-workers[6] and structurally characterised by Böttcher *et al.*[7]



2



3

The ^{31}P-$\{^1H\}$ NMR spectrum of **2** shows only one singlet at δ 151, the four phosphorus atoms being equivalent. The IR spectrum shows three absorptions in the area of terminal carbonyls, confirming the high symmetry of this molecule. In the ^1H NMR spectrum, **2** gives rise to a doublet of triplets centered at δ −17.70. The four hydrido ligands are equivalent, each hydride being coupled to the μ-phosphorus atom at the same Ru–Ru edge ($^2J_{HP} = 20$ Hz) and to the equivalent vicinal μ-phosphorus atoms ($^2J_{HP} = 10.4$ Hz).

The metal skeleton of complex **2** is saturated with respect to the noble gas rule, the electron count being 64. It consists of a nearly square-planar arrangement of four ruthenium atoms [Ru(2)–Ru(1)–Ru(4) 90.25(4), Ru(1)–Ru(2)–Ru(3) 90.59(4), Ru(2)–Ru(3)–Ru(4) 89.90°, Ru(1)–Ru(4)–Ru(3) 88.88(4)°] (Fig. 1, Table 1). The four edges are bridged by four μ-dicyclohexylphosphido ligands, the Ru–Ru bonds are quite long [Ru(1)–Ru(2) 3.006(1), Ru(1)–Ru(4) 3.047(1), Ru(2)–Ru(3) 3.011(1), Ru(3)–Ru(4) 3.061(1) Å]. These distances are longer than those in the known unsaturated complex $[Ru_4(CO)_8(PCy_2)_4]$ (mean 2.989 Å).[4] Two opposite edges of the Ru_4 square are bridged by the phosphido ligands [P(2), P(4)] situated above the plane and by the hydrido ligands situated below the plane. The other two Ru–Ru edges have the hydrido bridges above the

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† *Non-SI unit employed*: bar = 10^5 Pa.

Table 1 Selected bond lengths (Å) and angles (°) for complex **2***

Ru(1)–Ru(2)	3.006(1)	Ru(2)–P(2)	2.349(2)
Ru(1)–Ru(4)	3.047(1)	Ru(3)–Ru(4)	3.061(1)
Ru(1)–H(1)	1.81(7)	Ru(3)–H(2)	1.75(5)
Ru(1)–H(4)	1.81(6)	Ru(3)–H(3)	1.81(7)
Ru(1)–P(1)	2.376(2)	Ru(3)–P(2)	2.375(2)
Ru(1)–P(4)	2.365(2)	Ru(3)–P(3)	2.373(2)
Ru(2)–Ru(3)	3.011(1)	Ru(4)–H(3)	1.80(7)
Ru(2)–H(1)	1.86(7)	Ru(4)–H(4)	1.76(6)
Ru(2)–H(2)	1.85(5)	Ru(4)–P(3)	2.364(2)
Ru(2)–P(1)	2.354(2)	Ru(4)–P(4)	2.376(2)
Ru(2)–Ru(1)–Ru(4)	90.25(4)	Ru(2)–Ru(3)–Ru(4)	89.90(4)
H(1)–Ru(1)–P(1)	86(2)	H(2)–Ru(3)–P(2)	83(2)
H(1)–Ru(1)–P(4)	84(2)	H(2)–Ru(3)–P(3)	91(2)
H(4)–Ru(1)–P(1)	86(2)	H(3)–Ru(3)–P(2)	81(2)
H(4)–Ru(1)–P(4)	80(2)	H(3)–Ru(3)–P(3)	80(2)
Ru(1)–Ru(2)–Ru(3)	90.59(4)	Ru(1)–Ru(4)–Ru(3)	88.88(4)
H(1)–Ru(2)–P(1)	85(2)	H(3)–Ru(4)–P(3)	80(2)
H(1)–Ru(2)–P(2)	82(2)	H(3)–Ru(4)–P(4)	92(2)
H(2)–Ru(2)–P(1)	82(2)	H(4)–Ru(4)–P(3)	87(2)
H(2)–Ru(2)–P(2)	82(2)	H(4)–Ru(4)–P(4)	80(2)

* Numbers in parentheses are estimated standard deviations in the least significant digits.

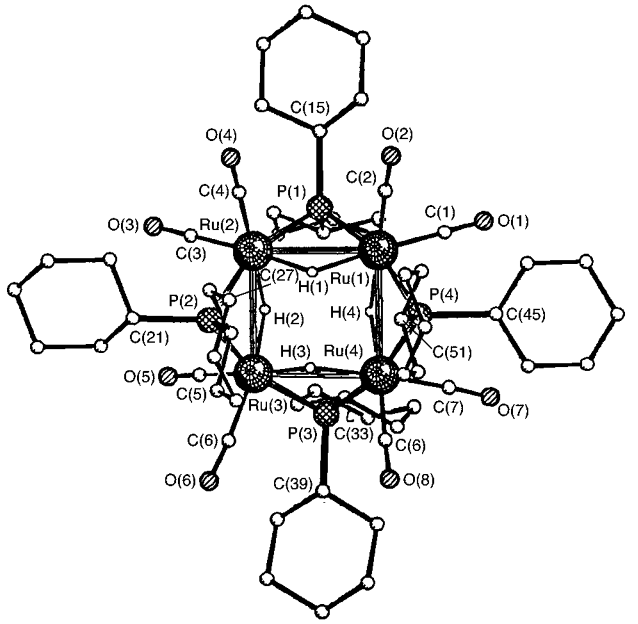

Fig. 1 Molecular structure of $[H_4Ru_4(CO)_8(PCy_2)_4]$ **2**

Table 2 Selected bond lengths (Å) and angles (°) for complex **3***

Ru(1)–Ru(2)	2.9699(9)	Ru(2)–P(2)	2.345(2)
Ru(1)–Ru(4)	2.7979(9)	Ru(3)–Ru(4)	2.9777(8)
Ru(1)–H(1)	1.52(5)	Ru(3)–H(2)	1.94(5)
Ru(1)–H(4)	1.92(5)	Ru(3)–H(3)	1.8(1)
Ru(1)–H(5)	1.48(5)	Ru(3)–P(2)	2.345(2)
Ru(1)–P(1)	2.325(3)	Ru(3)–P(3)	2.356(3)
Ru(2)–Ru(3)	3.005(1)	Ru(4)–H(3)	1.76(9)
Ru(2)–H(1)	1.92(6)	Ru(4)–H(4)	1.81(6)
Ru(2)–H(2)	2.02(5)	Ru(4)–H(5)	1.46(6)
Ru(2)–P(1)	2.361(3)	Ru(4)–P(3)	2.325(3)
Ru(4)–Ru(1)–Ru(2)	91.76(4)	Ru(4)–Ru(3)–Ru(2)	87.63(4)
H(1)–Ru(1)–P(1)	82(2)	H(2)–Ru(3)–P(2)	90(2)
H(4)–Ru(1)–P(1)	152(2)	H(2)–Ru(3)–P(3)	87(2)
H(5)–Ru(1)–P(1)	110(2)	H(3)–Ru(3)–P(2)	82(2)
Ru(1)–Ru(2)–Ru(3)	88.37(4)	H(3)–Ru(3)–P(3)	79(2)
P(2)–Ru(2)–P(1)	159.8(1)	P(2)–Ru(3)–P(3)	159.2(1)
H(1)–Ru(2)–P(1)	74(1)	Ru(1)–Ru(4)–Ru(3)	92.23(4)
H(1)–Ru(2)–P(2)	87(1)	H(3)–Ru(4)–P(3)	81(2)
H(2)–Ru(2)–P(1)	87(2)	H(4)–Ru(4)–P(3)	154(2)
H(2)–Ru(2)–P(2)	87(2)	H(5)–Ru(4)–P(3)	111(2)

* Numbers in parentheses are estimated standard deviations in the least significant digits.

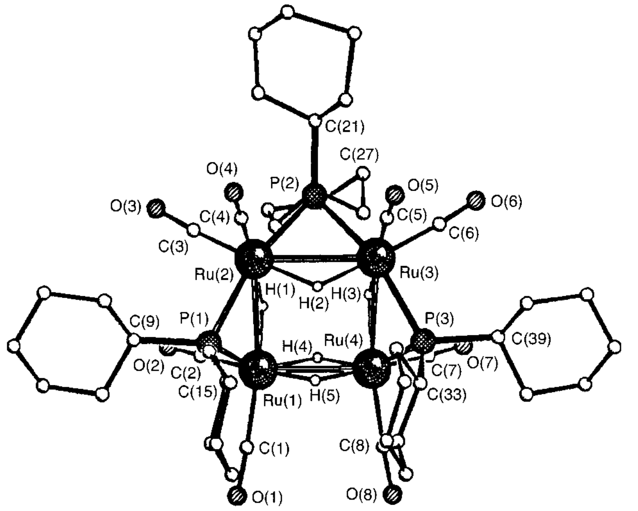

Fig. 2 Molecular structure of $[H_5Ru_4(CO)_8(PCy_2)_3]$ **3**

Ru_4 plane and the phosphido bridges [P(1), P(3)] below the plane. The inclination angle of the phosphido bridges with respect to the Ru_4 plane is 123.7° (average). The inclination angle of the hydrido bridges with respect to the Ru_4 plane is found to be 73.26° (average), the four hydrido ligands being closer to the Ru_4 skeleton than the phosphido ligands.

Complex **3** represents, with an electron count of only 62, an electron-deficient species. This electron-deficiency can be expressed either by formulating a Ru_2H_4 four-centre four-electron multicenter interaction or (more conventionally) by formulating a Ru=Ru double bond. We opted for the latter representation in the light of the Ru–Ru distances of **3**, as found in the single-crystal X-ray structure analysis.

The Ru_4 metal skeleton of **3** consists of a planar arrangement [torsion angle Ru(4)–Ru(1)–Ru(2)–Ru(3) = −0.29°] (Fig. 2, Table 2). Three of the four edges are bridged by both a dicyclohexylphosphido and a hydrido ligand. The fourth edge of the Ru_4 skeleton [Ru(1)–Ru(4)] is bridged by two hydrido ligands, thus resulting in a formal double bond between Ru(1) and Ru(4). This distance is indeed shorter [2.798(1) Å] than the other three Ru–Ru bonds (average 2.985 Å) which are similar to those observed in complex **2** (average 3.031 Å). The presence of a formal Ru=Ru double bond in the Ru_4 skeleton is responsible for the difference in the angles of the Ru_4 framework: Ru(4)–Ru(1)–Ru(2) [91.76(4)°] and Ru(1)–Ru(4)–Ru(3) [92.23(4)°] are superior to 90°, while Ru(1)–Ru(2)–Ru(3) [88.37(4)°] and Ru(4)–Ru(3)–Ru(2) [87.63(4)°] are inferior to 90°. The positions of the phosphido ligands are alternating below and above the Ru_4 plane. The average inclination angle of the phosphido ligands with respect to the Ru_4 skeleton is 123.7°, being similar to that observed in **2**. Owing to the different orientation of the cyclohexyl rings C(15) to C(20) and C(33) to C(38), there is no symmetry plane in the molecule.

In accordance with the molecular structure, the $^{31}P-\{^1H\}$ NMR spectrum of **3** shows two signals, a doublet at δ 216.6 (J_{PP} = 105 Hz) attributed to the two equivalent phosphorus atoms P(1) and P(3), and a triplet at δ 196.6 (J_{PP} = 105 Hz) assigned to the third phosphorus atom P(2). The angles P(2)–Ru(2)–P(1) [159.8(1)°] and P(2)–Ru(3)–P(3) [159.2(1)°] being different from 90° result in a large coupling (105 Hz) between the two signals. The ^1H NMR spectrum of **3** presents a complicated pattern between δ 1.06 and 2.36 corresponding to the cyclohexyl hydrogen atoms. In the hydride area, four signals are observed: the triplet at δ −7.46 (integral ratio 1) ($^2J_{HP}$ = 20 Hz) can be assigned to H(4) which is coupled to the two equivalent phosphorus atoms P(1) and P(3). This coupling is large because of the large angles H(4)–Ru(4)–P(3) [154(2)°] and H(4)–Ru(1)–P(1) [152(2)°]. The pseudo triplet at δ −13.76 (integral ratio 2) (${}^2J_{HP} = 14.3$, ${}^2J_{HP} = 15.6$ Hz) can be assigned to H(1) and H(3) which couple to P(1) and P(2) or to P(3) and P(2), respectively. The triplet at δ −17.02 (integral ratio 1) (${}^2J_{HP} = 9.3$ Hz) is attributed to H(5), coupled to P(1) and P(3), the coupling being smaller because of the smaller angles H(5)–Ru(4)–P(3) [111(2)°] and H(5)–Ru(1)–P(1) [110(2)°]. Finally, the multiplet at δ −18.04 (integral ratio 1) must be assigned to H(2), coupled to P(3) and P(1) as well as to P(2); it is the only signal showing in addition a homo-spin coupling [to H(1) and H(3)]. In the signal for H(1) and H(3) this coupling is not seen due to the broadening of the lines.

Conclusion

Tetranuclear ruthenium clusters which are unsaturated with respect to the noble gas configuration are quite rare. The 18-electron rule requires for a tetrahedral Ru_4 cluster 60 electrons, for a butterfly Ru_4 cluster 62 electrons, and for a square-planar Ru_4 cluster 62 electrons. Of the numerous square-planar Ru_4 clusters described hitherto, only a few have less then 64 electrons: the μ4-phosphinidyne clusters $[Ru_4(CO)_{11}(PPh)_2]$,[8] $[HRu_4(CO)_{10}(PPh)_2]^-$ [9] and $[Ru_4(CO)_8(PPhH)_2(PPh)_2]$,[10] reported by Haines and co-workers as well as $[Ru_4(CO)_8(PCy)_2(PCy_2)_2]$[4] and $[Ru_4(CO)_8(PPh)_2(PPh_2)_2]$[4,5] contain only 62 electrons, which can be explained by the fact that they represent a *closo* octahedral Ru_4P_2 framework with seven skeletal electron pairs according to the polyhedral skeleton electron pair theory.[11] The cluster $[H_4Ru_4(CO)_7(PPh_3)(PPh_2)_2(PPh)]$, containing only one PPh cap and giving rise to a tetragonal-pyramidal Ru_4P skeleton, also has an electron count of 62 electrons.[5] The only square-planar Ru_4 cluster with an electron count of 60 is the μ-phosphido bridged cluster $[Ru_4(CO)_8(PCy)_4]$ reported in 1994.[4] By contrast, the 64e clusters $[Ru_4(CO)_{13}(PR_2)_2]$ (R = Ph, Pr^i, OEt, NPr^i_2, Cy or Et)[12,13] and $[Ru_4(CO)_{10}(PPh_2)_4]$[13,14] are rhomboidal containing five metal–metal bonds. The two clusters reported in this paper, $[H_5Ru_4(CO)_8(PCy_2)_3]$ **3** and $[H_4Ru_4(CO)_8(PCy_2)_4]$ **2** complement the series of square-planar Ru_4 clusters with 60, 62, 64 electrons containing phosphorus ligands with bulky cyclohexyl substituents. Interestingly, the electron-deficiency in cluster **3** can be localised at the two ruthenium atoms carrying the two hydrido bridges by a formal Ru=Ru double bond with respect to the three Ru–Ru single bonds of the Ru_4 square.

Experimental

The organic solvents were refluxed over appropriate desiccants,[15] distilled and saturated with nitrogen prior to use. Thin layer chromatography (TLC) was performed using glass plates (20 × 20 cm) coated with Fluka Silica gel G. The NMR spectra were recorded on a Varian Gemini 200 BB instrument or on a Bruker AMX 400, chemical shifts were measured relative to $SiMe_4$ (${}^1H$, ${}^{13}C$) and to 85% H_3PO_4 (${}^{31}P$). The IR spectra were recorded with a Perkin-Elmer FTIR 1720X spectrophotometer (4000–400 cm^{-1}). Microanalytical data were obtained from the Mikroelementaranalytisches Laboratorium der ETH Zürich. Mass spectra were obtained with a LCQ Finnigan instrument using the ESI method. The starting compound $[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]$ was synthesised according to the published method.[4] Dicyclohexylphosphine was purchased from Strem Chemicals Co. and used without further purification.

Reaction of $[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]$ with H_2 (R = H or Me)

A solution of $[Ru_2(CO)_4(O_2CH)_2(PCy_2H)_2]$ (200 mg, 0.250 mmol) in 20 ml of cyclohexane was pressured with 60 bar of H_2 in a stainless-steel autoclave. The yellow solution was stirred at 160 °C for 2 h. After cooling and venting, the autoclave was opened, the red-brown solution evaporated to dryness, and the residue taken up in a minimum amount of CH_2Cl_2. Thin layer chromatography on silica gel using CH_2Cl_2–pentane (1:8) as eluent afforded a weak yellow and a strong red band. From the yellow band, crystals of $[H_4Ru_4(CO)_8(PCy_2)_4]$ (**2**, 12 mg, 8.45 μmol, 7%) were obtained by crystallisation from CH_2Cl_2–CH_3OH. IR (pentane): ν(CO) 2018vs, 1971m, 1963 (sh) cm^{-1}. ${}^1H$ NMR (C_6D_6): δ 1.03–2.83 (88 H, m, C_6H_{11}), −17.70 (4 H, dt, μ-H). ${}^{31}P$ NMR (C_6D_6): δ 151.1 (s); FAB MS: *m/z* 1421 (1420 based on ${}^{101}Ru$) (Found: C, 47.05; H, 6.61. Calc. for $C_{56}H_{92}O_8P_4Ru_4$: C, 47.32; H, 6.52%). The red band gives, upon extraction with CH_2Cl_2 and crystallisation from CH_2Cl_2–hexane, red crystals of $[H_5Ru_4(CO)_8(PCy_2)_3]$ (**3**, 85 mg, 70 μmol, 56%). IR (hexane): ν(CO) 2046 (sh), 2025vs, 1981m, 1970 (sh) cm^{-1}. ${}^1H$ NMR ($CDCl_3$): δ 1.06–2.36 (66 H, m, C_6H_{11}), −7.46 (1 H, t, 20), −13.76 (2 H, t, 15), −17.02 (1 H, t, 9.3 Hz), −18.04 (1 H, m). ${}^{31}P$ NMR 216.6 (d, ${}^2J_{PP} = 105$), 196.6 (t, ${}^2J_{PP} = 105$ Hz) (Found: C, 43.35; H, 5.80. Calc. for $C_{44}H_{71}O_8P_3Ru_4$: C, 43.13; H, 5.84%).

The analogous reaction of $[Ru_2(CO)_4(O_2CMe)_2(PCy_2H)_2]$ gives the same compounds **2** (yield 5%) and **3** (yield 46%).

Crystal structure of complex 2

A yellow crystal of compound **2** was mounted on a Stoe-Siemens AED2 four-circle diffractometer. Intensity data were measured using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) at −50 °C. The ω–2θ scan technique was used to a maximum 2θ value of 45°. The cell parameters were determined from a least-squares treatment of the setting angles of 24 reflections with 14.0 < θ < 21.0°. The intensity of one representative reflection was measured every 60 min. During data collection the intensity of the standards decreased by less than 1%. A semiempirical absorption correction was supplied using ψ scans ($T_{min} = 0.42$, $T_{max} = 0.51$).

The structure was solved by direct methods using the program SHELXS 86[16] and refined by full-matrix least squares on F^2 with SHELXL 97.[17] The positions of the four hydrides were derived from Fourier-difference maps, while the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL 97[17] default parameters. One distorted molecule of dichloromethane (four chlorine positions with an occupancy of 0.5 were derived), 0.5 molecule of water and 0.5 molecule of methanol per asymmetric unit was found in the molecular structure of **2**. The hydrogen atoms of the water molecule were found and fixed in their positions, while the remaining hydrogen atoms of the solvent molecules were included in calculated positions and refined as riding atoms using SHELXL default parameters.

Crystallographic details are given in Table 3 and significant bond lengths and angles are listed in Table 1. The figures were drawn with SCHAKAL.[18]

Crystal structure of complex 3

A red crystal of compound **3** was mounted on a Stoe Imaging Plate diffractometer System (Stoe & Cie, 1995) equipped with a one circle φ goniometer and a graphite-monochromator. Data collection was performed at −50 °C using Mo-Kα radiation (λ = 0.710 73 Å). 120 Exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with 0 < φ < 120° and with crystal oscillating through 0.5° in φ. The resolution was D_{min}–D_{max} 12.45–0.81 Å.

The structure was solved by direct methods using the program SHELXS 86[16] and refined by full-matrix least squares on F^2 with SHELXL 97.[17] The structure is pseudo-centrosymmetric as indicated by the Calc ADDSYM subroutine in PLATON,[19] which indicates the presence of a centre of symmetry at 0.0, 0.5, 0.25. All attempts to solve the structure in the centrosymmetric space group *Pnma* failed. The structure solution and refinement in the non-centrosymmetric space group

Table 3 Crystal data and data collection parameters for complexes **2** and **3**

	2	**3**
Formula	$C_{56}H_{92}O_8P_4Ru_4{\cdot}CH_2Cl_2{\cdot}0.5H_2O{\cdot}0.5CH_3OH$	$C_{44}H_{71}O_8P_3Ru_4{\cdot}CH_2Cl_2$
M	1531.41	1310.12
Crystal size/mm	0.53 × 0.46 × 0.19	0.25 × 0.20 × 0.20
T/K	223(2)	223(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
Colour	Yellow	Red
a/Å	13.505(5)	32.536(1)
b/Å	14.968(6)	14.362(1)
c/Å	16.933(5)	11.495(1)
α/°	89.82(3)	
β/°	80.21(3)	
γ/°	79.73(3)	
U/Å^3	3318(2)	5371.4(6)
Z	2	4
D_c/g cm^{-3}	1.533	1.620
μ/mm^{-1}	1.119	1.338
F(000)	1568	2648
θ Limits/°	1.56–22.5	2.17–22.5
Reflections measured	8684	12 405
Independent reflections	8684	5530 ($R_{int} = 0.027$)
Observed reflections	6634	4270
Goodness-of-fit on F^2	1.040	0.857
$R1$ [$I > 2\sigma(I)$], $R1$ (all data)	0.040, 0.060	0.027, 0.040
$wR2$ [$I > 2\sigma(I)$], $wR2$ (all data)	0.099, 0.1010	0.046, 0.048
Minimum, maximum residual electron density/e Å^{-3}	−0.986, 1.236	−0.385, 0.433

$Pna2_1$ was successful. The molecule possesses a pseudo-mirror plane which is perpendicular to the crystallographic mirror plane required for the centrosymmetric space group. The positions of the five hydrides were located from Fourier-difference maps and were refined with U_{iso} fixed at 0.02 Å^2. Their final coordinates were displaced from the observed positions by less than 0.05 Å. Two cyclohexyl rings [C(21)–C(26) and C(27)–C(32)] of the P(2) phosphine ligand are highly disordered. Distances and angles for their cyclohexyl rings were constrained to their theoretical values[20] with estimated standard deviations of 0.02 for the cycles C(27)–C(32) and C(27A)–C(32A) and 0.05 for the remaining disordered cyclohexyl rings, also the U_{eq} values were constrained to be equal in the rings. One molecule of dichloromethane per asymmetric unit was found in the molecular structure of **3**. No absorption correction was applied.

Crystallographic details are given in Table 3 and significant bond lengths and angles are listed in Table 2. The figures were drawn with SCHAKAL.[18]

CCDC reference number 186/1008.

See http://www.rsc.org/suppdata/dt/1998/2211/ for crystallographic files in .cif format.

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