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# Synthesis and X-Ray Structure of Cp*Rh(III)-Molybdate Complexes Derived from Bis(triphenylphosphineiminium) Mono- and Polymolybdates

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Reaction of $[\{Cp^*RhCl_2\}_2]$ ($Cp^*=\eta^5$-$C_5Me_5$) with the PPN ($PPN^+ = Ph_3P{=}N{=}PPh_3^+$) salts of iso- and heteropolymolybdates offers a good route to polyoxometallates containing organometallics; the syntheses and X-ray structures of $[(Cp^*Rh)_4(Mo_4O_{16})]$, containing a tris-cubane oxotetramolybdenum skeleton (derived from $(PPN)_2[MoO_4]\cdot 6H_2O$) and the ionic $[Cp^*RhCl_3RhCp^*]^+[PPN]^+_2[PMo_{12}O_{40}]^{3-}$ (derived from $(PPN)_2[Mo_2O_7]$) are described.

Organometallics anchored to polyoxoanions of early transition metals are currently of special interest,[1] as they provide useful models for oxide-supported metal catalysts, and also allow the study of soft acid (organometallic) – hard base (polyoxometallate) interactions. Since the synthesis of such complexes proceeds better in non-aqueous media, we have developed routes to the bis-triphenylphosphineiminium ($Ph_3P{=}N{=}PPh_3^+$,$PPN^+$) salts of oxometallate anions, which are soluble in organic solvents.

The following PPN iso- and heteropolyoxometallates were made by metathesis of PPN chloride with the appropriate salt or acid in water: $(PPN)_2[MoO_4]\cdot 6H_2O$ **1**, $(PPN)_2[WO_4]\cdot 4H_2O$ **2**, $(PPN)_2[Mo_2O_7]$ **3**, $(PPN)_2[Mo_6O_{19}]$ **4**, $(PPN)_3[PMo_{12}O_{40}]\cdot 2CHCl_3$ **5a**, $(PPN)_3[PMo_{12}O_{40}]\cdot(CH_3)_2CO$ **5b**, $(PPN)_3[PW_{12}O_{40}]\cdot 2CHCl_3$ **6** and $(PPN)_3[HV_{10}O_{28}]$ **7**.[2,†]

† Starting oxometallates and yields, based on [PPN]Cl (in brackets) were as follows: **1**, $Na_2[MoO_4]\cdot 2H_2O$ in 0.1 mol $dm^{-3}$ NaOH (88%); **2**, $Na_2[WO_4]\cdot 2H_2O$ in water (91%); **3**, $Na_2[MoO_4]\cdot 2H_2O$ in water (89%); **4**, $Na_2[Mo_6O_{19}]$ in 6 mol $dm^{-3}$ HCl (85% on Mo); **5** $(H_3O)_3[PMo_{12}O_{40}]\cdot 21H_2O$ [**5a**, recrystallized from $CHCl_3$, 65%]; **5b**, [recrystallized from acetone, 83%]; **6**, $(H_3O)_3[PW_{12}O_{40}]\cdot \sim 20H_2O$ (88%); **7**, $Na_6[V_{10}O_{28}]\cdot 18H_2O$ in 0.17 mol $dm^{-3}$ aqueous acetic acid (63%). Elemental analyses and $^1H$ NMR data fitted the formulations **1–7**.

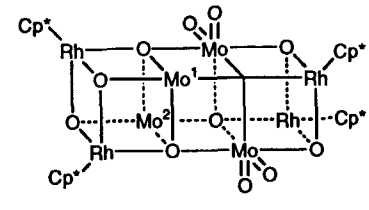


**Fig. 1.** Schematic representation of $[(Cp^*Rh)(Mo_4O_{16})]$ tris-cubane complex.[3] Two pairs of oxygen atoms adjacent to $Mo^1$ and $Mo^2$ are omitted.

All the salts had good solubility in acetonitrile, DMF or DMSO, were less soluble in acetone, $CH_2Cl_2$ or chloroform and poorly soluble in ether or benzene.

Both the PPN mono- and dimolybdate, **1** and **3**, reacted with pentamethylcyclopentadienylrhodium(III) chloride (acetonitrile, 20 °C) to give a crystalline complex, $Cp^*RhMoO_4\cdot CH_3CN$ **8**. Preliminary X-ray data of a single crystal of **8** showed its identity to be that obtained previously by the reaction of $[\{Cp^*RhCl_2\}_2]$ with $Na_2MoO_4\cdot 2H_2O$ in aqueous solution (followed by recrystallization from acentoni-

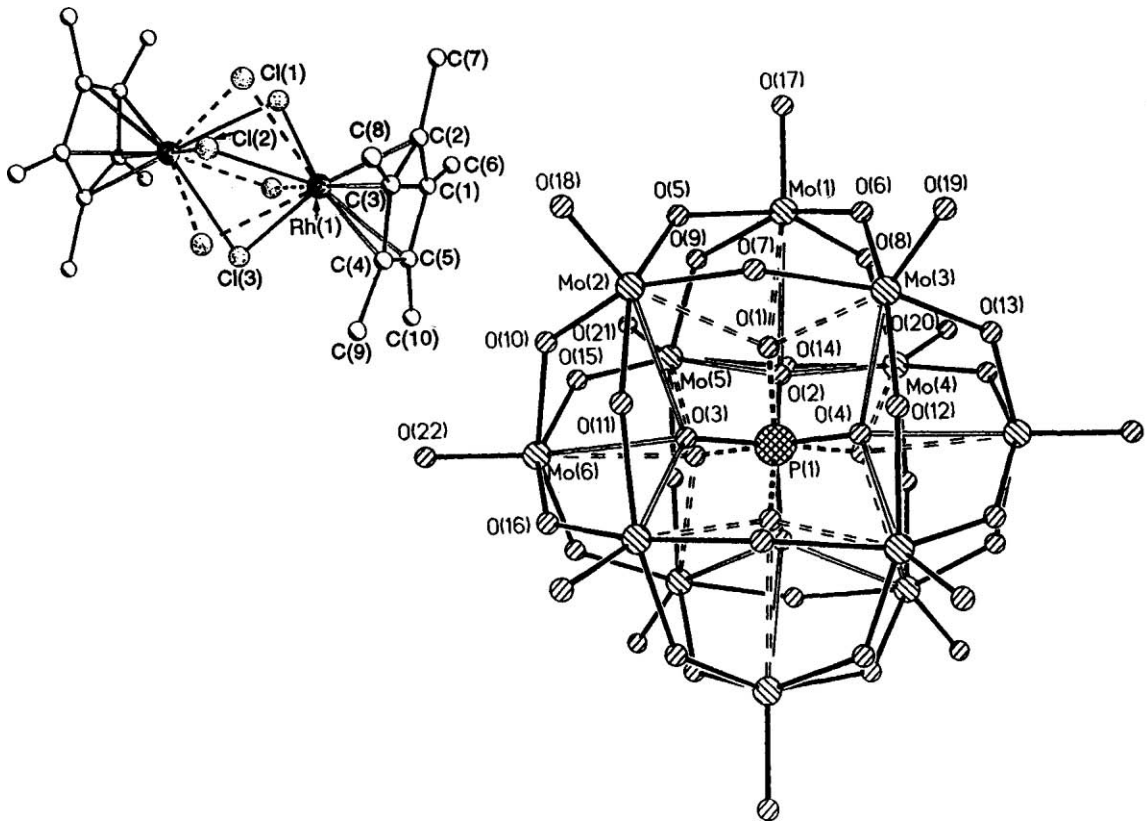


**Fig. 2.** The structure of the $[PMo_{12}O_{40}]^{3-}$ anion and of the $[Cp^*RhCl_3RhCp^*]^+$ cation in crystal **9** (bonds to the second positions of disordered atoms are shown by the dashed lines). Selected distances: P–O 1.50–1.54, Mo–O (inner) 2.44–2.51, Mo–O (bridging) 1.818–1.985, Mo=O (terminal) 1.643–1.667, Rh–Cl 2.379–2.468, Rh–C(Cp*) 2.11–2.16, Rh···Rh 3.220(1) Å.

trile)[3] (Fig. 1).‡ Thus, oligomerization of $MoO_4^{2-}$ anions to the tetrameric tris-cubane $[Mo_4O_{16}]^{8-}$ species also occurs in non-aqueous medium, and the Lewis acidity of $Cp^*Rh^{2+}$ seems to be the main driving force of the reaction (1).

$$[MoO_4]^2 + 2[\{Cp^*RhCl_2\}_2] \rightarrow [(Cp^*Rh)_4\{Mo_4O_16\}] \quad (1)$$

The complex $[\{Cp^*RhCl_2\}_2]$ also reacted easily with the PPN phosphopolymetallates **5b** and **6** ($CH_2Cl_2$, MeCN or DMF solution, 25 °C) to give crystalline products which contained, according to the elemental analysis and $^1H$, $^{31}P$ NMR data, $Cp^*RhCl^+$, $PPN^+$ and $[PMo_{12}O_{40}]^{3-}$ or $[PW_{12}O_{40}]^{3-}$ together with molecules of crystallization of solvent.

An X-ray diffraction study revealed that the crystal of complex **9** ($[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+[PPN]^+{}_2[PMo_{12}O_{40}]^{3-}\cdot 4DMF$), obtained from $[\{Cp^*RhC_2\}_2]$ and **5b** in DMF, contained $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+$ cations and $[PMo_{12}O_{40}]^{3-}$ anions (Fig. 2) in a 1:1 ratio, occupying special positions at the crystallographic inversion centres. The crystal also contains two $PPN^+$ and four DMF molecules per phosphomolybdate anions. The geometric parameters of the cation are close to those found in $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]BF_4\cdot 3H_2O$.[4] However, there is a difference since in **9** each of the three chloride bridges in $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+$ is disordered over two equally occupied positions, one of which is rotated by 60 ° with respect to the other.§ The $[PMo_{12}O_{40}]^{3-}$ anion has a Keggin-type heteropolyanion structure;[5] disorder of the oxygens of the inner $PO_4$ tetrahedron is seen of the same type that has previously been reported.[6] The stoicheiometry of complex **9**, derived from the X-ray structural results, fits the formulation, $[(Cp^*RhCl_3RhCp^*)\ (PPN)_2(PMo_{12}O_{40})]\cdot 4DMF$, in agreement with elemental analysis and NMR data.

Although a number of organometallics anchored to polyoxometallates have been reported, in most cases the polyoxoanions are lacunary and/or highly-charged of a non-Keggin type.[7] Few examples of transition metal complexes attached to true Keggin anions have as yet been reported and none has been

‡ Crystals of $[[Cp^*RhMoO_4]_4]$ were reported to be cubic with $a = 25.285(2)$ Å at room temperature;[3] our preliminary X-ray data shows them also to be cubic with $a = 24.86(1)$ Å at 158 K.

§ Complex **9** was prepared in the form of single crystals by slow diffusion of methanol vapour into the DMF reaction solution containing $[\{Cp^*RhCl_2\}_2]$ and **5b**. Crystal data for **9**: $C_{104}H_{118}Cl_3Mo_{12}N_6O_{44}P_5Rh_2$, $M = 3774.3$, triclinic, space group $P\bar{1}$, $a = 12.855(3)$, $b = 14.548(4)$, $c = 17.543(4)$ Å, $\alpha = 75.16(2)$, $\beta = 79.97(2)$, $\gamma = 82.79(2)°$, $V = 3112(1)$ Å$^3$, $Z = 1$, $D_c = 2.014$ g cm$^{-3}$. The $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+$ cation and $[PMo_{12}O_{40}]^{3-}$ anion occupy special positions in the inversion centres (the Cl atoms of the cation and four central O atoms of the anion are disordered over two positions). The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer ($T = 153$ K, graphite-monochromated Mo-$K_\alpha$ radiation, $\lambda = 0.71073$ Å, $\theta/2\theta$ scan technique, $2\theta < 53°$). The structure was solved by direct methods using SHELXTL PLUS programs (PC version). Anisotropic least-squares refinement [H atoms bonded to carbons included in calculated positions with the common refined $U_{iso}$ equal to 0.06(1), 0.044(6) and 0.12(2) Å$^2$ for the H atoms of the $[Cp^*RhCl_3RhCp^*]$, the PPN cations and the solvating DMF molecules, respectively] converged at $R = 0.0686$, $R_w = 0.0804$ for 8847 observed independent reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Commun.*, Issue 1, 1993.

structurally characterized.[8] So far as we are aware, the salt **9** is the first X-ray structurally characterized example of an organometallic salt of a Keggin heteropolyanion in the same crystal.

Our finding that the Cp*Rh is not attached covalently to the phosphomolybdate moiety in complex **9** agrees with the suggestion that the charge on the highly-symmetrical Keggin $[XM_{12}O_{40}]^{n-}$ anions is too delocalized for the oxygen atoms on the anion surface to be sufficiently nucleophilic to compete with donor solvent molecules (*e.g.*, $H_2$, ROH, RCN) in reactions with transition metal Lewis acids (such as the soft organometallic $Cp^*Rh^{2+}$).[8a] Further studies of PPN oxometallates in the preparation of polyoxometallate-anchored organometallics are in progress.

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