Hybrid Cyclic Dimers of Divacant Heteropolyanions: Synthesis, Mass Spectrometry (MALDI-TOF and ESI-MS) and NMR Multinuclear Characterisation

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In the field of organic-inorganic hybrid composites, functionalized polyoxometalates constitute a special class of inorganic nanobuilding blocks (NBBs). This study represents a first approach related to the formation of new oligomeric hybrid species based on the reaction of bis(electrophilic) groups with a divacant heteropolyanion as the NBB. Bis(phosphonates) such as *para*-$H_2O_3PCH_2(C_6H_4)_nCH_2PO_3H_2$ (n = 1 or 2) have been treated with the divacant heteropolyanion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ to form the hybrid cyclic dimer $[H_2\{(SiW_{10}O_{36})(O{=}PCH_2(C_6H_4)_nCH_2P{=}O)\}_2]^{6-}$. MALDI-TOF and ESI mass spectrometry have been used as essential analytical techniques for the characterization of such composite systems.

Introduction

"Hybrid organic-inorganic" is an old concept but still represents a current challenge because it allows combination of the specific properties of organic and inorganic components in a unique system.[1] This concept has experienced a notable expansion, especially since soft inorganic chemistry processes have been applied to new inorganic nanobuilding blocks (NBBs) such as oligosilsesquioxane derivatives,[2] organotin−oxo clusters,[3] transition metal−oxo clusters,[4] functionalized polyoxometalates and functionalized nanoparticles.[5] These NBBs have been chosen to cover a large domain of sizes and structures. The degree of organization and properties that can be obtained for such composites closely depends on the synergy between and the chemical nature of the organic and inorganic moieties. Thus, these hybrids can be categorized into two main classes depending on the nature of the interface and interactions shared by both components.[6] Class I corresponds to systems where no covalent or iono-covalent bonds exist between the inorganic and organic moieties, and class II refers to systems linked through strong chemical bonds (covalent bonds). For both classes, the chemical strategy depends largely on the functionalization of the NBBs.

Among these inorganic NBBs, polyoxometalates (POMs) based on Mo or W constitute a special class. In fact, these metallic oxo clusters play a great role in important areas such as catalysis, electro- and photochromism, magnetism, and medicine. Recently, the development of ordered assemblies of POMs within hybrid organic-inorganic materials has undergone considerable expansion, due to a large variety of electronic, magnetic, redox and photonic properties.[7] The main hybrid materials described in the literature belong to class I, being of anionic character and most of them are derived from Keggin heteropolyanions.[8] On the other hand, the materials of class II have appeared only very recently.[9] Indeed, their synthesis requires a prior covalent functionalization. Three different methods can be used to functionalize POM blocks. The first one proceeds by surface activation of POMs, resulting in the localization of the charge density at the oxygen atoms on the surface which permits covalent bonding with organometallic fragments.[10] In the second method, (organoimido)polyoxometalates[11] are used while the last one is based on multivacant polyoxotungstates showing an increased anionic charge density at the oxygen atoms on the lacunary surface. The highly nucleophilic character of the oxygen atoms permits

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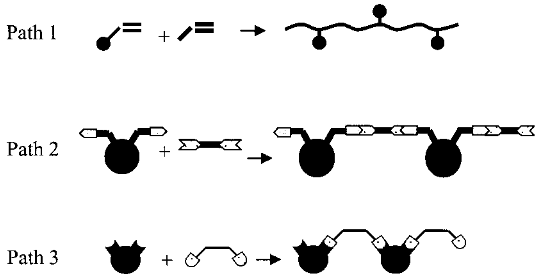
the covalent binding of electrophilic groups such as organotin groups[12] or organophosphorus groups.[13] A few hybrid materials have recently been described in class II by Maatta and co-workers who have reported (organoimido)-POMs as polystyrene pendants by co-polymerization of the monofunctional $[Mo_6O_{18}(NC_6H_4CH{=}CH_2)]^{2-}$ with a styrene monomer.[14] Mayer et al. have described the covalent entrapment in an organic matrix of $[\gamma\text{-}SiW_{10}O_{36}(OSi{-}\text{propyl methacrylate})_4]^{4-}$ by radical co-polymerization resulting in the formation of a hybrid gel.[15]

This work is focused on the formation of a new cyclic hybrid POM by reaction of the divacant heteropolyanion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with two bis(phosphonate) groups, *para*-$H_2O_3PCH_2(C_6H_4)_nCH_2PO_3H_2$, where $n = 1, 2$. These systems have been characterized by a combination of multinuclear NMR spectroscopy (^{183}W, ^{29}Si and ^{31}P) and mass spectrometry (MALDI-TOF and ESI-MS).

Results and Discussion

Linear or cyclic hybrid polymers can be obtained in three main ways as shown in Scheme 1. The first path is the most commonly used and corresponds to the radical co-polymerization of monofunctional inorganic NBBs with an organic monomer. The second way concerns the polycondensation of bifunctional inorganic NBBs with a bifunctional organic precursor. A third possibility could be to treat an inorganic NBB containing two nucleophilic sites with a bis(electrophilic) group.



Scheme 1. Schematic structure of polymer hybrids: Path 1: radical co-polymerization of monofunctional inorganic NBBs with an organic monomer; Path 2: polycondensation of bifunctional inorganic NBBs with a bifunctional organic precursor; Path 3: reaction of an inorganic NBB containing two nucleophilic sites with a bis-electrophilic group

We have focused our attention on the last method, starting from the divacant heteropolyanion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ and two types of bis(phosphonates). The choice of divacant POM was motivated by the ability of the four oxygen atoms of the vacancy to react with electrophilic phosphonate groups. This reaction was expected to lead to only one bifunctionalized POM.[16] Moreover, in recent works, this POM has been shown to be a good inorganic NBB precursor.[17,18] The choice of two bis(phosphonate) precursors, *para*-xylylenebis(phosphonate) (**LI**) and the homologue with a supplementary aromatic group (**LII**), was selected in order to check the influence of their organic chain lengths and to prevent the attachment of the two ending $\{-PO_3\}$ groups to the same POM. The synthesis of these bis(phosphonates) proceeds through an Arbuzov reaction, the two terminal halide ligands are first transformed into $\{-PO_3Et_2\}$ groups,[19] then hydrolyzed into acid functions. Hybrid systems have been obtained from the reaction of 1 equiv. of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ suspended in acetonitrile with 1 equiv. of bis(phosphonate) previously dissolved in a mixture of dimethylformamide and hydrochloric acid. Tetrabutylammonium bromide was used as transfer agent. After subsequent purification, the oligomer was characterized by several techniques including multinuclear NMR spectroscopy (^{183}W, ^{29}Si and ^{31}P) and mass spectrometry (MALDI-TOF and ESI-MS). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF), in particular, has been already used with success for the characterization of two organosilyl derivatives of POMs.[20] To the best of our knowledge, however, electrospray ionization mass spectrometry (ESI-MS) has never been performed on these types of inorganic NBBs although it has recently been utilized for lacunary Keggin-type POMs.[21]

Upon proton decoupling each ^{31}P NMR spectrum showed only one resonance attributable to the RPO groups. These single lines display satellites corresponding to the heteronuclear couplings $^{2}J(^{183}W\text{-}^{31}P)$ = 10.1 Hz for **LI** and 10.3 Hz for **LII**, respectively, as expected for the symmetric attachment of phosphonates groups to the polyanionic surface. No free phosphonate ligands were observed in the solution NMR spectra. The ^{183}W NMR spectra each exhibit three lines with relative intensities of 1:2:2 (Figure 1). The most shielded resonances appear as doublets due to the heteronuclear phosphorus-tungsten couplings $^{2}J(^{183}W\text{-}^{31}P)$ = 10.2 Hz (for **LI**) and 10.8 Hz (for **LII**), respectively, as already observed in the ^{31}P NMR spectra. These features confirm that the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ framework has retained its original C_{2v} symmetry after two organophosphonate units have been attached to the surface. Moreover, the shifting of the lines is quite close to that already observed for $[\gamma\text{-}SiW_{10}O_{36}(RPO)_2]^{4-}$ species.[16] Homonuclear tungsten-tungsten couplings were also observed and are presented in

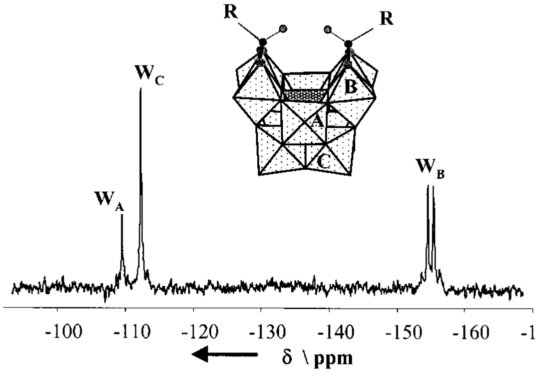


Figure 1. ^{183}W NMR (12.5 MHz) spectrum of **DII**, with a polyhedral representation of the polytungstate framework showing the three types of equivalent tungsten atoms

the Exp. Sect. Here, for simplification purposes, we use the symbolism used in previous works for these types of functionalized POMs, as illustrated in Figure 1.[16,20] The line with a relative intensity of 1 was assigned to the W(C) atoms, the most shielded line with heteronuclear coupling to the W(B) atoms and the last line to W(A) atoms. ^{31}P and ^{183}W NMR spectroscopic data suggest that a cyclic species has been obtained, containing at least two POMs interlinked by bis(phosphonate) ligands. Thus, two RPO groups could be covalently attached on the lacunary surface through P−O−W bridges, the C_{2v} symmetry of the starting POM being conserved. At this stage, however, nothing is known about the degree of oligomerization of the hybrid.

In order to check whether ESI-MS could be used reliably to determine the structures of the composites, we first performed analyses on $[Bu_4N]_3[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]$ (noted $\mathbf{[H(NBu_4)_3M]}$) used as a standard since it has already been fully characterized by X-ray diffraction methods.[16] The mass spectrum obtained from a 10^{-4} M solution in acetonitrile in the negative ion mode is shown in Figure 2 (a). Two signals have been detected at m/z = 896.7 and 1468.6 which have been attributed to $\mathbf{[HM]^{3-}}$ (calcd. m/z = 897.2) and $\mathbf{[H(NBu_4)_1M]^{2-}}$ (calcd. m/z = 1467.1), respectively. Although the presence of many tungsten atoms leads to a wide isotopic distribution with a Gaussian shape, in our case the resolution of the mass analyzer did not allow this distribution to be resolved and only rather large peaks representing an envelope of this distribution could be detected. The m/z values measured thus correspond to the centroid of the distribution which roughly amounts to an average molecular weight. Noticeably, no M^{4-} species were detected since a proton seemed to be strongly bound, probably through a P−O−H−O−P bridge between two terminal oxygen atoms of two {−P=O} groups. The presence of such a bound proton was also deduced from X-ray diffraction data.[16] It is quite usual in ESI-MS to detect a collection of multiply charged ions of different charge states corresponding to the attachment of various counterions. Here, the presence of two signals confirms the charge states as well as a double determination of the mass of the compound analyzed. In fact, in spite of the multiplicity of the signals, the interpretation of the mass spectrum remained straightforward, particularly since no fragmentation was observed.

The negative ion mass spectrum of the oligomer synthesized in this study is presented in Figure 2 (b), showing for the system based on **LII** three peaks at m/z = 905.5, 1135.5 and 1481.7. These signals were attributed to $\mathbf{[H_2D]^{6-}}$ (exp. m/z = 905.5, calcd. m/z = 905.9), $\mathbf{[H_2(NBu_4)_1D]^{5-}}$ (exp. m/z = 1135.5, calcd. m/z = 1135.6) and $\mathbf{[H_2(NBu_4)_2D]^{4-}}$ (exp. m/z = 1481.7, calcd. m/z = 1480.1), respectively, where D corresponds to the dimeric anion $[\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_2CH_2P{=}O]\}_2]^{8-}$. The highest charge state detected was 6−, *two* protons are necessarily bound to the polyanion. The sterically improbable monomeric ions $\mathbf{[HM]^{3-}}$ and $\mathbf{[H_2(NBu_4)M]^{2-}}$, where M is $\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_2CH_2P{=}O]\}^{4-}$, would have the same m/z values of 905.5 and 1480.1, respectively. The presence of a peak at m/z = 1135.5 undoubtedly confirms the charge states to be from 6− to 4− rather than 3− and 2−.

MALDI-TOF mass spectrometry was also performed to seek confirmation of the dimerization as it usually yields mostly singly-charged species. The mass spectrum obtained in the positive ion mode presents several peaks in the region of m/z = 6000−8000 [Figure 3 (a) and (b)], regularly spaced with 242.5 u, corresponding to the mass of the Bu_4N^+ counterion. These peaks were therefore assigned to the cationic entities $[D + x\ Bu_4N + (8 - x)\ H]^+$, with D corresponding to the mass of *two* $\{SiW_{10}O_{36}\}$ units and *two* $\{O{=}PCH_2(C_6H_4)_nCH_2P{=}O\}$ units (n = 1, 2). These observed experimental values are consistent, within the experimental accuracy estimated as ±2 u in the m/z = 6000−8000 range, with the calculated masses for the different cations as shown

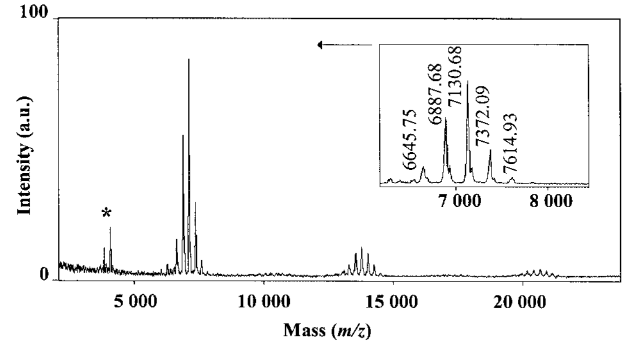


Figure 3. Positive ion MALDI-TOF mass spectra of **DII** and expansion of the m/z = 6000−8000 region, the asterisk indicates $[SiW_{12}O_{40}]^{4-}$ impurity

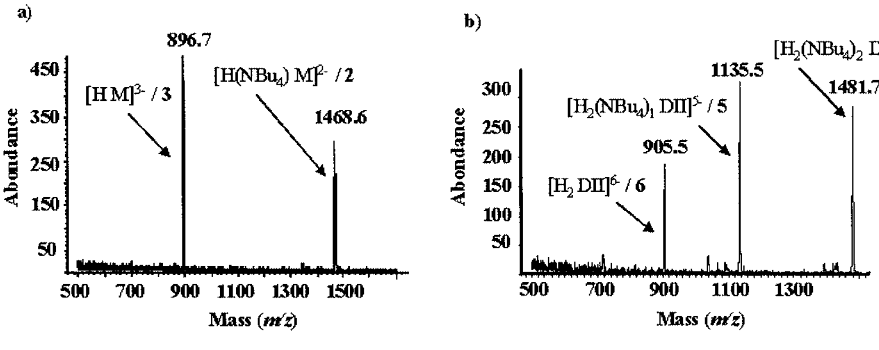


Figure 2. Negative ESI mass spectra of a) $[H\{\gamma\text{-}SiW_{10}O_{36}(PhPO)_2\}]^{3-}$ ($\mathbf{[HM]^{3-}}$) and b) $[H_2\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_2CH_2P{=}O]\}_2]^{6-}$ ($\mathbf{[H_2DII]^{6-}}$)

Table 1. MALDI-TOF MS data collected for $[\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_1CH_2P{=}O]\}_2]^{8-}$ (**DI**) and $[\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_2CH_2P{=}O]\}_2]^{8-}$ (**DII**) and calculated values

DI	+ 4 Bu_4N	+ 5 Bu_4N	+ 6 Bu_4N	+ 7 Bu_4N	+ 8 Bu_4N	+ 9 Bu_4N
Observed value	6249.4	6494.8	6734.7	6978.2	7220.4	7461.6
Calculated value	6251.2	6493.7	6736.1	6978.6	7221.1	7463.5
DII						
Observed value	–	6645.7	6887.7	7130.7	7372.1	7614.9
Calculated value	6403.4	6645.9	6888.3	7130.8	7373.3	7615.7

in Table 1. Other less intense signals were detected at higher *m*/*z* values (*m*/*z* = 12000–15000 and 19000–21000) as shown in Figure 3. These signals were most probably nonspecific noncovalent aggregates of the dimeric compound D which are often produced during the desorption process in MALDI-TOF mass spectrometry.

Both the MALDI-TOF and ESI-MS results undoubtedly point to the presence of cyclic species and indicate the degree of oligomerization, in this case dimeric species are indicated.

Conclusion

The synthesis of hybrid oligomers from inorganic NBBs has undergone considerable developments in the last few years. In this context, the $[\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_nCH_2P{=}O]\}_2]^{8-}$ (n =1, 2) species, as represented in Figure 4, constitute an alternative approach for obtaining hybrids with a high degree of oligomerization. Moreover, this work has shown that mass spectrometry (combination of MALDI-TOF and ESI-MS) was more than just an alternative tool, but an essential technique in the characterization of these hybrid systems. Other bis(phosphonates) with larger sizes and different topologies are in preparation and their reactivity towards POMs will be reported very shortly.

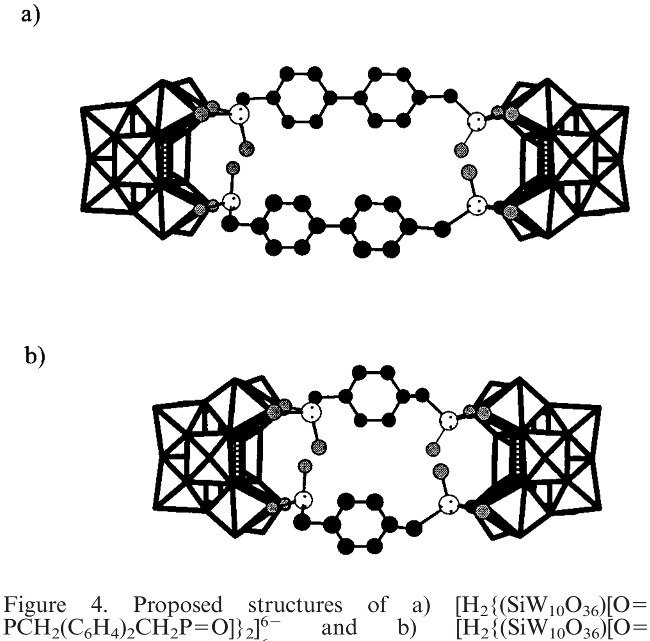


Figure 4. Proposed structures of a) $[H_2\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_2CH_2P{=}O]\}_2]^{6-}$ and b) $[H_2\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_1CH_2P{=}O]\}_2]^{6-}$

Experimental Section

General Procedures and Chemicals: $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O$ was prepared according to ref.[22] Other reagents and solvents were purchased from Aldrich and used as received. IR spectra (4000–250 cm^{-1}) were recorded with a Nicolet Magna 550 spectrometer in KBr pellets.

ESI-MS: The measurements were carried out using an HP 5989B single quadrupole mass spectrometer equipped with an electrospray source from Analytica of Branford. The instrument was operated in the negative ion mode. Source parameters were as follows: U_{needle} = 0 V, $U_{cyl.}$ = 3500 V, $U_{end.}$ = 3000 V, $U_{cap.}$ = 3500 V. Purified air was used as the nebulizing and drying gas, the presence of oxygen helping to prevent corona discharge which is often a problem during negative ion operation. The pressures of the nebulizing and drying gases were 0.34 and 1.70 bar, respectively, the nebulizing gas was heated to approximately 100 °C. Mass spectra were obtained by direct infusion with a Harvard Apparatus syringe pump of 10^{-4}, 5×10^{-5}, or 10^{-5} M sample solutions in pure distilled acetonitrile at a flow rate of 5 μL min^{-1}. The cone voltage U_c was varied, but was mostly set at low values of 10–40 V relative to the capillary exit voltage. Raising the cone voltage improves the ion transmission through the analyzer. It also increases the kinetic energy, which in turn enhances the formation of daughter ions by collisions with solvent and gas molecules within the region of primary stage pumping between the capillary exit and the sampling cone. The mass spectra shown are the result of approximately 20 scans summed from *m*/*z* = 50 to 1650. The mass axis was calibrated using the cluster ions observed from a 50 ng/μL solution of SDS (sodium dodecylsulfate) in acetonitrile.

MALDI-TOF MS: The spectra were recorded using a Voyager Elite Time-of-Flight Mass Spectrometer (PerSeptive Biosystems, Boston, MA, USA). In this apparatus, the pulsed N_2 laser beam (337 nm, 3 ns pulse duration, repetition rate 2 Hz) was focused onto the target with an angle of incidence of 45°. In all experiments the mass spectrometer was tuned in the linear mode using delayed extraction and a beam wire guide. The target voltage was set to +20 kV. The extraction delay and pulse voltage were adjusted to obtain the best mass resolution and the wire guide voltage was adjusted to obtain the best transmission. All mass spectra were recorded and averaged over 256 laser shots with a Tektronix TDS 520 oscilloscope (Beaverton, OR, USA). The samples were prepared as follows: the compound (2 mg) was dissolved in acetonitrile (500 µL; solution A), and dithranol (12 mg) was dissolved in CH_2Cl_2 (500 µL; matrix solution). 1 µL of solution A was then added to 50 µL of the matrix solution. An external calibration of the instrument with a POE 5000 standard was used.

NMR: The ^1H (300 MHz) NMR spectra were obtained at room temperature in 5-mm (o.d.) tubes with a Bruker AC 300 spectrometer equipped with a QNP probe head. Chemical shifts are given according to the IUPAC convention with respect to $SiMe_4$. The 12.5 MHz ^{183}W NMR spectra were recorded at 300 K in almost saturated DMF/CD_3CN (90:10, v/v) solutions in 10-mm (o.d.) tubes with the same spectrometer equipped with a low-frequency special VSP probe head. Chemical shifts are given with respect to 2 M aqueous Na_2WO_4 and were determined by the substitution method using a saturated D_2O solution of tungstosilicic acid $H_4SiW_{12}O_{40}$ as secondary standard ($\delta = -103.8$ ppm).

***para*-Xylylenebis(phosphonic acid) (LI):** α,α′-Dibromo-*p*-xylene (2.084 g, $7.9.10^{-3}$ mol) was suspended in deaerated triethyl phosphite (25 mL) and the mixture was heated to reflux at 138 °C with stirring for 3 h. The unreacted triethyl phosphite was removed in vacuo at 80 °C. Crystalline products were obtained by dissolving the yellow oil in diethyl ether and cooling to −35 °C overnight. *para*-Xylylenebis(diethyl phosphonate) (1 g, $2.64.10^{-3}$ mol) was then dissolved in HCl (60 mL, 12 M) and heated to reflux overnight. The pure phosphonic acid was obtained by removing hydrochloric acid with a rotary evaporator. Yield: 0.65 g, 31%. ^1H NMR (300.13 MHz, [D$_6$]DMSO, TMS): $\delta = 2.90$ (d, 2 H), 7.14 (s, 2 $H_{arom.}$) ppm. ^{31}P NMR (121.5 MHz, [D$_6$]DMSO, H_3PO_4): $\delta = 22.57$ ppm.

1,1′-Biphenylene-4,4′-bis(methylene)bis(phosphonic acid) (LII): The procedure was similar except that the starting material was 4,4′-bis(chloromethyl)-1,1′-biphenyl (0.6 g, $2.39.10^{-3}$ mol). Yield: 0.33 g, 40.3%. ^1H NMR (300.13 MHz, [D$_6$]DMSO, TMS): $\delta = 2.97$ (d, 2 H), 7.31 (d, 2 $H_{arom.}$), 7.54 (d, 2 $H_{arom.}$) ppm. ^{31}P NMR (121.5 MHz, [D$_6$]DMSO, H_3PO_4): $\delta = 22.38$ ppm.

$(NBu_4)_6H_2[\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)CH_2P{=}O]\}_2]$ (DI): A homogeneous mixture of **LI** (0.089 g, 0.333 mmol) and 12 M hydrochloric acid (0.35 mL) in dimethylformamide (2 mL) was added dropwise to a suspension of solid $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O$ (1 g, 0.333 mmol) and Bu_4NBr (0.35 g, 1 mmol) in acetonitrile (30 mL). The resultant mixture was heated to reflux with stirring overnight. Acetonitrile was then removed by evaporation, and the crude product was precipitated from the dimethylformamide solution by diffusion of diethyl ether through the gas phase. The precipitate was filtered and washed with ethanol and diethyl ether. Yield: 1.3 g (0.180 mmol, 54%). ^{31}P NMR (121.5 MHz, DMF/CD_3CN, H_3PO_4): $\delta = 23.23$ [$^2J(^{183}W,^{31}P) = 10.1$ Hz] ppm. ^{183}W NMR (12.5 MHz, DMF/CD_3CN, Na_2WO_4): $\delta = -109.1$ [s, 2 W, $^2J(^{183}W,^{183}W) = 21.6$, 12.1 Hz], −113.0 [s, 4 W, $^2J(^{183}W,^{183}W) = 12.7$, 16.5 Hz], −155.3 [d, 4 W, $^2J(^{183}W,^{183}W) = 21.35$, 16.5, $^2J(^{183}W,^{31}P) = 10.2$ Hz] ppm. IR (KBr): $\tilde{\nu} = 1160$ (vw), 1060 (vw), 1006 (vw), 975 (s), 939 (m), 907 (vs), 885 (vs), 835 (m), 763 (vs), 552 (vw), 363 (w), 331 (w) cm^{-1}.

$(NBu_4)_6H_2[\{(SiW_{10}O_{36})[O{=}PCH_2(C_6H_4)_2CH_2P{=}O]\}_2]$ (DII): The synthesis followed the same procedure, using **LII** (0.114 g, 0.333 mmol). Yield: 1.5 g (0.203 mmol, 61.1%). ^{31}P NMR (121.5 MHz, DMF/CD_3CN, H_3PO_4): $\delta = 22.80$ [$^2J(^{183}W,^{31}P) = 10.3$ Hz] ppm. ^{183}W NMR (12.5 MHz, DMF/CD_3CN, Na_2WO_4): $\delta = -109.6$ [s, 2 W, $^2J(^{183}W,^{183}W) = 7$, 21.6 Hz], −112.3 [s, 4 W, $^2J(^{183}W,^{183}W) = 7$, 20.3 Hz], −155.0 [d, 4 W, $^2J(^{183}W,^{183}W) = 20.35$, 21.6, $^2J(^{183}W,^{31}P) = 10.8$ Hz] ppm. IR (KBr): $\tilde{\nu} = 1160$ (vw), 1060 (vw), 1006 (vw), 975 (s), 939 (m), 907 (vs), 885 (vs), 835 (m), 763 (vs), 552 (vw), 363 (w), 331 (w) cm^{-1}.

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