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Synthesis and spectroscopic characterization of 1,2-divanadium(V)-substituted α-Dawson polyoxotungstate-based 1 : 1-type Cp*Rh^{2+} complex showing three different supporting sites of the Cp*Rh^{2+} group †

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A novel Dawson polyoxotungstate-based 1 : 1-type Cp*Rh^{2+} complex (Cp* = C_5Me_5), $(NBu_4)_6[(Cp^*Rh)(\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62})]$ **2**, was synthesized as an analytically pure, brown powder by 1 : 1 molar ratio reaction in ice-cooled CH_2Cl_2 under air of 1,2-divanadium(V)-substituted α-Dawson polyoxotungstate $(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ **1** with the dimeric precursor $[Cp^*RhCl_2]_2$ without the use of $AgBF_4$. The unprotonated polyoxotungstate support **1** was prepared *via* synthesis of $K_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$, $(NBu_4)_6H_2[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$, and deprotonation with aqueous NBu_4OH. Solution (^{51}V, ^{31}P, ^{183}W, ^1H and ^{13}C) NMR measurements in CD_2Cl_2 of **2** have revealed that it contained three species, **2a** with C_s symmetry, **2b** with C_1 symmetry and **2c** with C_s symmetry, based on different supporting sites of the Cp*Rh^{2+} group on the surface oxygen atoms in the three edge-shared octahedra (B-site, V_2W surface). The Cp*Rh^{2+} group in **2a**, **2b** and **2c** was covalently bound on the V_2W surface, and the distribution of the species in *ca.* 1 : 2 : 1 ratio was not dependent on the initial concentration of $[Cp^*RhCl_2]_2$ and temperature of the CH_2Cl_2 solution (from room temperature to −90 °C). The brown powder containing **2a**, **2b** and **2c** was readily crystallized in CH_2Cl_2 solution at −20 °C to give dark red crystals, which initially contained one predominant species, but, then, reverted to the 1 : 2 : 1 mixture of the three species during 5 h in CH_2Cl_2 solution at room temperature. The polyoxoanion-supported Cp*Rh^{2+} complex **2** is unique and can be compared with the previous Dawson polyoxotungstate-based organometallic complexes.

Numerous examples of Keggin and Dawson polyoxoanion-supported organometallic and transition-metal complexes have been so far described.[1–3] Examples of vanadium-substituted polyoxoanion-supported organometallics are seen, *e.g.* in $[(CpTi)(\beta\text{-}1,2,3\text{-}SiW_9V_3O_{40})]^{4-}$ (**4**, Cp = C_5H_5),[3] $[(Cp^*Rh)_4(V_6O_{19})]$,[4a] $[\{(cod)Ir\}(V_4O_{12})]^{3-}$ (cod = 1,5-cyclooctadiene),[4b] $[\{(cod)Ir\}_2(V_4O_{12})]^{2-}$,[4b] $[\{(cod)Ru(MeCN)_2\}(V_4O_{12})]^{2-}$,[4c] and $[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]^{4-}$ (**3**, Cp* = C_5Me_5).[5c] One example of Dawson trivanadium-substituted polyoxotungstate-based organometallics has been reported as an unusual site-bonding 1 : 1-type compound $(Bu_4N)_6[(CpTi)(\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62})]$ **5** with C_s symmetry,[5a] 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.[5b] 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–c] and $[\{(C_6H_6)Ru\}(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]^{7-}$.[1a,d] It has been proposed that either the Dawson-type tri-metal-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 $[\alpha\text{-}1,2,3\text{-}P_2W_{15}M_3O_{62}]^{9-}$.[5a]

In extending our work concerning the interaction of the Cp*Rh^{2+} group with three edge-shared vanadium octahedra (B-site, V_3 surface) in **6**, we aimed at synthesizing a novel Cp*Rh^{2+} complex supported on 1,2-divanadium(V)-substituted α-Dawson polyoxotungstate $[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]^{8-}$ (Fig. 1a), which can be expected to have still enough surface negative-charge density to support cationic organometallic groups. The water-soluble potassium salt of 1,2-divanadium(V)-substituted α-Dawson polyoxotungstate was first reported by Pope *et al.* in 1983,[6a] and later by Contant *et al.* in 1991,[6b] but its development to a polyoxoanion-support for organometallic complexes has not been studied to date. However, the protonated form of the polyoxotungstate, *e.g.* $(NBu_4)_6H_2[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$,[6b] potentially involves a serious issue in the formation of the supported organometallic complexes. ‡ Thus, we have here prepared the unprotonated form, *i.e.* $(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ **1** and used it as the polyoxotungstate support for the Cp*Rh^{2+} group.

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† Electronic supplementary information (ESI) available: results of ^{31}P and ^{51}V NMR characterization of the reaction solutions containing **2**, showing the dependence of the starting concentrations on the reaction products. See http://www.rsc.org/suppdata/dt/b1/b106459m/

‡ We have found in our recent synthesis of $[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]^{4-}$ **3**[5c] using the protonated polyoxotungstate support $(NBu_4)_4H_2[\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40}]$ that (1) the two protons decrease the surface negative-charge density of $[PW_9V_3O_{40}]^{6-}$, reducing the interaction with the cationic organometallic group, (2) the two protons also have a tendency to limit the bonding site of the organometallic groups on the surface oxygens of the polyoxometalate, because they are usually attached to the bridging oxygens at V–O–V or V–O–W sites,[3a] and (3) the use of the protonated polyoxotungstate support led to a formation of the compounds containing an organometallic counter cation species, *i.e.* $[Cp^*Rh(solvent)_3]H_2[(Cp^*Rh)(\alpha\text{-}1,4,9\text{-}PW_9V_3O_{40})]$.

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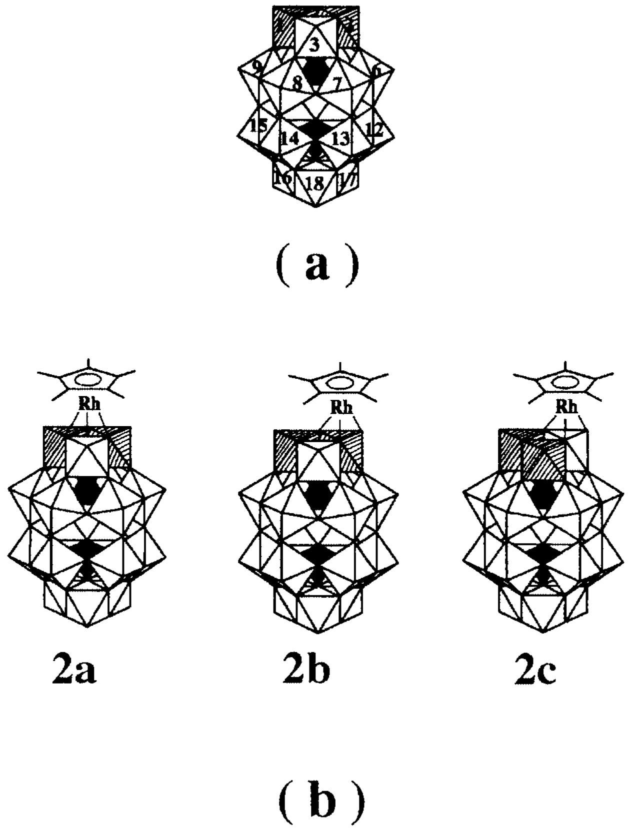

Fig. 1 Polyhedral representation of the Dawson polyoxotungstates [α-1,2-$P_2W_{16}V_2O_{62}$]$^{8-}$ (a), in which the two vanadiums are represented by hatched octahedra in the 1,2-positions (B-site). The WO_6 octahedra occupy the white octahedra, and two PO_4 groups are shown as the internal black tetrahedra. The three most plausible structures of [(Cp*Rh)(α-1,2-$P_2W_{16}V_2O_{62}$)]$^{6-}$ are shown in (b). The three supporting sites of the Cp*Rh^{2+} group are a central position of the B-site (**2a**, C_s symmetry), either one of two vanadium octahedra of the B-site (**2b**,C_1 symmetry), and a tungsten octahedron of the B-site (**2c**, C_s symmetry).

In this work, we have successfully prepared a novel Dawson polyoxotungstate-based 1 : 1-type Cp*Rh^{2+} complex, $(NBu_4)_6$-[(Cp*Rh)(α-1,2-$P_2W_{16}V_2O_{62}$)] **2** as an analytically pure brown powder by 1 : 1 molar ratio reaction in ice-cooled CH_2Cl_2 under air of **1** with [Cp*$RhCl_2$]$_2$ without the use of $AgBF_4$. Complex **2** of the brown powder contained three different supporting sites of the Cp*Rh^{2+} group on the B-site V_2W surface (Fig. 1b); the sites were a central position of the B-site (**2a**, C_s symmetry), either one of two vanadium octahedra of the B-site (**2b**, C_1 symmetry), and a tungsten octahedron of the B-site (**2c**, C_s symmetry). The Cp*Rh^{2+} group in **2a**, **2b** and **2c** was covalently bound on the V_2W surface, and the distribution of the species in *ca.* 1 : 2 : 1 ratio was not dependent on the initial concentrations of [Cp*$RhCl_2$]$_2$ and temperature of the CH_2Cl_2 solution (room temperature to −90 °C). By dissolving the brown powder in ice-cooled CH_2Cl_2 and placing the solution in a refrigerator at −20 °C for two days, dark-red crystals were formed, which contained only one species of **2a**, **2b** and **2c** predominantly just after dissolving, but they reverted to the 1 : 2 : 1 mixture of **2a**, **2b** and **2c** during 5 h in CD_2Cl_2 solution at room temperature. It was found from (^{51}V, ^{31}P and ^{1}H) NMR changes of the dark red crystals that the most intense signal in the 1 : 2 : 1 mixture was due to **2a** or **2c**, and not to **2b**.

The unique complex **2** can be compared with the previous Dawson polyoxotungstate-based organometallic complexes such as **5**,[5a] **6**[5b] and **7**.[1a–c] Herein, we report full details of the synthesis and spectroscopic characterization of the unprotonated polyoxotungstate support **1**, and the Cp*Rh^{2+} complex **2** both as a brown powder and as dark red crystals, with complete elemental analysis including oxygen, TG/DTA, FTIR and multiple (^{51}V, ^{31}P, ^{183}W, ^{1}H and ^{13}C) NMR spectroscopies.

Results and discussion

Synthetic reactions, compositional identification and general properties

The unprotonated polyoxotungstate-support **1** was prepared *via* synthesis of K_8[α-1,2-$P_2W_{16}V_2O_{62}$], then $(NBu_4)_6H_2$[α-1,2-$P_2W_{16}V_2O_{62}$], and deprotonation with aqueous NBu_4OH. The K_8 salt was prepared according to the literature.[6b] The $(NBu_4)_6H_2$ salt was prepared from reaction of the K_8 salt in water with excess amounts of solid NBu_4Br and purified by the first reprecipitation from the CH_3CN solution with pH 1.5 unbuffered water and the second reprecipitation from the CH_3CN solution with Et_2O. The molecular formulas of the $(NBu_4)_6H_2$ salt and the $(NBu_4)_8$ salt **1**, both isolated without any solvated molecules, were consistent with all data of complete elemental analysis (all elements including oxygen), TG/DTA, FTIR, and ^{31}P, ^{51}V and ^{183}W NMR spectra.

Complex **2** was obtained as a brown powder in 64.8% (0.30 g scale) yield by 1 : 1 molar-ratio, stoichiometric reaction in ice-cooled CH_2Cl_2 under air of the polyoxotungstate support **1** with [Cp*$RhCl_2$]$_2$ without the use of $AgBF_4$, followed by repeated reprecipitations from the ice-cooled CH_2Cl_2 solution with excess amounts of ice-cooled EtOAc. The molecular formula of **2** was consistent with all data of complete elemental analysis, TG/DTA, FTIR, and solution (^{51}V, ^{31}P, ^{183}W, ^{1}H and ^{13}C) NMR spectroscopies. The formation of **2** is shown in eqn. 1.

$$[\mathrm{Cp^*RhCl_2}]_2 + 2\,(\mathrm{NBu_4})_8[\alpha\text{-}1,2\text{-}\mathrm{P_2W_{16}V_2O_{62}}]\ \mathbf{1} \longrightarrow 2\,(\mathrm{NBu_4})_6[(\mathrm{Cp^*Rh})(\alpha\text{-}1,2\text{-}\mathrm{P_2W_{16}V_2O_{62}})]\ \mathbf{2} + 4\,\mathrm{NBu_4Cl} \quad (1)$$

In the present synthesis, compared with those of other polyoxoanion-based organometallics,[1,3,5a] there are several noteworthy points. (i) The work-ups of reaction and isolation required the ice-cooled temperature condition, because **2** in CH_2Cl_2 gradually decomposed at room temperature. Its decomposition was slowed under ice-cooled conditions. (ii) The reaction proceeded without the use of silver(I) salts such as $AgBF_4$ and $AgNO_3$, which have been usually used to remove the chloride ions from the precursors such as $CpTiCl_3$ and [Cp*$RhCl_2$]$_2$.[1,3] The chlorine analysis revealed that no Cl atom is contained in the final product of **2**, *i.e.* both in a brown powder and in dark red crystals. (iii) The appropriate solvent was CH_2Cl_2. The stability of **2** in coordinating solvents, *e.g.* CH_3CN and DMSO, was very low; in such solvents a part of the supported Cp*Rh^{2+} groups was removed from the polyoxoanion surface to produce [Cp*Rh(solvent)$_3$]$^{2+}$ which will be present as the counter cation of the polyoxotungstate-support.[5b] (iv) This reaction proceeded under air; an inert atmosphere was not required. (v) The synthetic stoichiometry to obtain a pure form of **2** in good yield was 1 : 1 molar ratio of **1** : [Cp*$RhCl_2$]$_2$, although all the starting molar ratios tested, *e.g.* 1 : 1/2, 1 : 1, 1 : 3/2, 1 : 5/2 and 1 : 5, gave complex **2** (see Table S in the electronic supplementary information (ESI)). (vi) The free NBu_4Cl as by-product was completely removed by reprecipitation with ice-cooled EtOAc, and **2** as a brown powder was isolated without any solvated molecules and any adducts. (vii) The UV-vis absorption titration experiments[2a] at 339 nm showed a formation of the 1 : 1-composition in CH_2Cl_2, because a break point of absorbance was found at the 1 : 1 ratio of [Cp*Rh]$^{2+}$/[$P_2W_{16}V_2O_{62}$]$^{8-}$.

The purity and molecular composition of **2** as a brown powder were established by complete elemental analysis (all elements including oxygen, and adding up to 99.26%), in which 0.74% difference from 100% can be attributed to only the difference of O analysis (calc. 17.13, found 16.40%). FTIR measurements confirm that the Dawson-type "$P_2M_{18}O_{62}{}^{n-}$" polyoxometalate framework remains intact under the conditions of synthesis (Fig. 2).[7] In the FTIR spectrum of the

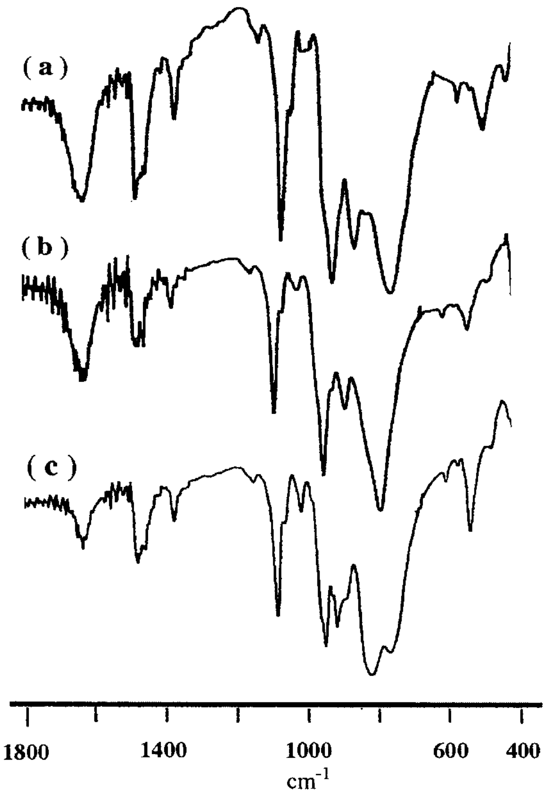

Fig. 2 FTIR spectra (KBr disks) of (a) $(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ **1**, (b) $(NBu_4)_6[(Cp^*Rh)(\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62})]$ **2** as the brown powder and (c) **2** as the dark red crystals. The observation of the characteristic Dawson-type polyoxoanion IR bands between 1100–400 cm^{-1} demonstrates that the $[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]^{8-}$ support-ion remains intact under the conditions of the synthesis.

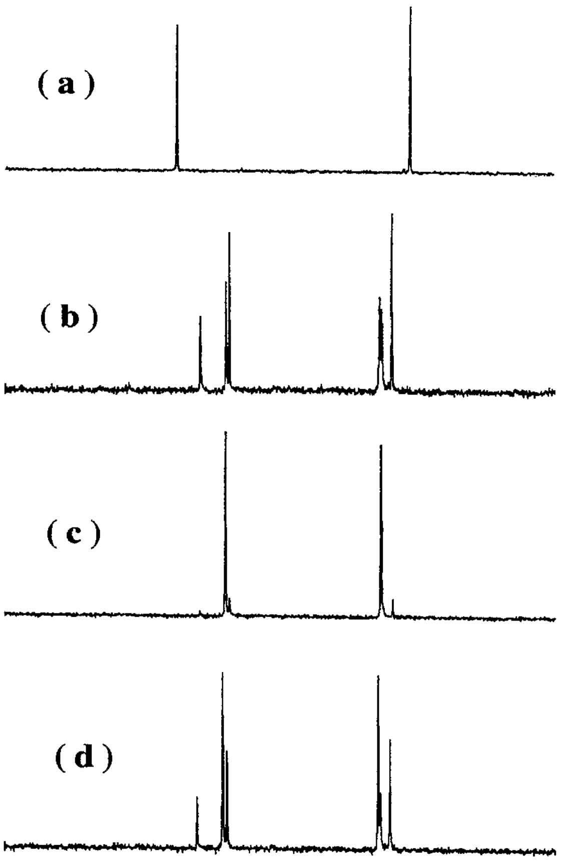

Fig. 3 ^{31}P NMR in CD_2Cl_2 with reference to external 25% H_3PO_4 in H_2O of (a) $(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ **1**, (b) $(NBu_4)_6[(Cp^*Rh)(\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62})]$ **2** as the brown powder, (c) **2** as the dark red crystals just after dissolving and (d) after standing the solution of the dark red crystals for 5 h at room temperature. In each case a very high level of purity is indicated (*i.e.* with respect to any other P-containing polyoxoanions).

brown powder, the major change relative to **1** was not seen in the polyoxometalate region.

The dark red granular crystals were also obtained in 21.6% (0.1 g scale) yield by dissolving the brown powder in ice-cooled CH_2Cl_2 and placing the solution in a refrigerator at −20 °C for two days, although the crystals were not suitable for X-ray structure analysis. The purity and the composition without any solvated molecules were also established by complete elemental analysis (all elements including oxygen, and adding up to 98.04%), where 1.96% difference from 100% can also be attributed to only the difference of O analysis (calc. 17.13, found 15.40%). In the FTIR of the dark red crystals, a major change was seen; the 942 and 781 cm^{-1} bands in **1**, respectively assignable to $M\text{–}O_{terminal}$ and $M\text{–}O_{edge}\text{–}M$ oxygens,[7] changed to the bands at 945 and (811, 759) cm^{-1}, respectively, and the 880 cm^{-1} band in **1** assignable to $M\text{–}O_{corner}\text{–}M$ oxygens[7] remarkably shifted to a higher energy band at 913 cm^{-1}.

Spectroscopic (^{51}V, ^{31}P, ^{183}W, ^{1}H and ^{13}C NMR) characterization

The polyoxotungstate-support precursor, *i.e.* the K_8 salt, showed a clean two-line spectrum of ^{31}P NMR in D_2O (δ_P −9.1, −13.7) and a very sharp single resonance of the ^{51}V NMR spectra in D_2O (δ_V −531.6), which were in good agreement with the literature data; δ_P −8.82, −13.44;[6b] δ_P −9.3, −13.9;[6a] δ_V −527.5 ($\Delta\nu_{1/2}$ 180 Hz);[6b] δ_V −528 ($\Delta\nu_{1/2}$ 70 Hz).[6a] The ^{31}P NMR data in CD_2Cl_2 of the $(NBu_4)_6H_2$ salt and the $(NBu_4)_8$ salt **1** showed a clean two-line spectrum at (δ_P −9.9, −13.2) and (δ_P −9.4, −14.1), respectively, confirming their homogeneity and purity (Fig. 3a). The ^{51}V NMR data of the $(NBu_4)_6H_2$ salt in DMSO-d_6 and the $(NBu_4)_8$ salt **1** in CD_2Cl_2 showed a very broad, single-line spectrum at δ_V −577.7 ($\Delta\nu_{1/2}$ 2261.9 Hz) and a relatively sharp single-line spectrum at δ_V −513.6 ($\Delta\nu_{1/2}$ 161.6 Hz), respectively (Fig. 4a). The line broadening of the $(NBu_4)_6H_2$ salt implies the presence of rapid transfers of two hydrogen ions on the V_2W surface.[3a] The ^{183}W NMR of **1** in CD_2Cl_2 showed a sharp seven-line (δ_W −99.7, −139.6, −167.4, −169.8, −179.5, −200.2, −201.6) plus a very broad two-line (δ_W −52.0, −157.8) spectrum as the expected nine-line spectrum (Fig. 5a), in which two broadened peaks around δ_V −57.0 and −157.8 are due to $^{51}V\text{–}^{183}W$ couplings.[3a]

The ^{31}P NMR in CD_2Cl_2 at room temperature of the polyoxotungstate-supported Cp^*Rh^{2+} complex **2** as a brown powder showed three sets of clear two-line ^{31}P NMR spectrum at (δ_P −10.4, −13.7), (δ_P −9.9, −13.5) and (δ_P −10.4, −13.5) with relative intensity ratio of *ca.* 2 : 1 : 1, respectively, suggesting the presence of three different species of the supported Cp^*Rh^{2+} group (Fig. 3b), and also a very high level of purity. The downfield resonance in each two-line ^{31}P NMR spectrum is assignable to the phosphorus (P(1) atom) closest to the V_2W site, whereas the upfield resonance is assignable to the phosphorus (P(2) atom) closest to the W_3 cap site. By bonding of the Cp^*Rh^{2+} group, the chemical shift of the P(1) atom is substantially changed from those of **1** (δ_P −9.4 in CD_2Cl_2). The ^{51}V NMR in CD_2Cl_2 at room temperature of the brown powder showed a four-line spectrum consisting of two major peaks at δ_V−547.8 ($\Delta\nu_{1/2}$ 289.1 Hz) and −564.2 ($\Delta\nu_{1/2}$ 313.2 Hz) and two minor peaks at δ_V −528.7 ($\Delta\nu_{1/2}$ 253.0 Hz), −536.4 ($\Delta\nu_{1/2}$ 397.6 Hz), in addition to the signal due to **1** at δ_V −514.3 which was produced by decomposition during the ^{51}V NMR measurements (Fig. 4b).

The ^{31}P and ^{51}V NMR spectral patterns of the brown powder were almost unchanged by varied temperature of the CD_2Cl_2 solution (25 to −90 °C) and, also, by the varied molar ratio of the starting materials, *i.e.* **1** : $[Cp^*RhCl_2]_2$ (1 : 1/2 to 1 : 5). (see

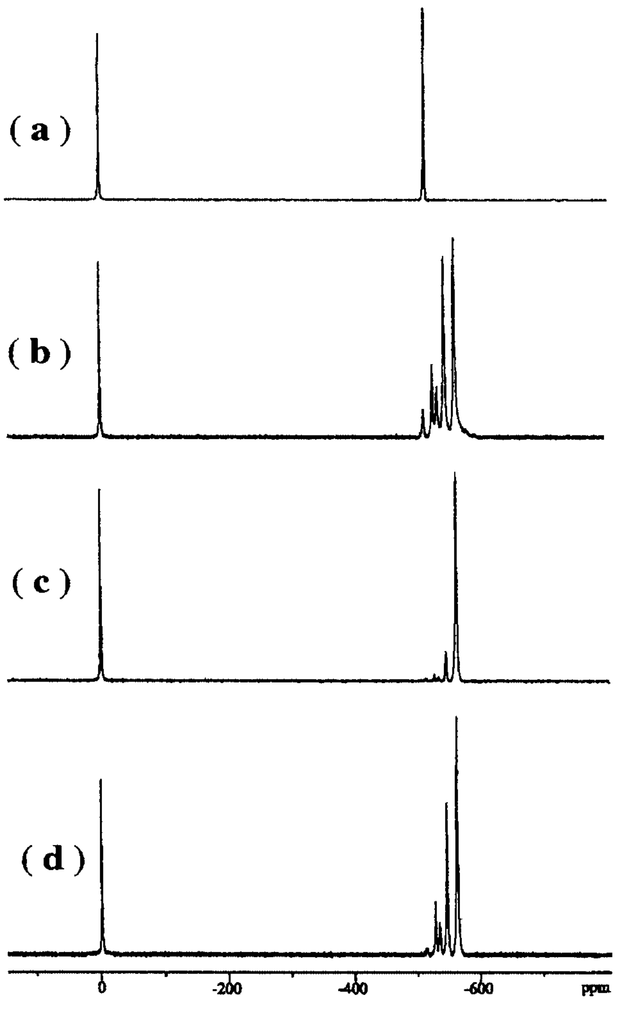

Fig. 4 ^{51}V NMR in CD_2Cl_2 with reference to external $VOCl_3$ of (a) $(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ **1**, (b) $(NBu_4)_6[(Cp^*Rh)(\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62})]$ **2** as the brown powder, (c) **2** as the dark red crystals just after dissolving and (d) after standing the solution of the dark red crystals for 5 h at room temperature.

the Experimental section and Table S in ESI). ^1H NMR in CD_2Cl_2 at room temperature of the brown powder showed three signals at δ_H 1.93, 1.91 and 1.89 due to the C_5Me_5 proton of the supported Cp^*Rh^{2+} group with *ca.* 1 : 2 : 1 ratio, respectively. Correspondingly, ^{13}C NMR in CD_2Cl_2 showed three carbon resonances due to three different methyl groups at δ_C 9.40, 9.32, 9.28. These facts strongly support the brown powder complex of **2** containing three different supporting sites of the Cp^*Rh^{2+} group on the V_2W surface. One Cp^*Rh^{2+} group is probably supported on a central position of the B-site (**2a**, C_s symmetry), one is on either one of two vanadium octahedra of the B-site (**2b**, C_1 symmetry), and one is on a tungsten octahedron of the B-site (**2c**, C_s symmetry) (Fig. 1b). The Cp^*Rh^{2+} group in **2a**, **2b** and **2c** will be covalently bound on the polyoxotungstate surface and the distribution of the species is in *ca.* 1 : 2 : 1 ratio. The multiple signals of the ^{183}W NMR in CD_2Cl_2 at room temperature were observed; for the expected 34-line spectrum (9 × 2 signals for two C_s symmetry species **2a** and **2c**, and 16 signals for C_1 symmetry species **2b**), more than 24 signals were detected (Fig. 5b). However, this ^{183}W NMR spectrum is very complex, because many signals of **1** formed by decomposition during measurements are contained, several true signals are potentially overlapped and several true signals are broadened due to $^{51}V-^{183}W$ couplings.

On the other hand, the ^{31}P and ^{51}V NMR in CD_2Cl_2 of **2** as dark red crystals, which were obtained by recrystallization of the brown powder from CH_2Cl_2 solution at −20 °C, have shown that one of three species (**2a**, **2b** and **2c**) is readily crystallized.

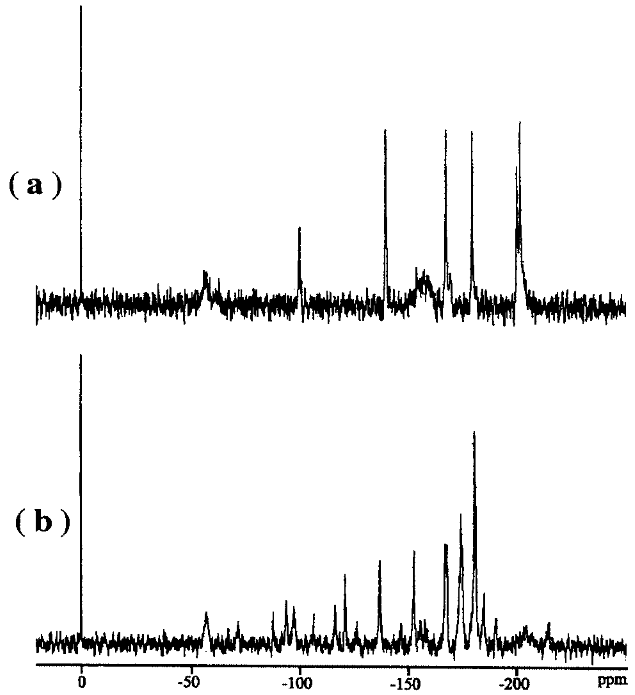

Fig. 5 ^{183}W NMR in CD_2Cl_2 with reference to external Na_2WO_4–D_2O saturated solution of (a) $(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ **1** and (b) $(NBu_4)_6[(Cp^*Rh)(\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62})]$ **2** as the brown powder. In (b), many signals of **1** formed by decomposition during measurements are contained, several true signals are potentially overlapped and several true signals are broadened due to ^{51}V–^{183}W couplings.

In fact, the dark red crystals of **2** contained one predominant species with NMR resonances (δ_H 1.91, δ_P −10.3 and -13.4, δ_V −563.4) in CH_2Cl_2 solution just after dissolving (Figs. 3c, 4c), but the species then changed to the *ca.* 1 : 2 : 1 mixture of **2a**, **2b** and **2c** (δ_H 1.89. 1.91, 1.94; δ_P (−10.4, −13.7), (−9.8, −13.5) and (−10.3, −13.4); δ_V −547.1, −563.3, −528.5, −535.2, in addition to a trace peak due to **1** at δ_V −515.0) by standing during 5 h in CH_2Cl_2 solution at room temperature (Figs. 3d, 4d).

Further, from the ^{51}V and ^{31}P NMR changes the dark red crystals have shown, at least one of the three species (**2a**, **2b** and **2c**) can be assigned. The ^{51}V NMR of species **2b** should be a two-line spectrum with equal intensity, while those of **2a** and **2c** should be a single-line spectrum, respectively. The ^{51}V NMR of the dark red crystals just after dissolving in CD_2Cl_2 showed one major peak at δ_V −563.4 and one minor peak at δ_V −547.2. After standing the solution for more than 5 h at room temperature, the ^{51}V NMR showed two major peaks at δ_V −547.1 and −563.3 and two minor peaks with almost equal intensity at δ_V −528.5 and −535.2. This ^{51}V NMR spectrum is the same as that of the solution of the powder sample. This spectral change suggests that two minor peaks with almost equal intensity at δ_V −528.5 and −535.2 are due to the species **2b**, and, therefore, two major peaks at δ_V −547.1 and −563.3 are due to either one of the species **2a** or **2c**, *vice versa*. Correspondingly, in the ^{31}P NMR of the dark red crystals just after dissolving in CD_2Cl_2, the minor peaks at δ_P (−9.8 and −13.5) are due to the species **2b**, and the major peaks observed at δ_P (−10.3 and −13.4) and minor peaks at δ_P (−10.4 and −13.7) are due to the species **2a** or **2c**, respectively.

The intensity ratios of ^{31}P and ^1H NMR of the brown powder show *ca.* 1 : 2 : 1 ratio of the three species. This ratio also corresponds to that observed in the ^{51}V NMR of the powder sample. Thus, the most intense peak in the 1 : 2 : 1 mixture is due to **2a** or **2c**, and not to **2b**.

Comparison of 2 with the related organometallic complexes

Compared with the recently prepared 2 : 1-type Cp^*Rh^{2+} complex, **6**,[5b] the reason why only one Cp^*Rh^{2+} group is supported on the V_2W surface in **2** is attributable to a lower surface charge of **1** than that of the $[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]^{9-}$. The three bonding sites of one Cp^*Rh^{2+} group in **2** are also unique, which can be compared with the previous examples, **5** with C_s symmetry[5a] and **7** with C_{3v} symmetry.[1a–c] The present work suggests that the Cp^*Rh^{2+} group can be supported on three adjacent oxygen atoms of any triangular place in the V_2W surface, as observed in the brown powder of **2**. Complex **2** gradually decomposed in CH_2Cl_2 at room temperature, but the decomposition was considerably slowed at ice-cooled temperature and/or in the presence of $[Cp^*RhCl_2]_2$. Further, when complex **2** was dissolved in coordinating solvents such as CH_3CN and DMSO, a part of the supported Cp^*Rh^{2+} groups in the three species (**2a**, **2b** and **2c**) was removed from the polyoxoanion surfaces.

It has also been elucidated that complex **6** is stable in CH_2Cl_2, but unstable in CH_3CN; when complex **6** was dissolved in CH_3CN, the supported Cp^*Rh^{2+} group was removed from the polyoxoanion surface to produce $[Cp^*Rh(CH_3CN)_3]^{2+}$, which was present as the counter cation.[5b] Such phenomena have not been observed in the supported Cp^*Rh^{2+} complexes on triniobium-substituted Keggin and Dawson polyoxometalates such as $[(Cp^*Rh)(\beta\text{-}SiW_9Nb_3O_{40})]$[5–8] and **7**.[1a–c] 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.

Conclusion

The B-type unprotonated Dawson polyoxotungstate **1** has been successfully prepared. Using **1** as the polyoxotungstate support for the Cp^*Rh^{2+} group, a novel Dawson polyoxotungstate-based 1 : 1-type Cp^*Rh^{2+} complex **2** is first isolated as an analytically pure brown powder, which was present as a 1 : 2 : 1 mixture of **2a**, **2b** and **2c** with three different supporting sites of the Cp^*Rh^{2+} group. The dark red crystals, obtained by crystallization of the brown powder in CH_2Cl_2, initially contained one predominant species, but it readily reverted to the 1 : 2 : 1 mixture of **2a**, **2b** and **2c** in CH_2Cl_2 solution at room temperature. Compound **1** as the polyoxotungstate support shows that it has still enough surface negative-charge density to support the cationic organometallic group,[9] but the support chemistry of **1** is in contrast to that of the related polyoxoanion, $[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]^{9-}$. This work can also be extended to molecular design of multifunctional polyoxometalate-based novel heterogeneous and homogeneous catalysts.

Experimental

Materials

The following were used as received: $Na_2WO_4\cdot 2H_2O$, 85% H_3PO_4, $NaVO_3$, KCl, NBu_4Br, 0.41 M aqueous NBu_4OH, 6.0 M aqueous HCl (quantitative analysis grade), diethyl ether, ethyl acetate, dichloromethane, ethanol, acetonitrile (all from Wako); D_2O, CD_2Cl_2, DMSO-d_6 (Isotec). The precursor $[Cp^*RhCl_2]_2$ was prepared according to literature methods,[10a,b] and identified with elemental analysis, ^1H and ^{13}C NMR. The precursor $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 19H_2O$ was prepared according to literature methods,[10c,d] and identified with elemental analysis, TG/DTA, FTIR and ^{31}P NMR.

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. The CHN analyses were performed using Perkin-Elmer PE2400 series II CHNS/O analyzer (Kanagawa University, Japan). Infrared spectra were recorded on a Jasco 300 FT-IR 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 per min 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 solutions 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 an internal TMS. Chemical shifts were 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 $VOCl_3$ by the substitution method. 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. ^{183}W NMR (16.50 MHz) spectra were recorded in 10 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data-processing system. These spectra were referenced to an external standard of saturated Na_2WO_4–D_2O solution by the substitution method. Chemical shifts were reported on the δ scale with resonances upfield of Na_2WO_4 (δ 0) as negative. In Figs. 4 and 5, the spectra were drawn by overlapping the reference peaks with the spectra measured by the substitution method.

Preparations

$K_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]\cdot 15H_2O$. This compound was prepared by a reaction of 50.0 g (10.0 mmol) of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 19H_2O$ in 250 mL water with 90 mL of 0.5 M aqueous $NaVO_3$ under refluxing conditions according to the literature.[6b] Water-soluble, orange needle crystals were obtained in 46.1% (10.8 g scale) yield by repeated recrystallization from hot (*ca.* 80 °C) water. TG/DTA data: weight loss of 5.91% observed below 451 °C with endothermic peaks at 71, 91 and 151 °C; calc. for $x = 15$, 5.78% and calc. for $x = 16$, 6.14% in $K_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]\cdot xH_2O$. FTIR bands (KBr disk) in 1700–400 cm^{-1} region (polyoxometalate region): 1624m, 1084s, 1015w, 946s, 921s, 785s, 599w, 528w, 473w cm^{-1}. ^{31}P NMR (D_2O, 22.0 °C): δ −9.1, −13.7. ^{51}V NMR (D_2O, 22.0 °C): δ −531.6.

$(NBu_4)_6H_2[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$. This compound was prepared by a reaction of 10.0 g (2.11 mmol) of $K_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]\cdot 15H_2O$ in 200 mL water with 60.0 g (186.2 mmol) of solid NBu_4Br, and purified by the first reprecipitation from the CH_3CN solution (10 mL) with pH 1.5 unbuffered water (200 mL) and then by the second reprecipitation from the CH_3CN solution (10 mL) with Et_2O (300 mL). Yellow–orange powder, soluble in CH_3CN, DMSO, EtOH and CH_2Cl_2 and insoluble in water and Et_2O, was obtained in 56.3% (6.6 g scale) yield {Found (repeat trial for CHN analysis): C, 20.76 (20.83); H, 4.13 (3.85); N, 1.69 (1.27); O, 16.40; P, 1.01; V, 1.78; W, 52.70; total 98.65%. Calc. for $C_{96}H_{218}N_6O_{62}P_2V_2W_{16}$ or $(NBu_4)_6H_2[P_2W_{16}V_2O_{62}]$: C, 20.76; H, 3.96; N, 1.51; O, 17.86; P, 1.12; V, 1.83; W, 52.96%}. Weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before analysis: 0.56% which shows this compound almost non-hygroscopic. TG/DTA data: no weight loss observed below 467 °C with exothermic peaks at 247, 275 and 391 °C. FTIR bands (KBr disk) in 1700–400 cm^{-1} region (polyoxometalate region): 1637m, 1483m, 1380m, 1086m, 951s, 915m, 788s, 600w, 527w cm^{-1}. ^{31}P NMR (DMSO-d_6, 23.0 °C): δ −9.2, −13.0. ^{31}P NMR (CD_2Cl_2, 22.7 °C): δ −9.9, −13.2. ^{51}V NMR (DMSO-d_6, 21.3 °C): δ −577.7 ($\Delta\nu_{1/2}$ 2261.9 Hz). ^{51}V NMR (CD_2Cl_2, 21.7 °C): δ −533.8, −577.1.

This compound in the solid state showed a color change from yellow-orange of the fresh sample to greenish after a couple of weeks at room temperature, and the ^{31}P and ^{51}V NMR showed several new minor peaks, in addition to the original major peaks.

$(NBu_4)_8[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ 1. The unprotonated polyoxotungstate-support **1** was prepared by deprotonation of 3.0 g (0.54 mmol) $(NBu_4)_6H_2[\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62}]$ in 50 mL of CH_3CN with 2.64 mL of 0.41 M aqueous NBu_4OH. The reaction solution was evaporated to dryness by a rotary evaporator at 40 °C. Orange powder, soluble in CH_3CN, DMSO and CH_2Cl_2, was obtained in 89.0% (2.9 g scale) yield {Found (repeat trial for CHN analysis): C, 25.61 (25.50); H, 5.10 (4.73); N, 1.97 (1.67); O, 16.30; P, 1.01; V, 1.72; W, 48.40; total 100.11%. Calc. for $C_{128}H_{288}N_8O_{62}P_2V_2W_{16}$ or $(NBu_4)_8[P_2W_{16}V_2O_{62}]$: C, 25.47; H, 4.81; N, 1.86; O, 16.43; P, 1.03; V, 1.69; W, 48.73%}. Weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before analysis: 1.98% which shows this compound slightly hygroscopic. TG/DTA data: no weight loss observed below 475 °C with exothermic peaks at 232, 278 and 475 °C. FTIR bands (KBr disk) in 1700–400 cm^{-1} region (polyoxometalate region): 1636m, 1485m, 1466m, 1381m, 1152w, 1084s, 1062m, 1037w, 1014w, 942s, 880m, 781s, 599w, 529w, 468w cm^{-1}. ^{31}P NMR (DMSO-d_6, 22.4 °C): δ −9.2, −13.8. ^{31}P NMR (CD_2Cl_2, 22.0 °C): δ −9.4, −14.1. ^{51}V NMR (DMSO-d_6, 23.0 °C): δ −515.9 ($\Delta\nu_{1/2}$ 308.2 Hz). ^{51}V NMR (CD_2Cl_2, 21.7 °C): δ −513.6 ($\Delta\nu_{1/2}$ 161.6 Hz). ^{183}W NMR (CD_2Cl_2, 23.0 °C): δ −57.0 (br), −99.7, −139.6, −157.8 (br), −167.4, −169.8, −179.5, −200.2, −201.6.

$(NBu_4)_6[(Cp^*Rh)(\alpha\text{-}1,2\text{-}P_2W_{16}V_2O_{62})]$ 2 as brown powder. Synthesis was performed under air. To 0.48 g (0.08 mmol) of $(NBu_4)_8[P_2W_{16}V_2O_{62}]$ dissolved in 10 mL of ice-cooled CH_2Cl_2 0.05 g (0.08 mmol) of solid $[Cp^*RhCl_2]_2$ was added. Stirring for 3 h was performed in an ice bath. The dark red clear solution was added dropwise into 500 mL of ice-cooled EtOAc, and the mixture was stirred for 30 min. The brown powder was collected on membrane filter (JG 0.2μm), thoroughly sucked and dried *in vacuo* for 2 h. The yield at this stage was 0.37 g. The brown powder of **2** was again reprecipitated by adding the solution dissolved in 5 mL of ice-cooled CH_2Cl_2 to 500 mL of ice-cooled EtOAc. Finally, brown powder obtained in 64.8% (0.30 g scale) yield was soluble in CH_2Cl_2, sparingly soluble in $CHCl_3$, but insoluble in EtOAc and Et_2O {Found (repeat trial for CHN analysis): C, 22.00 (22.38); H, 4.21 (2.99); N, 1.57 (1.40); Cl, 0.20; O, 16.40; P, 0.97; V, 1.78; Rh, 1.90; W, 50.20; total 99.26%. Calc. for $C_{106}H_{231}N_6O_{62}P_2V_2RhW_{16}$ or $(NBu_4)_6[(Cp^*Rh)P_2W_{16}V_2O_{62}])$: C, 21.99; H, 4.02; N, 1.45; Cl, 0.00; O, 17.13; P, 1.07; V, 1.76; Rh, 1.78; W, 50.80%}. Weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before analysis: 0.50% which shows this compound almost non-hygroscopic. TG/DTA data: weight loss of 0.53% observed below 146 °C; decomposition began around 150 °C with an exothermic peak at 258 °C. FTIR bands (KBr disk) in 1700–400 cm^{-1} region (polyoxometalate region): 1637m, 1484m, 1459m, 1380m, 1152w, 1085s, 1022w, 943vs, 920w, 881m, 785vs, 670w, 599w, 566w, 528w, 469w, 419w cm^{-1}. ^{1}H NMR (CD_2Cl_2, 23.1 °C): δ (C_5Me_5) (minor peak) 1.89, (major peak) 1.91, (minor peak) 1.93. ^{1}H NMR (CD_2Cl_2, −10.1 °C): δ (C_5Me_5) 1.90, 1.93, 1.95. ^{1}H NMR (CD_2Cl_2, −29.9 °C): δ (C_5Me_5) 1.90, 1.94, 1.95. ^{1}H NMR (CD_2Cl_2, −49.7 °C): δ (C_5Me_5) 1.91, 1.95. ^{1}H NMR (CD_2Cl_2, −90.4 °C): δ (C_5Me_5) 1.92, 1.96. ^{13}C NMR (CD_2Cl_2, 22.7 °C): δ (C_5Me_5) 9.28, 9.32, 9.40, (C_5Me_5) 94.7–94.9. ^{31}P NMR (CD_2Cl_2, 22.2 °C): δ (major peaks) (−10.4, −13.7), (minor peaks) (−9.9, −13.5), (−10.4, −13.5). ^{51}V NMR (CD_2Cl_2, 23.0 °C): δ (trace peak due to **1**) −514.3, (major peak) −547.8 ($\Delta\nu_{1/2}$ 289.1 Hz), −564.2 ($\Delta\nu_{1/2}$ 313.2 Hz), (minor peaks) −528.7 ($\Delta\nu_{1/2}$ 253.0 Hz), −536.4 ($\Delta\nu_{1/2}$ 397.6 Hz). ^{51}V NMR (CD_2Cl_2, 9.9 °C): δ (trace peak due to **1**) −514.0, (major peaks) −548.7, −565.3, (minor peaks) −528.5, −537.0. ^{51}V NMR (CD_2Cl_2, −10.0 °C): δ (trace peak due to **1**) −515.5, (major peaks) −550.4, −567.7, (minor peaks) −529.2, −539.4. ^{51}V NMR (CD_2Cl_2, −30.0 °C): δ (trace peak due to **1**) −516.9, (major peaks) −551.9, −570.4, (minor peaks) −529.8, −541.1. ^{51}V NMR (CD_2Cl_2, −50.0 °C): δ (major peaks) −553.7, −573.0, (minor peaks) −530.3, −543.2. ^{51}V NMR (CD_2Cl_2, −70.3 °C): δ (major peaks) −555.7, −576.5, (minor peaks) −531.5, −546.5. ^{51}V NMR (CD_2Cl_2, −90.4 °C): δ (major peak) −557.4, (minor peaks) −532.4, −548.6, −579.2. ^{183}W NMR (CD_2Cl_2, 22.6 °C): δ −37.6, −56.8, −71.5, −87.5, −93.5, −97.0, −106.2, −116.3, −120.7, −126.0, −136.7, −146.6, −152.5, −155.6, −157.6, −167.1, −167.8, −173.7, −174.3, −175.0, −180.6, −184.2, −184.9, −190.7, −214.7.

Since compound **2** in CH_2Cl_2 gradually decomposed at room temperature, the ^{183}W NMR spectrum is contaminated with signals due to **1** formed by decomposition during measurements. ^{31}P NMR measurements showed that its decomposition was slowed in ice-cooled temperature and/or in the presence of $[Cp^*RhCl_2]_2$. Further, the ^{31}P and ^{51}V NMR measurements showed that when this compound was dissolved in CH_3CN and DMSO, some of the supported Cp^*Rh^{2+} groups were removed from the polyoxoanion surfaces.

Crystallization of brown powder of 2 to dark red crystals. The brown powder of **2** was dissolved in 3 mL of ice-cooled CH_2Cl_2 and the solution was left to stand for two days in a refrigerator at −20 °C. The dark red granular crystals formed were collected on membrane filter (JG 0.2μm), washed with 2 mL of ice-cooled CH_2Cl_2 and dried *in vacuo* for 2 h. The crystals changed to a dark red powder. The dark red powder, soluble in CH_2Cl_2, sparingly soluble in $CHCl_3$, and insoluble in EtOAc and Et_2O, was obtained in 21.6% (0.1 g scale) yield {Found (repeat trial for CHN analysis): C, 21.96 (21.69); H, 4.15 (3.78); N, 1.46 (1.39); Cl, <0.1; O, 15.40; P, 1.02; V, 1.74; Rh, 1.81; W, 50.50; total 98.04%. Calc. for $C_{106}H_{231}N_6O_{62}P_2V_2RhW_{16}$ or $(NBu_4)_6[(Cp^*Rh)P_2W_{16}V_2O_{62}]$: C, 21.99; H, 4.02; N, 1.45; Cl, 0.00; O, 17.13; P, 1.07; V, 1.76; Rh, 1.78; W, 50.80%}. Weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before analysis: 0.88% which shows this compound almost non-hygroscopic. TG/DTA data: weight loss of 0.67% observed below 131 °C; decomposition began around 200 °C with exothermic peaks at 234, 283 and 427 °C. FTIR bands (KBr disk) in 1700–400 cm^{-1} region (polyoxometalate region): 1637m, 1483m, 1379w, 1152w, 1084s, 1015w, 945s, 913m, 811vs, 759s, 670w, 662w, 599w, 565w, 526m, 470w cm^{-1}. ^{1}H NMR (CD_2Cl_2, 26.6 °C): δ (C_5Me_5) (major peak) 1.91, (minor peaks) 1.89, 1.94. ^{1}H NMR (CD_2Cl_2, 26.6 °C; measured after standing the solution for 5 h at room temperature): δ (C_5Me_5) (major peak) 1.91, (minor peaks) 1.89, 1.94. ^{31}P NMR (CD_2Cl_2, 26.7 °C): δ (major peaks) (−10.3, −13.4), (minor peaks) (−10.4, −13.7). ^{31}P NMR (CD_2Cl_2, 27.5 °C; measured after standing the solution for 5 h at room temperature): δ (major peaks) (−10.3, −13.4), (minor peaks) (−9.8, −13.5), (−10.4, −13.7). ^{51}V NMR (CD_2Cl_2, 26.6 °C): δ (trace peak due to **1**) −515.2, (major peak) −563.4, (minor peak) −547.2, (trace peaks) −528.3, −535.2. ^{51}V NMR (CD_2Cl_2, 27.4 °C; measured after standing the solution for 5 h at room temperature): δ (trace peak due to **1**) −515.0, (major peaks) −547.1, −563.3, (minor peaks) −528.5, −535.2.

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