Organoimido-polyoxometalates as polymer pendants†

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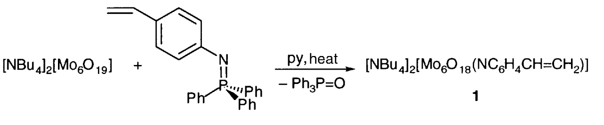
The *p*-styrenyl substituent borne by the organoimido ligand in the Lindqvist derivative $[NBu_4]_2[Mo_6O_{18}(NC_6H_4CH{=}CH_2)]$ 1 allows the polyoxometalate complex to be introduced as a pendant group in polystyrene compositions *via* conventional free radical-induced copolymerization.

Research involving polyoxometalates[1]—the multimetallic oxo-anions formed by Mo, W, V and, to a lesser extent, Nb and Ta—continues to increase in scope and pace, driven by the goal of harnessing these species' remarkable and versatile attributes for catalytic, medical and imaging applications, and for use in magnetic and photo- and electro-chromic materials.[2] In their solid state applications, polyoxometalates generally are employed as components embedded heterogeneously within various matrices, rather than as covalently bound integral elements.[3] The covalent incorporation of polyoxometalates into conventional polymeric systems therefore may provide additional opportunities for their technological development.

There are few examples of polymers bearing covalently attached polyoxometalate species. Knoth[4] has described the 'all-inorganic' polymer $[(OC)_3CoGe_2W_{11}SiO_{40}{}^{5-}]_n$. Difunctional polyoxotungstates $[(RSiOSiR)W_{11}SiO_{39}]^{4-}$ have been homo-polymerized by Judeinstein[5] and incorporated into siloxane compositions by Katsoulis and Keryk.[6] Very recently, Mayer, Thouvenot *et al.*[7] have reported well characterized acrylamide and methacrylate networks cross-linked by the polyoxometalates $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$ or $[\gamma\text{-}SiW_{10}O_{36}(R\text{-}SiOSiR)]^{4-}$ [R = $C_3H_6OC(O)C(Me){=}CH_2$]. Here, we describe a different approach to organic polymers bearing polyoxometalate pendants, involving co-polymerization of the styrylimido ligand in the Lindqvist derivative $[NBu_4]_2[Mo_6O_{18}(NC_6H_4CH{=}CH_2)]$ **1**.

Reaction of $[NBu_4]_2[Mo_6O_{19}]$ with $Ph_3P{=}NC_6H_4CH{=}CH_2$ in pyridine solution at 90 °C produces $Ph_3P{=}O$ and the red styrylimido-hexamolybdate complex **1** in high yield (Scheme 1).‡ To our knowledge, **1** represents the first example of a styrylimido complex.[8] In MeCN solution, cyclic voltammetry of **1** reveals a one-electron reduction at $E_{1/2}$ = – 886 mV (*vs.* Ag/Ag$^+$); this value is more negative than that of the $[Mo_6O_{19}]^{2-}$ parent ($E_{1/2}$ = −707 mV) and is typical of other monosubstituted $[Mo_6O_{18}(NR)]^{2-}$ systems.[9] **1** is soluble in polar organic solvents such as 1,2-dichloroethane and its solutions display good hydrolytic stability: the deliberate addition of H_2O (*ca.* 15 equiv.) to a CD_3CN solution of **1** produced no detecable amount of 4-vinylaniline after 4 d at 25 °C as monitored by ^1H NMR spectroscopy.

Crystals of **1** were grown by diffusion of Et_2O vapor into an acetonitrile solution, and the molecular structure was determined by X-ray crystallography (Fig. 1).§ The styrylimido ligand occupies a terminal position on the hexamolybdate cage and its metrical parameters [Mo(1)–N(1) 1.728(7) Å, Mo(1)–N(1)–C(1) 159.9(7)°] indicate substantial [Mo≡NR] triple bond character. Along the Mo(1)–O(1)–Mo(5) axis, the central O(1) atom is substantially nearer to the imido-bearing Mo(1) site [2.223(5) Å] than to the *trans* oxo site Mo(5) [2.353(5) Å].



Scheme 1 Synthesis of styrylimido-hexamolybdate complex **1**.

Co-polymerization of **1** (0.50 g, 0.34 mmol) and 4-methylstyrene (0.16 g, 1.34 mmol) initiated by AIBN [2,2′-azobis(2-methylpropionitrile), 0.010 g, 0.061 mmol] was conducted in 1,2-dichloroethane (5 mL) at 60 °C for 48 h, and led to the separation of an oily brown insoluble residue (0.435 g) from the brown solution. Dissolution of this residue in acetonitrile (10 mL), filtration to remove a small amount of gummy material, and evaporation to dryness afforded a green–brown solid **2**. In the IR spectrum of **2**, no bands were observed in the vinylic ν(C=C) region, and the presence of an imido-substituted hexamolybdate was confirmed by its characteristic 'doublet' pattern in the ν(Mo–O$_t$) stretching region [975(sh), 952s cm^{-1}]. The ^1H NMR spectrum of **2** taken in CD_3CN revealed features consistent with the formation of the expected co-polymer of **1** and 4-methylstyrene: the vinylic resonances of both precursors had disappeared; a pair of broadened aryl resonances were observed centered at δ *ca.* 7.0 and 6.5; a broad signal at δ 2.3 was assignable as the CH_3 resonance of the 4-methyl styrene component; the resonances of the $[NBu_4]^+$ cations were observed as virtually unbroadened signals in their characteristic regions; and broadened resonances assignable as the methine and methylene units of the polymer backbone were observed in the range δ 1.8–1.5 overlapped with the resonances of the interior CH_2 groups of the $[NBu_4]^+$ cations. A comparison of the relative intensities due to the aryl groups, the α-CH_2 groups of the $[NBu_4]^+$ cations, and the styrenic CH_3 group suggested a

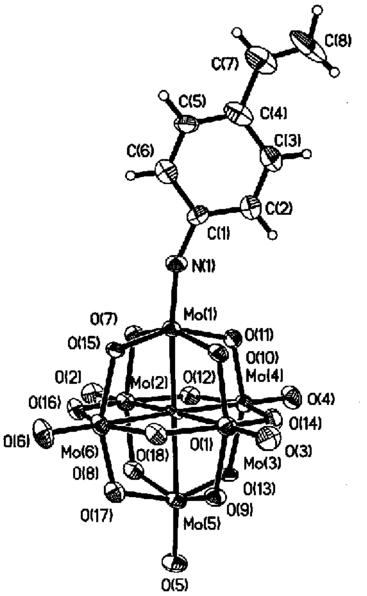


Fig. 1 ORTEP representation and labelling scheme for the $[Mo_6O_{18}(NC_6H_4CH{=}CH_2)]$ dianion within **1**. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.728(7), N(1)–C(1) 1.388(12), Mo(1)–O(1) 2.223(5), Mo(1)–O(7) 1.897(5), Mo(1)–O(10) 1.994(6), Mo(1)–O(11) 1.996(6), Mo(1)–O(15) 1.887(5), Mo(5)–O(1) 2.353(5), Mo(5)–O(5) 1.689(6), Mo(5)–O(8) 1.966(6), Mo(5)–O(9) 1.864(6), Mo(5)–O(13) 1.867(5), Mo(5)–O(17) 1.971(6); Mo(1)–N(1)–C(1) 159.9(7).

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† Electronic supplementary information (ESI) available: colour version of Fig. 2. See http://www.rsc.org/suppdata/cc/b0/b005022i/

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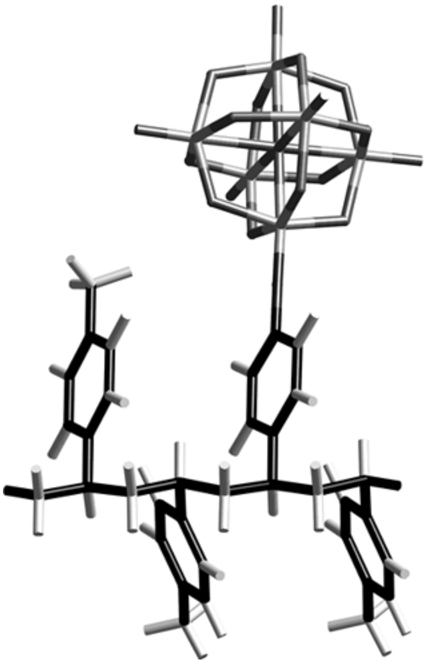

Fig. 2 Idealized representation of a segment within **2** (cations omitted for clarity). Colour version is shown as ESI†.

composition for **2** of nearly three 4-methyl styrene units per unit of **1**, as indicated in Fig. 2. Elemental analysis of **2** is consistent with this formulation. Molecular weight determinations of **2** are in progress.[10]

This work demonstrates that the styrylimido ligand can be employed as a reactive site capable of delivering its metal complex into a conventional polymeric environment. Similar methodology should be broadly applicable to the synthesis of other new classes of hybrid inorganic/organic polymers which incorporate covalently attached organoimido-metal complexes as exploitable backbone substituents. Further characterization of the properties of **2** is underway, as are studies on a variety of other polymerizable organoimido systems.

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Notes and references

‡ *Experimental procedure* for **1**: under an N_2 atmosphere, $[NBu_4]_2[Mo_6O_{19}]$ (6.54 g, 4.79 mmol) and $Ph_3P{=}NC_6H_4CH{=}CH_2$ (2.73 g, 7.19 mmol) were added to 20 mL pyridine and the mixture stirred for 5 d at 90 °C. After cooling to room temperature, the solution was filtered and solvent was removed under vacuum. The residue was washed successively with Et_2O (50 mL) and benzene (3 × 75 mL) and dried *in vacuo* to afford red–orange solid **1** (6.30 g, 89.7%). Anal. Calc. for $C_{40}H_{79}Mo_6N_3O_{18}$: C, 32.78; H, 5.43; N, 2.87. Found: C, 32.97; H, 5.55; N, 3.02%. δ_H(CD_3CN, 296 K): 7.49, 7.47, 7.21, 7.19 (AA′BB′ ‘quartet’, 4H, C_6H_4), 6.77 (m, 1H, CH), 5.79 (d, 1H, $=CH_2$ *cis*, ^3J 17.2 Hz), 5.26 (d, 1H, $=CH_2$ *trans*, ^3J 10.8 Hz), 3.08 (m, NCH_2, 16 H), 1.60 (m, CH_2, 16 H), 1.35 (m, CH_2, 16 H), 0.97 (t, CH_3, 24 H). IR (Nujol, cm^{-1}): ν(C=C) 1605 w; ν(Mo≡O), 975(sh), 952s. UV–VIS [MeCN; λ/nm (ε/M^{-1} cm^{-1})]: 272 (64200), 366 (50400).

§ *Crystal data* for $C_{40}H_{79}Mo_6N_3O_{18}$ **1**: orange–red crystals, $M_w = 1465.70$, monoclinic, space group $P2_1/n$, $a = 17.316(2)$, $b = 15.6017(17)$, $c = 20.774(2)$ Å, $\beta = 105.098(9)°$, $V = 5418.6(11)$ Å^3, $Z = 4$, $D_c = 1.797$ g cm^{-3}. Of the 8303 reflections collected [$T = 173(2)$ K, $2\theta_{max} = 47°$], 8001 were unique ($R_{int} = 0.0422$) and 6784 were observed [$I > 2\sigma(I)$]. Full-matrix least squares refinement on F^2 converged with $R_1 = 0.0450$ and $wR_2 = 0.1268$. CCDC 182/1742. See http://www.rsc.org/suppdata/cc/b0/b005022i/ for crystallographic files in .cif format.

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10 A composition for **2** incorporating an average of 2.7 (4-methylstyrene) units for each unit of **1** has the empirical formula $C_{64.3}H_{106}N_3Mo_6O_{18}$ and requires: C, 43.27; H, 5.99; N, 2.35. Found for **2**: C, 43.10; H, 6.08; N, 2.90%.