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Two types of tetrasubstitution in $[H_4Ru_4(CO)_{12}]$: spectroscopic characterization and crystal structure determination of $[H_4Ru_4(CO)_8(PMe_2Ph)_4]$ and $[H_2Ru_4(CO)_9(PMe_2Ph)_4]$

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Abstract

Two tetrasubstituted tetranuclear ruthenium clusters containing dimethylphenylphosphine $[H_4Ru_4(CO)_8(PMe_2Ph)_4]$ and $[H_2Ru_4(CO)_9(PMe_2Ph)_4]$ were prepared and characterized spectroscopically as well as by X-ray crystallography. Both compounds show a structure based on the usual 60-electron tetrahedral framework with each ruthenium atom being bonded to one phosphine ligand. In the case of the nonacarbonyl derivative, one of the ruthenium atoms has one terminal carbonyl groups and is also bonded to two semibridging carbonyl groups; two other metal–metal bonds are bridged by the hydride groups. In the case of the octacarbonyl compound all the ruthenium atoms are bonded to two terminal carbonyls and to two bridging hydrides. NMR spectroscopical information of $[H_4Ru_4(CO)_8(PMe_2Ph)_4]$ suggests the presence of two isomers in solution which we propose to have D_{2d} and C_s symmetries. The observation of the NMR properties gives some observations about conditions that favour coupling between substituents in different ruthenium atoms.

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1. Introduction

The chemistry of $[H_4Ru_4(CO)_{12}]$ has been studied in some detail [1] and several phosphine-substituted products have been prepared and characterized spectroscopically and structurally [2–4]. Substitution of carbonyl groups in cluster compounds with phosphorous ligands allows the introduction of some modifications in the electron density distribution in the cluster depending on the donor–acceptor abilities of the ligand [5]. The importance of tuning electronic properties of metal clusters has been discussed in the context of the role they could play in materials chemistry [6,7]. On the other hand, an additional tetranuclear hydrido ruthenium cluster $[H_2Ru_4(CO)_{13}]$ has been isolated and characterized [8,9] and thus these two compounds provide an entry into the study of the properties of both derivatives. However, to our knowledge, there is only one preliminary report of a monosubstituted derivative of the dihydride compound [10] and this was not fully characterized. This is not the case with tetrasubstituted derivatives of formula [H₄Ru₄(CO)₈L₄] where the crystal structure of the trimethyl phosphite compound has been described and shows a D_{2d} symmetry [11]. As part of a study on the chemistry of substituted metal clusters we now report the synthesis, spectroscopic characterization and structural determination of $[H_4Ru_4(CO)_8(PMe_2Ph)_4]$ (compound 1) and $[H_2Ru_4(CO)_0(PMe_2Ph)_4]$ (compound 2) which enables us to make a comparison between both types of structures having the same substituent. In addition, the analysis of NMR data allows the observation of how hydride or carbonyl bridges affect coupling between substituents in different ruthenium atoms. Results are described herein.

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2. Results and discussion

The reaction of $[H_4Ru_4(CO)_{12}]$ with an excess of PMe₂Ph in the presence of one equivalent of Me₃NO yields the products which result from substitution of three [13] or four carbonyl groups by the phosphine, compound **1**, and a small amount of $[H_2Ru_4(CO)_9 (PMe_2Ph)_4]$ (compound **2**), which could be considered a product from the carbonyl substitution of $[H_2Ru_4 (CO)_{13}]$.¹ Attempts to increase the yield of **2** by changing

temperature and pressure conditions or to prepare it through substitution reactions of $[H_2Ru_4(CO)_{13}]$ were not successful. However, we managed to obtain spectroscopic information of both compounds.

Both spectroscopic [14] and structural [11] studies of $[H_4Ru_4(CO)_8{P(OMe)_3}_4]$ show this compound to have the usual tetrahedral 60-electron cluster structure with one phosphite bonded to each ruthenium atom. We thus expected to have the same structure in the case of compound 1. The NMR spectra were obtained from solutions prepared with crystals of the compound obtained both at room temperature and at low temperature. The symmetry present in this structure would predict the presence of one signal in both the ³¹P NMR spectrum and in the hydride zone of the ¹H NMR spectrum. However, the ³¹P NMR spectum of the crystals obtained at room temperature showed two singlets, one more intense than the other and when the coupled spectrum was obtained, one of the signals became wider while the other (the smaller one) split into a septuplet.

The presence of two types of phosphine is confirmed when an analysis of the methyl zone of the spectrum is carried out. Once again there are two signals, one is a doublet $({}^{2}J({}^{1}H-{}^{31}P) = 9 Hz)$ while the other one shows a virtual triplet, similar to the one described for the trimethyl phosphite derivative [14] as can be appreciated in Fig. 1. This coupling pattern would thus be the result of the coupling of the methyl protons with two phosphorus atoms; one is the one to which the methyl group is directly bonded and the other is the one found in a pseudotrans position to this, $|{}^{2}J({}^{1}H-{}^{31}P) + {}^{5}J({}^{1}H-{}^{31}P)| = 7.4 Hz$. The relative intensities of the two signals are 10:24.



Fig. 1. Methyl zone of the ${}^{1}H$ NMR spectrum of the mixture of isomers present in the crystals of compound 1 obtained at room temperature.

¹ Synthesis of $[H_4Ru_34(CO)_8(PMe_2Ph)_4]$ (1) and $[H_2Ru_4(CO)_9]$ $(PMe_2Ph)_4$] (2). $[H_4Ru_4(CO)_{12}]$ [12] (0.131 g, 0.1759 mmol) was dissolved in 45 ml of dichloromethane and the flask was placed in an ultrasound bath, PMe₂Ph (126 µl, 0.8802 mmol) was then added. Afterwards a solution of Me₃NO (0.0132 g, 0.1757 mmol) in 53 ml of CH₃CN was added dropwise. The reaction mixture was kept under the action of utrasound for 3 h after which the solvent was removed under vacuum. The reaction mixture is purified by column chromatography (1.5:1; hexane:dichloromethane) to yield $[H_4Ru_4(CO)_9(PMe_2Ph)_3]$ (52.4% yield), [H₄Ru₄(CO)₈(PMe₂Ph)₄] (9.6% yield) and [H₂Ru₄ $(CO)_{9}(PMe_{2}Ph)_{4}$] (4.5% yield). The yield of compound 1 can be increased to over 30% yield if the reaction, carried out as described above, is stopped after 90 min, the solvent volume reduced and another 2.5 equivalents of phosphine and another equivalent of Me₃NO are added and the reaction mixture is maintained for another 2 h in the ultrasound bath. Spectroscopic data for 1: IR v_{CO} (cm⁻¹, in hexane): 2057(w), 2044(w), 2020(w), 2004(w), 1977(vs), 1969(vs) and 1946(m). ¹H NMR (in CDCl₃): -16.69(tt, $J({}^{1}\text{H}{-}{}^{31}\text{P}) = 7.2$ Hz), δ H(Ph) = 7.45 (m), $\delta H(Me, C_s) = 1.86$ (d, ${}^{2}J^{1}H^{-31}P = 9$ Hz), $\delta H(Me, D_{2d}) = 1.72$ (virtual triplet, $|({}^{2}J^{1}H-{}^{31}P) + ({}^{5}J^{1}H-{}^{31}P)| = 7.4$ Hz), ${}^{31}P$ NMR (in CDCl₃): 2.03(s, D_{2d}), 1.17(s, C_s), ${}^{31}P({}^{1}H) = 1.99(s)$, -1.22(sept), ${}^{13}C$ NMR (in CDCl₃): δ (CO, D_{2d}) = 200.75 (virtual triplet, $|J|^{13}$ Ci– $^{31}P) + J(^{13}Ci^{-31}P) = 7.32$ Hz), aromatics: $\delta(Ci, C_s) = 140.78$ (d, ${}^{1}J({}^{31}P{-}^{13}Ci) = 43.32 \text{ Hz}), \quad \delta(Cp, C_s) = 129.17 \quad (d, {}^{2}J({}^{13}C{-}^{31}P) = 129.17 \text{ Hz})$ 2.17 Hz), $\delta(\text{Ci}, \text{D}_{2d}) = 143.14$ (complex, $|(J^{13}\text{Ci}-^{31}\text{P} + J^{13}\text{Ci}-^{31}\text{P})| =$ 37.3 Hz), $\delta(Cp) = 128.63(s, br)$, $\delta(Co, D_{2d}) = 128.8$ (complex, $|J({}^{13}\text{Co}{}^{-31}\text{P}) + J({}^{13}\text{Co}{}^{-31}\text{P})| = 10.18 \text{ Hz}), \ \delta(\text{Cm}, \text{D}_{2d}) = 128.52 \text{ (com$ plex, $|J({}^{13}\text{Cm}{}^{-31}\text{P}) + J({}^{13}\text{Cm}{}^{-31}\text{P})| = 8.68 \text{ Hz}$, methyl: $\delta(\text{Me}, \text{C}_{\text{s}}) =$ 20.87 (d, ${}^{1}J({}^{31}P{}^{-13}C) = 29.1$ Hz), $\delta(Me, D_{2d}) = 22.47$ (complex, $|J({}^{13}C-{}^{31}P) + J({}^{13}C-{}^{31}P)| = 25.5$ Hz). FAB: 1185 uma. Microanalysis: C: 40.92(40.54)%, H: 4.12(4.08)%. Spectroscopic data for compound 2. IR v_{CO} (cm⁻¹, in hexane): 2058(w), 2044(w), 2020(m), 2004(s), 1988(m), 1980(m), 1962(m), 1950(m), 1942(m, sh). ^{1}H NMR (in CDCl₃): Hydrides: -18.49(tt, ${}^{2}J({}^{31}P{}^{-1}H) = 6.34$ Hz), $\delta(Me_{B}) = 1.94$ (s, br), $\delta(Me_{2A}) = 1.74(s, br), \ \delta(Me_{C}) = 1.61(s, br), \ \delta(Ph) = 7.39(m), \ ^{1}H$ NMR (in CDCl₃ at -30 °C) δ (Hydrides) = -18.69(tt, ²J(³¹P-¹H) = 5.86 Hz), $\delta(Me_B) = 1.97$ (d, ${}^{2}J({}^{31}P^{-1}H) = 9.77$ Hz), $\delta(Me_A) = 1.89$ (d, ${}^{2}J({}^{31}P-{}^{1}H) = 8.79$ Hz), $\delta(Me_A) = 1.69$ (d, ${}^{2}J({}^{31}P-{}^{1}H) = 7.81$ Hz), $\delta(\text{Me}_{\text{C}}) = 1.59 \text{ (d, } {}^{2}J({}^{31}\text{P}{-}^{1}\text{H}) = 8.79 \text{ Hz}), \ \delta(\text{Ph}) = 7.4(\text{m}). {}^{31}\text{P} \text{ NMR}$ (in CDCl₃): $\delta(P_B) = 14.55(s), \ \delta(2P_A) = 12.58(s), \ \delta(P_C) = -0.95(s);$ ³¹P NMR (at -30 °C, in CDCl₃): $\delta(P_B) = 15.44(t), \ \delta(2P_A) = 12.58(d, d)$ ${}^{3}J({}^{31}P-{}^{31}P) = 11.89$ Hz), $\delta(P_{B}) = -0.33(s); {}^{13}C$ NMR (in CDCl₃): carbonyls: 202.61(s, br); aromatics: δ 129.59(m), 128.7(m); methyls: $\delta(Me_C) = 21.97$ (d, ${}^{1}J({}^{31}P{}^{-13}C) = 26.22$ Hz), $\delta(Me_{A+B}) = 20.14$ (d, ${}^{1}J({}^{31}P{-}^{13}C) = 26.74$ Hz); ${}^{13}C$ NMR (at -30 °C, in CDCl₃): carbonyls: $\delta(4A) = 202.55(d, {}^{1}J({}^{31}P{}^{-13}C) = 5.5 \text{ Hz}); \ \delta(3B) = 203.95(s, br), \ \delta(3B) =$ $(2CO_{bridge}) = 197.96(s, br);$ aromatics: $\delta(Cp, Co, Cm) = 128.7(m),$ $\delta(Ci) = 142.27$ (d, ${}^{1}J({}^{31}P{}^{-13}C) = 40.9$ Hz), $\delta(Ci) = 141.52(d,$ ${}^{1}J({}^{31}P{-}^{13}C) = 34.66$ Hz), $\delta(Ci) = 140.21(d, {}^{-1}J({}^{31}P{-}^{13}C) = 43$ Hz); methyls: $\delta(Me_C) = 21.68$ (d, ${}^{1}J({}^{31}P{}^{-13}C) = 24.6$ Hz), $\delta(Me_B) =$ 17.83 (d, ${}^{1}J({}^{31}P-{}^{13}C) = 28.1$ Hz), $\delta(Me_{2A}) = 17.73$ (d, ${}^{1}J({}^{31}P-{}^{13}C) =$ 30.57 Hz). FAB: 1211 uma. Microanalysis: C=46.58(46.15)%, H = 5.29(5.12)%.





Heteronuclear (${}^{31}P{-}^{1}H$) irradiation experiments showed that the more intense ${}^{31}P$ signal is related to the more intense signals in the ${}^{1}H$ NMR spectrum and the same happens with the weaker signals in both spectra. The ${}^{13}C$ spectrum also shows two signals due to methyl groups, one doublet and a virtual triplet. The sample prepared with the crystals obtained at -10 °C only showed the more intense signals.

We believe this behaviour to be due to the existence of two isomers: a D_{2d} isomer mixed with a C_s isomer, the two isomeric types of structures already observed in monosubstituted $[H_4Ru_4(CO)_{11}L]$ derivatives [15] and which are shown in Scheme 1. Comparison of the spectra of 1 with those of $[H_4Ru_4(CO)_8{P(OMe)_3}_4]$ indicates that the more intense signals correspond to the



Scheme 2.

 D_{2d} isomer and the weaker signals are thus assigned to the Cs isomer. Virtual coupling is proposed to take place through one of the metal-metal bonds not bridged by a hydride. That coupling is not observed in the Cs isomer, where we propose the corresponding bond would be hydride-bridged. This behaviour could be explained by the fact that in the crystal structure results, P-Ru-Ru-P torsion angles in the hydride bridged metal-metal bonds fall in a range of 80.6-89.9° while those that involve a non-bridged metal-metal bond have torsion angle values of 31.17° and 40.2°. An analysis of the crystals obtained at room temperature shows the presence of two types of sample, with different unit cell dimensions. Unfortunately the quality of one of the types of crystals (presumably the C_s isomer) did not permit us to obtain the corresponding crystal structure.

The infrared spectrum of compound 2 shows it to have bridging carbonyl groups, similar to what is observed in $[H_2Ru_4(CO)_{13}]$ [8]. The NMR data of compound 2^{1} can be easily explained considering three types of phosphine ligands in the molecule where the three phosphorus signals in the ³¹P NMR spectrum obtained at room temperature do not show coupling between them. However, if the spectrum is obtained at -30 °C, the signal observed at higher frequency splits into a triplet while the central signal becomes a doublet and the third signal remains a singlet. This coupling pattern indicates that two of the phosphines are equivalent (P_A) while the two other ones are different $(P_B and$ $P_{\rm C}$) as shown in Scheme 2. The hydride signal appears as a triplet of triplets indicating coupling to all the phosphorus ligands. The methylic zone of the ¹H spectrum also supports the presence of three different phosphine groups although it has to be pointed out that if the spectrum is obtained at -30 °C, four doublets are

observed. Heteronuclear irradiation experiments suggest that the two signals assigned as bonded to P_A look as two doublets as a consequence of virtual coupling between the methyl groups of P_A with P_C . An analysis from the crystal structure results indicates that P-Ru-Ru-P torsion angles for the metal-metal bonds bridged by the carbonyl group have values of 9.92° and 9.95° while those bridged by the hydride groups have values of 64.03° and -67.97°. We believe that the phosphine groups involved in the virtual coupling are bonded to ruthenium atoms which have a semibridging carbonyl group between them (P_A and P_C).

3. Crystal structure results

Molecular plots for compounds 1 and 2² are shown in Figs. 2 and 3, respectively, and some selected bond lengths and angles are also reported there. Both compounds show the expected closo-tetrahedral 60-electron structure, but while in compound 1 we find the usual arrangement of four long, hydride bridged, and two short metal-metal bonds, in 2 the presence of the two semibridging carbonyl groups changes the distribution to two long (hydride-bridged), two short (CO bridged) and two intermediate (unbridged) metal-metal bonds. The phosphine groups are bonded one to each ruthenium atom. In the case of compound 1, the coordination sphere around each ruthenium atom is that of a



Fig. 2. Molecular structure of compound **1**. Selected bond lengths (Å) are Ru(1)–Ru(2) 2.9978(9), Ru(1)–Ru(3) 2.8009(6), Ru(1)–Ru(4) 3.0058(8), Ru(2)–Ru(3) 3.0126(6), Ru(2)–Ru(4) 2.7960(7), Ru(3)–Ru(4) 2.9775(6), Ru(1)–P(1) 2.3323(10), Ru(2)–P(2) 2.3339(11), Ru(3)–P(3) 2.3509(11) and Ru(4)–P(4) 2.3426(11).



Fig. 3. Molecular structure of compound **2**. Selected bond lengths (Å) and angles (°) are Ru(1)–Ru(2) 2.9689(10), Ru(1)–Ru(3) 2.7504 (9), Ru(1)–Ru(4) 2.9082(8), Ru(2)–Ru(3) 2.8271(10), Ru(2)–Ru(4) 2.9723(10), Ru(3)–Ru(4) 2.7537(9), Ru(1)–P(1) 2.350(2), Ru(2)–P(2) 2.330(2), Ru(3)–P(3) 2.338(2), Ru(4)–P(4) 2.346(2), Ru(1)–C(13) 2.384(9), Ru(3)–C(13) 1.953(10), Ru(3)–C(34) 1.970(9), Ru(4)–C(34) 2.326(8); O(13)–C(13)–Ru(1) 128.7(7), O(13)–C(13)–Ru(3) 153.3(7), O(34)–C(34)–Ru(3) 149.9(7) and O(34)–C(34)–Ru(4) 130.8(7).

² Crystal data and details of refinement. Compound 1: C₄₀H₄₈O₈ P_4Ru_4 , fw = 1184.94; cryst. size = $0.2 \times 0.12 \times 0.1$ mm; cryst. system: monoclinic; space group: P21/c; a = 15.252(3) Å, b = 14.757(3) Å, 1.721 M g/m³; $\mu = 1.483$ mm⁻¹; radiation: Mo-K α , $\lambda = 0.71073$ Å; 26; 2 Θ range: 6.82–55°; temp: 253(2) K; collected refl. = 132386; unique refl. = 10471; observed refl. $(F > 4\sigma(F)) = 8070; R_{int} = 0.1203;$ no. of variables = 529; GoF = 1.051; $R_{(4\sigma)} = 0.0349$; final wR2 (all data) = 0.0789; large res. peak = 0.867 e/Å³. Compound **2**: $C_{47}H_{58}O_9P_4Ru_4$, fw = 1295.09; cryst. size = $0.35 \times 0.21 \times 0.12$ mm; cryst. system: triclinic; space group: P-1; a = 10.3078(6) Å, b =15.7447(10) Å, c = 17.4434(11) Å, $\alpha = 75.500(2)^{\circ}$, $\beta = 99.10(3)^{\circ}$, $\gamma =$ $80.110(2)^{\circ}$; V = 2647.2(3) Å³; Z = 2; $\rho_{calcd.} = 1.625$ M g/m³; $\mu = 1.290$ mm⁻¹; radiation: Mo-K α , $\lambda = 0.71073$ Å; F(000) = 1296; index range: -12 > h > 12, -19 > k > 19, -20 > l > 21; 2 Θ range: 2.46-51.98°; temp: 293(2) K; collected refl. = 17568; unique refl. = 10368; observed refl. $(F > 4\sigma(F)) = 5420$; $R_{int} = 0.070$; no. of variables = 585; GoF = 0.864; $R_{(4a)} = 0.0551$; final wR2 (all data) = 0.1362; large res. $peak = 1.167 e/Å^3$. A molecule of cyclohexane is present in the asymmetric unit. In both compounds, hydrogen atoms from phenyl and methyl groups were fixed in idealized positions and their positions refined. Hydrogen atoms of the hydrides were localized in Fourier maps and their coordinates refined. Crystallographic data for compounds 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 198845 and 198846, respectively. Copies if 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.ac.uk, or http://www.ccdc.ac.uk).

distorted octahedron, as it had been observed in the trimethyl phosphite derivative [4]. In the case of compound 2, Ru(3), which is bonded to the two semibridging carbonyl and only one terminal carbonyl groups, shows angles with more different values from the ideal 90° or 180° expected in an ideal octahedron. This can be appreciated by comparing the one large (transoid) P-Ru-Ru angle sustained by each metal atom and which, for Ru(1), Ru(2) and Ru(4), have values of 167° and 170° while Ru(3) has two large angles of $143.00(7)^{\circ}$ and 149.28(8)°. This must be due to the larger steric bulk of the bridging carbonyl groups in comparison with that of the hydrides. The effect of the semibridging CO groups can also be appreciated by comparing the P-Ru-Ru-P torsion angles which have values close to 9° for the carbonyl bridged edge, to 65° for the hydride bridged and values of 2° and 160° for the non-bridged edges. The corresponding values for hydride bridged edges in compound 1 are closer to 80°, while those not bridged metal-metal bonds show P-Ru-Ru-P torsion angles of 31° and 40°.

There are no significant differences in the Ru–P bond lengths in either 1 or 2 and the values are also similar to what had been observed in $[H_4Ru_4(CO)_{11}(PMe_2Ph)]$ [15]. The semibridging nature of the two such CO groups in 2 can be appreciated by the two bond lengths observed for each CO (average values: 2.3545 Å for the longer bond and 1.961 Å for the shorter one).

It is important to point out that no evidence of a compound similar to 2 was obtained when $P(OMe)_3$ or $P(OEt)_3$ was used. Neither did we observe the presence of more than one isomer in the $[H_4Ru_4(CO)_8L_4]$ derivatives with the phosphites as ligands. The monosubstituted derivative $[H_4Ru_4(CO)_{11}(PMe_2Ph)]$ also shows a different structure from that derived from $P(OMe)_3$ or $P(OEt)_3$. This could be an effect of the cone angle shown by PMe_2Ph (122°) intermediate between the value for $P(OEt_3)$ (109°) and the corresponding values in PPh₃ (145°), a phosphine also used in reactivity studies of these systems [2]. Puga et al. [16] proposed that the stability of the C_s isomer in the $[H_4Ru_4(CO)_{10}(diphos$ phine)] systems they studied was due to the preference of the hydrides to be located as close as possible to the electron donating alkyl-substituted phosphine. This no longer stands for the tetrasubstituted systems since all

four ruthenium atoms are bonded to a phosphine group therefore suggesting that steric reasons could be the important factor affecting the relative stability of these systems.

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