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Synthesis and spectroscopic characterization of a Keggin α-1,4,9-trivanadium-substituted polyoxotungstate-supported $Cp^{*}Rh^{2+}$ complex, $[(Cp^{*}Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]^{4-}$

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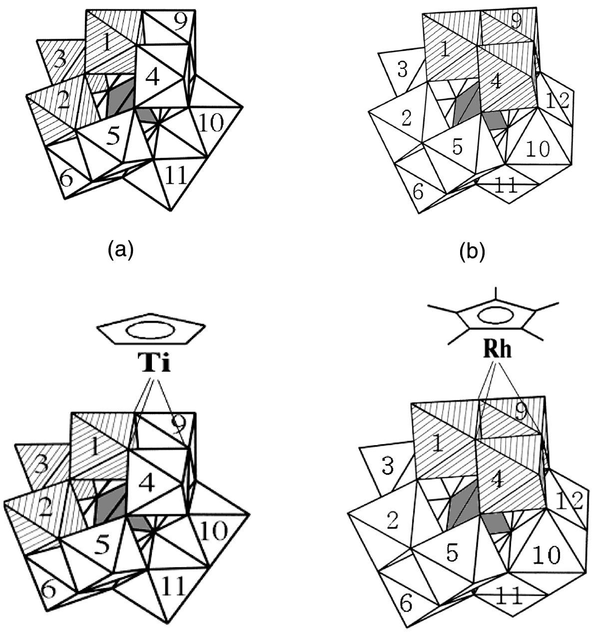
A novel Keggin polyoxotungstate-based 1 : 1-type $Cp^{*}Rh^{2+}$ complex ($Cp^{*} = C_5Me_5$), $[Cp^{*}Rh(DMSO)_3]$-$H_2[(Cp^{*}Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]\cdot 3DMSO\cdot 0.5MeCN$ **2**, was synthesized by reaction in MeCN–DMSO mixed solvent at 80 °C under nitrogen, of the α-Keggin-type 1,4,9-trivanadium-substituted polyoxotungstate $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ **1** with $[Cp^{*}Rh(MeCN)_3]^{2+}$. Characterization was performed with complete elemental analysis, TG/DTA, FTIR, and multiple (^{51}V, ^{31}P, ^{1}H and ^{13}C) NMR spectroscopies. Complex **2** contains two different types of $Cp^{*}Rh^{2+}$ groups; one is covalently bonded to the surface oxygen atoms of three edge-shared vanadium octahedra while the other is present as a DMSO-solvated counter ion. The composition of complex **2** is unique and can be compared with previous Keggin and Dawson polyoxotungstate-based organometallic complexes.



(a) (b)

(c) (d)

Fig. 1 Polyhedral representation of the Keggin polyoxotungstates $[\beta\text{-}1,2,3\text{-}SiW_9V_3O_{40}]^{7-}$ (a) and $[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]^{6-}$ (b). In (a) and (b), the three vanadiums are represented by hatched octahedra in the 1,2,3-positions (A-site) and 1,4,9-positions (B-site), respectively. The WO_6 octahedra occupy the white octahedra, and an XO_4 (X = Si or P) group is shown as the internal, black tetrahedron. One of the two most plausible C_s symmetry structures of $[(CpTi)(\beta\text{-}1,2,3\text{-}SiW_9V_3O_{40})]^{4-}$ is shown in (c) and the other most plausible structure involves bonding of the organometallic moiety to two bridging W–O–V oxygens and a terminal V=O oxygen. Polyhedral representation of $[(Cp^{*}Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]^{4-}$, prepared in this work, is shown in (d). Although the sites of two protonations in **1** can be assumed to be bridging oxygens in V–O–V or V–O–W sites, the observed single ^{51}V NMR signal has suggested the presence of rapid proton-transfer in solution. In **2**, although the bonding of $Cp^{*}Rh^{2+}$ group on the V_3 surface implies two protonations at V–O–W sites, it is not determined whether the symmetry is C_s or C_1.

Numerous examples of Keggin and Dawson polyoxoanion-supported organometallics have been so far described.[1] Recently, the Dawson triniobium-substituted polyoxotungstate-supported transition metal complexes $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})\{M(MeCN)_x\}]^{n-}$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, Zn^{II}) and oxygenation catalysis by these all-inorganic, oxidation-resistant precatalysts have been reported.[2] In particular, as a model of catechol dioxygenase, oxygenation of 3,5-di-*tert*-butylcatechol by the trivanadium-substituted polyoxotungstate-supported iron(II) complex $(NBu_4)_7[(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})\{Fe^{II}(MeCN)_x\}]$ is noteworthy.[2c]

Examples of vanadium-substituted polyoxoanion-supported organometallics are $[(CpTi)(\beta\text{-}1,2,3\text{-}SiW_9V_3O_{40})]^{4-}$ ($Cp = C_5H_5$) **3** [Fig. 1(c)],[3] $[(Cp^{*}Rh)_4V_6O_{19}]$,[4a] $[\{(cod)Ir\}V_4O_{12}]^{3-}$ (cod = cycloocta-1,5-diene)[4b] and $[\{(cod)Ir\}_2V_4O_{12}]^{2-}$.[4b] One example of a Dawson trivanadium-substituted polyoxotungstate-based organometallics has been reported as an unusual site-bonding 1 : 1-type compound $(NBu_4)_6[(CpTi)(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **5** with C_s symmetry,[5] and not the initially anticipated C_{3v} symmetry. In relation to this complex, we have very recently been successful in isolating a novel Dawson polyoxoanion-supported 2 : 1-type $Cp^{*}Rh^{2+}$ complex, *i.e.* $(NBu_4)_5[(Cp^{*}Rh)_2(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **6** with C_s symmetry.[6] These complexes are in contrast to the Dawson triniobium-substituted polyoxotungstate-based 1 : 1-type organometallic complexes with C_{3v} symmetry such as $[(Cp^{*}Rh)(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]^{7-}$ **7**[1a,b,d,f] and $[\{(C_6H_6)Ru\}(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]^{7-}$ **8**.[1a,d] It has been proposed that either the Dawson-type trimetal-substituted polyoxometalate-support $[P_2W_{15}M_3O_{62}]^{9-}$ (M = V^{V} *vs.* Nb^{V}) or the organometallic group with different charge ($CpTi^{3+}$ *vs.* $Cp^{*}Rh^{2+}$), or both, are variables for kinetic control process (C_s symmetry) *vs.* thermodynamic control process (C_{3v} symmetry) of the organometallic group in the support chemistry of $[\alpha\text{-}1,2,3\text{-}P_2W_{15}M_3O_{62}]^{9-}$.[5]

To verify the interaction of the $Cp^{*}Rh^{2+}$ group with three edge-shared vanadium octahedra (B-site V_3 surface), we aimed at synthesizing a novel $Cp^{*}Rh^{2+}$ complex supported on a Keggin-type α-1,4,9-trivanadium-substituted polyoxotungstate $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ **1** [Fig. 1(b)]. The α-1,4,9-substituted Keggin polyoxotungstate **1** was first reported as an

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isomer of an α-1,2,3-substituted compound by Domaille and Watunya in 1986,[7] but its development to a polyoxoanion-support for organometallic complexes has not, as yet, been studied. In this work, we have successfully prepared a novel Keggin polyoxotungstate-based 1 : 1-type Cp^*Rh^{2+} complex $[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]\cdot 3DMSO\cdot 0.5MeCN$ **2** as an analytically pure, yellow–brown powder by a 1 : 3 molar ratio reaction in MeCN–DMSO mixed solvent at 80 °C under nitrogen of **1** with the $[Cp^*Rh(MeCN)_3]^{2+}$ ion. In **2**, one Cp^*Rh^{2+} group is covalently bonded to, *i.e.* directly supported on, the V_3 surface oxygens [Fig. 1(d)], and the other group is present as a counter ion with coordinated DMSO molecules. The unique composition of **2** can be compared with the previous Keggin-type organometallics family $(NBu_4)_4[(CpTi)(\beta\text{-}1,2,3\text{-}SiW_9V_3O_{40})]$ **3**[3b–d,5] and $(NBu_4)_5[(Cp^*Rh)(\beta\text{-}1,2,3\text{-}SiW_9Nb_3O_{40})]$ **4**,[8a,b] and also with the Dawson-type family $(NBu_4)_6[(CpTi)(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **5**,[5] $(NBu_4)_5[(Cp^*Rh)_2(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **6**[6] and $(NBu_4)_7[(Cp^*Rh)(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]$ **7**.[1a,d,f] Examples of polyoxometalates with organometallic counter cations have previously been reported as bifunctional solid catalysts based on the classic Keggin polyoxometalates, *i.e.* $[(Ph_3P)_2Rh(CO)(MeCN)]_n[XM_{12}O_{40}]$ (M = P, Si, X = Mo, W).[9] Herein, we report full details of the synthesis and spectroscopic characterization of **2**.

Results and discussion

Synthetic reactions, compositional identification and general properties

The molecular formula of **1**, $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$, prepared according to ref. 7, was consistent with all data (complete elemental analysis, TG/DTA, FTIR, ^{31}P and ^{51}V NMR spectra), and also in good agreement with the literature data.[7] This compound was isolated without any molecules of solvation. The ^{31}P NMR spectrum of **1** in DMSO-d_6 showed the presence of an unavoidable minor species assumed to be the 1,2,3-isomer [see Fig. 4(a)] also consistent with the literature report.[7]

Complex **2** was formed by a 1 : 3 molar ratio stoichiometric reaction, in MeCN–DMSO mixed solution under nitrogen, of the Keggin polyoxotungstate-support **1** with the separately *in situ*-derived $[Cp^*Rh(MeCN)_3](BF_4)_2$, and was purified by repeated reprecipitation from DMSO solution, initially with excess EtOAc and then with excess MeCN. The molecular formula of **2**, obtained in 69.2% yield (0.31 g scale) as a DMSO-soluble, MeCN-insoluble yellow–brown powder, was consistent with all data [complete elemental analysis, TG/DTA, FTIR and solution (^{51}V, ^{31}P, ^{1}H and ^{13}C) NMR spectroscopies]. The formation of **2** is shown in eqns. (1) and (2).

$$[Cp^*RhCl_2]_2 + 4\,AgBF_4 + 6\,MeCN \longrightarrow 2\,[Cp^*Rh(MeCN)_3](BF_4)_2 + 4\,AgCl \quad (1)$$

$$\underset{\mathbf{1}}{(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]} + 2\,[Cp^*Rh(MeCN)_3](BF_4)_2 + 3\,DMSO \longrightarrow \underset{\mathbf{2}}{[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]} + 4\,NBu_4BF_4 + 6\,MeCN \quad (2)$$

In the present synthesis, there are several key points. (i) The appropriate solvent for preparation is a MeCN–DMSO mixed solvent, because the starting polyoxotungstate-support **1** is MeCN- and DMSO-soluble but CH_2Cl_2-insoluble, while the product **2** is soluble only in DMSO. In fact, the Cp^*Rh^{2+} complex supported on **1** was formed only in lower yield under refluxing conditions in pure MeCN. (ii) The synthetic stoichiometry to obtain **2** in good yield is a 1 : 3 molar ratio of **1** : $[Cp^*Rh(MeCN)_3](BF_4)_2$. (iii) The most interesting point is the fact that all NBu_4^+ counter ions of **1** are completely replaced with $[Cp^*Rh(solvent)_3]^{2+}$ (solvent = MeCN, DMSO). This phenomenon has not been found previously in the formation of organometallic complexes supported on both Keggin and Dawson triniobium-substituted polyoxotungstates.[1,8] (iv) The by-product NBu_4BF_4 in the formation of **2** was completely removed by repeated reprecipitation with EtOAc and then with MeCN, and **2** was isolated in an analytically pure form.

For control experiments relating to point (iii), the ^{1}H NMR spectrum in DMSO-d_6 of the MeCN-insoluble orange powder obtained after 17 h refluxing of the starting 1 : 3 molar-ratio mixture in MeCN revealed that the compound did not contain the counter cation NBu_4^+. ^{31}P and ^{51}V NMR spectra in DMSO-d_6 of the orange powder showed that it contained two major species with an intensity ratio of *ca.* 1 : 2 (δ_P −10.95 and −12.02, and δ_V −547.9 and −562.6); one is probably $[Cp^*Rh(MeCN)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]$ **2** (δ_P −12.02, δ_V −547.9) and the other is probably $[Cp^*Rh(MeCN)_3]_2H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ (δ_P −10.95, δ_V −562.6). By dissolving the orange powder in DMSO-d_6 and monitoring variable-temperature ^{31}P NMR (from room temperature to 90 °C), we found that the ^{31}P NMR signal due to the supported Cp^*Rh^{2+} complex increased as the temperature is elevated and the ^{31}P NMR signal due to the single species at 90 °C appeared at δ −11.31. Thus, in polar solvents such as DMSO and MeCN, the following reaction is presumed to occur [eqn. (3)].

$$\underset{\mathbf{1}}{(NBu_4)_4H_2[(1,4,9\text{-}PW_9V_3O_{40})]} \longrightarrow [Cp^*Rh(solvent)_3]_2H_2[(1,4,9\text{-}PW_9V_3O_{40})] \longrightarrow \underset{\mathbf{2}}{[Cp^*Rh(solvent)_3]H_2[(Cp^*Rh)(1,4,9\text{-}PW_9V_3O_{40})]} \quad (3)$$

These facts are also in contrast to the recent preparation in less-polar CH_2Cl_2 of the Dawson-type species $(NBu_4)_5[(Cp^*Rh)_2(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **6** isolated as a brown powder which is unstable in MeCN,[6] in the preparation of which the CH_2Cl_2-soluble, deprotonated form, $(NBu_4)_9[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]$, was allowed to react with an equimolar amount of $[Cp^*RhCl_2]_2$ in ice-cooled CH_2Cl_2 without the use of $AgBF_4$.

The purity and molecular composition of **2** were established by complete elemental analysis (all elements including oxygen, and adding up to 100.53%). No presence of NBu_4^+ ions is evidenced by ^{1}H NMR in DMSO-d_6. The evidence for the presence of the coordinating and/or solvated DMSO is also obtained by FTIR as multiple intense vibrational bands at 1500–1300 cm^{-1} region [Fig. 2(b)] and also by ^{13}C NMR as a signal at δ 40.2. The presence of the two different types of Cp^*Rh^{2+} groups has been evidenced by ^{1}H NMR with signals at δ 1.64 and 1.84 due to the methyl group of Cp*, and also by ^{13}C NMR with signals at δ 8.16 and 8.97 due to the methyl carbon and signals at δ 93.0 and 95.3 due to the quaternary carbon of Cp*.

In the FTIR spectrum of **2** in the polyoxometalate region [Fig. 2(b)], the major change relative to **1** was seen in the polyoxometalate region; the (969 and 956 cm^{-1}) bands of **1** assignable to $M\text{–}O_{terminal}$ and the 809 cm^{-1} band of **1** assignable to edge-sharing M–O–M oxygens,[10] changed to bands at 954 and 802 cm^{-1} of **2**, respectively, and the 882 cm^{-1} band of **1** assignable to corner-sharing M–O–M oxygens[10] shifted to a lower energy band at 876 cm^{-1} of **2**. The (1152, 1123 and 1090 cm^{-1}) bands of **1** seem to be shifted to the 1111 cm^{-1} band of **2**, and the 1054 cm^{-1} band (P–O) of **1** seems to be shifted to the (1038 and 1019 cm^{-1}) bands of **2**.

Spectroscopic (^{51}V, ^{31}P, ^{1}H and ^{13}C NMR) characterization

The ^{51}V NMR spectrum in DMSO-d_6 of **1** showed a broad single resonance at δ −557.9 [Fig. 3(a)]. Two protonations at V–O–V or V–O–W sites would reduce the symmetry from C_{3v}

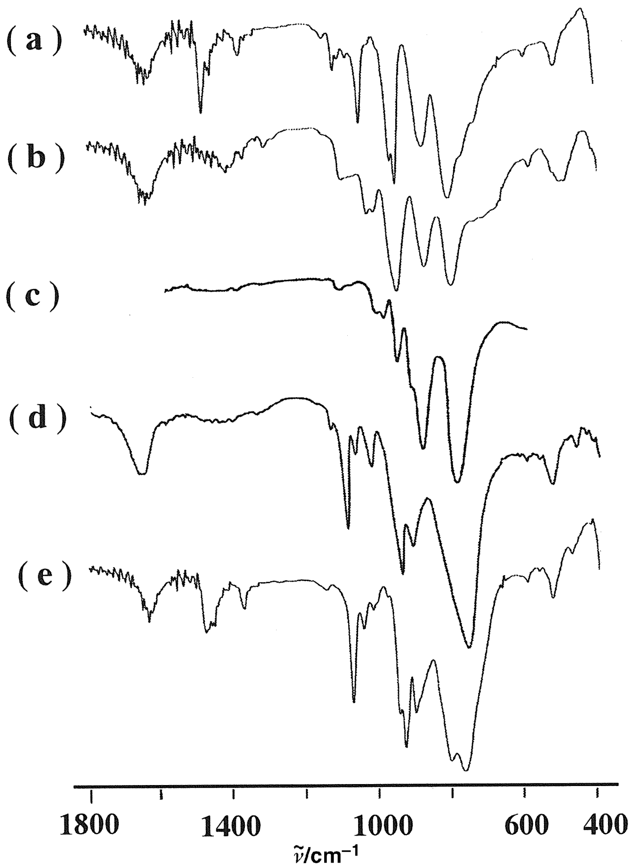

Fig. 2 FTIR spectra (KBr disks) of (a) $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ **1**, (b) $[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]\cdot 3DMSO\cdot 0.5MeCN$ **2**, (c) $Na_5[(Cp^*Rh)(\beta\text{-}1,2,3\text{-}SiW_9Nb_3O_{40})]\cdot 3DMSO\cdot 2H_2O$, (d) $Na_7[(Cp^*Rh)(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]\cdot 7DMSO\cdot 5H_2O$, and (e) $(NBu_4)_5[(Cp^*Rh)_2(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]\cdot 0.2NBu_4Cl$. In (a) and (b), the observation of the characteristic Keggin-type polyoxoanion IR bands in the range 1100–700 cm^{-1} demonstrates that the $[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]^{6-}$ support-ion remains intact under the conditions of the synthesis. In spectrum (b), in place of the very intense C–H vibrations due to the NBu_4^+ counter cations in (a), very intense and broad bands are observable in the range 1500–1300 cm^{-1}; these are attributed to the vibrations of the coordinating DMSO molecules on the Cp^*Rh^{2+} group. The bands due to the supported Cp*Rh groups and the solvated DMSO molecules have been observed as very weak and broad bands in the 1500–1300 cm^{-1} region, as shown in the sodium salts (c) and (d).[1b,8d] In (e),[6] the vibrational bands due to the two Cp^*Rh^{2+} groups supported on the B-site V_3 surface of the Dawson polyoxotungstate could not be observed, owing to the presence of intense vibrational bands characteristic of NBu_4^+ (1490–1370 cm^{-1}).

to C_s or C_1, and these would affect the ^{51}V NMR spectra.[3a] The broad single signal observed in **1** ($\Delta\nu_{1/2}$ 2395 Hz) probably implies the presence of rapid proton-transfer in solution. On the other hand, the ^{51}V NMR in DMSO-d_6 of **2** showed a clean, single resonance at δ −546.7 [Fig. 3(b)], suggesting that the Cp^*Rh^{2+} group was attached to the B-site V_3 surface in a way that yielded three equivalent vanadium atoms. Two protonations in **2** should also reduce the symmetry from C_{3v}. However, the ^{183}W NMR measurements have been unsuccessful, because of too low a concentration of the saturated DMSO-d_6 solution. Thus, the symmetry of **2** can not be deduced, although the bonding of Cp^*Rh^{2+} group on the V_3 surface implies two protonations at V–O–W sites. Fig. 3 shows that the ^{51}V spectral line of **2** ($\Delta\nu_{1/2}$ 586 Hz) is narrowed when the Cp^*Rh^{2+} group is bound on **1**. One possible reason for this is a change in the electric field gradient caused by bonding of the Rh^{III} (d^6) metal nucleus, as previously discussed by Leparulo-Loftus and Pope.[11]

The ^{31}P NMR spectrum in DMSO-d_6 of **2** showed one resonance at δ −12.7 (Fig. 4), substantially different from the δ −11.0 resonance of **1**. The ^{31}P NMR spectrum confirmed the homogeneity of **2** and, thus, the support-site regiospecificity in **2**.

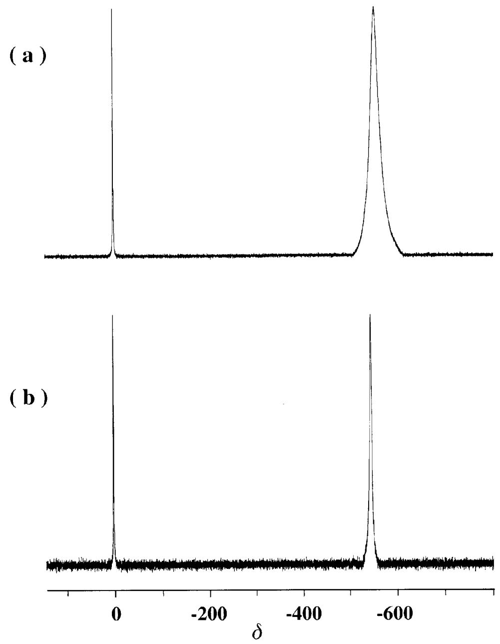

Fig. 3 ^{51}V NMR spectra in DMSO-d_6 with reference to external $VOCl_3$ of (a) $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ **1** and (b) $[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]\cdot 3DMSO\cdot 0.5MeCN$ **2**.

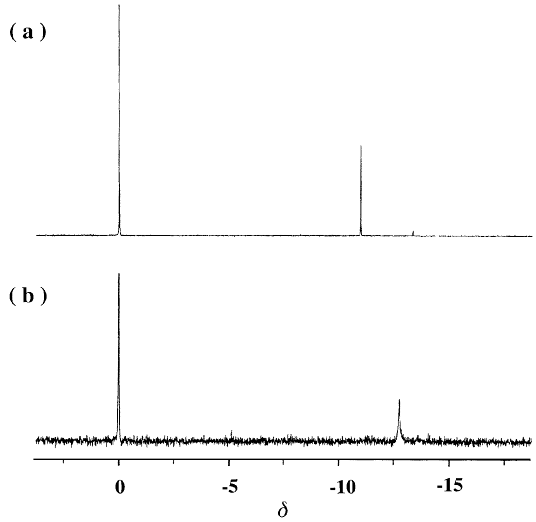

Fig. 4 ^{31}P NMR spectra in DMSO-d_6 with reference to external 25% H_3PO_4 in H_2O of (a) $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ **1** and (b) $[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]\cdot 3DMSO\cdot 0.5MeCN$ **2**. For both, a very high level of purity is indicated (*i.e.*, with respect to any other, P-containing polyoxoanions such as the 1,2,3-isomer or other materials).

Further evidence for the single product nature of **2** came from the Cp* resonances in DMSO-d_6 seen in the ^1H NMR at δ 1.84 (Cp*Rh group supported) and at δ 1.64 (Cp*Rh group as counter ion) and in the ^{13}C NMR at δ 8.16 (Cp*Rh group as counter ion) and 8.97 (Cp*Rh group supported) and their quaternary carbon resonances at δ 93.0 and 95.3, respectively. These assignments are based on our control experiments, *i.e.* ^1H and ^{13}C NMR measurements of the DMSO-d_6 solution of $[Cp^*Rh(DMSO)_3](BF_4)_2$, which was derived by a reaction in DMSO-d_6 of $[Cp^*RhCl_2]_2$ with stoichiometric amounts of $AgBF_4$, followed by filtering off AgCl. The ^1H NMR signal of the methyl proton of the Cp* group in $[Cp^*Rh(DMSO)_3](BF_4)_2$ was observed at δ 1.55, and the ^{13}C NMR signals of the methyl carbon and quaternary carbon were found at δ 7.13 and 92.0, respectively.

Comparison of 2 with the related organometallic complexes

All attempts at deprotonation of the B-type protonated Keggin polyoxotungstate **1** have been unsuccessful (see Experimental section). There are several problems in the two protons contained in **1**. (1) The protonated form of the polyoxotungstate-support restricts the solvents, *i.e.* **1** is soluble in polar solvents such as DMSO and MeCN, but insoluble in less-polar CH_2Cl_2 (the deprotonated form has been expected to be also soluble in CH_2Cl_2 in addition to DMSO and MeCN[6]). (2) The two protons decrease the surface negative-charge density of $[PW_9V_3O_{40}]^{6-}$, which has an extra 3− charge in comparison with parent anion $[PW_{12}O_{40}]^{3-}$, reducing the interaction with the cationic, organometallic group (see also the next section). (3) The two protons also may have a tendency to hinder the bonding of the cationic, organometallic groups to the surface oxygens of polyoxometalates, because they are usually attached to the bridging oxygens at V–O–V or V–O–W sites. (4) The protons in the polyoxometalates could also act as catalysts for an isomerization, *e.g.* from the β- to α-Keggin framework. In fact, it has been elucidated by Kawafune and Matsubayashi that the isomerization of $(NBu_4)_4H_2[\beta\text{-}1,2,3\text{-}PW_9V_3O_{40}]$ to $(NBu_4)_4H_2[\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]$ takes place through an intramolecular acid-catalysis.[12] However, this will not be the case, because **1** is an α-Keggin species. Thus, in spite of points (1)–(3), we can isolate the supported Cp^*Rh^{2+} complex **2** as an analytically pure compound.

Compared with the recently prepared 2 : 1 type complex $(NBu_4)_5[(Cp^*Rh)_2(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **6**,[6] the reason why only one Cp*Rh group is supported on the V_3 surface in **2** is probably attributable to the presence of surface protons and hence a lower surface charge in **1**; it is related to the points (2) and (3) above.

It has also been elucidated that the complex **6** is stable in CH_2Cl_2, but unstable in MeCN; for **6** dissolved in MeCN, the supported Cp*Rh group is removed from the polyoxoanion surface to produce $[Cp^*Rh(MeCN)_3]^{2+}$, which is present as the counter cation.[6] Such phenomena have not been observed in the supported Cp*Rh complexes on triniobium-substituted Keggin and Dawson polyoxometalates such as $(NBu_4)_5[(Cp^*Rh)(\beta\text{-}1,2,3\text{-}SiW_9Nb_3O_{40})]$ **4**[8a,b] and $(NBu_4)_7[(Cp^*Rh)(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]$ **7**.[1a,d,f] It should be, therefore, noted that the bonding interaction between the Cp^*Rh^{2+} group and the edge-shared M_3O_6 triads ($M = Nb^V$ *vs.* V^V) is significantly different. This difference may be more pronounced in the bonding of an organometallic group with higher positive-charge such as $CpTi^{3+}$ on the M_3O_6 triads.

Organometallic counter cation complexes

Examples of cationic rhodium complexes as counter ions of polyoxometalates are $[(Ph_3P)_2Rh(CO)(MeCN)]_4[SiW_{12}O_{40}]$ and $[(Ph_3P)_2Rh(CO)]_4[SiW_{12}O_{40}]$.[9] Addition of MeCN to the latter regenerates the former and, therefore, the reaction between them is reversible. These complexes which have been reported as bifunctional catalysts capable of activating carbon monoxide and hydrogen at the rhodium centers as well as oxygen at tungsten, have been previously found, in which the $(Ph_3P)_2Rh(CO)^+$ units are located in interstitial lattice sites and are not covalently bonded to the oxygen atoms of the surrounding metal oxide clusters. The non-bonding property of the cationic organometallic group has been attributed to the low basicity of the surface oxygens in the polyoxoanion $[SiW_{12}O_{40}]^{4-}$, *i.e.* $[(SiO_4)^{4-}(W_{12}O_{36})]$.[13] Thus, the polyoxometalate **2** also provides a new guideline for the molecular design of multifunctional catalysts.

Conclusion

In conclusion, a novel Keggin polyoxotungstate-based organometallic complex, *i.e.* the α-1,4,9-trivanadium-substituted Keggin polyoxotungstate-based 1 : 1-type Cp^*Rh^{2+} complex **2** has been isolated in an analytically pure form, accompanied with one $[Cp^*Rh(DMSO)_3]^{2+}$ counter cation, rather than NBu_4^+. In this preparation, the protonated form of the Keggin polyoxometalate-support **1** is used, which has been suspected to be inappropriate for formation of the supported organometallic complexes. In **2**, the composition containing two different Cp^*Rh^{2+} groups is noteworthy. This work can also be extended to molecular design of novel multifunctional polyoxometalate-based heterogeneous and homogeneous catalysts.

Experimental

Materials

The following were used as received: $Na_2WO_4\cdot 2H_2O$, 25% H_3PO_4, $NaVO_3$, KCl, NBu_4Br, $AgBF_4$, 12.0 M and 6.0 M aqueous HCl (both are quantitative analysis grade), diethyl ether, ethyl acetate, acetonitrile (all from Wako); D_2O, DMSO-d_6 (Isotec). The precursor $[Cp^*RhCl_2]_2$ was prepared according to literature methods,[14] and identified by elemental analysis, ^1H and ^{13}C NMR spectroscopy.

Instrumentation/analytical procedures

Complete elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature under 10^{-3}–10^{-4} Torr overnight before analysis. IR spectra were recorded on a Jasco 300 FTIR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 4 °C min^{-1} between 20 and 500 °C.

^1H (399.65 MHz), $^{13}C\text{-}\{^1H\}$ (100.40 MHz), ^{31}P NMR (161.70 MHz) and ^{51}V NMR (104.95 MHz) spectra in DMSO-d_6 solution were recorded in 5-mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and JEOL EX-400 NMR data-processing system. ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were referenced to internal TMS. Chemical shifts are reported as positive for resonances downfield of TMS (δ 0). ^{31}P NMR spectra were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary and the ^{51}V NMR spectra referenced to an external standard of $VOCl_3$. Chemical shifts were reported on the δ scale with resonances upfield of H_3PO_4 (δ 0) as negative and with resonances upfield of $VOCl_3$ (δ 0) as negative, respectively.

Preparations

$(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ 1. This compound was prepared according to the literature[7] including syntheses of $Na_9[B\text{-}PW_9O_{34}]\cdot 7H_2O$ and $K_6[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]\cdot 8H_2O$, and then a change of the counter ions to $(NBu_4)_4H_2$, and identified with complete elemental analysis, TG/DTA, FTIR, ^{31}P and ^{51}V NMR. The analytically pure, orange crystals obtained in 34.6% (0.27 g scale) yield were soluble in MeCN and DMSO, but insoluble in CH_2Cl_2, EtOAc and diethyl ether {Found: C, 22.05; H, 4.25; N, 1.62; O, 17.6; P, 0.95; V, 4.80; W, 48.1; K, <0.05; total 99.37%. Calc. for $C_{64}H_{146}N_4O_{40}PV_3W_9$ or $(NBu_4)_4H_2[PW_9V_3O_{40}]$: C, 22.28; H, 4.27; N, 1.62; O, 18.55; P, 0.90; V, 4.43; W, 47.96; K, 0.00%}. TG/DTA data: no weight loss observed before decomposition temperature; decomposition began around 250 °C with an exothermic peak at 250 °C. FTIR bands (KBr disk) in the 1500–400 cm^{-1} region (polyoxometalate region): 1483s, 1459m, 1382m, 1363w, 1152w, 1123m, 1090m, 1054vs, 969vs, 956vs, 882vs, 809vs, 595w, 512m cm^{-1}. ^{31}P NMR (DMSO-d_6, 23.3 °C): (major peak) δ −11.0; (minor peak due to the 1,2,3-isomer) −13.3. ^{51}V NMR (DMSO-d_6, 23.5 °C): δ −557.9 ($\Delta\nu_{1/2}$ 2395 Hz).

Complex **1** is soluble in MeCN and DMSO, but insoluble in CH_2Cl_2. All attempts at preparing an unprotonated species, expected to be CH_2Cl_2-soluble, such as passing through a NBu_4^+-type ion-exchange resin column and reaction with NBu_4OH, were unsuccessful. In such work-ups, a conversion to the α-1,2,3-isomer was observed.

$[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]\cdot 3DMSO\cdot 0.5MeCN$ 2. All work-ups were performed in a glove box under dry nitrogen ($[O_2] < 55$ ppm). 0.12 g (0.19 mmol) of solid $[Cp^*RhCl_2]_2$ was suspended in 20 mL of dry MeCN. Solid $AgBF_4$ (0.15 g; 0.77 mmol; 4 equiv.) was added to the slurry causing the immediate formation of an AgCl precipitate. The mixture was stirred for several minutes *via* a magnetic stir bar, and then filtered through a folded filter paper (Whatman No. 2) directly into the stirred, red solution of 0.45 g (0.13 mmol) of **1** dissolved in 20 mL dry MeCN. To it 60 mL DMSO were added. After stirring for 30 min at room temperature, a further 40 mL DMSO was added to the dark-red suspension. The solution was stirred at 80 °C for 1 h. Acetonitrile was removed from the dark-red solution by a rotary evaporator at 120 °C. The clear black solution was added to 1500 mL ethyl acetate to form a yellow–brown precipitate, which was collected on a membrane filter (JG 0.2 μm) and dried *in vacuo* for 2 h. The yellow–brown powder was redissolved in 20 mL DMSO and the solution added to 300 mL acetonitrile. The yellow–brown precipitate formed was collected on a membrane filter (JG 0.2 μm), thoroughly dried by suction, and then dried *in vacuo*.

The hygroscopic, yellow–brown powder obtained in 69.2% (0.31 g) yield was soluble in DMSO, but insoluble in EtOAc, MeCN and diethyl ether {Found: C, 11.74; H, 2.05; N, 0.21; O, 21.3; P, 0.93; S, 5.93; V, 4.71; Rh, 5.66; W, 48.0; total 100.53%. Calc. for $C_{33}H_{69.5}N_{0.5}O_{46}PS_6V_3Rh_2W_9$ or $[Cp^*Rh(DMSO)_3]H_2[(Cp^*Rh)PW_9V_3O_{40}]\cdot 3DMSO\cdot 0.5MeCN$): C, 11.50; H, 2.03; N, 0.20; O, 21.36; P, 0.90; S, 5.58; V, 4.43; Rh, 5.97; W, 48.02%}. TG/DTA data: weight loss due to adsorbed water was observed below 50 °C, suggesting that it is hygroscopic; decomposition began around 228 °C with exothermic peaks at 228 and 373 °C. FTIR bands (KBr disk) in the 1500–400 cm^{-1} region (polyoxometalate region): 1419m, 1318m, 1111m, 1038s, 1019s, 954vs, 876vs, 802vs, 592m, 506m cm^{-1}. ^1H NMR (DMSO-d_6, 21.5 °C): δ 1.64, 1.84 (C_5Me_5). ^{13}C NMR (DMSO-d_6, 22.0 °C): δ 8.16, 8.97 ($C_5\mathit{Me}_5$), 93.0, 95.3 (C_5Me_5). In the ^1H and ^{13}C NMR spectra, the lower-field signals are assigned to the Cp*Rh group supported on **1** and the higher-field signals are assigned to the Cp*Rh group as counter ion. ^{31}P NMR (DMSO-d_6, 22.0 °C): δ −12.7. ^{51}V NMR (DMSO-d_6, 22.0 °C): δ −546.7 ($\Delta\nu_{1/2}$ 586 Hz). The ^{183}W NMR measurements were unsuccessful, due to the low concentration of the saturated DMSO-d_6 solution.

Control experiments. ^1H and ^{13}C NMR measurements of the DMSO-d_6 solution of $[Cp^*Rh(DMSO)_3](BF_4)_2$, which was obtained by stirring for >15 min $[Cp^*RhCl_2]_2$ and stoichiometric amounts of $AgBF_4$ in DMSO-d_6, followed by removal of AgCl. ^1H NMR (DMSO-d_6, 24.8 °C): δ 1.55 (C_5Me_5). ^{13}C NMR (DMSO-d_6, 24.4 °C): 7.13 ($C_5\mathit{Me}_5$), 92.0 (C_5Me_5).

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