Reduction of the Phosphododecamolybdate Ion by Phosphonium Ylides and Phosphanes

Vincent Artero[a] and Anna Proust*[a]

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The reaction of phosphonium ylides with $[PMo_{12}O_{40}]^{3-}$ consists of successive single electron transfers leading to the formation of the 1e- and 2e-reduced polyoxomolybdates $[PMo_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{5-}$. The ylide is converted into the corresponding phosphonium cation via a radical-cation intermediate. The reaction of phosphanes follows the same pathway but subsequent reactions with residual water produce protons which induce the disproportionation of $[PMo_{12}O_{40}]^{4-}$. Authentic samples of heteropoly blues in different protonation states have been obtained from the reaction of phenyllithium with $[PMo_{12}O_{40}]^{3-}$ and subsequent protonation with triflic acid. On the basis of electrochemical and spectroscopic data, the reaction product of $[PMo_{12}O_{40}]^{3-}$ with triphenylphosphane, which has been previously described as the oxygen-deficient species $[PMo_{12}O_{39}]^{3-}$, is reformulated as $[H_2PMo_{12}O_{40}]^{3-}$.

Introduction

Early transition metals in their highest oxidation states form a large class of oxo−metal cluster anions called polyoxometalates.[1] For the past ten years, our group has been involved in a systematic study of the functionalization of polyoxometalates.[2] One subclass of derivatized polyoxometalates include compounds that derive from parent polyoxometalates through the replacement of terminal oxo ligands by other multiply bonded ligands. The oxo, imido, nitrido and cyclopentadienyl groups are formally six-electron donors. Thus imido,[3] nitrido[4] and cyclopentadienyl[5] derivatives of polyoxometalates are effectively isoelectronic with the parent polyoxometalates. On the other hand, the $[MoO]^{4+}$, $[Mo(NO)]^{3+}$ and $[Mo(NNR)]^{3+}$ groups are isolobal, so that the formation of nitrosyl[6] and diazenido[7] polyoxomolybdates can easily be rationalized. The oxo ligand can also act as a four-electron donor and, as such, is isoelectronic with alkylidene groups. These considerations led us to look for alkylidene derivatives of polyoxometalates. Our aims were threefold: (i) to provide structural and spectroscopic models for metathesis reactions on oxide surfaces; (ii) to identify the reactive species when $[Mo_6O_{19}]^{2-}$ is used as a precatalyst;[8] (iii) to design new metathesis catalysts or precatalysts in a special oxo environment that could be further tuned through size, shape or charge modifications. One strategy for the functionalization of polyoxometalates relies on the analogy between oxometal units and organic functionalities. This has been established by Floriani et al. for oxovanadium groups.[9] The analogy also holds to some extent for oxomolybdenum groups. Indeed, hydrazido[4,7b,10] and imido[3a,11,12] derivatives of polyoxomolybdates have been obtained from the reactions of *N*,*N*-disubstituted hydrazines and iminophosphoranes or isocyanates with polyoxomolybdates. The formation of imido derivatives is reminiscent of the aza Wittig reaction and is thought to proceed by a net [2 + 2] cycloaddition of the P=N and Mo=O bonds.[13] Intermetal exchange of oxo, imido and alkylidene ligands has been shown to occur readily, at least at coordinatively unsaturated metal centres.[14] 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 $[MoO_2(mesityl)_2(CH_2PBu_3)]$.[15] We have investigated the reactions of a number of phosphonium ylides with $(nBu_4N)_3[PMo_{12}O_{40}]$ in acetonitrile and we have found that only 1e- and/or 2e-reduced derivatives of $[PMo_{12}O_{40}]^{3-}$ are formed.

Another route to functionalized polyoxometalates involves lacunary polyoxometalates. This has been widely applied to the rational synthesis of metal-substituted polyoxometalates. On the other hand, polyoxometalates with oxygen vacancies would be potential precursors for the synthesis of ligand-substituted polyoxometalates. The only oxygen-deficient polyoxometalates that have been reported so far are the species $[PMo_{12}O_{40-x}]^{3-}$ ($x = 1$, 2 or 3) which were obtained by Kawafune et al. by reaction of $[PMo_{12}O_{40}]^{3-}$ with PPh_3 in acetonitrile.[16] However, these results have not been confirmed by Mattes et al., who isolated $[HPMo_{12}O_{40}]^{4-}$ from Kawafune's reaction.[17] Furthermore, Bond et al. have recently shown that the similar reaction of the Dawson-type polyanion $[S_2Mo_{18}O_{62}]^{4-}$ yields plenary reduced species.[18] This led us to revisit the reaction of $[PMo_{12}O_{40}]^{3-}$ with phosphanes. We have shown that only plenary reduced anions are formed in these reactions and that the compound formulated as $(nBu_4N)_3[PMo_{12}O_{39}]$ by Kawafune et al. is actually $(nBu_4N)_3[H_2PMo_{12}O_{40}]$. Identification of the reduced species formed in the reactions of $[PMo_{12}O_{40}]^{3-}$ with phosphonium ylides or phosphanes has been based on the comparison with the samples ob-

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[a] Laboratoire de Chimie Inorganique et Matériaux Moléculaires,
unité C.N.R.S. 7071, Université Pierre et Marie Curie,
Case Courrier 42, 4 place Jussieu 75252 Paris Cedex 05, France
Fax: (internat.) + 33-1/44273841
E-mail: proust@ccr.jussieu.fr

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tained by reduction of $[PMo_{12}O_{40}]^{3-}$ by phenyllithium. Thus this report deals with interrelated studies of the reactions of $[PMo_{12}O_{40}]^{3-}$ with phosphonium ylides, phenyllithium and phosphanes.

Results

From here on, the Keggin anions $[PMo_{12}O_{40}]^{3-}$, $[PMo_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{5-}$ will be designated by the numerals **0**, **I** and **II**, respectively, according to their reduction state. Unless otherwise stated, they were isolated as tetrabutylammonium salts. Other cations will be specified when appropriate. Thus, **LiII** refers to $(n\mathrm{Bu}_4N)_4Li[PMo_{12}O_{40}]$ while **H** $\mathbf{H_2II}$ refers to $(n\mathrm{Bu}_4N)_3[H_2PMo_{12}O_{40}]$.

1e- and 2e-Reduced Derivatives of $[PMo_{12}O_{40}]^{3-}$

In nonaqueous solvents, most often MeCN and DMF, 1e- and 2e-reduced derivatives of $[PMo_{12}O_{40}]^{3-}$ have usually been obtained by electrolysis and characterized in situ. Only in a few cases were the reduced derivatives isolated. Phenyllithium proved to be a convenient reagent for the synthesis of **I** and **LiII** from **0** in MeCN. Reduction of **0** by phenyllithium was first recognized when an excess of phenyllithium was inadvertently used in the synthesis of the benzylidene ylide, which was subsequently added to a solution of $(n\mathrm{Bu}_4N)_3[PMo_{12}O_4]$ in MeCN. When the reaction of $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{40}]$ with PhLi in MeCN was monitored by ^{31}P NMR spectroscopy, it was found that **I** is quantitatively formed upon addition of one equivalent of PhLi, while addition of a second equivalent yields **II**. The reduction does not proceed beyond the 2e-reduced state. The 1e- and 2e-reduced derivatives were readily isolated as $(n\mathrm{Bu}_4N)_4[PMo_{12}O_{40}]$ (**I**) and $(n\mathrm{Bu}_4N)_4Li[PMo_{12}O_{40}]$ (**LiII**). Acidification of the solution of **LiII** with triflic acid allowed the isolation of $(n\mathrm{Bu}_4N)_4[HPMo_{12}O_{40}]$ (**HII**) and $(n\mathrm{Bu}_4N)_3[H_2PMo_{12}O_{40}]$ ($\mathbf{H_2II}$). In this way, a full set of spectroscopic data could be obtained for the 1e- and 2e-reduced derivatives of $[PMo_{12}O_{40}]^{3-}$. Indeed, only **0** and **I** had been previously fully characterized by IR,[19] UV/Vis,[20] ^{31}P NMR[3b,21] and (for **I**) by EPR spectroscopy.[20] IR data for **HII** and $\mathbf{H_2II}$, UV/Vis data for **II** and $\mathbf{H_2II}$, and ^{31}P NMR data for **II** and $\mathbf{H_2II}$ have now been obtained and are reported herein. ^{31}P NMR data are gathered in Table 1. The electrochemical behaviour of **HII** and $\mathbf{H_2II}$ in MeCN had been previously studied by Himeno et al.[22] As electrochemical data will be at the centre of the discussion, they were examined further. The results reported in Table 2 are in agreement with those reported by Himeno et al. Solution data for **HII** and $\mathbf{H_2II}$ were measured both for these species formed in situ by acidification of **LiII** and after isolation of $(n\mathrm{Bu}_4N)_4[HPMo_{12}O_{40}]$ and $(n\mathrm{Bu}_4N)_3[H_2PMo_{12}O_{40}]$, respectively. No significant discrepancy was observed.

The ^{31}P NMR chemical shift of **II** steadily moves to higher frequency as the proton content increases. The values characteristic of **II**, **HII** and $\mathbf{H_2II}$ are $\delta = -5.4, -5.2$ and -5.0, respectively, in CH_3CN. **I** undergoes disproportionation upon acidification. Indeed, the ^{31}P NMR spectrum of an equimolecular mixture of **I** and triflic acid displays two signals with equal intensities at $\delta = -2.3$ and -5.0 which can be unambiguously assigned to **0** and $\mathbf{H_2II}$, respectively, indicating the full disproportionation of **I** according to Equation (1).

$$2\,[PMo_{12}O_{40}]^{4-} + 2\,H^+ \rightarrow [PMo_{12}O_{40}]^{3-} + [H_2PMo_{12}O_{40}]^{3-} \quad (1)$$

On the other hand, the ^{31}P NMR spectrum of a solution of **I** with half an equivalent of triflic acid displays three signals at $\delta = +1.4, -2.3$ and -5.2, which are respectively assigned to **I**, **0** and **HII**. Further, the same spectrum is obtained for an equimolar solution of **0** and **HII**. This

Table 1. ^{31}P NMR chemical shift of some relevant species, referenced to external 85% H_3PO_4

	$\delta_{(CH_3CN/CD_3CN)}$ [ppm]	$\delta_{(DMSO/[D_6]DMSO)}$ [ppm]		$\delta_{(CH_6CN/CD_6CN)}$ [ppm]
$[PMo_{12}O_{40}]^{3-}$	−2.3	−2.9	$Bu_3PCH_3^+$	33.5
$[PMo_{12}O_{40}]^{4-}$	1.4 [21]	0.8	Bu_3PO	47.5
$[PMo_{12}O_{40}]^{5-}$	−5.4	−5.8	Bu_3P	−30.8
$[HPMo_{12}O_{40}]^{4-}$	−5.2[a]	–	$Ph_3P{=}CHPh$	9.3
$[H_2PMo_{12}O_{40}]^{3-}$	−5.0	−5.5	$Ph_3PCH_2Ph^+$	24.2
			Ph_3PO	27.5
			Ph_3P	−4.5
			Ph_4P^+	24.4

[a] This value aggrees with that reported by Mattes et al. for $[K(18\text{-crown-6})]_2[N(PPh_3)_2]_2[HPMo_{12}O_{40}]$ when locking the value for **0** at −2.3 ppm.[17]

Table 2. Electrochemical data[22] for $[H_xPMo_{12}O_{40}]^{n-}$ species, 1 mm in MeCN, at a platinum electrode

		$E_{1/2}$ [V/SCE]	$1/2(E_{pa}+E_{pc})$	$E_{1/2}$ [V/SCE]	$1/2(E_{pa}+E_{pc})$
$[PMo_{12}O_{40}]^{4-}$	**I**	0.14 ($1e^-$, ox)[a]	0.18 (rev.)[b]	−0.28 ($1e^-$, red)	−0.24 (rev.)
$\{Li[PMo_{12}O_{40}]\}^{4-}$	**LiII**	0.17 ($1e^-$, ox)	0.22 (rev.)	−0.10 ($1e^-$, ox)	−0.11 (rev.)
$[HPMo_{12}O_{40}]^{4-}$	**HII**	0.56 ($1e^-$, ox)	irrev.	0.2 ($1e^-$, ox)	irrev.
$[H_2PMo_{12}O_{40}]^{3-}$	$\mathbf{H_2II}$	0.56 ($2e^-$, ox)	irrev.	0.1 ($1e^-$, red)	irrev.

[a] ox and red for oxidation and reduction processes, respectively. – [b] rev. and irrev. for reversible and irreversible processes, respectively.

shows that **0**, **I** and **HII** are in equilibrium according to Equation (2).

$$2\,[PMo_{12}O_{40}]^{4-} + H^{+} \leftrightarrows [PMo_{12}O_{40}]^{3-} + [HPMo_{12}O_{40}]^{4-} \qquad (2)$$

It follows therefore that $[HPMo_{12}O_{40}]^{3-}$ cannot be isolated. Whether the more positive oxidation wave of $[HPMo_{12}O_{40}]^{4-}$ at 0.56 V/SCE is due to the 1e-oxidation of **HI**, as assumed by Himeno et al.,[22] or to the 2e-oxidation of **H$_2$II** resulting from the disproportionation of **HI**, remains to be established. Indeed, the R.D.E. voltammogram of an equimolar mixture of **I** and triflic acid is identical to that of an equimolar mixture of **0** and **H$_2$II** at the same overall polyanion concentration.

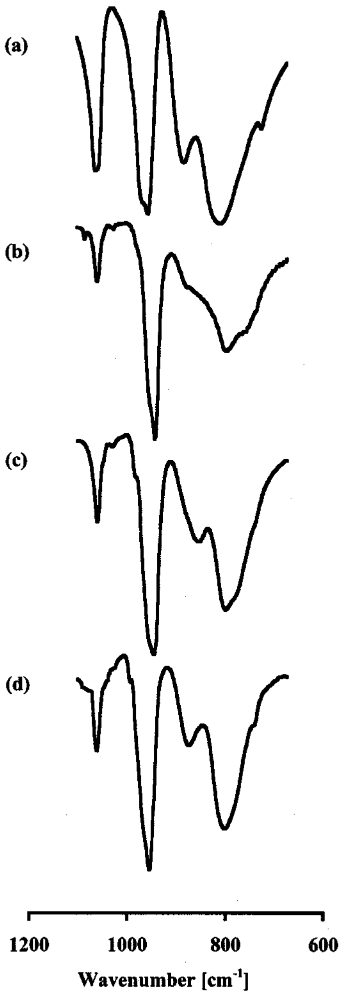

Figure 1. Infrared spectra of $(nBu_4N)_3[PMo_{12}O_{40}]$ (**0**, a), $Li(nBu_4N)_4[PMo_{12}O_{40}]$ (**LiII**, b), $(nBu_4N)_4[HPMo_{12}O_{40}]$ (**HII**, c) and $(nBu_4N)_3[H_2PMo_{12}O_{40}]$ (**H$_2$II**, d)

The IR spectra of **0**, **LiII**, **HII**, and **H$_2$II** (Figure 1 and Table 3) all display the characteristic pattern of α-Keggin anions, with four bands arising from the P−O, Mo=O$_t$, and Mo−O−Mo stretching vibrations.[23] The progressive decrease in both the intensity and the energy of the P−O and Mo−O−Mo bands upon reduction has been fully discussed in the literature.[17,19] The energy of the Mo=O$_t$ stretching mode also decreases upon reduction. However, the corresponding band shifts to higher frequencies upon protonation so that the values are fortuitously the same for **0** and **H$_2$II**.

Reactions of Phosphonium Ylides with $[PMo_{12}O_{40}]^{3-}$

Various phosphonium ylides $R_3P{=}CR^1R^2$ (R = Bu, $R^1 = R^2 =$ H; R = Ph, R^1 = H, R^2 = Ph, C(O)Me, C(O)N(Me)OMe; R = Ph, $R^1R^2 = (CH_2)_4$; R = Ph, R^1 = Me, R^2 = CHO) were used. In each case, the addition of a phosphonium ylide to a solution of $(nBu_4N)_3[PMo_{12}O_{40}]$ in MeCN results in the formation of reduced species as evidenced by the strong blue colour of the resulting solutions. However, the reaction proceeds most cleanly with $Bu_3P{=}CH_2$. Immediately after the addition of one equivalent of $Bu_3P{=}CH_2$ to a solution of $(nBu_4N)_3[PMo_{12}O_{40}]$ in CH_3CN, the ^{31}P NMR spectrum displays two signals, assigned to **I** and to the phosphonium cation $Bu_3PCH_3^+$, respectively (Figure 2). Subsequent addition of a second

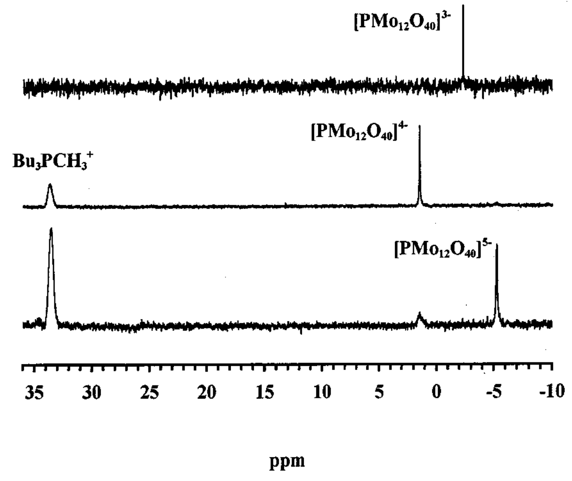

Figure 2. ^{31}P NMR spectra (referenced to external 85% H_3PO_4) in acetonitrile: $(nBu_4N)_3[PMo_{12}O_{40}]$ (top); $(nBu_4N)_3[PMo_{12}O_{40}]$ + 1 equiv. $Bu_3P{=}CH_2$ (center); $(nBu_4N)_3[PMo_{12}O_{40}]$ + 2 equiv. $Bu_3P{=}CH_2$ (bottom)

Table 3. Spectroscopic data for $[H_xPMo_{12}O_{40}]^{n-}$ species

Anion		Electronic λ_{max} (solvent) [nm]	Infrared [cm^{-1}] $10^{-3}\varepsilon$ [mol^{-1}·L·cm^{-1}]	ν(PO)	ν(Mo=O)	ν(MoOMo)
$[PMo_{12}O_{40}]^{3-}$ [23]	**0**	–	–	1063	965sh, 956	880, 807
$[PMo_{12}O_{40}]^{4-}$ [19][20]	**I**	800 (DMF)	1.3	1058	952, 942	858, 794
$[LiPMo_{12}O_{40}]^{4-}$	**LiI**	715 (CH_3CN)	3.4	1058	950 sh, 941	860, 794
$[HPMo_{12}O_{40}]^{4-}$ [17]	**HII**	724 (CH_3CN)	3.9	1059	952 sh, 942	852, 800
$[H_2PMo_{12}O_{40}]^{3-}$	**H$_2$II**	740 (CH_3CN)	4.5	1061	955	872, 800

equivalent of $Bu_3P{=}CH_2$ leads to the reduction of **I** to **II** with formation of another equivalent of phosphonium cation. The reduction products were further identified as **I** and **II** by R.D.E. measurements. According to ^{31}P NMR and electrochemical analyses, the reactions are quantitative. When $(Ph_4P)_3[PMo_{12}O_{40}]$ was used instead of $(nBu_4N)_3[PMo_{12}O_{40}]$, precipitation of $(Ph_4P)_4[PMo_{12}O_{40}]$ occurred after addition of one equivalent of ylide.

A similar pattern was observed for the reaction of $Ph_3P{=}CHPh$ with $(nBu_4N)_3[PMo_{12}O_{40}]$, with the exception of the initial formation of a green precipitate, which proved to be a mixture of oxidized and reduced phosphodecamolybdates containing lithium, tetrabutylammonium and phosphonium cations. This was followed by the precipitation of $(nBu_4N)_4[PMo_{12}O_{40}]$ which could be recrystallized from DMSO.

Reactions of Phosphanes with $[PMo_{12}O_{40}]^{3-}$

Phosphanes react with $(nBu_4N)_3[PMo_{12}O_{40}]$ in MeCN to yield reduced species, as indicated by the blue colour of the resulting solutions. In a typical experiment, a solution of $(nBu_4N)_3[PMo_{12}O_{40}]$ (510 mg, 0.200 mmol) and PPh_3 (52.5 mg, 0.200 mmol) in distilled MeCN (20 mL) was heated to reflux and samples were periodically analysed by ^{31}P NMR spectroscopy, which showed a progressive decrease in the signals of PPh_3 and $[PMo_{12}O_{40}]^{3-}$at $\delta = -4.5$ and -2.3, respectively, and a concomitant increase in two new signals, one at $\delta = 27.5$, which is unambiguously assigned to Ph_3PO, the second at $\delta = -5.0$, which is consistent with $[H_2PMo_{12}O_{40}]^{3-}$. These observations are in agreement with those reported by Kawafune et al.[16] However, contrary to these authors, we found that the complete disappearance of $[PMo_{12}O_{40}]^{3-}$ in distilled acetonitrile required more than one equivalent of PPh_3. A pure product with analytical and spectroscopic features identical to those reported by Kawafune et al. for $(nBu_4N)_3[PMo_{12}O_{39}]$, was then isolated after heating a solution of $(nBu_4N)_3[PMo_{12}O_{40}]$ and a 10-fold excess of PPh_3 at reflux for 17 h (see Experimental Section). It was subsequently found that only one equivalent of phosphane is needed if the reaction is carried out in the presence of a sufficient amount of water. Analytical, spectroscopic and electrochemical data for the compounds obtained either in distilled acetonitrile, but in the presence of an excess of PPh_3, or in wet acetonitrile are identical to those of **H$_2$II** as well as to the analytical and spectroscopic data reported by Kawafune for $(nBu_4N)_3[PMo_{12}O_{39}]$. The latter has thus to be reformulated as $(nBu_4N)_3[H_2PMo_{12}O_{40}]$ and the reaction could be thought to proceed according to Equation (3).[24,25]

$$[PMo_{12}O_{40}]^{3-} + PPh_3 + H_2O \rightarrow [H_2PMo_{12}O_{40}]^{3-} + Ph_3PO \quad (3)$$

The reaction of tributylphosphane with $[PMo_{12}O_{40}]^{3-}$ is much faster than that of PPh_3 and proceeds according to a different stoichiometry. The reaction was monitored by ^{31}P NMR spectroscopy (Figure 3). For molar ratios less than 0.5 phosphane per polyanion, three signals are observed, which are unambiguously assigned to $[PMo_{12}O_{40}]^{3-}$ (**0**), $[H_2PMo_{12}O_{40}]^{3-}$ (**H$_2$II**) and Bu_3PO. For ratios from 0.5 to ca. 1.0, five signals are observed: The first three are unambiguously assigned to **0**, **I** and Bu_3PO; the fourth, which shifts from $\delta = -5.0$ to $\delta = -5.2$ as the ratio increases, is tentatively assigned to a mixture of **HII** and **H$_2$II**; the fifth, which appears as a broad doublet ($\delta = 14-35$, $J_{PH} = 400$ Hz), is assigned to Bu_3PH^+. Its chemical shift varies widely, which might be indicative of proton exchange with other species such as reduced polyoxometalates. Complete disappearance of **0** is observed for ratios in the range 1 to 1.1. Control experiments have shown that the reduction of **I** by PBu_3 is quite slow at room temperature.

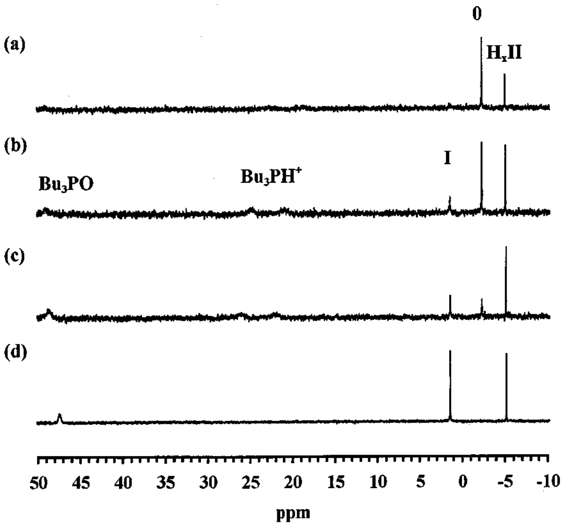

Figure 3. ^{31}P NMR spectra (referenced to external 85% H_3PO_4) in acetonitrile: (a) $(nBu_4N)_3[PMo_{12}O_{40}]$ + 0.5 equiv. PBu_3; (b) $(nBu_4N)_3[PMo_{12}O_{40}]$ + 0.75 equiv. PBu_3; (c) $(nBu_4N)_3[PMo_{12}O_{40}]$ + 1 equiv. PBu_3; (d) $(nBu_4N)_3[PMo_{12}O_{40}]$ + 2 equiv. PBu_3

Discussion

Reactions of Phosphonium Ylides with $[PMo_{12}O_{40}]^{3-}$

The addition of a phosphonium ylide to a solution of $(nBu_4N)_3[PMo_{12}O_{40}]$ in MeCN only results in the formation of reduced species **I** and **II**, whatever ylide is used. We could not obtain any evidence for the formation of an alkylidene derivative of $[PMo_{12}O_{40}]^{3-}$. The more reducing the ylide is, the cleaner the reaction. The reactions of Bu_3PCH_2 with **0** and **I** are fast. Both the reduction of **0** in **I** and that of **I** in **II** involve one equivalent of ylide and yield one equivalent of the parent phosphonium ion. The stoichiometry of the reactions is consistent with Equations (4) and (5).

$$[PMo_{12}O_{40}]^{3-} + R_3P{=}CR^1R^2 \rightarrow [PMo_{12}O_{40}]^{4-} + [R_3P{=}CR^1R^2]^{\bullet +} \quad (4)$$

$$[PMo_{12}O_{40}]^{4-} + R_3P{=}CR^1R^2 \rightarrow [PMo_{12}O_{40}]^{5-} + [R_3P{=}CR^1R^2]^{\bullet +} \quad (5)$$

The formation of ylide-derived radical-cations is known. Indeed, $[Ph_3P{=}CPh_2]^{\bullet +}$ has been obtained and characterized by electrochemical oxidation of $Ph_3P{=}CPh_2$ in MeCN in the probe of an EPR spectrometer.[26] However, direct evidence for the formation of $[R_3P{=}CR^1R^2]^{\bullet+}$ could not be obtained. Indirect evidence for the formation of a radical is nevertheless provided by the formation of diphenyl disulfide when the reaction was carried out in the presence of thiophenol. Diphenyl disulfide was isolated by extraction with ether and characterized by TLC and IR spectroscopy. Control experiments showed that thiophenol is not oxidized by **0** on the reaction timescale.

The formation of the parent phosphonium ion $[R_3PCHR^1R^2]^+$ by reaction of the ylide with solvent can be excluded since $Ph_3P{=}CHPh$ proved to be stable in the absence of $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{40}]$. Indeed, complete "spontaneous" transformation of $Ph_3P{=}CHPh$ into $[Ph_3PCH_2Ph]^+$ requires more than 12 h in MeCN at room temperature. The formation of phosphonium ions in the reactions of various ylides with dioxomolybdenum complexes in CH_2Cl_2 has been observed by Lai et al. and ascribed to transylidation between residual ylide and an oxometallabetaine initially formed.[15] However, such a pathway could not account for the complete transformation of the ylide into the parent phosphonium ion. We have reinvestigated the reactions of various ylides with $[MoO_2(dedtc)_2]$ (dedtc = diethyl dithiocarbamate) in MeCN and we have found that addition of the ylide is followed by the precipation of the purple compound $[Mo_2O_3(dedtc)_4]$. The formation of this complex most probably accounts for the violet colour observed by Lai et al. in their experiments and suggests that a redox pathway also occurs in the reaction of ylides with dioxomolybdenum complexes.

The actual source (XH) of the hydrogen atom in the formation of the phosphonium ion from the ylide-derived radical cation (Equation 6) has not been definitively established.

$$[R_3P{=}CR^1R^2]^{\bullet+} + XH \rightarrow [R_3P{-}CHR^1R^2]^+ + X^\bullet \quad (6)$$

It is unlikely that either the ylide or the tetrabutylammonium ion acts as XH. Indeed the ylide is quantitatively transformed into the parent phosphonium ion and the course of the reaction is not altered upon the replacement of tetrabutylammonium by tetraphenylphosphonium, which does not act as an hydrogen donor. Thus XH is most likely MeCN or residual H_2O.

Reactions of Phosphanes with $[PMo_{12}O_{40}]^{3-}$

Reactions of phosphanes with oxomolybdenum complexes have been largely investigated in relation to modelling studies of molybdenum oxotransferases.[27] Oxo transfer reaction from $[MoO_2L_n]$ to PR_3 is initiated by nucleophilic attack on an $Mo^{VI}{=}O$ unit and the formation of a (μ-oxo)Mo^V dimer $[Mo_2O_3L_{2n}]$ often competes with that of the Mo^{IV} complex $[MoOL_n]$. Kawafune et al. were the first to extend such reactions to polyoxoanions by investigating the reaction of PPh_3 with $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{40}]$ in MeCN.[16] They claimed to have obtained the oxygen-deficient reduced species $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{40-x}]$ (x = 1, 2 or 3) by successive oxo transfer reactions. Although it is commonly accepted that oxygen-deficient species are formed in the course of heterogeneous catalytic oxidations with polyoxometalates,[28] the formation of such species in solution may be questioned. The reaction has been revisited by Mattes et al. who isolated **HII** by reaction of PPh_3 with $[K(18\text{-crown-}6)][N(PPh_3)_2]_2[PMo_{12}O_{40}]$ and subsequent workup.[17] It should also be noted at this point that the UV/Vis and ^{31}P NMR spectra of $[HPMo_{12}O_{40}]^{4-}$ are not in agreement with those reported by Kawafune et al. for the so-called $[PMo_{12}O_{39}]^{3-}$ species. Mattes et al. assumed that $[PMo_{12}O_{39}]^{3-}$, once formed, reacts with residual water. Indeed we found the reaction of PPh_3 with $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{40}]$ to be dependent on the residual amount of water in the solvent. The reaction did not go to completion when distilled acetonitrile was used, probably due to kinetically competitive phosphane-consuming side-reactions. Only in the presence of a sufficient amount of water did the reaction go to completion with one equivalent of PPh_3. The product obtained in this way displays all the features reported by Kawafune et al. for $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{39}]$ and will be referred to as Kawafune's compound. Analytical data reasonably conform to the formula $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{39}]$, but would equally be consistent with either $(n\mathrm{Bu}_4N)_3[HPMo_{12}O_{40}]$ or $(n\mathrm{Bu}_4N)_3$-$[H_2PMo_{12}O_{40}]$. IR features are clearly indicative of a reduced Keggin anion by the reduced intensity of P−O and Mo−O−Mo stretching bands. Moreover, the $Mo{-}O_t$ stretching band is almost unaltered with respect to $[PMo_{12}O_{40}]^{3-}$, which suggests that both compounds have the same charge. Again, this would be consistent with any of the three formulas above. In any case, the formation of $[PMo_{12}O_{40}]^{5-}$ (**II**) can be ruled out since this species could not coexist with $[PMo_{12}O_{40}]^{3-}$ in solution. The hypothesis of a 1e-reduced product may also be ruled out since the observed ^{31}P signal is shielded with respect to that of $[PMo_{12}O_{40}]^{3-}$. Neither does the product correspond to $[HPMo_{12}O_{40}]^{4-}$ (**HII**) as described by Mattes et al. Definitive evidence for the true nature of the product is provided by electrochemistry which shows that the behaviour of the product is identical to that of $(n\mathrm{Bu}_4N)_3[H_2PMo_{12}O_{40}]$ (**H₂II**). Indeed the R.D.E. voltammogram (Figure 4) displays a 2e-oxidation wave at +0.56 V/SCE and becomes indistinguishable from those of $[HPMo_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{5-}$ upon addition of one and two equivalents of tetrabutylammonium hydroxide, respectively. Finally, electrochemical, ^{31}P NMR, IR and UV/Vis data are identical to those of $(n\mathrm{Bu}_4N)_3[H_2PMo_{12}O_{40}]$. Thus, Kawafune's compound, which was postulated to be $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{39}]$, is actually $(n\mathrm{Bu}_4N)_3[H_2PMo_{12}O_{40}]$.

While only **H₂II** was obtained by reaction of PPh_3 with $(n\mathrm{Bu}_4N)_3[PMo_{12}O_{40}]$, **I**, **HII** and **H₂II** have been characterized from the products of the reaction with PBu_3, depending on the amount of phosphane. This can be explained on the basis of the mechanism postulated by Bond et al. for the reduction of $[S_2Mo_{18}O_{62}]^{4-}$ by phosphanes [Equation (7) to Equation (9)].[18]

$$[PMo_{12}O_{40}]^{3-} + R_3P \rightarrow [PMo_{12}O_{40}]^{4-} + R_3P^{\bullet+} \quad (7)$$

$$R_3P^{\bullet+} + H_2O \rightarrow R_3POH^\bullet + H^+ \quad (8)$$

$$[PMo_{12}O_{40}]^{3-} + R_3POH^\bullet \rightarrow [PMo_{12}O_{40}]^{4-} + R_3PO + H^+ \quad (9)$$

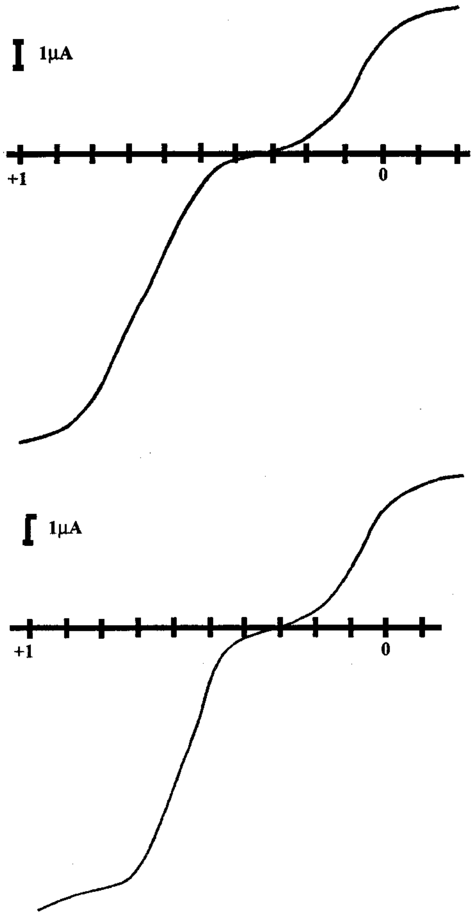

Figure 4. R.D.E. voltammogram of the reaction product of PPh_3 with $(nBu_4N)_3[PMo_{12}O_{40}]$ (top) and $(nBu_4N)_3[H_2PMo_{12}O_{40}]$ (bottom), both 1 mM in MeCN, *E* in Volt vs. SCE at a platinum electrode

The net reaction can then be written as Equation (10).

$$2\,[PMo_{12}O_{40}]^{3-} + R_3P + H_2O \rightarrow 2\,[PMo_{12}O_{40}]^{4-} + R_3PO + 2\,H^+ \qquad (10)$$

As **I** disproportionates in the presence of protons, the final products will depend upon the relative basicities of the different species. When a strong base such as triethylamine is added to the reaction mixture, the reaction stops after addition of half an equivalent of PBu_3 and the ^{31}P NMR spectrum only displays the signal of **I**, in agreement with Equation (11).

$$2\,[PMo_{12}O_{40}]^{3-} + PBu_3 + H_2O + 2\,Et_3N \rightarrow 2\,[PMo_{12}O_{40}]^{4-} + Bu_3PO + 2\,Et_3NH^+ \qquad (11)$$

In the absence of any additional base, the products depend on the basicity of the phosphane. PPh_3 is a weak base so that **I** undergoes disproportionation according to Equation (1), and the overall reaction reduces to Equation (3). On the other hand, PBu_3 is more basic than PPh_3 and competes with **I** for protonation. For low phosphane-to-polyanion ratios, $\mathbf{H_2II}$ is the only product observed while a mixture of **I**, $\mathbf{H_2II}$ and/or **HII** is found for higher ratios.

While this mechanism is consistent with the experimental results, the following alternative mechanism [Equation (12) to Equation (15)] might equally account for the stoichiometry of the reaction of $(nBu_4N)_3[PMo_{12}O_{40}]$ with PBu_3 in the presence of NEt_3.

$$[PMo_{12}O_{40}]^{3-} + R_3P \rightarrow [PMo_{12}O_{39}]^{3-} + R_3PO \qquad (12)$$

$$[PMo_{12}O_{39}]^{3-} + H_2O \rightarrow [H_2PMo_{12}O_{40}]^{3-} \qquad (13)$$

$$[H_2PMo_{12}O_{40}]^{3-} + 2\,NEt_3 \rightarrow [PMo_{12}O_{40}]^{5-} + 2\,Et_3NH^+ \qquad (14)$$

$$[PMo_{12}O_{40}]^{3-} + [PMo_{12}O_{40}]^{5-} \rightarrow 2\,[PMo_{12}O_{40}]^{4-} \qquad (15)$$

As no evidence could be obtained for either $R_3P^{\bullet+}$ or $[PMo_{12}O_{39}]^{3-}$, it is not possible to discriminate between these two mechanisms.

Concluding Remarks

Phenyllithium and phosphonium ylides act as 1e-reducing reagents towards $[PMo_{12}O_{40}]^{3-}$. The former is a convenient reagent for the millimolar-scale preparation of **I**, **LiII**, **HII** and $\mathbf{H_2II}$, which have been fully characterized. To the best of our knowledge, the only previous mention of the reduction of polyoxometalates by organometallic reagents is the report by McCann et al. of the catalytic norbornene ROMP by a single crystal of $(nBu_4N)_2[Mo_6O_{19}]$, in the presence of $EtAlCl_2$.[8] On the other hand, phosphanes act as 2e-reducing reagents, although it could not be established whether the reactions proceed through oxo transfer or via phosphane-based radical intermediates. Whatever the actual mechanism, the so-called oxygen-deficient compound $(nBu_4N)_3[PMo_{12}O_{39}]$ previously reported by Kawafune is actually $(nBu_4N)_3[H_2PMo_{12}O_{40}]$.

Experimental Section

Reagents and Solvents: Reactions were routinely carried out under inert atmospheres unless otherwise stated. Solvents were dried and freed of oxygen using standard procedures. $(nBu_4N)_3[PMo_{12}O_{40}]\cdot xH_2O$ was prepared as previously described[2,3] and further dried overnight at 80 °C under vacuum; $(Ph_4P)_3[PMo_{12}O_{40}]$ was obtained by a similar procedure, using Ph_4PBr instead of nBu_4NBr. Other chemicals were used as supplied.

Methods and Instrumentation: Infrared spectra were recorded from KBr pellets with a Bio-Rad FT 165 spectrophotometer and electronic absorption spectra on Shimadzu UV-2101 spectrophotometer. − Elemental analyses were performed at the Service Central d'Analyse of the CNRS (Vernaison, France). − ^{31}P NMR spectra (121.5 MHz, external 85% H_3PO_4) were recorded on CH_3CN/CD_3CN or DMSO/[D$_6$]DMSO solutions (0.3 mL − 0.1 mL) with a Bruker AC300 spectrometer equipped with a QNP probehead. − All electrochemical measurements were carried in 0.1 M $(nBu_4N)BF_4$ CH_3CN solutions under nitrogen at room temperature using a standard three-electrode cell [platinum rotating disk working electrode, auxiliary platinum wire and aqueous KCl saturated double junction calomel electrode (SCE)]. Rotating disk electrode voltammograms were recorded with a Tacussel PRG3 device at the rate of 5 $mV\cdot s^{-1}$. Cyclic voltammograms were recorded with a PAR 273A instrument at the rate of 100 $mV\cdot s^{-1}$.

Ylide Syntheses: Tributyl(methylene)phosphorane $Bu_3P{=}CH_2$ was prepared from tributyl(methyl)phosphonium iodide and butyllithium and distilled under vacuum.[29] − A slurry of benzyltriphenylphosphonium bromide (433 mg, 1.00 mmol) in CH_3CN (10 mL) was cooled in an ice bath. Phenyllithium solution (1 equiv.) was then added via syringe. The reaction mixture quickly turned orange and was filtered via canula after stirring for 15 min at 0 °C. The solution of benzylidenetriphenylphosphorane was then directly used in the reaction on $[PMo_{12}O_{40}]^{3-}$.

Reduced Phosphododecamolybdates. − $(n\mathbf{Bu_4N})_4[\mathbf{PMo_{12}O_{40}}]$: Phenyllithium (1.00 mmol) was added slowly to a solution of $(nBu_4N)_3[PMo_{12}O_{40}]$ (2.55 g, 1.00 mmol) in acetonitrile (90 mL). The blue solution was filtered when necessary and $(nBu_4N)BF_4$ (320 mg, 1.00 mmol) was added. Cooling to −40 °C afforded a blue-green precipitate coated with a brown oil and was isolated by filtration. Pure $(nBu_4N)_4[PMo_{12}O_{40}]$ was obtained by washing the blue-green powder with tetrahydrofuran and methanol until the filtrate was colourless. Further crops of the product can be isolated by successive additions of $(nBu_4N)BF_4$ (320 mg, 1.00 mmol) followed by cooling, filtration and washing. The powder can be handled in air and its solutions in MeCN, DMF or DMSO are stable towards oxidation. Yield: 2.1 g (75%). − $C_{64}H_{144}N_4PMo_{12}O_{40}$ (2792.0824): calcd. C 27.53, H 5.2, Mo 41.23, N 2.01, P 1.11; found C 27.57, H 5.23, Mo 40.86, N 2.05, P 1.19. − Recrystallization in DMSO led to dark-blue crystals of $(nBu_4N)_4[PMo_{12}O_{40}]$: tetragonal, $a = b = 18.72(2)$ Å, $c = 14.548(3)$ Å, $V = 5094(2)$ Å^3.[3b]

$\mathbf{Li}(n\mathbf{Bu_4N})_4[\mathbf{PMo_{12}O_{40}}]$: The same procedure with two equivalents of phenyllithium afforded pure $Li(nBu_4N)_4[PMo_{12}O_{40}]$. Yield: 2.3 g (82%). − $C_{64}H_{144}LiMo_{12}N_4O_{40}P$ (2799.0234): calcd. C 27.46, H 5.19, Li 0.25, N 2, P 1.11; found C 27.46, H 5.40, Li 0.21, N 2.22, P 1.14.

$(n\mathbf{Bu_4N})_4[\mathbf{HPMo_{12}O_{40}}]$: A solution of triflic acid in acetonitrile (1.00 mL, 200 mM) was slowly added to a solution of $Li(nBu_4N)_4[PMo_{12}O_{40}]$ (560 mg, 0.200 mmol) in acetonitrile (10 mL). Subsequent addition of $(nBu_4N)BF_4$ (320 mg, 1.00 mmol) and cooling to −40 °C afforded a blue precipitate of $(nBu_4N)_4[HPMo_{12}O_{40}]$, which was washed with THF and dried in vacuum. Yield: 0.42 g (0.15 mmol, 75%). − $C_{64}H_{145}Mo_{12}N_4O_{40}P$ (2793.0903): calcd. C 27.52, H 5.23, Mo 41.22, N 2.01, P 1.11; found C 27.36, H 5.21, Mo 40.20, N 2.07, P 1.22.

$(n\mathbf{Bu_4N})_3[\mathbf{H_2PMo_{12}O_{40}}]$: The same procedure using 2.00 mL of the 200 mM solution of triflic acid in acetonitrile afforded $(nBu_4N)_3[H_2PMo_{12}O_{40}]$. Yield: 0.29 mg (57%). − $C_{48}H_{110}Mo_{12}N_3O_{40}P$ (2551.6311): calcd. C 22.59, H 4.35, N 1.65, P 1.21; found C 22.92, H 4.83, N 1.76, P 1.30.

Typical Experiment for the Reaction of $(n\mathbf{Bu_4N})_3[\mathbf{PMo_{12}O_{40}}]$ with Phosphonium Ylide or Tributylphosphane: In a typical experiment, $(nBu_4N)_3[PMo_{12}O_{40}]$ (510 mg, 0.200 mmol) was dissolved in acetonitrile (20 mL) or DMSO (5 mL) and the desired amount of reagent was added via syringe or transferred via canula (benzylidenetriphenylphosphorane solution). The reaction mixture was stirred for 10 min at room temperature. A sample (0.3 mL) was then placed in an NMR tube, purged with argon, and CD_3CN (0.1 mL) was added.

$(\mathbf{Ph_4P})_4[\mathbf{PMo_{12}O_{40}}]$: To a solution of $(Ph_4P)_3[PMo_{12}O_{40}]$ (1.0 g, 0.35 mmol) in acetonitrile (100 mL) was added a slight excess of Bu_3PCH_2 (85 mg, 0.40 mmol) via syringe. The solution turned dark green and a blue precipitate formed immediately. Yield: 0.6 g. Recrystallization in DMF led to dark-blue crystals of composition $(Ph_4P)_4[PMo_{12}O_{40}]\cdot 2DMF$: triclinic, $a = 13.973(2)$ Å, $b = 14.378(4)$ Å, $c = 15.193(2)$ Å, $\alpha = 71.17(2)°$, $\beta = 77.97(1)°$, $\gamma = 79.40(2)°$, $V = 2803$ (1) Å^3. − $C_{102}H_{94}Mo_{12}N_2O_{42}P_5$ (3325.9860): calcd. C 36.83, H 2.85, Mo 34.61, N 0.84, P 4.66; found C 37.16, H 2.8, Mo 33.85, N 0.98, P 4.59.

Reaction of $(n\mathbf{Bu_4N})_3[\mathbf{PMo_{12}O_{40}}]$ with Triphenylphosphane: $(nBu_4N)_3[PMo_{12}O_{40}]$ (510 mg, 0.200 mmol) and PPh_3 (525 mg, 2.00 mmol) were heated at reflux in acetonitrile (20 mL) for 17 h. The solvent was then evaporated in vacuum and the blue residue washed with ethyl ether and THF until the filtrate was colourless. Yield: 0.40 g (78%). − $C_{48}H_{110}Mo_{12}N_3O_{40}P$ (2551.6311): calcd. C 22.59, H 4.35, Mo 45.12, N 1.65, P 1.21; found C 23.39, H 4.37, Mo 46.45, N 1.64, P 1.26. − ^{31}P NMR (CD_3CN): $\delta = -5.0$. − IR (cm^{-1}): $\tilde{\nu} = 1062$ (m), 955(s), 880(m), 807(s). − UV/Vis (CH_3CN): $\lambda_{max} = 740$ nm ($\varepsilon = 5.4\ 10^3$ mol$^{-1}\cdot$L$\cdot$cm^{-1}).

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