Functionalization of polyoxometalates: towards advanced applications in catalysis and materials science

Anna Proust,* René Thouvenot* and Pierre Gouzerh*

Received (in Cambridge, UK) 8th October 2007, Accepted 30th November 2007
First published as an Advance Article on the web 24th January 2008
DOI: 10.1039/b715502f

Functionalization *via* covalent grafting of organic functions allows to tune the redox and acid–base properties, and the solubility of polyoxometalates, to enhance their stability and biological activity and to reduce their toxicity, to facilitate their implementation in extended structures and functional devices. We discuss herein the electronic and binding connections, and the various synthesis methodologies. We emphasize on organonitrogen, organosilyl and organophosphonyl derivatives with special attention to synthesis, characterization and potential applications in catalysis and materials science. We also consider the giant molybdenum oxide-based clusters especially the porous capsule-type clusters (Keplerates) which have high relevance to this context.

1 Introduction

Early transition-metals (M = V, Nb, Ta, Mo, W) in their highest oxidation state form discrete oxygen cluster anions (polyoxometalates, or POMs) which may also include a variety of heteroatoms (X). This class of inorganic compounds is unmatched not only in terms of molecular structural diversity but also regarding reactivity and relevance to analytical chemistry, catalysis, medicine and materials science.[1] POMs reveal a huge variety of shapes, sizes and compositions, from small (*e.g.*, $[Mo_6O_{19}]^{2-}$ [2]) to nanosized species (*e.g.* $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$, $\{Mo_{368}\}$).[3a] Their structures are based upon $\{MO_p\}$ and $\{XO_q\}$ polyhedra sharing vertices, edges or, more rarely, faces. A large variety of POMs can be obtained by linking metal-oxygen building units either as existing or virtual species. The approach has been elegantly exploited by Müller *et al.* to produce remarkable wheel-type and porous capsule-type nano-objects.[3b,c] Some basic structures are shown in Fig. 1.[4]

Owing to their sizes, structures, and properties, POMs are often referred to as soluble metal-oxide fragments and, as such, are receiving considerable attention. While their biological properties are the subject of increasing interest,[5] catalysis and materials science are still the two main fields of applications of POMs today. In that context, one of the most significant properties of POMs is the ability of many of them, *i.e.* "type I" POMs, according to the classification of Pope,[6a] to accept and release specific numbers of electrons reversibly, under marginal structural rearrangement.[6–8]

There are numerous applications of POMs as acid and oxidation catalysts, including several large scale industrial processes, both in heterogeneous and in homogeneous conditions.[9–12] POM-based catalysts however present some drawbacks. (i) In the solid state, the catalytic activities of POMs are limited owing to their low specific surface area. The problem may be overcome by various strategies, *e.g.* dispersing or immobilizing POMs onto various supports or entrapping them

Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071, FR 2769, Université Pierre et Marie Curie-Paris6, 4 Place Jussieu, 75252 Paris cedex 05, France. E-mail: proust@ccr.jussieu.fr, rth@ccr.jussieu.fr, pg@ccr.jussieu.fr

Pierre Gouzerh, Anna Proust and René Thouvenot

Anna Proust, born in 1967, received her PhD in Chemistry from the Université Pierre et Marie Curie in 1992. She was appointed Professor of Chemistry at this University in 2000 and Junior Member of the Institut Universitaire de France in 2006. René Thouvenot (right), born in 1946, obtained his Doctorate in Chemistry at the Université Pierre et Marie Curie in 1978. He is presently Directeur de Recherche at the CNRS. Pierre Gouzerh (left), born in 1943, obtained his Doctorate in Chemistry in 1973 at the Université Pierre et Marie Curie where he is Professor of Chemistry since 1990. Their research interests are focused on organometallic oxides, magnetic polyoxometalates and functionalized polyoxometalates, in particular with multiple metal–nitrogen bonds, organosilyl or organophosphonyl functions, and also include reactivity of multiple metal-ligand bonds, coordination chemistry of redox-active ligands and multinuclear NMR.

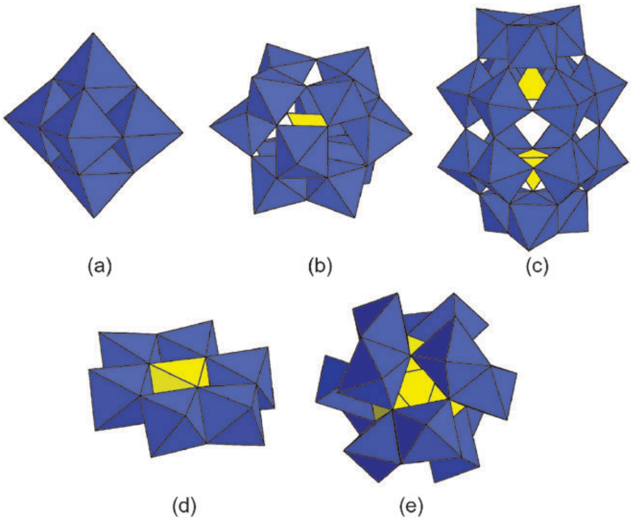

Fig. 1 Some basic POM structures in polyhedral representation: $[M_6O_{19}]^{n-}$,[2,4a] $[\alpha\text{-}XM_{12}O_{40}]^{n-}$,[4b] $[\alpha\text{-}X_2M_{18}O_{62}]^{n-}$,[4c] $[H_xXMo_6O_{24}]^{n-}$,[4d] $[XM_{12}O_{42}]^{8-}$.[4e] Colour code: MO_6 octahedra, blue; XO_n polyhedra, yellow.

into various matrices, which can also be used to convert homogeneous to heterogeneous catalytic processes.[12a,b,13] (ii) In comparison to many homogeneous catalytic systems, an apparent weakness of POMs is the absence of pathway to direct the substrate towards the catalytically active center, which could be bypassed by a suitable modification of the POM surface (*vide infra*).

Generally speaking, POMs are attractive components for the design of advanced materials and devices.[14–17] However, the development of functional POM-based materials has been rather slow because POMs usually are crystalline solids that are hard to process. Recent progress has been made in the synthesis of POM nanoarchitectures, *e.g.* nanocrystals and nanowires.[18] However the most common route to the integration of POMs into functional architectures and devices rests on inorganic/organic hybrids.

Several strategies have been considered to modify POMs while retaining their structural integrity and their intrinsic properties, and facilitating their implementation into extended structures. One procedure is based on the exchange of POMs counterions with cationic surfactants resulting in the formation of discrete, hydrophobic, surfactant-encapsulated clusters (SECs).[19–21] SECS have been obtained for various POMs, among them large polyoxomolybdates, *e.g.* $\{Mo_{57}V_6\}$,[19a] $\{Mo_{132}\}$,[19b,c] $\{Mo_{72}Fe_{30}\}$[19f] and $\{Mo_{176}\}$,[20a] and several europium-containing polyoxotungstates.[20b,21] A subclass of SECs include dendron-encapsulated POMs (dendrizymes) which could combine the catalytic activity of POMs with the steric properties of the dendritic surfactants.[19d] Besides SECs there is also a growing interest for biopolymer-encapsulated POMs (liposomes and polysaccharides) for biomedical applications.[22]

Thin films of SECs are readily obtained by the Langmuir–Blodgett (LB) technique and solvent-casting methods. Various well-ordered arrays such as honeycomb-structured films[19f,21e] and lamellar[21d] and columnar[20] liquid-crystal phases have been reported. Surfactant-encapsulated europium-containing POMs are particularly attractive for use in electroluminescent devices.[21f] Besides SEC films, LB films composed of monolayers of POMs with different shapes, sizes and charges, and bilayers of cationic surfactants have also been obtained by the semiamphiphilic method.[23–27] Their magnetic,[23a–c] luminescent,[24a,25,27] and electrochemical[24b,c,26a] properties have been reported.

The electrostatic layer-by-layer self-assembly (ELSA) which is based on alternating adsorption of oppositely charged components from dilute solutions provides an alternative method for the fabrication of thin films of POMs.[28–31] Nanocomposite multilayers that behave as bifunctional electrocatalysts,[30] electro- and photochromic dual-mode devices,[29c,j] sensors,[29d,h] or exhibit thermotropic liquid crystal behaviour,[29f] have been reported.

Most of these POMs-based hybrids are ‘‘class I’’ materials, *i.e.* the POM and organic components are linked through non-covalent interactions, *e.g.* van der Waals contacts, hydrogen bonding and/or ionic interactions.[31] Covalent POM-based hybrids, *i.e.* ‘‘class II’’ materials, are less developed. Examples include polymeric hybrids based on covalently linked POMs and transition-metal complexes,[32–34] POM-dendrimers,[35] POMs incorporated into polymers by copolymerization,[36–38] and conjugated polymer-POM hybrids.[39] Nevertheless the covalent approach offers several advantages since covalent link improves the stability of the hybrid and might enhance the interaction between the inorganic and organic components and facilitate the construction of POM-based integrated nanosystems.[14] Thus there is clearly a need for the development of functionalized POMs.[40] Here we first review synthetic methodologies for the functionalization of POMs, then we emphasize on organonitrogen, organosilyl, and organophosphonyl derivatives. Finally we consider the giant ring- and ball-shaped polyoxomolybdates which are of the highest importance for the development of functional materials.

2 Electronic and binding connections

The oxo, O^{2-}, imido, HN^{2-}, and nitrido, N^{3-}, ligands are isoelectronic, flexible four- or six-electron donor ligands. Furthermore, the imido and cyclopentadienyl ligands are isolobal.[41a] Thus it should be possible to replace terminal oxo ligands by imido, nitrido or cyclopentadienyl ligands. Indeed, that has been achieved, as shown by the extensive series of derivatives of $[Mo_6O_{19}]^{2-}$, which include nitrido,[42] hydrazido,[42] imido,[43a–45] diazoalkane,[43b] and cyclopentadienyl derivatives (Fig. 2).[46,47]

While the replacement of multiply bonded terminal oxo ligands by similar σ-donor/π-donor ligands is—at least formally—straightforward, it was less obvious that they could be replaced by σ-donor/π-acceptor ligands. Yet nitrosyl and diazenido derivatives of POMs have been obtained, *e.g.* $[Mo_6O_{18}(NO)]^{3-}$,[48] and $[Mo_6O_{18}(NNAr)]^{3-}$.[49] The short Mo–N, N–O or N–N bond distances, and the linearity of the Mo–N–O and Mo–N–N moieties, suggest extensive delocalization and significant multiple bond character throughout the MoNO an MoNNAr functions. In such coordination modes, nitrosyl and diazenido ligands are commonly considered as NO^+ and $ArNN^+$ ligands, respectively,[50a] and

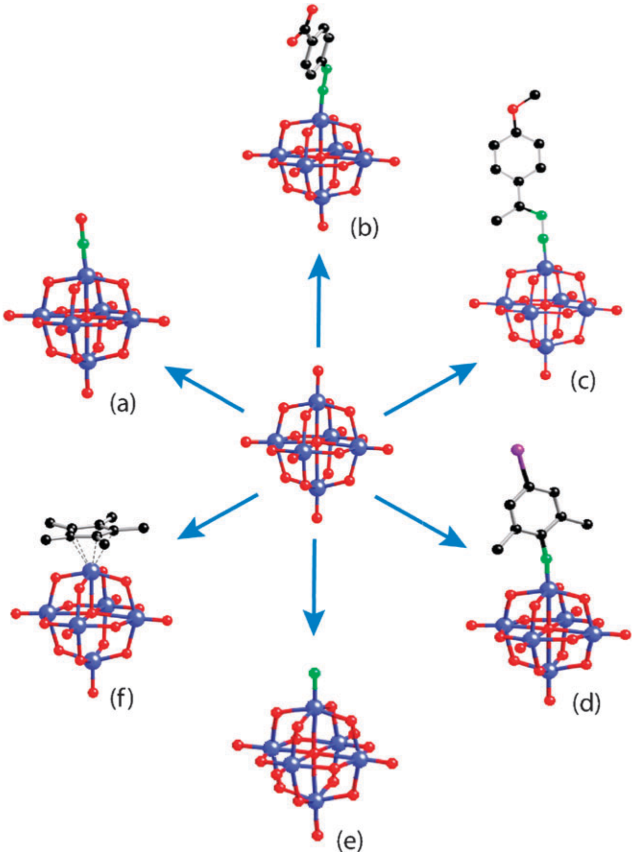

Fig. 2 Some derivatives of $[Mo_6O_{19}]^{2-}$. (a) $[Mo_6O_{18}(NO)]^{3-}$,[48] (b) $[Mo_6O_{18}(N_2C_6H_4\text{-}4\text{-}CO_2H)]^{3-}$,[49b] (c) $[Mo_6O_{18}\{N_2C(C_6H_4\text{-}4\text{-}OCH_3)CH_3\}]^{3-}$,[43b] (d) $[Mo_6O_{18}(NC_6H_2\text{-}2,6\text{-}(CH_3)_2\text{-}4\text{-}I)]^{2-}$,[45a] (e) $[Mo_6O_{18}(N)]^{3-}$,[42] (f) $[Mo_6O_{18}(\eta^5\text{-}C_5Me_5)]^{-}$.[46b] Colour code: Mo, blue; O, red; N, green; C black.

accordingly, the $Mo(NO)^{3+}$ and $Mo(NNAr)^{3+}$ functions would contain a d^4-Mo^{II} center. However DFT calculations on mono-NNR complexes suggest that the formal oxidation state of the diazenido ligand is close to −1 when linearly coordinated.[50b] Thus it seems more appropriate to describe the $Mo(NO)^{3+}$ and $Mo(NNAr)^{3+}$ functions as $\{MoNO\}^4$ or $\{MoNNAr\}^4$ functional groups, using the notation of Enemark and Feltham.[50c]

Hence some electronic connections emerge between high- and low-valent fragments though they are not strictly isolobal according to Hoffmann's definition.[41b] Thus the sets of structurally related complexes $[Mo_4O_{10}(OMe)_6]^{2-}$,[51] $[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$ [52a] and $[Mo_2O_6(OMe)_4\{Ru(\eta^6\text{-arene})\}_2]$[53a] on the one hand (Fig. 3), $[Mo_8O_{24}(OMe)_4]^{4-}$, $[Mo_6O_{20}(OMe)_2\{Ru(\eta^6\text{-arene})\}_2]^{2-}$ and $[Mo_6O_{20}(OMe)_2\{Rh(\eta^5\text{-}C_5Me_5)\}_2]^{2-}$ on the other, are indicative of an analogy between the fragments d^0-*fac*-$\{MoO_2(OR)\}^+$ and d^6-*fac*-$\{ML_3\}^{n+}$ (M = Mn, Ru, Rh).[52]

In a similar way Pope has pointed up the topological equivalence of a $\{ML\}^{n+}$ group, where L is a monodentate σ-donor ligand, and that of a chelated transition metal such as $\{Co^{III}(en)\}^{3+}$, to the MO_t and *cis*-MO_2 units, respectively.[54]

3 Synthesis methodologies

3.1 Self-assembly reactions

POMs usually are formed in self-assembly reactions. As regards polyoxomolybdates, $[MoO_4]^{2-}$ is a convenient precursor in aqueous solutions while $[Mo_2O_7]^{2-}$ or α-$[Mo_8O_{26}]^{4-}$ (as tetralkylammonium salts) are used in non-aqueous solvents. A number of alkoxo derivatives of POMs have been obtained in this way. Thus the formation of $[MnMo_6O_{18}\{RC(CH_2O)_3\}_2]^{3-}$ occurs according to the following stoichiometry:[55]

$$3\,[Mo_2O_7]^{2-} + 2\,RC(CH_2OH)_3 + Mn^{3+} \rightarrow \\ [MnMo_6O_{18}\{RC(CH_2O)_3\}_2]^{3-} + 3\,H_2O$$

The procedure also applies to organometallic oxides, *e.g.*:[47,53b,c]

$$2\,[Cp^*{}_2Mo_2O_5] + 4\,[MoO_4]^{2-} + 8\,H^+ \rightarrow [Cp^*{}_2Mo_6O_{17}] + 4\,H_2O_4$$

$$[MoO_4]^{2-} + 4\,\{Ru(\eta^6\text{-arene})\}^{2+} \rightarrow [Mo_4O_{16}\{Ru(\eta^6\text{-arene})\}_4]$$

Even when the framework of the POM is retained in the course of functionalization, *e.g.* in the formation of $[Mo_6O_{18}(NAr)]^{2-}$ by reaction of $[Mo_6O_{19}]^{2-}$ with ArNCO, it can not be excluded that the reaction proceeds with decondensation and reaggregation. Indeed the reaction is activated by pyridine,[44c] and, moreover, the same product is obtained from $[\alpha\text{-}Mo_8O_{26}]^{4-}$ (*vide infra*).

3.2 Metathetical exchange of oxo ligands and condensation-type reactions

Terminal, *i.e.* multiply-bonded, oxo ligands usually are rather unreactive. The {Mo=O} function however can experience metathetical exchange with other multiply-bonded ligands as well as condensation-type reactions reminiscent of the reactivity of the carbonyl function {C=O}. Thus numerous imido derivatives have been obtained through reaction of $[Mo_6O_{19}]^{2-}$ with imino-phosphoranes, isocyanates and

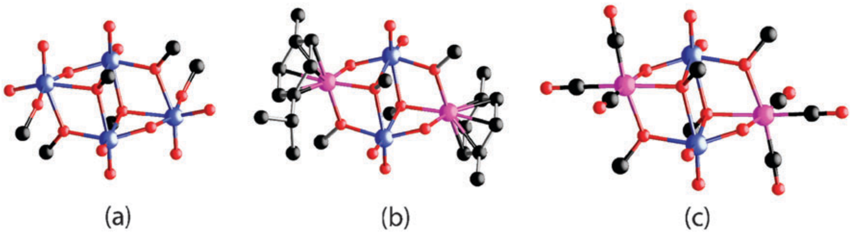

Fig. 3 Topologically equivalent tetranuclear complexes: (a) $[Mo_4O_{10}(OMe)_6]^{2-}$,[51] (b) $[Mo_2O_6(OMe)_4\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$,[53a] and (c) $[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$.[52a] Colour code: Mo, blue; Ru and Re, pink; O, red; C black.

sulfinylamines.[43,44] These reactions are supposed to proceed through tandem [2 + 2] cycloaddition–cycloreversion sequences.[56] Imido derivatives of $[Mo_6O_{19}]^{2-}$ can also be obtained from amines, albeit in rather drastic conditions such as prolonged reflux in benzonitrile.[57] However, it has been discovered that condensation of amines with polyoxomolybdates is greatly facilitated in the presence of dicyclohexylcarbodiimide (DCC) and the procedure is largely used now.[45]

Reaction of hydrazines is more easy: disubstituted hydrazines, $RR'NNH_2$, react with $[\alpha\text{-}Mo_8O_{26}]^{4-}$ to yield hydrazido(2−) complexes that contain *cis*-$\{Mo(NNRR')_2\}^{2+}$ or *cis*-$\{MoO(NNRR')\}^{2+}$ functions, while monosubstituted hydrazines, $RNHNH_2$, produce diazenido derivatives that contain $\{Mo(NNR)\}^{3+}$ or *cis*-$\{Mo(NNR)_2\}^{2+}$ functions. Some insight into the mechanism of the reactions of hydrazines with molybdenum–oxo complexes has been obtained by Chatt *et al.* on mononuclear complexes. The formation of hydrazido-complexes presumably involves initial coordination of the hydrazine followed by proton transfer to an oxo ligand.[58a] Mixed hydrazido–diazenido-complexes are apparently intermediates in the formation of the bis(diazenido)-complexes and indeed they have been isolated when the hydrazine is a carbazate.[58b]

The mechanism of the reductive nitrosylation of molybdenum– and vanadium–oxo complexes with hydroxylamine is better established. The formation of mononitrosyl complexes $\{M(NO)\}^4$ proceeds *via* high-valent $\{M(\eta^2\text{-}HNO)\}$ intermediates which undergo an intramolecular two-electron transfer and subsequent deprotonation. In the formation of the dinitrosyl-metal complexes $\{M(NO)_2\}$ the η^2-hydroxylamido ligand of the precursor $\{M(NO)(H_2NO)\}^4$ is oxidized either by dioxygen or by hydroxylamine in excess.[59]

The oxo ligand can act as a four-electron donor and, as such, is isoelectronic with the methylidene ligand. However, attempts to achieve the replacement of an oxo ligand by an alkylidene ligand have so far failed. For instance, the reaction of *cis*-$[MoO_2(mesityl)_2]$ with Bu_3PCH_2 has afforded the stable betaine-like $[(2,4,6\text{-}Me_3C_6H_2)Mo^-O_2(CH_2P^+Bu_3)]$.[60] We have investigated the reactions of a number of phosphonium ylides with $(^nBu_4N)_3[PMo_{12}O_{40}]$ in acetonitrile and we have demonstrated that only 1e- and/or 2e-reduced derivatives of $[PMo_{12}O_{40}]^{3-}$ are formed.[61a]

In our hands, in a general way, metathetical exchange of oxo ligands or condensation-type reactions on Keggin-type POMs have failed to give the targeted derivatives[61] and, to the best of our knowledge, all the Keggin-type functionalized POMs reported to date have been obtained from lacunary POMs (see section 3.3).

3.3 Transition metal-substituted POMs

Lacunary POMs react with a large variety of transition metals to give transition metal-substituted POMs (TMSPs). In particular a great deal of complexes of the type $[XM_{11}O_{39}M'(H_2O)]^{x-}$ and several nitrosyl,[62a] diazenido,[62b] imido,[62c] and nitrido[63] derivatives have been obtained from monovacant Keggin-type POMs which may be generated *in situ* by alkaline degradation of the parent complete POMs.

TMSPs can be further derivatized at the hetero-transition metal. Thus the aquo ligand of the $[XM_{11}O_{39}M'(H_2O)]^{n-}$ complexes can be replaced by other ligands, notably nitrogenous ligands.[64] For example pyrazine forms a 1 : 1 complex with $[SiW_{11}O_{39}Co^{III}(H_2O)]^{5-}$ while 4,4′-bipyridyl forms both 1 : 1 and dumbbell-shaped 2 : 1 complexes.[64c,d] Coordination or coupling of chiral amines has allowed to differentiate between the enantiomers of $[\alpha_1\text{-}P_2W_{17}O_{61}Ln(H_2O)_x]^{7-}$,[65a,66c] and those of $[\alpha_1\text{-}P_2W_{17}O_{61}SnCH_2CH_2CO_2H]^{7-}$.[66a,b] These results open the way to potential resolution of the chiral $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ polyoxoanion. Chiral polyoxometalates are attracting growing interest. In this context it is noteworthy that enantiopure pure polyoxotungstates have been obtained by reacting the achiral polyoxotungstate $[P_2W_{15}O_{56}]^{12-}$ with zirconyl nitrate and homochiral tartrate or malate.[67] The chiral ligand induces the formation of a single enantiomer and, at least for the tartrate complex, significant chirality transfer on the inorganic part.

Complexes of the type $[XM_{11}O_{39}M'(H_2O)]^{x-}$ show many analogies to metalloporphyrins.[68] In particular, monovacant Keggin-type POMs afford convenient platforms for the stabilization of unusually high-oxidation-state metal–oxo species. Thus Mn(V)–oxo POM intermediates are formed in the reaction of $[\alpha_2\text{-}P_2W_{17}O_{61}Mn^{III}(H_2O)]^{7-}$ with $C_6F_5I(OCOCF_3)_2$ in 1 : 1 CH_2Cl_2–MeCN.[69a] The analogy of such species to metalloporphyrins or corroles, as well as to the active site of cytochrome P-450, raises a number of questions that have been theoretically addressed. These studies have provided insight into the electronic structures of the fundamental and low-lying excited states of various high-valent metal–oxo complexes.[69] Similarly high-valent metal–nitrido-substituted POMs are attracting growing interest as potential catalysts in nitrogen-atom transfer reactions.[63]

To conclude this section it must be mentioned that multivacant POMs allow the rational synthesis of magnetic clusters with diverse nuclearities and topologies.[70–73] In this field, our group has focused recently on the reactivity of the tri- and hexavacant derivatives of $\alpha\text{-}[P_2W_{18}O_{62}]^{6-}$.[73] On the other hand lanthanide cations are ideal linkers for the assembly of large polyoxotungstates from lacunary POM fragments.[74]

3.4 Grafting of electrophilic groups

Complete (plenary) POMs usually are weakly basic and nucleophilic, except when the surface charge is increased either by substitution of metals from groups 4 or 5 for Mo or W, *e.g.* $[Nb_2W_4O_{19}]^{4-}$,[75] or by reduction. Lacunary POMs have higher charges, hence increased basicity and nucleophilicity than their parent complete species. Thus they react quite easily with a variety of electrophilic groups in water or in non-aqueous solvents. A large variety of hybrid derivatives, *e.g.* $[\alpha\text{-}A\text{-}PW_9O_{34}(RPO)_2]^{5-}$,[76] $[\alpha\text{-}A\text{-}PW_9O_{34}(^tBuSiO)_3(SiR)]^{3-}$,[77] $[\alpha\text{-}A\text{-}PW_9O_{34}(Me_2Si)_3]^{3-}$,[77] $[(\beta\text{-}A\text{-}PW_9O_{34})_2(PhSnOH)_3]^{12-}$,[78] and $[(A\text{-}XW_9O_{34})_{12}\{SnMe_2(H_2O)\}_{24}\{SnMe_2\}_{12}]^{36-}$ [79] have been obtained by reactions of organophosphonic acids, $RPO(OH)_2$, organosilanes, $RSiCl_3$ and R_2SiCl_2, and organotin species, $RSnCl_3$ and Me_2SnCl_2, with lacunary heteropolyoxotungstates.

3.5 Derivatization of hybrid platforms

In some cases the organic part of a POM hybrid can be modified through common organic reactions so that the original hybrid behaves as a platform from which further derivatives are

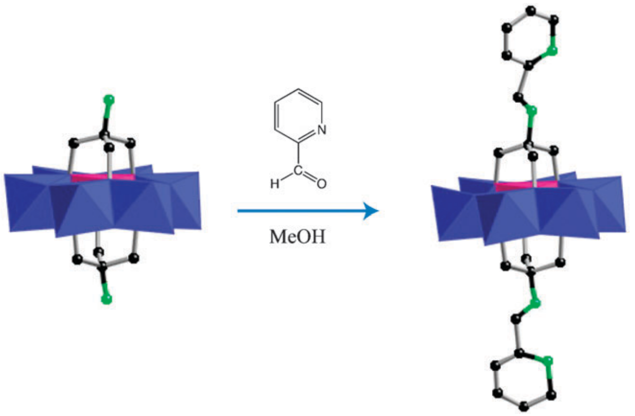

Fig. 4 Developing remote binding sites in $[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]^{3-}$.[55b] Colour code: MoO_6 octahedra, blue; MnO_6 octahedron, pink; N, green; C, black.

conveniently prepared. In principle the method offers greater simplicity than direct functionalization although the reactivity of the incorporated organic group is sometimes altered with respect to the "free" group and the reagents should also be chosen to preserve the POM from competitive degradation or reduction. The method has been successfully applied to post-functionalization of $[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]^{3-}$ (Fig. 4),[55b] $[P_2W_{15}V_3O_{59}\{(OCH_2)_3CNH_2\}_2]^{6-}$,[80] α_1- and α_2-$[P_2W_{17}O_{61}SnCH_2CH_2CO_2H)]^{7-}$,[66a,b] $[\alpha\text{-}PW_{11}O_{39}SnCH_2CH_2CO_2H]^{4-}$,[66b,81] $[Mo_6O_{18}(NC_6H_2\text{-}2,6\text{-}Me_2\text{-}4\text{-}I)]^{2-}$, and $[Mo_6O_{17}\{NC_6H_2\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}I\}_2]^{2-}$ (Fig. 5).[34,82]

4 Nitrogenous derivatives with multiple metal–nitrogen bonds

4.1 Imido derivatives

Athough the imido and nitrido ligands are quite common in coordination chemistry, only recently have they been introduced in POM chemistry. Organoimido and nitrido POMs were reported first by Kang and Zubieta, who briefly mentioned the Lindqvist-type derivatives $[Mo_6O_{18}(NTol)]^{2-}$ and $[Mo_6O_{18}(N)]^{3-}$, which were obtained by condensation of $[Mo_2O_7]^{2-}$ with $[Mo(NTol)Cl_4(thf)]$ and $[MoNCl_4]^-$, respectively.[42] However it was Maatta and co-workers that gave a decisive impetus to the chemistry of imido derivatives of POMs. They found that arylimido derivatives of the type $[Mo_6O_{18}(NAr)]^{2-}$ can be obtained by reaction of iminophosphoranes or isocyanates with $[Mo_6O_{19}]^{2-}$ in pyridine.[43a,83] Our group had independently started a programme aiming at the synthesis of imido POMs[44] and the two groups eventually collaborated.[83e] An extensive series of mono-imido derivatives $[Mo_6O_{18}(NC_6H_4\text{-}p\text{-}X)]^{2-}$ has been obtained.[38,43a,44,83c,f] A linear relationship has been observed between the reduction potential of the cluster and the Hammett constant of the substituent X, which demonstrates transmission of electronic effects through the imido ligand.[44b,c] A striking feature of organoimido hexamolybdates is the tendency for multifunctionalization,[44a,83a,d,e] and it has even proved possible to replace the six terminal oxo ligands of $[Mo_6O_{19}]^{2-}$ by 2,6-(diisopropyl)phenylimido ligands (Fig. 6).[83d] An homologous series $[Mo_6O_{19-x}(NAr)_x]^{2-}$ has been obtained, which provides an unique opportunity to study in detail what perturbations arise within the POM framework as a result of oxo/imido substitution. Cyclic voltammetry studies indicate that a continuous build-up of electron density accompanies increasing arylimido incorporation. Multinuclear NMR studies suggest that this electron density accumulates preferentially at the terminal oxo ligands, and to a lesser extent at the imido nitrogen atoms, rather than within the $\{Mo_6O_{13}\}$ core.[83e] Contrary to expectations based on steric considerations, the substitution pattern reveals a preference for mutual *cis*-coordination of imido ligands.[44a,83a,e] The question of the preference for the *cis* rather than the *trans* structure in disubstituted derivatives has been addressed by density functional theory (DFT) studies.[84a] Kinetically-controlled *trans*-bifunctionalized organoimido hexamolybdates have been recently obtained in mild conditions.[85a,b]

As noted above, amines are rather unreactive towards $[Mo_6O_{19}]^{2-}$. However an efficient reaction protocol has been introduced by Peng and co-workers who discovered that DCC can dramatically facilitate the reaction of $[Mo_6O_{19}]^{2-}$ with

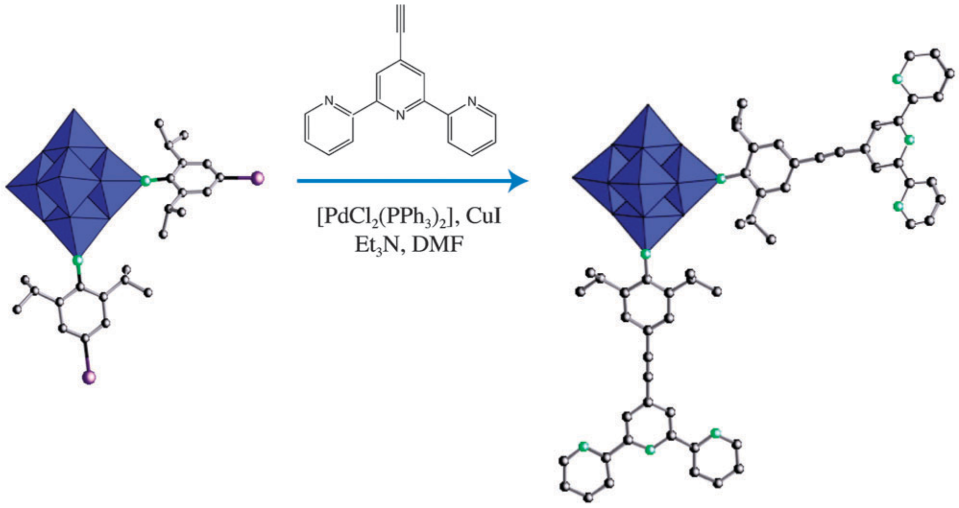

Fig. 5 Derivatizing $[Mo_6O_{17}(NC_6H_2\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}I)_2]^{2-}$.[34] Colour code: MoO_6 octahedra, blue; N, green; C, black; I, violet.

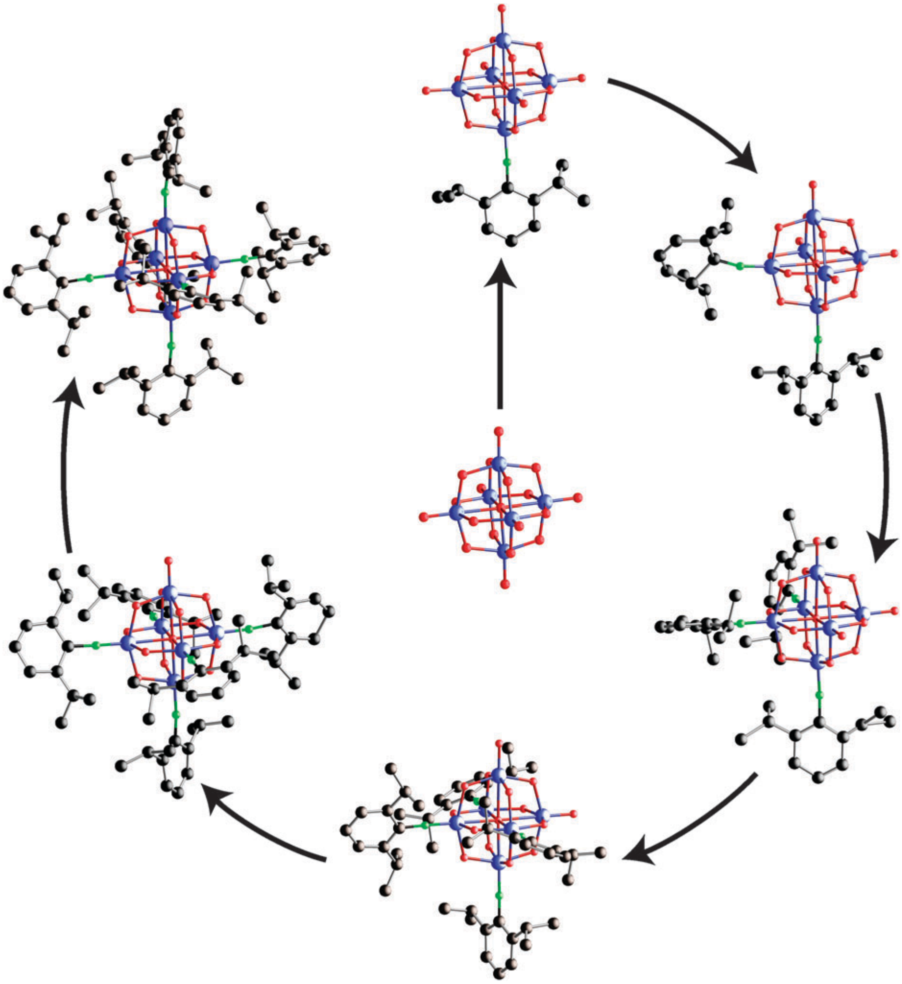

Fig. 6 Multifunctionalization of $[Mo_6O_{19}]^{2-}$: $[Mo_6O_{19-x}(NC_6H_3\text{-}2,6\text{-}Me_2)_x]^{2-}$ (x = 1–5);[83e] $[HMo_6O_{13}(NC_6H_3\text{-}2,6\text{-}Me_2)_6]^{-}$.[83d] Colour code: Mo, blue; O, red; N, green; C, black.

aromatic amines.[45] This method can tolerate a variety of organic functional groups and it has now supplanted other methods.[85] In particular, it has been used for the synthesis of iodo- and ethynyl-functionalized hexamolybdates which can undergo Pd-catalyzed coupling reactions to give novel hybrid materials.[34,82]

While numerous Lindqvist-type organoimido molybdates are now known, only one imido hexatungstate has been reported.[86] This reflects the low reactivity of the $\{W{=}O\}^{4+}$ functionality with respect to $\{Mo{=}O\}^{4+}$. Extension to Keggin-type derivatives also came up upon difficulties. Thus, $[\alpha\text{-A-PW}_9Mo_3O_{40}]^{3-}$ and $[\alpha\text{-PW}_{11}MoO_{40}]^{3-}$ are reduced by arylamines, iminophosphoranes or isocyanates without any evidence of the formation of the expected imido derivative.[61b] The reaction of $[H_3PW_{11}O_{39}]^{4-}$ with $[Re(NPh)Cl_3(PPh_3)_2]$ in acetonitrile and in the presence of NEt_3 has provided the first Keggin-type organoimido derivative $[PW_{11}O_{39}\{Re(NPh)\}]^{4-}$.[62c] While an earlier attempt to prepare $[PW_{12}O_{39}(NC_6H_4\text{-}p\text{-}Me)]^{3-}$ by reacting $(^nBu_4N)_4[H_3PW_{11}O_{39}]$ with $[W(NC_6H_4\text{-}p\text{-}Me)Cl_4]_2$ was unsuccessful,[87a] the related phenylimido derivative $[\alpha\text{-PW}_{12}O_{39}(NPh)]^{3-}$ has been recently obtained by a similar synthetic approach.[87b]

At the beginning, studies of imido derivatives of polyoxomolybdates were motivated by the search for structural and, possibly, functional homogeneous models for ammoxidation chemistry. Thus the reaction of $[Mo_6O_{19}]^{2-}$ with $Ph_3P{=}NCH_2Ph$ replicates key features of heterogeneous ammoxidation chemistry by producing moderate yields of benzonitrile through the proposed intermediary of $[Mo_6O_{18}(NCH_2Ph)]^{2-}$.[88] Otherwise, unexpected C=C bond formation *via* doubly dehydrogenative coupling of two sp^3 C–H bonds have been observed by refluxing *n*-propylamine hydrochloride, $(^nBu_4N)_4[\alpha\text{-Mo}_8O_{26}]^{4-}$ and DCC in dry acetonitrile.[89] However current studies are mainly directed towards the synthesis of novel organic/inorganic hybrids with potential applications in molecular electronic and photonic. Large second- and third-order polarizability coefficients have been predicted by DFT calculations.[84b,c] Several dumbbells, in which two POM units are connected through an extended π-conjugated,[57a,83b,90,91] or flexible, saturated,[92] organic bridge, are now known. Strong electronic interactions are observed in conjugated dumbbells and an intramolecular charge separation has even been suggested in the phenanthroline-POM hybrid compound reported by Neumann and coworkers.[91] Polymeric hybrids have been obtained by free radical-induced copolymerization,[38] by coordination or by palladium-catalyzed coupling reactions.[34,39] The potential of

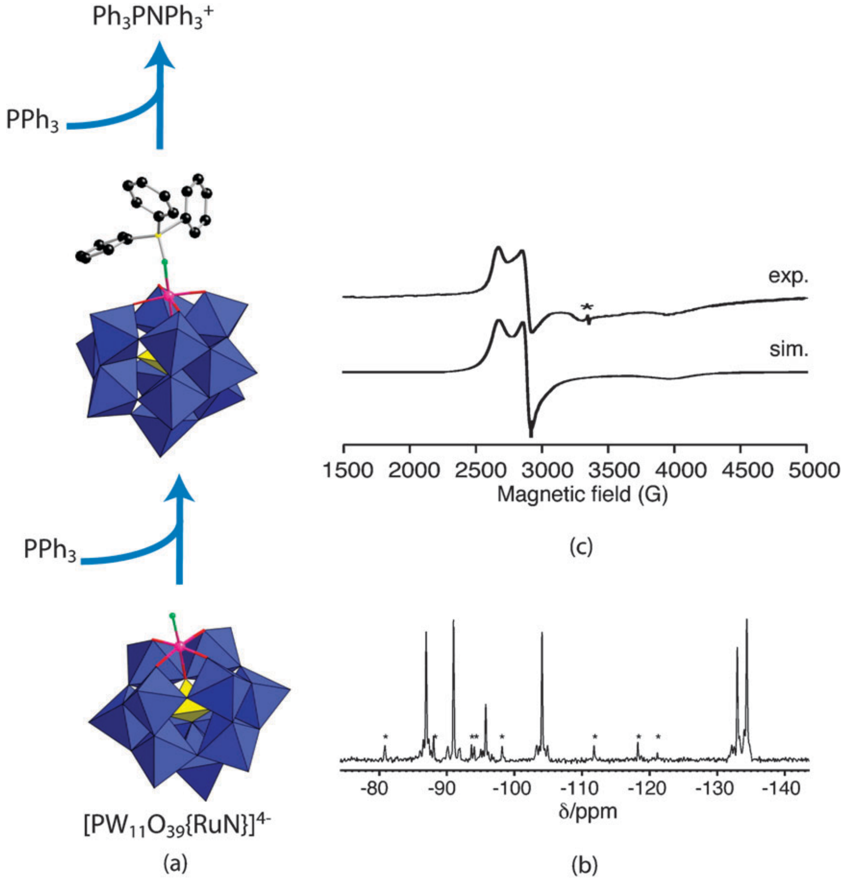

Fig. 7 (a) Reactivity of $[PW_{11}O_{39}\{Ru^{VI}N\}]^{4-}$ towards phosphines; (b) ^{183}W NMR spectrum of $[PW_{11}O_{39}\{Ru^{VI}N\}]^{4-}$; (c) EPR spectrum of $[PW_{11}O_{39}\{Ru^{V}NPPh_3\}]^{3-}$.[63b,c] Colour code: MoO_6 octahedra, blue; PO_4 tetrahedron and P, yellow; Ru, pink; N, green; C, black.

conjugated polymers containing POMs as side-chain pendants or embedded into the main chain for applications in photovoltaic cells has been demonstrated.[34] On the other hand an imido hexamolybdate has been tested for controlled modulation of conductance of pseudo-metal oxide semiconductor field-effect transistors *via* covalent grafting on the channel region.[93]

4.2 Nitrido derivatives

Although di- and tetra-nuclear nitrido/oxo complexes were obtained by reaction between MoO_3 and hexamethyldisilazane,[94] there is no report of similar reactions with polyoxomolybdates. Only two nitrido derivatives of POMs which had been obtained by self-assembly reactions,[42] or by reaction of monovacant heteropolyoxotungstates with mononuclear nitrido complexes,[95] were known when, in collaboration with the group of Maatta, we started a joint programme with the aim of enlarging the range of nitrido derivatives and of assessing their potential in nitrogen-atom transfer reactions.[63] The species $[\alpha\text{-}PW_{11}O_{39}Re^{VI}N]^{4-}$, $[\alpha\text{-}PW_{11}O_{39}Os^{VI}N]^{4-}$, $[\alpha_1\text{-}P_2W_{17}O_{61}Os^{VI}N]^{7-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}Os^{VI}N]^{7-}$ have now been obtained by reaction of the monovacant species $[\alpha\text{-}PW_{11}O_{39}]^{7-}$, $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with the nitrido complexes $[Re^{VI}NCl_4]^-$ and $[Os^{VI}NCl_4]^-$, either in aqueous solution or in acetonitrile, and they have been isolated as tetrabutylammonium salts. Reaction of $(^nBu_4N)_4[\alpha\text{-}H_3PW_{11}O_{39}]$ with $[Re^{V}NCl_2(PPh_3)_2]$ in CH_3CN in the presence of Et_3N provides an alternative route to the synthesis of $(^nBu_4N)_4[\alpha\text{-}PW_{11}O_{39}\{Re^{VI}N\}]$. Work in progress in our group deals with the reactivity of nitrido derivatives of POMs towards nucleophilic or electrophilic reagents, and nitrogen atom transfer to olefins. We have demonstrated that $[\alpha\text{-}PW_{11}O_{39}Ru^{VI}N]^{4-}$ reacts with PPh_3 to give the Ru-phosphoraniminato derivative $[\alpha\text{-}PW_{11}O_{39}Ru^{V}NPPh_3]^{3-}$ with subsequent release of the $Ph_3P{=}N{=}PPh_3{}^+$ cation (Fig. 7).[63c]

4.3 Organodiazenido derivatives

Monosubstituted hydrazines easily react with isopolymolybdates, *e.g.* $[Mo_6O_{19}]^{2-}$ and $[\alpha\text{-}Mo_8O_{26}]^{4-}$, in non-aqueous solvents. The thermodynamically favoured products are tetranuclear and hexanuclear complexes containing one, two or three *cis*-$\{Mo(NNAr)_2\}^{2+}$ units.[96] However the $\{Mo(NNAr)\}^{3+}$ unit is formed in mild conditions, and a series of compounds of the type $(^nBu_4N)_3[Mo_6O_{18}(NNAr)]$ have been prepared by treatment of $(^nBu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ with the appropriate arylhydrazines in acetonitrile or in methanol. The presence of reactive groups, *e.g.* $\text{–}CO_2H$, on the aromatic ring allows further derivatization.[49b]

5 Organosilyl derivatives

Organosilyl derivatives of polyoxometalates have been first reported by Knoth who obtained the anions $[\alpha\text{-}SiW_{11}O_{39}\text{-}$

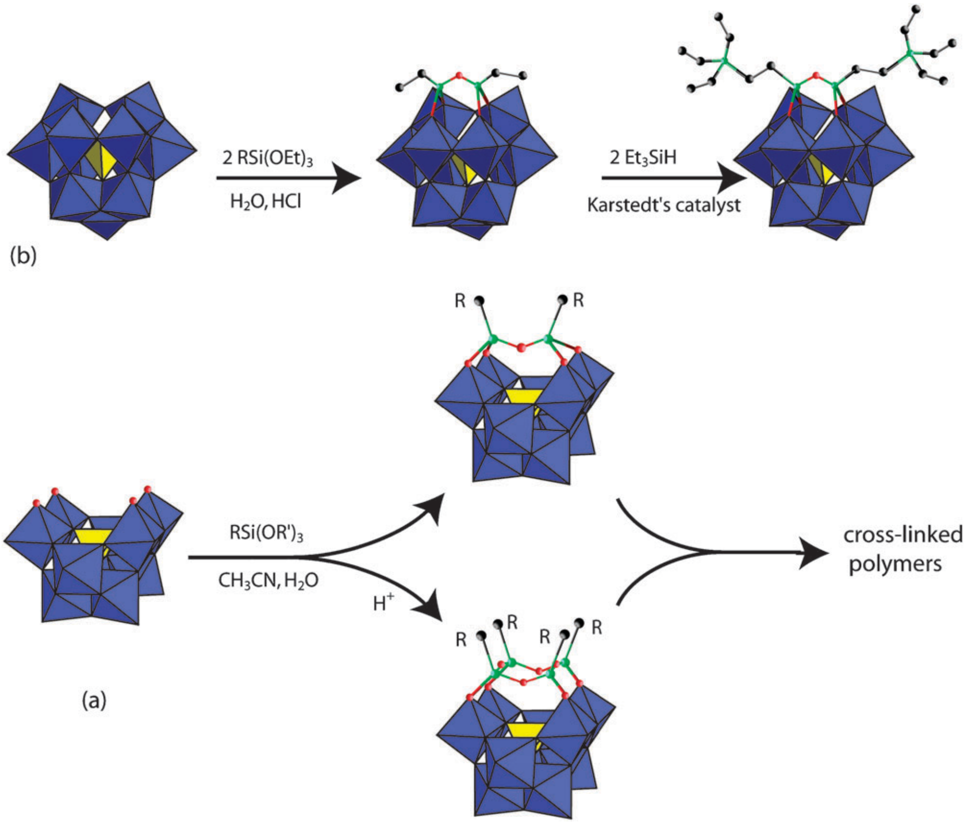

Fig. 8 Organosilyl derivatives of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ (a)[104a,c] and $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ (b).[100] From discrete species to materials.[37] Colour code: MoO_6 octahedra, blue; PO_4 and SiO_4 tetrahedra, yellow; organic Si, green; C, black.

$\{O(SiR)_2\}]^{4-}$ by reacting $RSiCl_3$ (R = Et, Ph, C_3H_5) with $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ in unbuffered aqueous solution.[97] These reactions have been reproduced and extended by Judeinstein and Hill.[98,99] Although no crystal structure is available for any of these complexes, spectroscopic data provide definite structural evidence:[98a] (i) IR indicates the presence of a μ-oxo disilyl linking unit; (ii) ^{183}W NMR establishes that all the complexes retain the lacunary unit $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$; (iii) ^{29}Si NMR indicates that the two SiR groups are equivalent.[99a] Similar compounds have been obtained from $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$. Hydrosilylation of monomers (R = H, vinyl) has been achieved (Fig. 8).[98b,100]

There is a continuing interest for hybrids of the type $[\text{XW}_{11}\text{O}_{39}\{O(SiR)_2\}]^{n-}$ in view of their potential in various areas: (i) they exhibit substantial hydrolytic stability, and high therapeutic indices in cell culture against HIV-1;[99] (ii) polymers have been obtained by radical polymerization of vinyl, allyl and methacryl derivatives.[36] Both monomers and polymers turn reversibly blue upon UV irradiation or electrochemical reduction, which makes them interesting materials for applications in photochromic and electrochromic devices.[100] The amphiphilic bis(dodecyl) derivative $(^n\text{Bu}_4\text{N})_4$-$[\text{SiW}_{11}\text{O}_{39}(O\{Si(CH_2)_{11}Me\}_2)]$ has been incorporated into monolayer and multilayer thin films using Langmuir–Blodgett techniques.[101] (iii) Some applications in catalysis have been devised by Neumann and co-workers who prepared organometallic-POM hybrid compounds from $[\alpha\text{-SiW}_{11}\text{O}_{39}\text{-}\{O(SiR)_2\}]^{4-}$.[102] In metallosalen-POM compounds obtained from the bis(amine) derivative $[\alpha\text{-SiW}_{11}\text{O}_{39}(O\{Si(CH_2)_3NH_2\}_2)]^{4-}$, it was shown that the POM exerts a significant intramolecular effect on the metallosalen moiety leading to the stabilization of higher oxidation states.[102a] Otherwise the Wilkinson's type complex obtained from bis(phosphine) derivative $[\alpha\text{-SiW}_{11}\text{O}_{39}(O\{Si(CH_2)_2PPh_2\}_2)]^{4-}$ has been used as an effective recyclable catalyst for hydrogenation of alkenes.[102b]

Besides organosilyl derivatives of Keggin monovacant heteropolytungstates, those of the monovacant Dawson tungstophosphate $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\{O(SiR)_2\}]^{6-}$ have been reported for various terminal groups R, including thiol, vinyl and methacryl groups.[103] It has been established by multinuclear NMR spectroscopy[103a] and later confirmed by single-crystal X-ray structure analysis,[103c,d] that each RSi unit forms two Si–O–W bonds with two different diads of the POM framework. The thiol derivative has been grafted on nanolatex particles, leading to a nanocomposite material.[103b]

The reactivity of organosilanes with multivacant heteropolytungstates was first investigated by our group. In a series of extensive studies we have demonstrated that it is possible to control the nature of the oligomeric organosiloxane framework grafted onto the POM surface. In an acetonitrile/water mixture the divacant anion $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ reacts with trialkoxysilanes in the presence of hydrochloric acid to give $[\gamma\text{-SiW}_{10}\text{O}_{36}\{O(SiR)_2\}]^{4-}$ and $[\gamma\text{-SiW}_{10}\text{O}_{36}(OSiR)_4]^{4-}$ (R = H, vinyl, $(CH_2)_3OCOC(Me){=}CH_2$, phenyl). The structures of these hybrid anions have been inferred from multinuclear

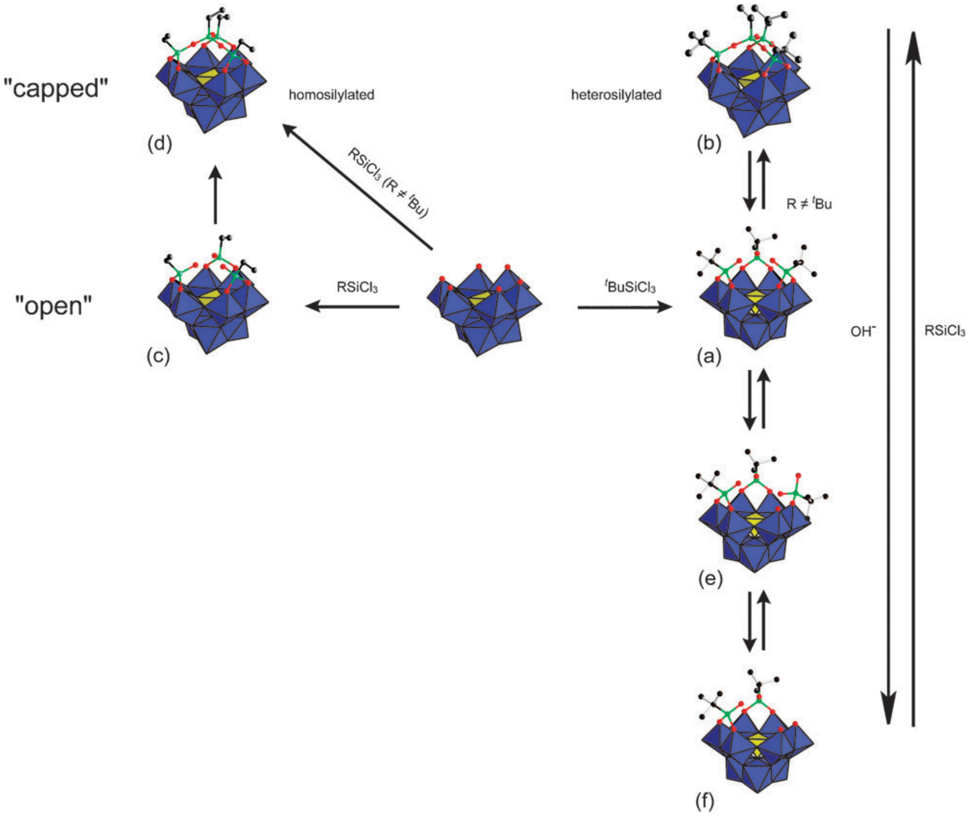

Fig. 9 Organosilyl derivatives obtained from $[\alpha\text{-PW}_9\text{O}_{34}]^{7-}$: (a) $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_3]^{3-}$, (b) $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiO})_3(\text{SiEt})]^{3-}$, (c) $[\alpha\text{-A-PW}_9\text{O}_{34}(\text{EtSiOH})_3]^{3-}$, (d) $[\alpha\text{-A-PW}_9\text{O}_{34}(\text{EtSiO})_3(\text{SiEt})]^{3-}$, (e) $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_2\{^t\text{BuSi(OH)}_2\}]^{4-}$, (f) $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})]^{5-}$. Colour code: MoO_6 octahedra, blue; PO_4 tetrahedron, yellow; organic Si, green; C, black.

NMR solution studies and from MALDI-TOF mass spectrometry.[104a] On the other hand, $^t\text{BuSiCl}_3$ reacts with $\text{Cs}_7[\gamma\text{-PW}_{10}\text{O}_{36}]\cdot x\text{H}_2\text{O}$ under phase-transfer conditions to give $[\gamma\text{-PW}_{10}\text{O}_{36}(^t\text{BuSiOH})_2]^{3-}$. This anion has an "open" structure with two nonequivalent ^{t}BuSiOH groups in the solid where the two silanol groups are linked by a relatively strong O–H···O bond. It reacts cleanly with Me_2SiCl_2 in homogeneous conditions to yield $[\gamma\text{-PW}_{10}\text{O}_{36}(^t\text{BuSiO})_2(\text{SiMe}_2)]^{3-}$ where the ^{t}BuSi groups are linked to the capping group, $SiMe_2$, through two siloxo bridges.[104b]

The chemistry of these hybrids has been developed in various ways. Thus the water-soluble methacryl hybrid $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{OSiR})_4]^{4-}$ allows the formation of gels by radical copolymerization with monomers such as acrylamide (Fig. 8). Such gels can incorporate magnetic particles of maghemite, leading to hybrid hydroferrogels which are expected to have applications in the areas of biomaterials and optics.[37] A nanoscale hybrid system based on gold nanoparticles linked to $[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{O[Si(CH}_2)_3\text{SiH]}_2\}]^{4-}$ has been characterized.[104c] Three-dimensionally ordered macroporous silica materials have been prepared by reaction of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with 1,2-bis(triethoxysilyl)ethane under acidic conditions, followed by condensation with tetraethoxysilane around polystyrene colloidal crystals.[105] Hybrid films with ultra-low dielectric constant have been obtained *via* copolymerization of $[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{O(SiR)}_2\}]^{4-}$ (R = $(CH_2)_3NH_2$) with poly(amic acid).[106] Moreover, fullerene-containing hybrids of the type $[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{O(SiR)}_2\}]^{4-}$ have been synthesized and found to be catalytically active for photooxidation in water under heterogeneous conditions, using visible light irradiation.[107]

Under phase-transfer conditions, the trivacant anion $[\alpha\text{-A-SiW}_9\text{O}_{34}]^{10-}$ reacts with trichlorosilanes, $RSiCl_3$, to give the "capped-structure" derivatives $[\alpha\text{-A-SiW}_9\text{O}_{34}(\text{RSiO})_3(\text{SiR})]^{4-}$ (R = H, Et, ^{n}Bu, Ph, vinyl, ...). It is noteworthy that the correct C_{3v} structure of these hybrids was obtained from a thorough multinuclear (^{1}H, ^{29}Si, ^{183}W) NMR study before crystal structures were available.[108a] These reactions have been extended to other $[\text{A-XW}_9\text{O}_{34}]^{n-}$ trivacant Keggin species (X = Ge, n = 10; X = P^V or As^V, n = 9) and to a variety of silanes.[108,109] All the species $[\alpha\text{-A-XW}_9\text{O}_{34}(\text{RSiO})_3(\text{SiR})]^{(n-6)-}$ characterized to date contain a $\{\alpha\text{-A-XW}_9\}$ framework. For X = P, where $\text{Na}_8\text{H}[\beta\text{-A-PW}_9\text{O}_{34}]\cdot24\text{H}_2\text{O}$ is the common precursor, grafting is followed by a rapid β → α isomerization of the $\{PW_9\}$ framework. The crystal structures of several compounds of the type $(^n\text{Bu}_4\text{N})_3[\alpha\text{-A-PW}_9\text{O}_{34}(\text{RSiO})_3(\text{SiR})]$ (R = Me, Et, Ph, vinyl) have been recently reported by the group of Li.[109] Whereas $^n\text{BuSiCl}_3$ reacts with $[\text{A-PW}_9\text{O}_{34}]^{9-}$ to give the "capped-structure" anion $[\alpha\text{-A-PW}_9\text{O}_{34}(^n\text{BuSiO})_3(\text{Si}^n\text{Bu})]^{3-}$, the corresponding reaction with $^t\text{BuSiCl}_3$ yields the "open-structure" anion $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_3]^{3-}$, presumably because of steric crowding (Fig. 9). The arsenic species $[\alpha\text{-A-AsW}_9\text{O}_{34}(^t\text{BuSiOH})_3]^{3-}$ and $[\text{B-AsW}_9\text{O}_{33}(^t\text{BuSiOH})_3]^{3-}$ were similarly obtained from $[\alpha\text{-A-AsW}_9\text{O}_{34}]^{9-}$ and $[\text{B-HAsW}_9\text{O}_{33}]^{8-}$, respectively. Both $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_3]^{3-}$ and $[\text{B-AsW}_9\text{O}_{33}(^t\text{BuSiOH})_3]^{3-}$ have been crystallographically characterized as tetrabutylammonium salts. Each of the three chemically equivalent $^t\text{BuSiOH}$ units is attached to the polyoxotungstate backbone through two W–O–Si bridges.[77] On the one hand, controlled degradation of $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_3]^{3-}$ by $^n\text{Bu}_4\text{NOH}$ successively yields $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_2\{^t\text{BuSi(OH)}_2\}]^{4-}$ and $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_2]^{5-}$ (Fig. 9).[110] On the other hand, $[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{BuSiOH})_3]^{3-}$ reacts cleanly with various electrophilic reagents, *e.g.* RECl_3 (E = Si, Ge or Sn) and VOCl_3 in homogeneous conditions to give "capped-structure" anions.[108c] Here again the structures of the products were established by multinuclear NMR spectroscopy before the crystal structure of $(^n\text{Bu}_4\text{N})_3[\alpha\text{-A-PW}_9\text{O}_{34}(^t\text{SiBuO})_3(\text{SiCH}_2\text{CH}{=}\text{CH}_2)]$ was eventually obtained.[111]

Whereas $[\beta\text{-A-PW}_9\text{O}_{34}]^{9-}$ and $[\text{B-HAsW}_9\text{O}_{33}]^{8-}$ react with dichlorosilanes R_2SiCl_2 (R = Me, Ph) to afford $[\alpha\text{-A-PW}_9\text{O}_{34}(\text{SiR}_2)_3]^{3-}$ and $[\text{B-AsW}_9\text{O}_{33}(\text{SiR}_2)_3]^{3-}$, respectively, $[\text{B-SbW}_9\text{O}_{33}]^{9-}$ leads to $[\text{B-SbW}_9\text{O}_{33}(\text{SiR}_2)_2]^{5-}$ even in the presence of an excess of R_2SiCl_2, likely because of the larger size of the Sb^{III} lone pair. Multinuclear NMR results are consistent with $C_{3\text{v}}$ symmetry for the As^{III} species and C_s symmetry for the Sb^{III} derivative.[108c]

Beside the numerous organosilyl derivatives of lacunary POMs, there are also a few derivatives of complete POMs. These relate to niobium-substituted polyoxotungstates where the electrophilic organosilyl fragment binds selectively to the terminal ONb oxygen atom.[75,112,113]

6 Organophosphonyl and organoarsonyl derivatives

The chemistry and the structural properties of $\text{M/O/O}_3\text{ER}$ systems where M = Mo or W, E = P or As, have been extensively reviewed,[114] and this section will be restricted to the self-assembly of molybdophosphonates and molybdoarsonates and to the reaction of organophosphonates towards lacunary polyoxotungstates.

The pentamolybdobisphosphonates $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^{n-}$, where R = Me,[115] Et,[115a] Ph,[115a,116] $\text{C}_2\text{H}_4\text{NH}_3^+$,[115] $p\text{-CH}_2\text{C}_6\text{H}_4\text{NH}_3^+$,[115a,117] were among the first organic derivatives of POMs to be characterized. Other members of the family, *e.g.* those with cyclic aminoethylphosphonates [118] and those with carboxylatophosphonates,[119] have been reported since then. Several of these compounds lend themselves for additional functionalization, at least in principle, *via* coordination of metal ions or attachment of organic or organometallic fragments. A few pentamolybdobisarsonates have also been characterized,[120] although hexamolybdobisarsonates $[(\text{RAs})_2\text{Mo}_6\text{O}_{24}]^{4-}$ and $[(\text{RAs})_2\text{Mo}_6\text{O}_{24}(\text{H}_2\text{O})]^{4-}$ are the predominant species in weakly acid solution,[121] while species of the type $[(\text{RAs})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$ are formed at pH <1.[122] The latter display an inverted Keggin structure with a tetrahedral arrangement of organic groups that can be used for the formation of *n*D networks. The architecture of the crystalline materials obtained from these clusters depends on the hydrogen bonding ability of the organic group and of the solvent, and the oxophilicity of the counterions.[122c,d] A new family of functionalized heteropolymolybdates, $[\text{RPMo}_6\text{O}_{21}(\text{O}_2\text{CCH}_2\text{NH}_2)_3]^{2-}$, has been reported.[123a] They consist of a central hetero group surrounded by a ring of six MoO_6 octahedra sharing edges and corners alternatingly. Three glycine molecules are each bound to two edge-sharing Mo centres *via* their carboxylate functionality on the same side of the ring. The same structure can be formed with lone-pair-containing heteroatoms and for a variety of amino acids as seen in $[\text{XMo}_6\text{O}_{21}(\text{O}_2\text{CRNH}_2)_3]^{2-}$.[123b]

Organophosphonic acids RPO(OH)_2 and organophosphonic dichlorides RPOCl_2 react with lacunary heteropolytungstates in homogeneous solution or under phase transfer conditions. By contrast to organosilyl groups, only two RPO^{2+} electrophilic groups are grafted even when multivacant Keggin tungstates are used. The group of Hill was the first to report the synthesis of $[\alpha\text{-XW}_{11}\text{O}_{39}(\text{PhPO})_2]^{(8-n)-}$ by reaction of $[\alpha\text{-XW}_{11}\text{O}_{39}]^{(12-n)-}$ with PhPOCl_2 in acetonitrile. The crystal structure of $(^n\text{Bu}_4\text{N})_2\text{H}[\text{PW}_{11}\text{O}_{39}(\text{PhPO})_2]$ has been determined. The collective ^{1}H, ^{31}P and ^{183}W NMR data provide evidence that the $[\text{PW}_{11}\text{O}_{39}(\text{PhPO})_2]^{3-}$ complex retains the C_s symmetry in solution.[124] Sun *et al.* have extended these reactions to other monovacant Keggin anions ($\text{X}^{n+} = \text{B}^{3+}, \text{Ga}^{3+}$) and to organothiophosphonic dichlorides.[125] For our part we focused on the reactivity of multivacant heteropolytungstates. Derivatives of the type $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RPO})_2]^{4-}$ (R = H, Et, ^{n}Bu, ^{t}Bu, Ph, $\text{C}_2\text{H}_4\text{CO}_2\text{H}$) have been obtained by reaction of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with the appropriate phosphonic acid in acetonitrile. These hybrids have been characterized by multinuclear NMR and by X-ray crystallography. Solution NMR data agree with the virtual $C_{2\text{v}}$ solid-state structure of $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$.[126a] Bisphosphonic acids $p\text{-(HO)}_2\text{P(O)CH}_2(\text{C}_6\text{H}_4)_n\text{CH}_2\text{P(O)(OH)}_2$ give cyclic dimers.[126b] In the presence of $^n\text{Bu}_4\text{NBr}$ acting as phase-transfer reagent, organophosphonic acids react in acetonitrile with the trivacant compound $\text{Na}_8\text{H}[\beta\text{-A-PW}_9\text{O}_{34}]\cdot 24\text{H}_2\text{O}$ to give $(^n\text{Bu}_4\text{N})_3\text{Na}_2[\alpha\text{-A-PW}_9\text{O}_{34}(\text{RPO})_2]$ (R = Et, ^{n}Bu, ^{t}Bu, Ph). The B-type derivatives $[\text{XW}_9\text{O}_{33}(\text{RPO})_2]^{5-}$ (X = As and Sb) have been obtained similarly. The solution structure of these anions has been inferred from multinuclear (^{31}P, ^{183}W) NMR studies. Each RPO group is connected to two terminal oxygen atoms belonging to the same diad. Therefore only four of the six nucleophilic oxygen atoms of the original trivacant anion become saturated. The remaining two oxygen atoms together with those of the RPO groups define a new lacuna which should allow the binding of other cations.[108e]

7 Nanosized polyoxomolybdates with multifunctionality

Compounds described in sections 3 to 6, including those obtained by self-assembly or decomposition–reaggregation processes, are relatively small species. In order to delineate the scope of the functionalization of POMs, it is appropriate to consider nanosized POMs, some of which are briefly mentioned in the introduction. In POM chemistry, as in other areas, self-assembly may result in the emergence of new properties especially if larger systems are considered.[127] Increasing the size and the complexity of POMs is expected to generate multifunctionality of interest in materials science. An impressive illustration of this concept has been provided by

Müller and his co-workers in the field of polyoxomolybdates. Reduction of acidified aqueous solutions of molybdates leads to remarkable nanosized blue wheel-shaped clusters while the deliberate addition of linkers such as $Mo^{V}{}_2O_4{}^{2+}$, Fe^{3+}, Cr^{3+} or VO^{2+} to a dynamic library containing pentagonal units of the type $(Mo)Mo_5$ leads to hollow porous capsules.[3,128] Ring-shaped polyoxomolybdates have also been obtained by the group of Zhang[129] and are also formed upon irradiation of isopolymolybdates in aqueous solutions containing electron donors.[130] Molybdenum oxide based clusters are unique in that they not only form fascinating structures, but most important, they display versatile reactivity and unprecedented materials properties which depend not only on their specific type of surface functionalities, but also on their size as well as on their shape.[128]

According to the Bielefeld group studies, ring-shaped clusters are the basic building units of soluble molybdenum blues (which were known by Scheele and Berzelius)[131*a*] and they have the composition $[(\{Mo^{VI}{}_2O_5(H_2O)_2\}^{2+})_n(\{Mo^{VI/V}{}_8O_{28}H(H_2O)_3Mo^{VI/V}\}^{3-})_n]^{n-} \equiv [\{(MoO_3)_{11}H(H_2O)_5\}_n]^{n-}$ ($\{Mo_{154}\}$ for $n = 14$, $\{Mo_{176}\}$ for $n = 16$).[131*b*] They exhibit a nanosized toroidal cavity (*ca.* 2 nm for $\{Mo_{154}\}$) and have an extended hydrophilic inner and outer surface, *n* tetrahedral $\{O_4\}$ sites as well as *n* $\{Mo_6O_6\}$-type ring receptors. The $\{Mo_{154}\}$ and $\{Mo_{176}\}$ clusters display different reactivities. Thus with regard to the $\{Mo_{154}\}$ wheel, the $\{O_4\}$ sites can incorporate paramagnetic metal centres such as Cu^{2+},[132*a*] the $\{Mo_6O_6\}$ pores can act as receptors for cations such as protonated urea,[132*b*] and the internal surface functionalities can be altered by the incorporation of multiphilic ligands such as cystine.[132*c*] The larger $\{Mo_{176}\}$ host allows various processes including the size-specific non-covalent incorporation of up to three metal porphyrins,[132*d*] the size- and surface-dependent integration of an unusual 64 membered ring comprising 16 K^+ and 16 $SO_4{}^{2-}$ ions,[132*e*] and an unprecedented growth process leading to the covalent closing of the cavity with two $\{Mo_{36}\}$-type caps.[132*f*]

Spherical capsules have the composition $(Pentagon)_{12}(Linker)_{30}$ where the pentagonal unit is made of a central MoO_7 pentagonal bipyramid sharing edges with five MoO_6 octahedra. They were called Keplerates by Müller[133*a*]—a term now widely used[133*b*]—and are remarkable for their symmetry and beauty.[133*c*] Various spherical clusters, *e.g.* $\{Mo_{132}\}$,[134*a*] $\{Mo_{102}\}$,[134*b*] $\{Mo_{72}Fe_{30}\}$,[134*c*] $\{Mo_{72}V_{30}\}$,[134*d,e*] $\{Mo_{72}Cr_{30}\}$,[134*f*] $\{Mo_{75}V_{20}\}$[134*g*] and $\{Mo_{80}V_{22}\}$[134*h*] have been characterized, among which the seminal[133*b*] $\{Mo_{72}Fe_{30}\}$ cluster has received very special attention since its discovery. The Müller type Keplerates have unique features: they have 20 openings and a cavity connected to the outside *via* 20 channels, the size and the charge of the capsule can be tuned by changing the linkers, the shell functionality of the internal cavity can be tuned by changing the ligands, and the $\{Mo_9O_9\}$ pores of $\{Mo_{132}\}$-type Keplerates have 20 crown-ether like functions which allows supramolecular chemistry on a sphere surface. The pores can be opened and shut with noncovalently bonded substrates such as amidinium cations. As a result of this, many applications have been developed such as modelling passive cation transport through membranes,[135] encapsulation and nano-separation chemistry,[136] generating structures of confined water,[137] coordination chemistry under confined conditions[138*a,b*] as well as modelling ligand exchange at oxide mineral surfaces (Fig. 10).[138*c*]

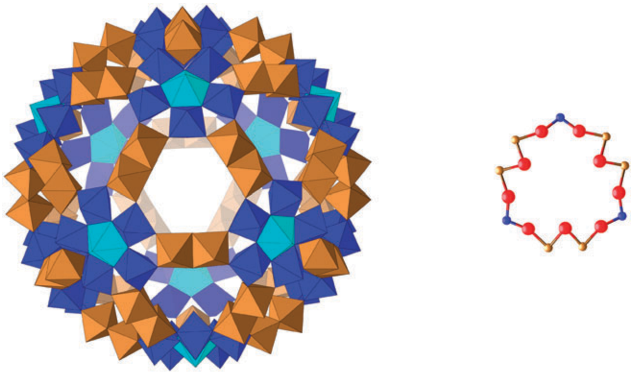

Fig. 10 Polyhedral representation of the Keplerate $[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(CH_3CO_2)\}_{30}]^{42-}$, view along a C_3 axis. One of the 20 $\{Mo_9O_9\}$ pores is shown in ball-and-stick representation. Colour code: MoO_7 pentagonal bipyramid, light blue; $Mo^{VI}O_6$ octahedra, dark blue; $Mo^{V}O_6$ octahedra, brown.

The magnetic properties of Keplerates of the type $\{Mo^{VI}{}_{72}M_{30}\}$ (M = Fe^{III}, Cr^{III}, V^{IV}) have received a lot of attention due to their spherical network of corner-shared magnetic triangles resulting in geometrical frustration[134*c–e*,139]—analogous to what occurs for the planar Kagomé lattices—which plays a central role in several key materials.[140]

An essential feature of Keplerates for current and future applications is their stability under well-defined conditions—especially under exclusion of oxygen—in aqueous and non-aqueous solutions. This has been proven by several experiments, *e.g.* ultracentrifugation,[141*a*] Raman spectroscopy,[3*b*,141*b*] small angle scattering on $\{Mo_{132}\}$-type solutions,[141*c*] NMR studies of cation uptake and release equilibrium,[135] as well as isolation with cationic surfactants from the solution with subsequent analyses of the well defined SECs.[19*a–c*]

A unique feature of molybdenum oxide based wheels and capsules, is their linking versatility, which is a consequence of their nanoscaled structured and functionalized surfaces.[142] Self-structuring has been detected in the gas phase by MALDI TOF mass spectrometry for two neutral Keplerates,[143] while several anions, such as $\{Mo_{154}\}$,[144] $\{Mo_{72}Fe_{30}\}$,[145] and $\{Mo_{132}\}$[146] self-assemble into giant hollow spherical vesicles in aqueous solution. These aggregates have been studied by different methods including small-angle X-ray scattering,[144*a*] static and dynamic light scattering,[144*a*,145] dielectric relaxation,[144*c*] kinetic precipitation followed by electronic microscopy,[147*a*] and flow field-flow fractionation.[147*b*] In the solid state, linking to 1-D and 2-D networks through Mo–O–Mo or Fe–O–Fe linkages is possible even in a room-temperature solid-state reaction for $\{Mo_{72}Fe_{30}\}$.[130*b*,148,149]

While wheels and capsules are easy to handle from a materials science point of view, they can also take advantage of the patterning methods outlined in the introduction section, *e.g.* exchange of POM counterions with cationic surfactants, and solvent-casting and LB techniques. Thus self-patterning of surfactant-encapsulated Keplerates into highly ordered nanostructures has been demonstrated at the air/water interface.[19f] Moreover introduction of $\{Mo_{132}\}$ as well as $\{Mo_{176}\}$ and clusters into silica *via* a sol–gel process results in hybrid materials where the structural integrity and the reactivity of the POMs are maintained.[150] In a quite different type of application, $\{Mo_{84}Fe_{30}\}$ and $\{Mo_{72}Fe_{30}\}$ clusters have been used to generate at high temperature bimetallic particles which act as catalysts for the synthesis of carbon nanotubes.[151] Thus it is quite apparent that giant molybdenum oxide based wheels and spheres find a large variety of applications in fundamental and applied science.

8 Conclusions and perspectives

The area of POM-based inorganic/organic hybrids has greatly expanded over the last three decades. Besides hybrids where the components assemble *via* weak interactions, those with covalent links develop steadily. We have focused here on three families of organically-derivatized POMs, namely those with multiple molybdenum–nitrogen (imido and diazenido derivatives), and organosilyl and organophosphonyl derivatives. However many other organic derivatives of POMs have been reported, in particular carboxylato,[71a] alkoxo[32,35,55,152] and organostannyl derivatives.[66a,b,153] While work on POM-based hybrids so far largely focused on their structural characterization, interesting properties have also been demonstrated. The organic component may direct the formation of frameworks and networks. Functionalization can stabilize otherwise unstable frameworks, *e.g.* the lacunary Lindqvist-type anions $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ and $[Mo_5O_{13}(OMe)_4(N_2Ar)]^{3-}$. It allows to tune the redox and acid–base properties, and the solubility of primary POMs, *e.g.* imido derivatives of the type $[Mo_6O_{19-x}(NAr)_x]^{2-}$. Encapsulation enhances cell-penetration, and the stability and biological activity of POMs, and reduces their toxicity. Functionalization might improve the efficiency and the selectivity of catalytic processes. Illustrative examples are provided by the organosilyl and organophosphonyl derivatives of lacunary polyoxotungstates which prove high-performance catalysts for oxidation with hydrogen peroxide under microwave irradiation.[154] Furthermore evidence of enantioselective oxygen transfer has been obtained with the 1-aminoethylphosphonic derivative of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$.[154] The electrochemical properties of POMs are maintained in polymers and polyelectrolyte matrices, which paves the way for applications as sensors or heterogeneous catalysts. Furthermore POM-based hybrids can combine several properties, *e.g.* magnetic and electrical properties,[15] or chirality and electrical properties.[155] Enhancement of the interaction between components *via* covalent linkage should increase the interaction of their properties, could result in synergetic effects and even lead to novel effects. On the other hand, due to their size and especially to their multifunctionality giant POMs set to play an important role in the development of new materials. The current challenge is to incorporate POMs into functional devices. Both covalent derivatization and self-assembly (bottom-up approach) should play a key role in this step as they are complementary.

Acknowledgements

This work was supported by the Université Pierre et Marie Curie, the CNRS and the Institut Universitaire de France from whom A. P. is a member.

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