Synthesis and Spectroscopic Characterization of a Dawson Trivanadium-Substituted Polyoxotungstate-Supported $\{(Cp^*Rh)_2\}^{4+}$ Complex; $(Bu^n{}_4N)_5[(Cp^*Rh)_2P_2W_{15}V_3O_{62}]$

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A novel polyoxotungstate-based 2 : 1-type Cp^*Rh^{2+} complex, $(Bu^n{}_4N)_5[(Cp^*Rh)_2P_2W_{15}V_3O_{62}]$ ($Cp^* = C_5Me_5$), was synthesized by a direct reaction of the Dawson trivanadium-substituted polyoxotungstate $(Bu^n{}_4N)_9[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]$ with an equimolar amount of $[Cp^*RhCl_2]_2$ in ice-cooled CH_2Cl_2, without use of silver(I) salts to remove the chloride ions of the precursor.

Numerous examples of Dawson polyoxoanion-supported organometallics have been so far described.[1] Recently, the Dawson triniobium-substituted polyoxotungstate-supported transition metal complexes, $[(CH_3CN)_xM]^{n+}$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, Zn^{II}) plus $[\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62}]^{9-}$, and oxygenation catalysis by their 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, $(Bu^n{}_4N)_7[\{(CH_3CN)_xFe^{II}\}P_2W_{15}V_3O_{62}]$, is noteworthy.[2c] Examples of vanadium-substituted polyoxoanion-supported organometallics are $[(CpTi)SiW_9V_3O_{40}]^{4-}$,[3] $[(Cp^*Rh)_4V_6O_{19}]$,[4a] $[\{(cod)Ir\}V_4O_{12}]^{3-}$ (cod = 1,5-cyclooctadiene)[4b] and $[\{(cod)Ir\}_2V_4O_{12}]^{2-}$.[4b] The only one example of the Dawson trivanadium-substituted polyoxotungstate-based organometallics is an unusual site-bonding 1 : 1-type compound $(Bu^n{}_4N)_6[(CpTi)\ P_2W_{15}V_3O_{62}]$ with C_s symmetry,[5] and not the initially anticipated C_{3v} symmetry.

In this work, we were successful in isolating a novel polyoxoanion-supported 2 : 1-type Cp^*Rh^{2+} complex, i.e., $(Bu^n{}_4N)_5[(Cp^*Rh)_2P_2W_{15}V_3O_{62}]$ **1** with C_s symmetry. Herein, we report the synthesis and spectroscopic characterization of **1**.

The complex **1** without solvated molecules was prepared by a direct reaction of $(Bu^n{}_4N)_9[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]$[3] with an equimolar amount of $[Cp^*RhCl_2]_2$[6] in ice-cooled CH_2Cl_2, and was purified by repeated reprecipitation with ice-cooled EtOAc.[7] The molecular formula of **1** obtained in 59% (0.27 g scale) yield was consistent with all data of complete elemental analysis, TG/DTA, FT-IR, and solution (^{183}W, ^{51}V, ^{31}P, ^{1}H and ^{13}C) NMR spectroscopies.[8] The formation of **1** is shown in Eq 1.

$$(Bu^n{}_4N)_9[P_2W_{15}V_3O_{62}] + [Cp^*RhCl_2]_2 \rightarrow (Bu^n{}_4N)_5[(Cp^*Rh)_2P_2W_{15}V_3O_{62}] + 4\ Bu^n{}_4NCl \quad (1)$$

The reaction of the B-type deprotonated polyoxotungstate $(Bu^n{}_4N)_9[P_2W_{15}V_3O_{62}]$ with $[Cp^*RhCl_2]_2$ proceeds in CH_2Cl_2 solvent. In the present synthesis, compared with those of other polyoxoanion-based organometallics,[1,3,5] there are several noteworthy points. (i) The work-ups of reaction and isolation require the ice-cooled temperature condition. (ii) The reaction proceeds without 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 $[Cp^*RhCl_2]_2$. (iii) The appropriate solvent is CH_2Cl_2. Since the reaction does not take place in a coordinating solvent such as CH_3CN, the reaction does not proceed via $[Cp^*Rh(CH_3CN)_3]^{2+}$ which has been *in situ* used for preparation of the traditional polyoxoanion-supported Cp^*Rh^{2+} complex.[1a,b] (iv) The synthetic stoichiometry to obtain **1** in good yield is 1 : 1 ratio of $(Bu^n{}_4N)_9[P_2W_{15}V_3O_{62}]$: $[Cp^*RhCl_2]_2$. Other starting ratios, e.g., the 1 : 0.5 ratio in CH_2Cl_2 gave a mixture of several species, including 1 : 1- and 2 : 1-type products, but not a single species. (v) The free by-product $Bu^n{}_4NCl$ was completely removed by the repeated reprecipitation with EtOAc, and **1** was isolated as an adduct with 0.2 $Bu^n{}_4NCl$. (vi) The stability of **1** in a coordinating solvent, e.g., CH_3CN, is very low; the supported Cp^*Rh^{2+} group is removed from the polyoxoanion surface to produce $[Cp^*Rh(CH_3CN)_3]^{2+}$ which is present as the countercation of the $[P_2W_{15}V_3O_{62}]^{9-}$. (vii) The UV-vis absorption titration experiments[2a] at 320 nm showed a formation of the 2 : 1-composition in CH_2Cl_2, because a break point of absorbance was found at the 2 : 1 ratio of $[Cp^*Rh]^{2+}/[P_2W_{15}V_3\ O_{62}]^{9-}$ (Figure 1). Thus, the composition of **1** is kept in CH_2Cl_2 solution.

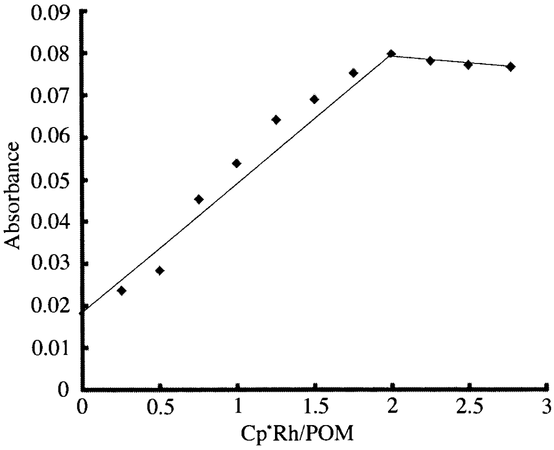

Figure 1. Plots of absorbance vs Cp^*Rh^{2+}/polyoxometalate (POM) molar ratio as UV-vis absorption titration curves at 320 nm in CH_2Cl_2.

The purity and molecular composition of **1** were established by complete elemental analysis (all elements, and adding up to 99.09%). No solvation was also confirmed by TG/DTA measurements. In the FT-IR spectrum of **1**, the major change relative to $(Bu^n{}_4N)_9[P_2W_{15}V_3O_{62}]$ was seen in the polyoxometalate region; the 936 and 776 cm^{-1} bands, respectively assignable to $M\text{-}O_{terminal}$ and edge-sharing M-O-M oxygens,[9] changed to explicit split bands at (957, 941) and (816, 778) cm^{-1}, respectively, and the 877 cm^{-1} band assignable to corner-sharing M-O-M oxygens[9] remarkably shifted to lower energy band at 912 cm^{-1}.

The ^{183}W NMR in CD_2Cl_2 (Figure 2) confirmed the C_s

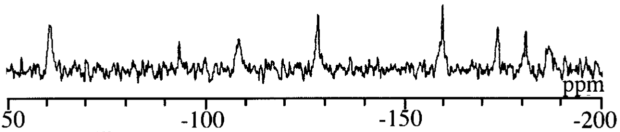

Figure 2. ^{183}W NMR spectrum of **1** in CD_2Cl_2.

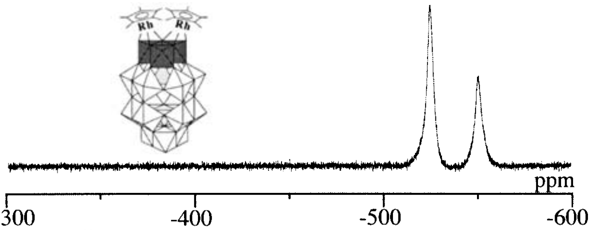

Figure 3. ^{51}V NMR spectrum of **1** in CD_2Cl_2.

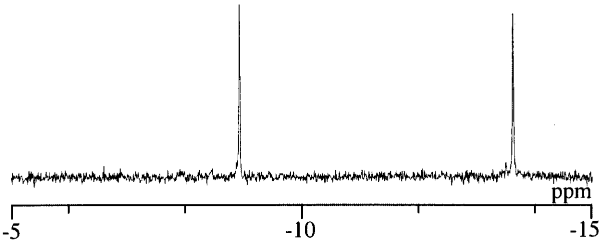

Figure 4. ^{31}P NMR spectrum of **1** in CD_2Cl_2.

symmetry by exhibiting an eight-line spectrum with relative intensities of 2 : 1 : 2 : 2 : 2 : 2 : 2 : 2 at -60.7, -93.3, -108.4, -128.3, -159.8, -173.7, -180.8 and -186.7 ppm, respectively. The line at -186.7 ppm was considerably broadened. The ^{51}V NMR in CD_2Cl_2 showed a clean, two-line spectrum of resonances at -524.9 and -550.3 ppm with 2 : 1 intensity ratio (Figure 3), suggesting that the Cp^*Rh^{2+} groups were attached to the $[P_2W_{15}V_3O_{62}]^{9-}$ polyoxotungstate in a way that yielded an overall C_s symmetry complex. The ^{31}P NMR spectrum in CD_2Cl_2 showed a simple two-line spectrum with resonances at -8.96 and -13.66 ppm (Figure 4), substantially different from the -6.74 and -14.48 ppm resonances of $(Bu^n_4N)_9[P_2W_{15}V_3O_{62}]$. The ^{31}P NMR spectrum confirms the homogeneity of **1** and, thus, the support-site regiospecificity in **1**. Further justification for the single product nature of the Cp^*Rh^{2+} complex comes from the single Cp^* resonance in CD_2Cl_2 seen in the ^{1}H NMR at 2.12 ppm ($C_5\mathit{Me}_5$), and ^{13}C NMR at 9.4 ($C_5\mathit{Me}_5$) and 95.1 ppm (C_5Me_5), respectively.

In summary, the formation of the 2 : 1-type Cp^*Rh^{2+} complex **1** is a rare example, and **1** is the second example which follows the trivanadium-substituted Dawson polyoxotungstate-based 1 : 1-type $CpTi^{3+}$ complex $(Bu^n_4N)_6[(CpTi)P_2W_{15}V_3O_{62}]$.[5]

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7 Synthesis of **1**: One precursor $(Bu^n_4N)_9[P_2W_{15}V_3O_{62}]$ was isolated via syntheses of $Na_{12}[P_2W_{15}O_{56}]\cdot 18H_2O$, $K_8H[P_2W_{15}V_3O_{62}]\cdot 9H_2O$ and $(Bu^n_4N)_5H_4[P_2W_{15}V_3O_{62}]$, and a deprotonation of the $(Bu^n_4N)_5H_4$ salt with Bu^n_4NOH,[3a] and identified with elemental analysis, FT-IR, ^{31}P and ^{51}V NMR. The other precursor $[Cp^*RhCl_2]_2$ was prepared according to literature methods,[6] and identified with elemental analysis, ^{1}H and ^{13}C NMR. To an orange solution of 0.50 g (0.081 mmol) of $(Bu^n_4N)_9[P_2W_{15}V_3O_{62}]$ dissolved in 10 cm^3 ice-cooled CH_2Cl_2, 0.050 g (0.081 mmol) of solid $[Cp^*RhCl_2]_2$ was added. After 3 h-stirring the resulting dark-red solution in ice-cooled bath, it was added dropwise to 500 cm^3 of ice-cooled EtOAc. A brown powder formed. After further 30 min-stirring the suspension, the brown precipitate was collected on a membrane filter (JG 0.2 μm). At this stage yield was 0.35 g. This powder was redissolved in ca. 2 cm^3 of ice-cooled CH_2Cl_2. The dark-red solution was added dropwise to 500 cm^3 of ice-cooled EtOAc. After 30 min-stirring, the brown precipitate was collected on a membrane filter (JG 0.2 μm), thoroughly dried by suction, and then dried *in vacuo*. The brown powder obtained in 59% (0.27 g) yield was soluble in CH_2Cl_2, but insoluble in EtOAc.

8 **1**: Anal. Found (repeat trials for CHN analysis): C, 21.92 (21.69); H, 3.96 (3.86); N, 1.38 (1.22); Cl, 0.25; O, 16.4; P, 1.07; V, 2.61; Rh, 3.20; W, 48.3; total 99.09% (from Mikroanalytisches Labor Pascher, Germany). Calcd for $C_{103.2}H_{217.2}N_{5.2}Cl_{0.2}O_{62}P_2V_3Rh_2W_{15}$ ($(Bu^n_4N)_5[(Cp^*Rh)_2P_2W_{15}V_3O_{62}]\cdot 0.2Bu^n_4NCl$): C, 21.71; H, 3.84; N, 1.28; Cl, 0.12; O, 17.38; P, 1.09; V, 2.68; Rh, 3.61; W, 48.31%. TG/DTA data: no weight loss was observed below 150 °C, suggesting no solvation; decomposition began around 192 °C with an exothermic peak at 260 °C. IR bands in 1700 - 400 cm^{-1} region (KBr disk): 1636m, 1483m, 1378m, 1153w, 1084s, 1053m, 1026w, 957s, 941s, 912s, 816s, 778s, 670w, 661w, 599w, 565w, 528w, 474w cm^{-1}. ^{1}H NMR (399.65 MHz, CD_2Cl_2, 25 °C): 2.12 ppm. ^{13}C NMR (100.40 MHz, CD_2Cl_2, 25 °C): 9.4 ($C_5\mathit{Me}_5$), 95.1 (C_5Me_5) ppm. ^{31}P NMR (161.70 MHz, CD_2Cl_2, 25 °C): -8.96, -13.66 ppm. ^{51}V NMR (104.95 MHz, CD_2Cl_2, 25 °C): -524.9, -550.3 ppm. ^{183}W NMR (16.59 MHz, CD_2Cl_2, 25 °C): -60.7, -93.3, -108.4, -128.3, -159.8, -173.7, -180.8, -186.7 ppm.

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