Polyoxoanion-supported, Atomically Dispersed Cyclooctadieneruthenium(II) Complexes*

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The cation $[Ru(C_8H_{12})]^{2+}$ was supported on $[P_3O_9]^{3-}$, $[V_4O_{12}]^{4-}$ and $[Nb_2W_4O_{19}]^{4-}$ polyoxoanions. All the complexes were stable in air and were characterized by elemental and thermogravimetric analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy. The crystal and molecular structure of $[NBu_4][Ru(C_8H_{12})(MeCN)(P_3O_9)]\cdot Et_2O$ has been determined [space group *C2/c*, *a* = 38.359(4), *b* = 9.907(5), *c* = 26.437(3) Å, β = 127.720(4)°]. Ruthenium(II) is octahedrally co-ordinated to the two C_8H_{12}-diene groups, to one acetonitrile molecule and through three O atoms to the $P_3O_9^{3-}$ ligand. In the case of $[Ru(C_8H_{12})(MeCN)_2(HV_4O_{12})]^-$ and $[Ru(C_8H_{12})(MeCN)_2(V_4O_{12})]^{2-}$ where a bidentate co-ordination to the polyanion is observed, two MeCN molecules are co-ordinated by Ru, resulting in the 18-valence-electron configuration. The $[Nb_2W_4O_{19}]^{4-}$ anion behaves differently: its reaction with $[RuCl(C_8H_{12})(MeCN)_3]PF_6$ leads to a product which, on the basis of IR, elemental analysis and the literature, we formulate as $[NBu_4]_3[\{RuCl(C_8H_{12})(MeCN)\}_5(Nb_2W_4O_{19})_2]\cdot 3H_2O$. In this case two $Nb_2W_4O_{19}^{4-}$ anions are probably linked, face to face, by five organometallic centres.

Although the importance of the oxygen–metal interaction in heterogeneous catalysis is well recognized, very little is known about how an O-donor ligand affects organometallic chemistry and homogeneous catalysis.[1] The exhibition of heterogeneous catalysis by atomically dispersed organometallic fragments supported on oxide surfaces is promising[2] if we consider *e.g.* the results obtained by Siedle and co-workers[3] in the solid-state C–H bond-activation reactions of the complex $[\{IrH_2(PPh_3)_2\}_3PW_{12}O_{40}]$; here the organometallic fragment is only held as a cationic species (not supported, *i.e.* covalently bonded) in a matrix comprised of anionic molecular metal oxide clusters.

Polyoxoanions as soluble models of solid metal oxides[4] are now receiving attention in the literature as supporting materials for organometallic catalytically active moieties.[5] For such systems the composition and structure of the active site can be determined;[6] generally they present only one type of active site, thus facilitating comprehension of the catalytic process and the design of new catalytic systems.

Here we report on polyoxoanion-supported ruthenium(II) complexes; as polyoxoanions we chose $[P_3O_9]^{3-}$, $[V_4O_{12}]^{4-}$ and $[Nb_2W_4O_{19}]^{4-}$ because they offer sufficient anionic charge density for the transition metal.[7] As organometallic fragment we chose $Ru^{II}(C_8H_{12})$; ruthenium(II) shows extensive application in the homogeneous catalysis of many different reaction types.[8] The ligand C_8H_{12} being not very tightly bound to the metal (also relevant to the possible formation of an allylic system[9]) can greatly enhance the catalytic properties of the metal centre.

Experimental

Reagents.—Acetonitrile, methylene chloride and ethanol were distilled from CaH_2 under N_2. Diethyl ether was distilled from sodium–benzophenone under N_2. The compounds $[RuCl(C_8H_{12})(MeCN)_3]PF_6$,[10] $[NBu_4]_3[P_3O_9]$,[7d] NBu_4VO_3[7g] and $[NBu_4]_4[Nb_2W_4O_{19}]$[7b] were prepared according to the literature methods; $[NBu_4]_3[HV_4O_{12}]$ is obtained by alkalinization of a MeCN solution of $[NBu_4]_4[V_{10}O_{26}]$ with NBu_4OH in 40% water in the ratio 1 : 5. All manipulations were carried out in air. The products are hygroscopic and the water content determined by thermal gravimetric analysis (TGA) (loss at low temperature) is not really significant. Elemental analyses (C,H,N) were performed either by the Servizio Microanalitico, Area della Ricerca di Roma, Consiglio Nazionale delle Ricerche (CNR), or by H. Malissa Analitische Laboratorien, Elbach, Germany (other elements).

Physical Measurements.—Thermal gravimetric analysis was carried out under dry nitrogen on a Stanton-Redcroft STA-781 thermoanalyser. Infrared spectra were recorded on a Perkin Elmer 983-G spectrometer, ^1H, ^{13}C and ^{31}P NMR spectra by the Servizio NMR, Area della Ricerca di Roma, CNR, using a Bruker WP-200 spectrometer operating at 200, 50.3 and 81 MHz respectively.

Preparations.—$[NBu_4][Ru(\eta^4\text{-}C_8H_{12})(MeCN)(P_3O_9)]\cdot Et_2O$ **2**. A solution of $[RuCl(C_8H_{12})(MeCN)_3]PF_6$ (0.55 g, 1.1 mmol) in EtOH (20 cm³) was added dropwise to a stirred solution of $[NBu_4]_3[P_3O_9]\cdot 2.5H_2O$ (1.1 g, 1.1 mmol) in EtOH (4 cm³). After 20 min of stirring at 80 °C and overnight refrigeration, the by-product NBu_4PF_6 was filtered off (320 mg, 77% compared to PF_6^-). Diethyl ether was added to the alcoholic solution until a supernatant cloudy layer was formed, and bright yellow X-ray-quality crystals appeared within 1 h. When removed from its mother-liquors, complex **2** loses its crystallinity due to the replacement of the molecule of diethyl ether by a molecule of water (Found: C, 41.55; H, 7.10; N, 3.55; P, 12.75; Ru, 13.90. Calc. for $C_{26}H_{51}N_2O_9P_3Ru\cdot H_2O$: C, 41.80; H, 7.15; N, 3.75; P, 12.45; Ru, 13.50%). TGA: 70 °C, −2.36% (calc.: H_2O, 2.41%); 180 °C, −5.5% (calc.: MeCN, −5.7%). IR(KBr pellet, 1350–500 cm⁻¹): 1302vs, 1279vs, 1129vs, 992w, 956vs, 941s, 885vw, 772s, 742vw, 722vw 703m, 552s and 534m cm⁻¹. NMR(CD_2Cl_2, 22 °C): ^1H (200 MHz), δ 4.18 (m, 2, CH), 4.05 (m, 2, CH), 2.55 (m, 2, CH_2), 2.24 (m, 2, CH_2), 2.05 (m, 2, CH_2) and 1.95 (m, 2, CH_2) (all C_8H_{12}); 2.65 (s, 3, CH_3, MeCN);

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3.18 (m, 8), 1.65 (m, 8), 1.42 (m, 8) and 1.01 (m, 12) (all NBu_4); ^{13}C, δ 92.73 (CH), 86.85 (CH), 30.13 (CH_2) and 28.74 (CH_2) (all C_8H_{12}); 59.53 (CH_2), 24.55 (CH_2), 20.38 (CH_2) and 14.12 (CH_3) (all NBu_4); 128.07 (CN) and 6 (CH_3) (MeCN); ^{31}P (H_3PO_4, reference), δ −7.73 (d, $^2J_{PP}$ 21) and −10.44 (t, $^2J_{PP}$ 21 Hz); δ −20.66 (free $P_3O_9{}^{3-}$).

If instead an excess of diethyl ether was added to the alcoholic solution a tacky solid or oil separated which solidified to a light brown powder upon washing with diethyl ether (3 × 20 cm^3) and scratching with a spatula. This solid was identified as a mixture of the chlorinated intermediate $[RuCl(C_8H_{12})(MeCN)(P_3O_9)]^{2-}$ **1** and complex **2**. Attempts to obtain the pure intermediate proved unsuccessful. The elemental analysis revealed the presence of Cl. IR(KBr pellet, 1500–500 cm^{-1}): 1484s, 1462s, 1382m, 1302s, 1283s, 1132s, 1107s, 986s, 948s, 884w, 834w, 771s, 705s, 558s and 535 cm^{-1}. NMR: ^1H[200 MHz, $(CD_3)_2CO$, 22 °C], δ 4.1 (m), 2.8 (m) and 1.8 (m) (br, C_8H_{12}); ^{31}P(CD_2Cl_2, 22 °C), δ −7.73 (d, $^2J_{PP}$ 21), −8.50 (d, $^2J_{PP}$ 24.5), −10.44 (t, $^2J_{PP}$ 21) and −20.96 (t, $^2J_{PP}$ 24.5 Hz).

$[NBu_4][Ru(C_8H_{12})(MeCN)_2(HV_4O_{12})]\cdot H_2O\cdot 0.5MeCN$ **3**. To a stirred solution of $[NBu_4]_3[HV_4O_{12}]\cdot H_2O$ (0.150 g, 0.133 mmol) in MeCN (3 cm^3) was added a solution of $[RuCl(C_8H_{12})(MeCN)_3]PF_6$ (0.065 g, 0.127 mmol) in MeCN (2 cm^3). After stirring for 1 h at room temperature (r.t.) the light brown product was precipitated upon addition of Et_2O, washed several times with Et_2O and dried. Yield: 65 mg, 50% compared to $[NBu_4]_3[HV_4O_{12}]$ (Found: C, 36.00; H, 5.95; N, 5.20; Ru, 10.25; V, 21.35. Calc. for $C_{29}H_{58.5}N_{3.5}O_{13}RuV_4$: C, 35.95; H, 6.10; N, 5.05; Ru, 10.45; V, 21.05%). TGA: 35 °C, −1.76% (calc.: H_2O, −1.86%); 70 °C, −2.17% (calc.: 0.5 MeCN, −2.15%). IR(KBr pellet, 1000–700 cm^{-1}): 975m, 934s, 895w, 836 (br) and 722 s cm^{-1}. NMR: $^1H[(CD_3)_2SO$, 22 °C], δ 4.6, 4.4 (m, 4, CH), 2.5 (m, 4, CH_2) and 2.2 (m, 4, CH_2) (all C_8H_{12}); 2.85 (s, 3) and 2.81 (s, 3) (MeCN); 3.18 (m, 8), 1.6 (m, 8), 1.3 (m, 8) and 0.95 (t, 12) (all NBu_4); $^{13}C[(CD_3)_2SO$, 22 °C], δ 110.39 (CH), 92.22 (CH), 29.68 (CH_2) and 28.30 (CH_2) (all C_8H_{12}); 58.41 (CH_2), 23.94 (CH_2), 20.09 (CH_2) and 14.37 (CH_3) (all NBu_4): 131.31 (CN), 129.28 (CN), 5.16 (CH_3) and 2.05 (CH_3) (all MeCN).

Alternatively, use of NBu_4VO_3 instead of $[NBu_4]_3[HV_4O_{12}]$ and work-up of the reaction as before gave $[NBu_4]_2[Ru(C_8H_{12})(MeCN)_2(V_4O_{12})]\cdot H_2O$ **4**. Proton NMR spectroscopy showed a fluxional behaviour of the complex in CD_2Cl_2 down to low temperatures (−80 °C) (Found: C, 43.25; H, 7.90; N, 2.60; Ru, 9.35; V, 18.25. Calc. for $C_{40}H_{86}N_2O_{13}RuV_4$: C, 43.35; H, 7.75; N, 2.55; Ru, 9.15; V, 18.45%). TGA: 50 °C, −1.63% (calc.: H_2O, −1.63%). IR(KBr pellet, 1000–700 cm^{-1}): 965s (sh), 950s, 920 (sh), 860w, 807m, 795m, 774m and 705w cm^{-1}.

$[NBu_4]_3[\{RuCl(C_8H_{12})(MeCN)\}_5(Nb_2W_4O_{19})_2]\cdot 3H_2O$ **5**. A solution of $[NBu_4]_4[Nb_2W_4O_{19}]\cdot 1.5H_2O$ (1.97 g, 0.90 mmol) in CH_2Cl_2 (10 cm^3) was added with stirring to a solution of $[RuCl(C_8H_{12})(MeCN)_3]PF_6$ (1.15 g, 2.25 mmol) in CH_2Cl_2 (8 cm^3). The colour immediately turned red-brown. The mixture was gently heated and stirred for 1 h, then the solvent was evaporated, the product dissolved in MeOH (20 cm^3) and precipitated with diethyl ether (10 cm^3). The brown precipitate was washed three times with diethyl ether and dried (900 mg, 43% compared to $Nb_2W_4O_{19}{}^{4-}$) (Found: C, 24.70; H, 4.05; Cl, 3.65; N, 2.20; Nb, 7.80; Ru, 10.85; W, 31.25. Calc. for $C_{98}H_{189}Cl_5N_8Nb_2O_{41}Ru_5W_8$: C, 25.25; H, 4.10; Cl, 3.80; N, 2.40; Nb, 7.95; Ru, 10.85; W, 31.55%). TGA: 30 °C, −1.15% (calc.: $3H_2O$, −1.16%); 95 °C, −4.6% (calc.: 5MeCN, −4.45%). IR(KBr pellet, 1000–700 cm^{-1}): 952s, 909m, 820s (sh), 799s (br) and 730s (br) cm^{-1}. ^1H NMR[200 MHz, $(CD_3)_2SO$, 22 °C]: δ 5.3, 4.2, 2.9, 2.5 and 2.1 (br, all C_8H_{12}).

Crystallographic Data Collection and Structure Refinement.— Crystals of compound **2** contain one molecule of diethyl ether (detectable by ^1H NMR) spectroscopy which is lost very rapidly in air while the sample loses crystallinity. After many attempts a well formed yellow crystal, mounted in a glass capillary in the presence of its mother-liquor, was found suitable for X-ray analysis and was used for collecting the entire set of reflections. The intensities were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-Kα radiation and 12 kW rotating-anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $39 < 2\theta < 40°$. The data were collected using the ω–2θ scan technique to a maximum 2θ of 120.30°. Weak reflections $[I < 10\sigma(I)]$ were rescanned (maximum of two rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time to the background counting time was 2 : 1. Of the 6425 reflections collected, 6314 were unique (R_{int} = 0.130); equivalent reflections were merged. The intensities of three representative reflections, measured after every 50, remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Cu-Kα is 47.8 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.64 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $0.951\,88 \times 10^{-7}$). The crystallographic data are summarized in Table 1.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures with minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o{}^2)$. The hydrogen atoms were introduced into calculated positions and not refined. All the non-hydrogen atoms were allowed to vibrate anisotropically. The final cycle of full-matrix least-squares refinement was based on 3682 observed reflections $[I > 3\sigma(I)]$ and 420 variable parameters and converged (largest parameter shift was 0.56 times its e.s.d.) with unweighted and weighted agreement factors of R = 0.086 and R' = 0.129. Though these R values were not satisfactory, no further attempts were made to improve the refinement because of the poor quality of data and the presence of the disordered diethyl ether molecule which could not be located. The standard deviation of an observation of unit weight was 3.62. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to down-weight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map were at 1.15 and −4.24 e Å^{-3}, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_{calc};[12] the values for f' and f'' were those of Cromer.[13] All calculations were performed using the TEXSAN[14] package on a VAX Station 3520 computer. Final atomic parameters of the non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Synthesis and Spectroscopic Properties.—$[NBu_4][Ru(C_8H_{12})(MeCN)(P_3O_9)]\cdot H_2O$ **2**. Reaction of $[RuCl(C_8H_{12})(MeCN)_3]PF_6$ with $[NBu_4]_3[P_3O_9]$ in EtOH solution and subsequent displacement of Cl^- [equations (1) and (2)] results

$$[RuCl(C_8H_{12})(MeCN)_3]PF_6 + [NBu_4]_3[P_3O_9] \xrightarrow{-NBu_4PF_6} \underset{\mathbf{1}}{[NBu_4]_2[RuCl(C_8H_{12})(MeCN)(P_3O_9)]} \quad (1)$$

$$\mathbf{1} \xrightarrow{-NBu_4Cl} \underset{\mathbf{2}}{[NBu_4][Ru(C_8H_{12})(MeCN)(P_3O_9)]} \quad (2)$$

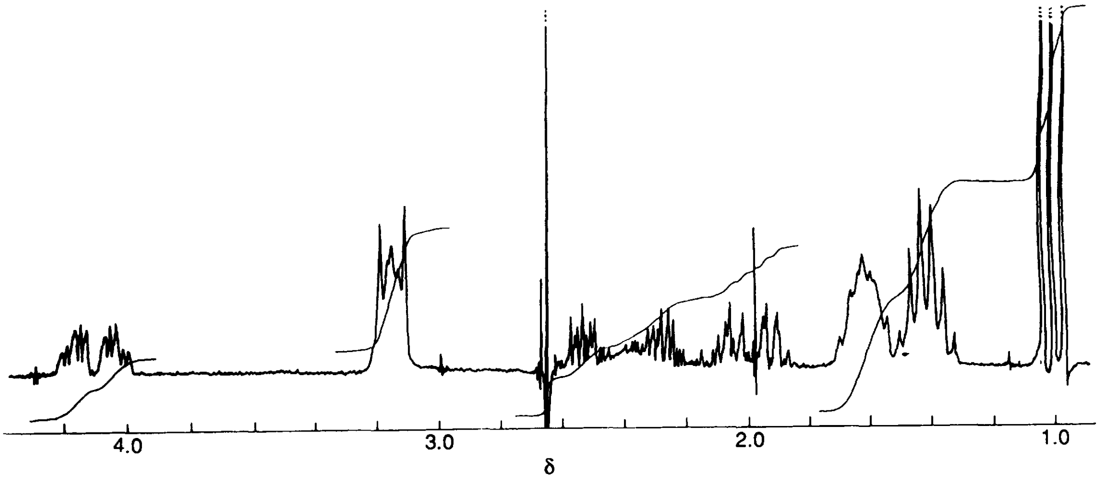

Fig. 1 Proton NMR spectrum of $[NBu_4][Ru(C_8H_{12})(MeCN)(P_3O_9)]\cdot Et_2O$ **2**

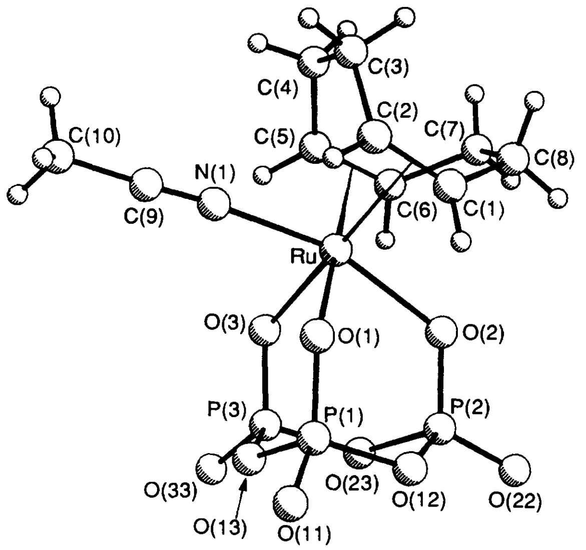

Fig. 2 A PLUTO[15] drawing of the complex anion $[Ru(C_8H_{12})(MeCN)(P_3O_9)]^-$ showing the atom numbering

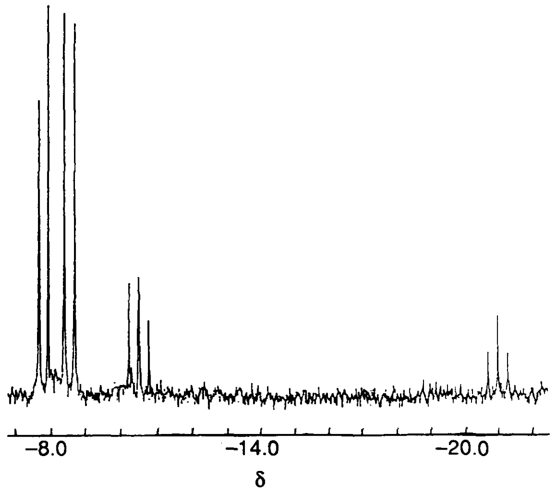

Fig. 3 The ^{31}P NMR spectrum of the mixture of complexes **1** and **2** (see Discussion)

in the formation of a few bright yellow prismatic crystals of complex **2**. Proton, ^{13}C, and ^{31}P NMR data are consistent with a tridentate co-ordination of the $P_3O_9{}^{3-}$ and a dihapto co-ordination of C_8H_{12} to Ru. The ^{31}P NMR spectrum shows two symmetry-non-equivalent types of phosphorus atoms in the ratio 2:1 forming an A_2B system; both signals are shifted to higher frequency relative to that of free $P_3O_9{}^{3-}$, denoting co-ordination to the metal. Proton (Fig. 1) and ^{13}C NMR measurements indicate two non-equivalent types of methyne cyclooctadiene groups and four signals, for the methylene C_8H_{12} groups. Co-ordination of acetonitrile to the metal is demonstrated by, besides its high-temperature dissociation from the metal (see Experimental section), the ^1H and ^{13}C NMR spectra, which exhibit a shift of the MeCN signals to higher frequency relative to the free molecule. The IR spectrum is comparable in the region 700–1300 cm^{-1}, where the P–O bonds are observed, to those of $[ML(P_3O_9)]^{n-}$ complexes [L = $(CO)_3$ or C_5Me_5; M = Mn, Re or Rh].[7d] In all cases complexation lowers the P–O stretching energy of the free ligand (979 cm^{-1}) by about 20–30 cm^{-1}. The similarity with the previous spectra, which correspond to a tridentate triphosphate ligand, suggests for the present compound an isostructural metal phosphate framework.

All these data support the octahedral symmetry typical of ruthenium(II) six-co-ordinated complexes,[8] and is confirmed by X-ray analysis (see below); the 18-valence-electron configuration is obtained through co-ordination to three P_3O_9 oxygen atoms (two equatorial, one axial) as found for example in $[NBu_4]_2[Ir(C_8H_{12})(P_3O_9)]$,[7e] to the axial MeCN molecule and to the two equatorial symmetry-equivalent cyclooctadiene double bonds (Fig. 2). In the case of $[Ir(C_8H_{12})(P_3O_9)]^{2-}$ the authors observed only one ^1H NMR signal for the two non-equivalent C_8H_{12} methine groups, whereas we found two. The intramolecular pseudo-rotation supposed in the case of the five-co-ordinated complex is prevented here owing to the presence of the MeCN molecule in the sixth co-ordination position.

When the reaction solution is treated with an excess of diethyl ether a tacky brown solid is obtained, which turns to a vitreous powder after scratching with a spatula and drying under vacuum. Its ^{31}P NMR spectrum shows an A_2B and an A_2X system (see Experimental section): no line broadening is observed suggesting that there is no exchange between the two systems (Fig. 3). The A_2B system denotes the presence of complex **2** (see Experimental section) where the organometallic fragment is *O*,*O*′,*O*″-coordinated to the triphosphate. The A_2X system indicates the presence of a *O*,*O*′-co-ordination; the chemical shift of X is very similar to that of the free ligand.

Support for the presence of a bidentate $P_3O_9{}^{3-}$ ligand is also given by the ^1H NMR spectrum in CD_2Cl_2, which is fluxional and shows broad multiplets in the CH and CH_2 regions of C_8H_{12}. A similar fluxional behaviour is exhibited by complex **4** where dihapto co-ordination of the tetravanadate ligand is well

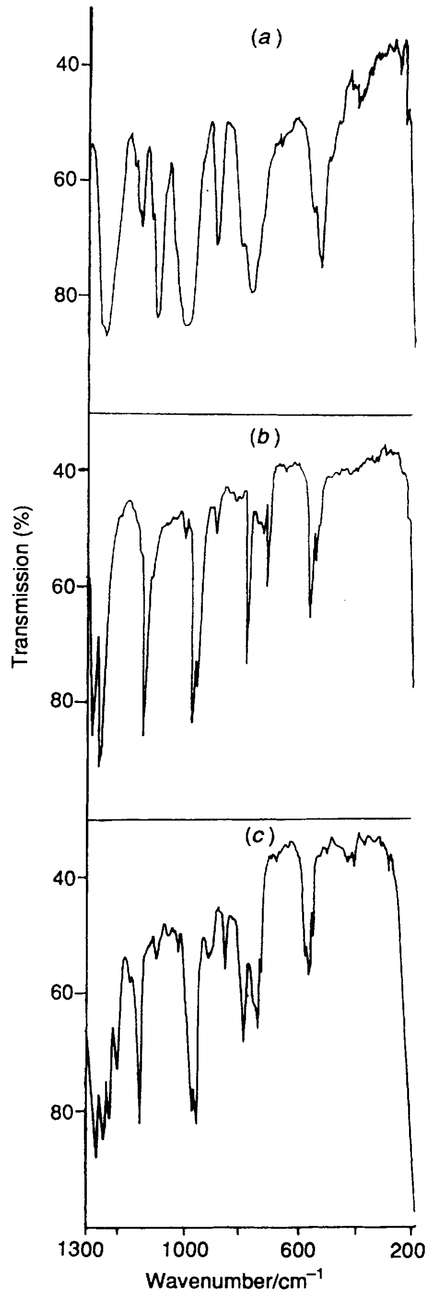

Fig. 4 Infrared spectra of (*a*) $[NBu_4]_3[P_3O_9]$, (*b*) complex **2**, and (*c*) the mixture of complexes **1** and **2**

Table 1 Crystallographic data for compound **2**

Molecular formula	$C_{26}H_{51}N_2O_9P_3Ru$
M	729.69
Crystal dimensions (mm)	0.450 × 0.300 × 0.400
Crystal system	Monoclinic
Space group	$C2/c$ (no. 15)
a/Å	38.359(4)
b/Å	9.907(5)
c/Å	26.437(3)
β/°	127.720(4)
U/Å^3	7947(6)
Z	8
D_c/g cm^{-3}	1.220
F(000)	3056
Radiation	Cu-Kα (λ = 1.541 78 Å)
Scan rate/° min^{-1}	32.00 (in ω)
Reflection/parameter ratio	8.77

established (see below). In addition the IR spectrum in the 700–1300 cm^{-1} region, Fig. 4(*c*), displays the same principal absorptions as those present in the spectrum of **2** with an additional band at 834 cm^{-1} also observed[7d] in the case of $[Rh(C_7H_8)(P_3O_9)]^{2-}$ where a bidentate triphosphate ligand was assumed. The presence of bi- and tri-dentate ligand molecules as well as the other experimental results suggest that this product is a mixture of complexes **1** and **2**. Unfortunately pure samples of the chlorinated intermediate could not be obtained and full characterization of complex **1** was not possible.

$[NBu_4][Ru(C_8H_{12})(MeCN)_2(HV_4O_{12})]\cdot H_2O\cdot 0.5MeCN$ **3**. This compound is obtained by reaction of the organometallic fragment $Ru(C_8H_{12})^{2+}$ with $[HV_4O_{12}]^{3-}$ whereas using $[VO_3]^-$ the complex $[NBu_4]_2[Ru(C_8H_{12})(MeCN)_2(V_4O_{12})]$ is formed. The differences observed in the IR spectra are due to the bent-ring configuration of HV_4O_{12}[7h] compared with the planar one of V_4O_{12}.[7g] In CD_2Cl_2 both compounds exhibit complex ^1H NMR spectra characteristic of fluxional behaviour: the signals of the C_8H_{12} but not the ones of free and co-ordinated MeCN, appear as broad bands down to −80 °C. The fluxional behaviour of compound **3** is attenuated in $(CD_3)_2SO$: the inequivalence of the two methine signals of C_8H_{12} is larger than for **2** (differences in the ^{13}C NMR are 12 and 6 ppm, respectively). The six-co-ordination of the ruthenium centre is completed by two oxygen atoms of the $V_4O_{12}{}^{4-}$ {bidentate co-ordination was also observed in the case of $[Ir(C_8H_{12})(V_4O_{12})]^{2-}$}. The enhanced mobility of the organometallic fragment on going from *O,O′,O″*- to *O,O′*-co-ordination significantly contributes to the solution fluxional behaviour of the compound.

$[NBu_4]_3[\{RuCl(C_8H_{12})(MeCN)\}_5(Nb_2W_4O_{19})_2]\cdot 3H_2O$ **5**. By reaction of $[NBu_4]_4[Nb_2W_4O_{19}]$ with $[RuCl(C_8H_{12})(MeCN)_3]PF_6$ in a CH_2Cl_2 solution complex **5** was obtained [equation (3)]. The elemental analyses are consistent with a 5:2

$$5[RuCl(C_8H_{12})(MeCN)_3]^+ + 2[Nb_2W_4O_{19}]^{4-} \longrightarrow [\{RuCl(C_8H_{12})(MeCN)\}_5(Nb_2W_4O_{19})_2]^{3-} \quad (3)$$

adduct and the IR spectrum is very similar to that of $[NBu_4]_3[\{Ir(C_8H_{12})\}_5(Nb_2W_4O_{19})_2]$[7e] and $[NBu_4]_3[\{Rh(C_7H_8)\}_5(Nb_2W_4O_{19})_2]$.[7a] Proton NMR measurements in CD_2Cl_2 showed a fluxional behaviour. In $(CD_3)_2SO$ two broad complex multiplets are observed for the CH groups of C_8H_{12} centred at δ 5.3 and 4.2 as observed for $[\{Ir(C_8H_{12})\}_5(Nb_2W_4O_{19})_2]^{3-}$. The anion is therefore assumed to have the C_{2v} structure where the two octahedral $Nb_2W_4O_{19}{}^{4-}$ anions are linked together in a face-to-face fashion by five organometallic centres, three of the five Ru atoms being bonded to doubly bridging ONbW or ONbNb oxygens and the other two to terminal ONb oxygen.

Crystal Structure of $[NBu_4][Ru(C_8H_{12})(MeCN)(P_3O_9)]\cdot Et_2O$ **2**.—The structure consists of $[Ru(C_8H_{12})(MeCN)(P_3O_9)]^-$ complex anions and $NBu_4{}^+$ cations. A perspective view of the complex anion is shown in Fig. 2 and bond lengths and angles with their standard deviations are given in Table 3. The Ru atom is six-co-ordinated by the three terminal oxygens of the tridentate triphosphate ligand, by the nitrogen atom of acetonitrile and by the double bonds of the chelating cyclooctadiene ligand in a distorted-octahedral geometry. The four Ru–C distances are within the range expected. They vary from 2.16(2) to 2.21(2) Å (average 2.18 Å), with distances from the metal to the midpoints of the co-ordinated double bonds of 2.07 and 2.08 Å.

The three Ru–O bond distances are equivalent (average 2.12 Å). They are shorter than the equatorial Rh–O bond distances [2.229(5), 2.231(5) Å] in the analogous five-co-ordinated

Table 2 Positional parameters

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.347 42(4)	0.077 0(1)	0.056 6(1)	C(8)	0.446(1)	0.068(4)	0.165(1)
P(1)	0.309 9(1)	−0.095 2(4)	−0.069 7(2)	C(9)	0.267(1)	−0.001(2)	0.053(1)
P(2)	0.371 3(2)	0.106(1)	−0.041 1(2)	C(10)	0.230(1)	−0.036(2)	0.050(1)
P(3)	0.285 4(2)	0.183 9(5)	−0.088 3(2)	N(2)	0.347 8(4)	−0.545(1)	0.324(1)
O(1)	0.326 1(3)	−0.097(1)	−0.001 8(4)	C(11)	0.344 9(5)	−0.432(2)	0.283(1)
O(2)	0.386 8(3)	0.116(1)	0.026(1)	C(12)	0.333(1)	−0.478(2)	0.217(1)
O(3)	0.299 7(3)	0.200(1)	−0.021 4(4)	C(13)	0.323(1)	−0.352(2)	0.176(1)
O(11)	0.291 5(4)	−0.214(1)	−0.110(1)	C(14)	0.312(1)	−0.391(2)	0.114(1)
O(12)	0.350 2(3)	−0.040(1)	−0.068 9(5)	C(21)	0.364 0(5)	−0.490(2)	0.387(1)
O(13)	0.275 1(3)	0.028(1)	−0.106 6(5)	C(22)	0.375(1)	−0.577(2)	0.439(1)
O(22)	0.403 1(4)	0.134(2)	−0.051(1)	C(23)	0.390(1)	−0.504(2)	0.498(1)
O(23)	0.328 8(4)	0.201(1)	−0.083 7(5)	C(24)	0.401(1)	−0.600(2)	0.533(1)
O(33)	0.249 7(4)	0.266(1)	−0.140(1)	C(31)	0.378(1)	−0.656(2)	0.334(1)
N(1)	0.295 8(4)	0.030(1)	0.057(1)	C(32)	0.425(1)	−0.618(2)	0.366(1)
C(1)	0.409(1)	−0.026(2)	0.129(1)	C(33)	0.451(1)	−0.738(3)	0.379(1)
C(2)	0.381(1)	−0.046(2)	0.143(1)	C(34)	0.499(1)	−0.700(4)	0.415(1)
C(3)	0.383(1)	0.028(3)	0.195(1)	C(41)	0.303 4(5)	−0.607(2)	0.293(1)
C(4)	0.365(1)	0.168(2)	0.182(1)	C(42)	0.265 3(5)	−0.507(2)	0.272(1)
C(5)	0.353(1)	0.229(2)	0.123(1)	C(43)	0.224 1(5)	−0.594(2)	0.250(1)
C(6)	0.386(1)	0.248(2)	0.116(1)	C(44)	0.185(1)	−0.499(2)	0.229(1)
C(7)	0.434(1)	0.218(4)	0.165(1)				

Table 3 Bond distances (Å) and angles (°) with standard deviations on the last significant figure in parentheses

Ru–O(1)	2.11(1)	C(1)–C(2)	1.36(2)	P(1)–O(13)	1.62(1)	C(11)–C(12)	1.56(2)
Ru–O(2)	2.13(1)	C(1)–C(8)	1.46(3)	P(2)–O(2)	1.50(1)	C(12)–C(13)	1.55(2)
Ru–O(3)	2.11(1)	C(2)–C(3)	1.52(3)	P(2)–O(12)	1.60(1)	C(13)–C(14)	1.47(2)
Ru–N(1)	2.05(1)	C(3)–C(4)	1.49(3)	P(2)–O(22)	1.43(1)	C(21)–C(22)	1.51(2)
Ru–MP(1)*	2.07	C(4)–C(5)	1.47(2)	P(2)–O(23)	1.60(1)	C(22)–C(23)	1.48(2)
Ru–MP(2)*	2.08	C(5)–C(6)	1.36(3)	P(3)–O(3)	1.50(1)	C(23)–C(24)	1.56(3)
Ru–C(1)	2.18(2)	C(6)–C(7)	1.51(4)	P(3)–O(13)	1.60(1)	C(31)–C(32)	1.51(2)
Ru–C(2)	2.17(2)	C(7)–C(8)	1.55(4)	P(3)–O(23)	1.60(1)	C(32)–C(33)	1.44(3)
Ru–C(5)	2.21(2)	C(9)–C(10)	1.41(2)	P(3)–O(33)	1.45(1)	C(33)–C(34)	1.53(3)
Ru–C(6)	2.16(2)	N(2)–C(11)	1.52(2)	N(1)–C(9)	1.09(2)	C(41)–C(42)	1.56(2)
P(1)–O(1)	1.50(1)	N(2)–C(21)	1.51(2)	C(1)–C(2)	1.36(2)	C(42)–C(43)	1.56(2)
P(1)–O(11)	1.45(1)	N(2)–C(31)	1.49(2)	C(1)–C(8)	1.46(3)	C(43)–C(44)	1.56(2)
P(1)–O(12)	1.63(1)	N(2)–C(41)	1.49(2)				
O(1)–Ru–O(2)	85.5(4)	O(3)–Ru–C(5)	89.4(6)	O(12)–P(2)–O(22)	109.8(8)	C(1)–C(8)–C(7)	116(2)
O(1)–Ru–O(3)	92.2(4)	O(3)–Ru–C(6)	93.3(7)	O(12)–P(2)–O(23)	101.5(6)	N(1)–C(9)–C(10)	177(2)
O(1)–Ru–N(1)	83.0(4)	O(3)–Ru–MP(1)*	177	O(22)–P(2)–O(23)	111.9(9)	C(11)–N(2)–C(21)	106(1)
O(1)–Ru–C(1)	89.3(6)	O(3)–Ru–MP(2)*	91	O(3)–P(3)–O(13)	107.5(6)	C(11)–N(2)–C(31)	112(1)
O(1)–Ru–C(2)	91.5(6)	N(1)–Ru–C(1)	115.1(6)	O(3)–P(3)–O(23)	106.6(6)	C(11)–N(2)–C(41)	110(1)
O(1)–Ru–C(5)	159.8(6)	N(1)–Ru–C(2)	79.4(6)	O(3)–P(3)–O(33)	120.1(7)	C(21)–N(2)–C(31)	111(1)
O(1)–Ru–C(6)	163.2(9)	N(1)–Ru–C(5)	77.2(6)	O(13)–P(3)–O(23)	100.5(6)	C(21)–N(2)–C(41)	111(1)
O(1)–Ru–MP(1)*	90	N(1)–Ru–C(6)	113.4(9)	O(13)–P(3)–O(33)	109.9(7)	C(31)–N(2)–C(41)	106(1)
O(1)–Ru–MP(2)*	175	N(1)–Ru–MP(1)*	97	O(23)–P(3)–O(33)	110.5(7)	N(2)–C(11)–C(12)	116(1)
O(2)–Ru–O(3)	85.3(4)	N(1)–Ru–MP(2)*	95	Ru–O(1)–P(1)	123.9(6)	C(11)–C(12)–C(13)	110(1)
O(2)–Ru–N(1)	163.2(4)	MP(1)–Ru–MP(2)*	85	Ru–O(2)–P(2)	125.1(6)	C(12)–C(13)–C(14)	111(2)
O(2)–Ru–C(1)	77.0(6)	O(1)–P(1)–O(11)	121.9(7)	Ru–O(3)–P(3)	124.2(6)	N(2)–C(21)–C(22)	115(1)
O(2)–Ru–C(2)	113.3(6)	O(1)–P(1)–O(12)	107.1(6)	Ru–N(1)–C(9)	174(1)	C(21)–C(22)–C(23)	111(2)
O(2)–Ru–C(5)	114.7(6)	O(1)–P(1)–O(13)	108.3(6)	C(2)–C(1)–C(8)	122(2)	C(22)–C(23)–C(24)	112(2)
O(2)–Ru–C(6)	79.1(8)	O(11)–P(1)–O(12)	108.3(6)	C(1)–C(2)–C(3)	124(2)	N(2)–C(31)–C(32)	117(1)
O(2)–Ru–MP(1)*	95	O(11)–P(1)–O(13)	108.6(6)	C(2)–C(3)–C(4)	118(2)	C(31)–C(32)–C(33)	110(2)
O(2)–Ru–MP(2)*	175	O(12)–P(1)–O(13)	100.5(6)	C(3)–C(4)–C(5)	116(2)	C(32)–C(33)–C(34)	110(2)
O(3)–Ru–N(1)	82.8(5)	O(2)–P(2)–O(12)	109.2(6)	C(4)–C(5)–C(6)	119(2)	N(2)–C(41)–C(42)	116(1)
O(3)–Ru–C(1)	162.1(6)	O(2)–P(2)–O(22)	116.4(7)	C(5)–C(6)–C(7)	128(2)	C(41)–C(42)–C(43)	107(1)
O(3)–Ru–C(2)	161.2(6)	O(2)–P(2)–O(23)	107.0(7)	C(6)–C(7)–C(8)	113(2)	C(42)–C(43)–C(44)	110(1)

* MP(1) is the midpoint of C(1)=C(2) and MP(2) of C(5)=C(6).

complex $[NBu_4]_2[Rh(C_7H_8)(P_3O_9)]$.[7d] The dimensions of the triphosphate ligand correspond to those found in $[NBu_4]_2[Rh(C_7H_8)(P_3O_9)]$[7d] and $[NBu_4]_2[Ir(C_8H_{12})(P_3O_9)]$.[7e] The three P–O(terminal) bond lengths average 1.46 Å, the three P–O bond lengths, with O bound to Ru, 1.53 Å and the six P–O bond lengths, with O bound to P, 1.60 Å. The angles at the P atoms are close to the tetrahedral values except for the larger O(terminal)–P–O_{Ru} angles which average 119.5° and the smaller O_P–P–O_P which average 100.8°.

The cyclooctadiene ligand has the usual 'tub' conformation. The C–C single-bond distances average 1.50 Å and the C(1)–C(2) and the C(5)–C(6) double bonds are equal to 1.36(2) and 1.36(3) Å with no apparent lengthening on co-ordination.

Conclusion

The aim of this work was the synthesis and characterization of $Ru(C_8H_{12})$ supported on polyoxoanions. As recent work has demonstrated, Ir-supported polyoxoanions are catalytically active both in hydrogenation and in oxygenation reactions of olefins.[5c,d] The polyoxoanion itself is highly resistant to oxidation but the organometallic polyoxoanion complex is very air-sensitive, a drawback not shown by ruthenium polyoxoanion-supported complexes. The [Ru(C_8H_8)(C_8H_{12})] complex has recently been used for the linear codimerization of butadiene and acetylene[16] and its derivatives have shown that they can undergo many hydrogen-transfer reactions.[17] They show however stability problems that could be overcome by the more stable Ru(C_8H_{12}) polyoxoanion derivatives. Further, we observed that the latter, when the anion is bidentate, are fluxional in solution: this property, as the recent literature has demonstrated, could have a great influence in enhancing their catalytic properties. Further studies are planned better to investigate their solution behaviour and test their catalytic properties.

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