The unexpected reactivity of *p*-tolylisocyanate towards the Keggin anion α-$[PMo_{12}O_{40}]^{3-}$

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In pyridine, *p*-tolylisocyanate reacts with $[NBu^n{}_4]_3[\alpha\text{-}PMo_{12}O_{40}]$ to give a number of products, among which are the highly functionalized neutral species $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}(py)_2O_{18}]$, the azo compound *p*-$MeC_6H_4N{=}NC_6H_4Me$-*p*, and reduced derivatives of α-$[PMo_{12}O_{40}]^{3-}$.

Transition-metal imido chemistry has experienced remarkable growth in recent years.[1] Although oxo–imido complexes of early transition metals have been known for some time, imido derivatives of polyoxometalates have only been characterised very recently.[2–5] Imido derivatives of $[Mo_6O_{19}]^{2-}$ have been obtained from phosphinimines[2a,3] or isocyanates,[2b–d,4a] through amine deprotonation reactions,[4b] or by self-assembly through the controlled hydrolysis of $[Mo_2O_7]^{2-}$with an imido complex.[5] The most significant achievements have been the multiple functionalization of $[Mo_6O_{19}]^{2-}$,[2b,3,4b] and the bridging of two hexametalate cages by a diimido ligand.[2c] To our knowledge, all imido derivatives of polyoxometalates characterized to date belong to the Lindqvist-type series.[2–5] This prompted us to explore the reactivity of isocyanates towards other polyoxometalates. For a start, we have focused on α-$[PMo_{12}O_{40}]^{3-}$, since its reactions can be conveniently monitored by ^{31}P NMR spectroscopy, which should further provide an opportunity to gain some insight into their mechanisms. We report here the results of our preliminary studies of the reaction of *p*-MeC_6H_4NCO with $[NBu^n{}_4]_3[\alpha\text{-}PMo_{12}O_{40}]$.

In a typical experiment, 1 equiv. of *p*-MeC_6H_4NCO was added to a suspension of 1 equiv. of $[NBu^n{}_4]_3[\alpha\text{-}PMo_{12}O_{40}]$ in pyridine and the mixture was heated for *ca.* 18 h at 80 °C. The resulting green–brown solution was evaporated to dryness and MeCN was added to the residue. At this stage, some unreacted $[NBu^n{}_4]_3[\alpha\text{-}PMo_{12}O_{40}]$ was removed by filtration, and the brown filtrate was divided into two parts: one was set aside while Et_2O was added to the other one, which led to the precipitation of a green–brown powder. A brown solid consisting of brown needles of $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}(py)_2O_{18}]$ **1**† lying on a brown powder of distinct composition **2**, was obtained from the MeCN–Et_2O filtrate within a few days. Later on, the filtrate produced orange needles of azotoluene, *p*-$MeC_6H_4N{=}NC_6H_4Me$-*p* **3**, characterized by mass spectrometry and X-ray analysis, and a white powder identified as *p*-$MeC_6H_4NHCONHNC_6H_4Me$-*p* **4** by mass spectrometry. Meanwhile the part of the MeCN filtrate that had been set aside gave a mixture of brown needles **1**, identified by IR spectroscopy,‡ yellow–orange needles and blue polyhedral crystals **5**. The ^{31}P NMR spectrum of **5** displays a single signal at δ 1.5 in MeCN–$(CD_3)_2CO$ [δ 0.8 in $(CD_3)_2SO$], while that of the green–brown powder initially obtained by addition of Et_2O presents in MeCN–$(CD_3)_2CO$ five signals at δ +1.5, −2.4, −2.6, −5.2, −5.5 and, in some cases, a weak extra signal at δ −3.8.

The molecular structure of the unreduced polyimido $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}(py)_2O_{18}]$ species is depicted in Fig. 1. This centrosymmetrical complex can be viewed as being composed of two '$Mo_3O_7(NC_6H_4Me\text{-}p)_6$' groups held together by four extra molybdenum units. These groups are made of three edge-sharing distorted octahedra, Mo(1), Mo(2) and Mo(3), and are reminiscent of the 'Mo_3O_{13}' building blocks of the α-$[PMo_{12}O_{40}]^{3-}$ Keggin anion. While each of the Mo(1), Mo(2) and Mo(3) sites displays MoO_3N_3 coordination, the remaining two independent molybdenum atoms, Mo(4) and Mo(5), display respectively distorted tetrahedral MoO_4 and distorted trigonal-bipyramidal MoO_4N surroundings. Each of the Mo(1), Mo(2) or Mo(3) centres is connected to both Mo(4) [or Mo(4′)] and Mo(5) [or Mo(5′)] through μ-bridging oxo ligands. The originality of this complex obviously relies on the high degree of functionalization of the '$Mo_3O_7(NC_6H_4Me\text{-}p)_6$' groups, similar to the structurally characterized discrete tritungstate $[W_3(NBu^t)_3(NPh)_3Cl_7]^-$.[7] Another striking feature is provided by the location of the tolyl groups at the surface of the compound so that it could be described as a layer of oxide sandwiched between two organic layers.

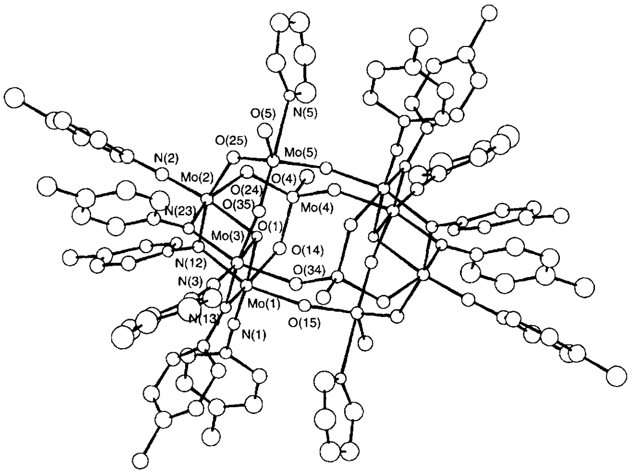

Fig. 1 Molecular drawing of $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}(py)_2O_{18}]$.[11] Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.73(2), Mo(2)–N(2) 1.74(1), Mo(3)–N(3) 1.75(1), Mo(1)–N(12) 2.03(1), Mo(1)–N(13) 1.96(1), Mo(2)–N(12) 1.99(1), Mo(2)–N(23) 1.99(1), Mo(3)–N(13) 2.02(1), Mo(3)–N(23) 2.01(1), Mo(1)–O(1) 2.06(1), Mo(2)–O(1) 2.07(1), Mo(3)–O(1) 2.08(1), Mo(1)–O(14) 2.13(1), Mo(1)–O(15′) 2.04(1), Mo(2)–O(24) 2.10(1), Mo(2)–O(25) 2.06(1), Mo(3)–O(34′) 2.06(1), Mo(3)–O(35) 2.05(1), Mo(4)–O(4) 1.70(1), Mo(4)–O(14) 1.77(1), Mo(4)–O(24) 1.79(1), Mo(4)–O(34) 1.77(1), Mo(5)–O(5) 1.69(1), Mo(5)–O(15) 1.77(1), Mo(5)–O(25) 1.80(1), Mo(5)–O(35) 1.81(1), Mo(5)–N(5) 2.39(2), O(1)–Mo(1)–N(1) 174.4(5), Mo(1)–N(1)–C(11) 174.5(13), O(1)–Mo(2)–N(2) 171.1(6), Mo(2)–N(2)–C(21) 175.1(15), O(1)–Mo(3)–N(3) 171.4(6), Mo(3)–N(3)–C(31) 175.0(15), Mo(1)–N(12)–Mo(2) 105.7(7), Mo(1)–N(13)–Mo(3) 104.6(6), Mo(2)–N(23)–Mo(3) 104.9(6), O(4)–Mo(4)–O(14) 106.4(6), O(4)–Mo(4)–O(24) 108.8(6), O(4)–Mo(4)–O(34) 107.5(6), O(14)–Mo(4)–O(24) 106.4(5), O(14)–Mo(4)–O(34) 115.2(5), O(24)–Mo(4)–O(34) 112.2(6), O(5)—Mo(5)–O(15) 113.9(6), O(5)–Mo(5)–O(25) 113.9(6), O(15)–Mo(5)–O(25) 124.1(5). Primed atoms are generated by the crystallographic inversion centre.

An unexpected feature of the reaction of p-MeC_6H_4NCO with $[NBu^n_4]_3[\alpha\text{-}PMo_{12}O_{40}]$ is the formation of reduced derivatives as evidenced by the isolation of the dark blue compound **5**. Thus it is useful to connect our results with those of Kawafune and Matsubayashi who have reported the reduction of $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$ by PPh_3 in MeCN.[8] According to these authors, this reaction would produce the oxygen-defect reduced $\alpha\text{-}[PMo_{12}O_{39}]^{3-}$ or $\alpha\text{-}[PMo_{12}O_{38}]^{3-}$ anions, depending on the amount of PPh_3, together with Ph_3PO. Actually, we have observed ^{31}P NMR signals at δ −5 or −5.2 in MeCN–$(CD_3)_2CO$ after reduction of $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$ with respectively 1 or 2 equiv. of PPh_3, in close agreement with the literature,[8] when making allowance for the difference in standards.§ However, MeCN solutions of the supposed $[NBu^n_4]_3[\alpha\text{-}PMo_{12}O_{39}]$ appeared to evolve in time as a new signal at δ +1.3 developed. It is noteworthy that the chemical shifts of δ *ca.* −5 and +1.3 are close to the values observed respectively for the 1e- and 2e-reduced $\alpha\text{-}[PMo_{12}O_{40}]^{4-}$ and $\alpha\text{-}[PMo_{12}O_{40}]^{5-}$ anions in Me_2SO–$(CD_3)_2SO$.¶ Moreover, $[NBu^n_4]_4[\alpha\text{-}PMo_{12}O_{40}]$, which we have obtained independently and characterized by X-ray crystallography,† gives also a signal at δ +1.3 in MeCN–$(CD_3)_2CO$. Thus, returning to the ^{31}P NMR spectrum of the green–brown mixture, the signal at δ −2.4 is assigned to unreacted $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$, while that at δ +1.5 can be confidently attributed to the 1e-reduced $\alpha\text{-}[PMo_{12}O_{40}]^{4-}$ anion. In other respects, the signal at δ −2.6 is tentatively assigned to an imido derivative retaining the Keggin structure. Following Kawafune and Matsubayashi it would be tempting to assign the signals at δ −5.2 and −5.5 to oxygen-defect reduced $\alpha\text{-}[PMo_{12}O_{40-x}]^{3-}$ anions. However, Kawafune's views have been recently questioned by Mattes and coworkers,[10] who suggested that the transferred oxygen atoms are immediately replaced by those of water molecules on the basis of the identification of the $\alpha\text{-}[HPMo_{12}O_{40}]^{4-}$ anion after some work-up. Whether the species we have obtained are thus complete or oxygen-defect reduced species remain to be solved.

The reduction of $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$ by p-MeC_6H_4NCO in pyridine brings up the question of the mechanism of the reaction. If the reaction proceeds exclusively *via* net [2 + 2] cycloaddition as is usually assumed,[1] there would be no reason for a reduction to occur. Now, if p-MeC_6H_4NCO is able to abstract an oxygen atom through a non-concerted pathway, then the formation of p-$MeC_6H_4N{=}NC_6H_4Me$-p as well as those of the 1e- and 2e-reduced derivatives of $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$, possibly through the intermediacy of $[PMo_{12}O_{39}]^{3-}$, could be reasonably explained.

We are currently pursuing studies of this very promising system. Further work is planned to characterize the products of the reaction of p-MeC_6H_4NCO with $[NBu^n_4]_3[\alpha\text{-}PMo_{12}O_{40}]$, to substantiate the mechanism of the reaction, and to explore the reactivity of $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}(py)_2O_{18}]$.

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Footnotes

† *Crystal data*: **1**, triclinic, space group $P\bar{1}$, a = 13.269(8), b = 13.62(2), c = 16.527(5) Å, α = 69.71(8), β = 72.97(3), γ = 85.829(2)°, U = 2677 Å^3, Z = 1, D_c = 1.66 g cm^{-3}; structure solution and refinement based on 3253 reflections with $I > 3\sigma(I)$ [λ(Mo-Kα) = 0.71069 Å] converged at a conventional R of 0.051. $[NBu^n_4]_4[\alpha\text{-}PMo_{12}O_{40}]$, tetragonal, space group $I\bar{4}$, a = 18.76(2), c = 14.601(1) Å, U = 5138 Å^3, Z = 2, D_c = 1.81 g cm^{-3}; structure solution and refinement based on 1545 reflections with $I > 3\sigma(I)$ [λ(Mo-Kα) = 0.71069 Å] converged at a conventional R of 0.054.[6] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/208.

‡ Main IR features for $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}(py)_2O_{18}]$ [KBr pellet, ν/cm^{-1})]: 1595w, 1490w, 955w, 845s, 830s, 770s, 690w.

§ All chemical shifts reported here are referenced to external 85% H_3PO_4, in place of 30% H_3PO_4 as in ref. 8.

¶ Controlled potential reduction of $[NBu^n_4]_3[\alpha\text{-}PMo_{12}O_{40}]$ was performed at a platinum electrode in Me_2SO and monitored by coulometry and ^{31}P NMR spectroscopy. Two signals at δ −2.9 and +0.8 were observed for mixtures of $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$ and $\alpha\text{-}[PMo_{12}O_{40}]^{4-}$, which indicates that the rate of the intermolecular electron exchange is slow on the NMR timescale. The signal for $\alpha\text{-}[PMo_{12}O_{40}]^{5-}$ was observed at δ −5.8. The respective deshielding and shielding of the 1e- and 2e-reduced derivatives with respect to $[PMo_{12}O_{40}]^{3-}$ follow the trend observed in the $[PW_{12}O_{40}]^{n-}$ system (n = 3–5).[9]

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