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A New Method for the Synthesis of Organopolyoxometalate Hybrid Compounds

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The reaction of a quaternary ammonium salt of the tin chloride-substituted polyoxometalate, $[PSn(Cl)W_{11}O_{39}]^{4-}$, with a variety of *n*-nucleophiles including primary, secondary, and tertiary amines and a tertiary phosphine, yielded tin-centered Lewis acid–base adducts, $[PSn(Cl)W_{11}O_{39}]^{4-}$–*n*-nucleophile; with more nucleophilic secondary amines such as diisopropylamine, apparently some $[PSnN[CH(CH_3)_2]_2W_{11}O_{39}]^{4-}$ was formed as a minor product. The compounds were identified by ^{1}H, ^{119}Sn, ^{15}N, ^{31}P, and ^{183}W NMR, ESI-MS, and elemental analyses. The key connectivity of the Sn–Cl center with the amine was clarified by the observation of ^{3}J Sn–H couplings (Sn from the polyoxometalate cluster and H from the amine moiety) in a 2D ^{119}Sn–^{1}H heteronuclear multiple-bond correlation NMR experiment. This new, rather simple synthetic method was also utilized for preparing amino acid–polyoxometalate hybrid compounds.

Introduction

The formation of hybrid compounds between polyoxometalates and organic or metal−organic species has significant potential in many areas of polyoxometalate chemistry ranging from applications in catalysis, materials science, and biologically relevant environments. The preparation of such organic−polyoxometalate hybrid compounds with predesigned structure and traits requires synthetic protocols that should be as simple as possible. A perusal of the known methods for such preparations reveals that there is a relative paucity of synthetic approaches available, and in all, one can discern two general approaches. The first group of synthetic methods involves the creation of hybrid materials via electrostatic interactions between the anionic polyoxometalates and cationic species that can be organic, for example, ammonium salts or metal organics, for example, metals with appropriate ligands.[1] Since the negative charge of the polyoxometalate anion is polarized over the entire structure, the hybrid compounds formed generally have little element of design; the structures formed are determined after the fact, generally by X-ray crystallography.[1] These compounds are sometimes insoluble, especially with more rigid cations, although solubility can often be obtained in apolar solvents or using surfactants. The second group of methods involves a covalent, site-selective link between an organic moiety and the polyoxometalate. One of the most notable methodologies is the reaction of amines with polyoxometalates via the substitution of terminal oxo moieties by organoimines.[1a,2] In practice, this procedure is largely limited to the reaction of hexamolybdates, $Mo_6O_{19}^{2-}$ or $MoW_5O_{19}^{2-}$, and to aniline derivatives with electron-donating groups. Aniline derivatives with electron-withdrawing substituents and aliphatic amines usually do not react; it is sometimes difficult to control the degree of substitution, further derivitization is complicated,

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(1) (a) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77. (b) Coronado, E.; Gomez-García, C. J. *Chem. Rev.* **1998**, *98*, 273. (c) Marcoux, P. R.; Hasenknopf, B.; Vaissermann, J.; Gouzerh, P. *Eur. J. Inorg. Chem.* **2003**, *13*, 2406.

(2) (a) Peng, Z. H. *Angew. Chem., Int. Ed.* **2004**, *43*, 930. (b) Wu, P. F.; Li, Q.; Ge, N.; Wei, Y. G.; Wang, Y.; Wang, P.; Guo, H. Y. *Eur. J. Inorg. Chem.* **2004**, *14*, 2819. (c) Wei, Y. G.; Lu, M.; Cheung, C. F. C.; Barnes, C. L.; Peng, Z. H. *Inorg. Chem.* **2001**, *40*, 5489. (d) Du, Y.; Rheingold, A. L.; Maatta, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 346. (e) Clegg, W.; Errington, R. J.; Fraser, K. A.; Lax, C.; Richards, D. G. In *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; p 113. (f) Clegg, W.; Errington, R. J.; Fraser, K.; Holmes, S. A.; Schäfer, A. *J. Chem. Soc., Chem. Commun.* **1995**, 455. (g) Wei, Y.; Xu, B.; Barnes, C. L.; Peng, Z. *J. Am. Chem. Soc.* **2001**, *123*, 4083. (g) Bar-Nahum, I.; Narasimhulu, K. V.; Weiner, L.; Neumann, R. *Inorg. Chem.* **2005**, *44*, 4900.

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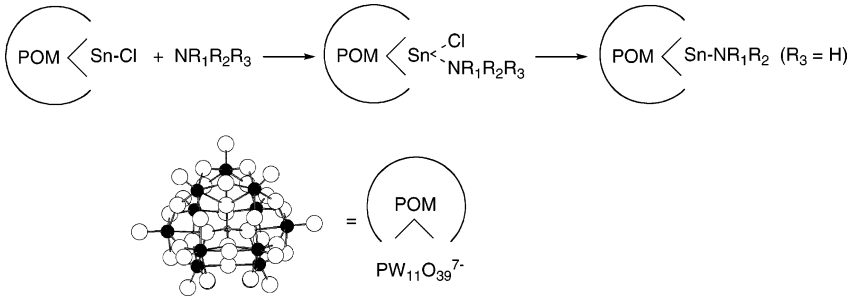
Scheme 1. Synthetic Route for the Preparation of Organopolyoxometalate Hybrid Compounds



and the hydrolytic stability is low. A second common methodology is the substitution of reactive organic−main metal species usually of the general formula RMX_3 or $RP(O)X_2$, where M = Si, Ge, Sn, and some others and X = halide or alkoxide, into a lacunary polyoxometalate compounds.[1a,3] This technique is largely limited by the availability of the specific RMX_3 or $RP(O)X_2$ compounds. Furthermore, there are relatively few organic substituents, R, that have functional units that are compatible with the synthetic technique and that are also useful for further derivatization; this derivatization is also often fraught with significant problems in the purification of the product since such reactions are usually incomplete and thus require a complicated separation of the highly charged substrate and product.[4]

In this paper we present a *new simple* synthetic methodology whereby primary, secondary, and tertiary amines, $NR_1R_2R_3$, and also phosphines can be reacted with readily prepared tin chloride-substituted polyoxometalates (POMs) of the common Keggin and Well-Dawson structures such as $[PSn(Cl)W_{11}O_{39}]^{4-}$ or $[P_2Sn(Cl)W_{17}O_{61}]^{7-}$ to yield the polyoxometalate−amine or phosphine adduct (Scheme 1). As will be clear from the multinuclear NMR results described below, initially, a Lewis acid−base couple, $POMSn(Cl)-NR_1R_2R_3$ is formed, followed in some cases, for secondary amines, by an apparent partial formation of an amide with a Sn−N covalent bond. In this context, it should also be noted that in the past tin hydroxide moieties within the polyoxometalate structure have been used in the opposite reaction, that is, in reacting a nucleophilic polyoxometalate with an electrophilic substrate.[5]

Results and Discussion

The lacunary Keggin polyoxometalate compound, $Q_3H_4PW_{11}O_{39}$, where Q = tetrahexylammonium, was prepared according to the known literature procedure.[6] A tin chloride moiety was then inserted into the defect position of the lacunary Keggin cluster to yield $Q_3HPSn(Cl)W_{11}O_{39}$.[7] The latter was analyzed by elemental analysis, ^{1}H NMR, ^{31}P NMR (see the Experimental Section), and by electrospray ionization mass spectroscopy (ESI-MS) in the negative ion mode (Figure 1). Importantly, the soft ionization technique used in the mass spectral analysis allows the observation of the molecular anion of $Q_3HPSn(Cl)W_{11}O_{39}$ with a cluster centered at m/z = 3895. The spectrum also indicates that the chloride anion is not hydrolyzed; that is, there is no peak attributable to $Q_3HPSn(OH)W_{11}O_{39}$. Furthermore, the ESI-MS analysis also demonstrates that dimerization via the formation of a Sn−O−Sn bond has not occurred. Further fragments of the molecular peak are consistent with the lacunary phosphotungstates[8] and/or $Q_3HPSn(Cl)W_{11}O_{39}$ as annotated on the spectrum. It is also worthwhile to note that the ESI-MS results of $Q_3HPSn(Cl)W_{11}O_{39}$ with positive ion detection showed only the peak of the tetrahexylammonium cation.

The organopolyoxometalate hybrid compounds were obtained by reacting $Q_3HPSn(Cl)W_{11}O_{39}$ with an excess of amine in THF (THF = tetrahydrofuran) at room temperature whereupon the product either quickly precipitated from the solution or was precipitated from solution by the addition of diethylether. Importantly, no purification was needed except for the washing of the precipitate by THF, water, ethanol, and then ether. Unfortunately, despite many attempts with many amines, we were generally unable to obtain single crystals suitable for analysis by X-ray diffraction. In one case, for the polyoxometalate−aniline complex formulated as $Q_3HSnClPW_{11}O_{39}-PhNH_2$ (see below), single crystals were obtained. Unfortunately, the compound crystallized in a highly symmetrical rhombohedral space group $R\bar{3}c$ (No. 167) with only two independent addenda atoms per asymmetric unit, which precluded the differentiation of Sn from W. In addition, refinement to only R = 0.1144 was possible and only 48 out of the 78 carbon atoms in the compound (see the elemental analysis below) could be located due to

(3) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 2211. (b) Judenstein, P.; Deprun, C.; Nadjo, L. *J. Chem. Soc., Dalton Trans.* **1991**, 1991. (c) Weeks, M. S.; Hill, C. L.; Schinazi, R. F. *J. Med. Chem.* **1992**, *35*, 1216. (d) Mazeaud, A.; Ammari, N.; Robert, F.; Thouvenot, R. *Angew. Chem., Int. Ed. Eng.* **1996**, *35*, 1961. (e) Zonnevijlle, F.; Pope, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 2731. (f) Judenstein, P. *Chem. Mater.* **1992**, *4*, 4. (g) Ammari, N.; Nervé, G.; Thouvenot, R. *New J. Chem.* **1991**, *15*, 607. (h) Mayer, C. R.; Thouvenot, R.; Lalot, T. *Macromolecules* **2000**, *33*, 4433. (i) Mayer, C. R.; Thouvenot, R. *J. Chem. Soc., Dalton Trans.* **1998**, 7. (j) Mayer, C. R.; Herson, P.; Thouvenot, R. *Inorg. Chem.* **1999**, *38*, 6152. (k) Mayer, C. R.; Fournier, I.; Thouvenot, R. *Chem.—Eur. J.* **2000**, *6*, 105. (l) Mayer, C. R.; Neven, S.; Cabuil, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 501. (m) Xin, F. B.; Pope, M. T.; Long, G. J.; Russo, U. *Inorg. Chem.* **1996**, *35*, 1207.
(4) (a) Bareyt, S.; Piligkos, S.; Hasenknopf, B.; Gouzerh, P.; Lacôte, E.; Thorimbert, S.; Malacria, M. *J. Am. Chem. Soc.* **2005**, *127*, 6788. (b) Sazani, G.; Pope, M. T. *Dalton Trans.* **2004**, *13*, 1989. (c) Bar-Nahum, I.; Cohen, H.; Neumann, R. *Inorg. Chem.* **2003**, *42*, 3677.
(5) Chorghade, G. S.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 5134.
(6) Combs-Walker, L. A.; Hill, C. L. *Inorg. Chem.* **1991**, *30*, 4016.
(7) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198.
(8) Bonchio, M.; Bortolini, O.; Conte, V.; Sartorel, A. *Eur. J. Inorg. Chem.* **2003**, 699.

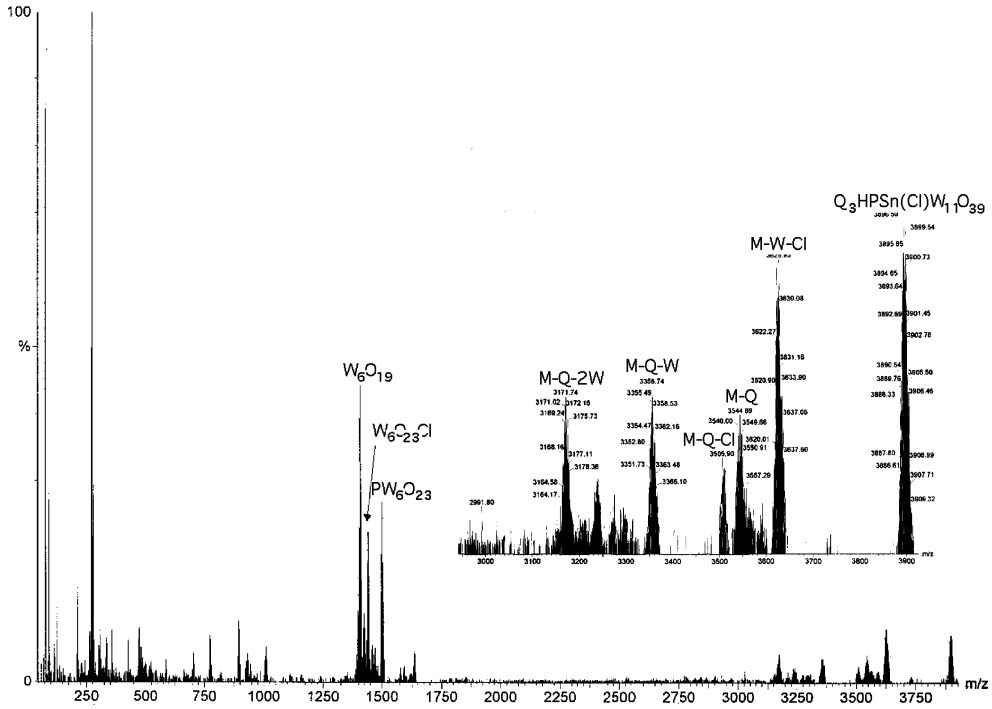


Figure 1. ESI-MS spectrum of $Q_3HPSn(Cl)W_{11}O_{39}$ in the negative anion mode.

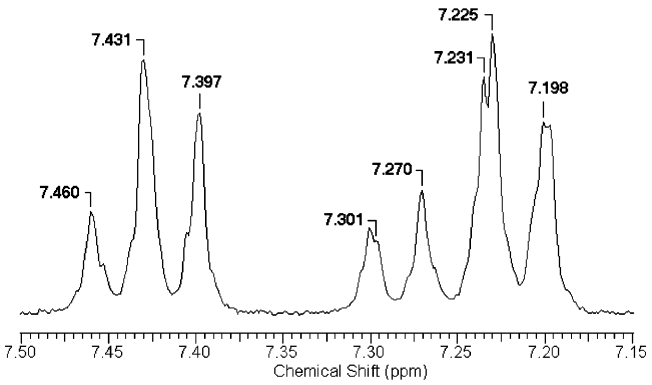


Figure 2. ^1H NMR spectrum of $Q_3HSn(Cl)W_{11}PO_{39}-PhNH_2$ (aromatic region only).

disorder. The crystallographic data is included in the Supporting Information.

The characterization of the isolated solids was achieved by solution-phase techniques. The reaction between $Q_3HSn(Cl)PW_{11}O_{39}$ and aniline to yield a polyoxometalate−aniline adduct was initially studied to characterize the nature of the polyoxometalate−amine interaction. The ^1H NMR spectrum showed a 1:1 adduct with a downfield shift for the aromatic hydrogen atoms (Figure 2 and Table 1).

A comparison of the ^{15}N NMR spectrum of $Ph^{15}NH_2$ with that of a polyoxometalate−$Ph^{15}NH_2$ adduct also showed a significant shift from 59.74 to 50.88 ppm. Thus, the electronic environment of aniline changed significantly, according to both the ^1H NMR and ^{15}N NMR spectra. Likewise, the ^{31}P NMR, ^{119}Sn NMR, and ^{183}W NMR spectra of the polyoxometalate−aniline adduct showed smaller but discernible differences compared with the original spectra of $Q_3HSn(Cl)PW_{11}O_{39}$ (Table 1). It should be noted that the ^{183}W NMR spectrum of $Q_3HSnClPW_{11}O_{39}-PhNH_2$ (Figure 3) shows the expected 2:2:2:2:1:2 peak ratio and also the expected satellite peaks. No other polyoxometalate compounds could be discerned in the spectrum; that is, no peaks associable to such possible contaminants such as a Linqvist anion ($W_6O_{19}^{2-}$; +58.9 ppm), a Keggin anion ($PW_{12}O_{40}^{3-}$; −99.4 ppm), or a lacunary Keggin anion ($PW_{11}O_{39}^{7-}$; −97 (2), −102 (2), −109 (2), −117 (1), −132 (2), and −152 (2) ppm) are observed.[9]

From the combined NMR data (including peak integration of the hydrogen atoms), the elemental analysis, and the observation of downfield shifts on the aniline moiety only, we hypothesized that the reaction between $Q_3HSnClPW_{11}O_{39}$ and aniline was a Lewis acid−base reaction at the tin center to yield a donor−acceptor organopolyoxometalate adduct, $Q_3HSn(Cl)PW_{11}O_{39}-PhNH_2$ (Scheme 1). To solidify this hypothesis, a series of necessary experiments was carried out. For example, an alternative explanation for the formation of the polyoxometalate−amine adduct could be the formation of a complex through a nonspecific acid−base type reaction between the proton associated with $Q_3\mathbf{H}SnClPW_{11}O_{39}$ and $Ph\mathbf{N}H_2$ although it should be noted that the pK_a (in H_2O) of aniline is 4.63. Indeed, the reaction between the protonated lacunary polyoxometalate $Q_3H_4PW_{11}O_{39}$ without substituted Sn−Cl showed no precipitation and *no reaction* with aniline in solution by ^1H NMR.

Next, the specificity of the reaction at the Sn−Cl center of $Q_3HSn(Cl)PW_{11}O_{39}$ was examined using diisopropylamine as a more basic (pK_a = 11.05 in water) and more nucleophilic substrate. The reaction revealed a more complicated process. From the ^{31}P NMR results, one observes peaks at −12.19 ppm (85%) and −12.03 ppm (15%) that can be associated

(9) (a) Chen, Y-G.; Gong, J.; Qu, L.-Y. *Coord. Chem. Rev.* **2004**, *248*, 245. (b) Brevard, C.; Schimpf, R.; Tourné, G.; Tourné, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059.

Table 1. NMR Shifts for Different Nuclei and Elemental Analysis for $Q_3HSn(Cl)PW_{11}O_{39}$ and the Aniline Adduct[a]

compound	^{1}H NMR[b]	^{31}P NMR	^{15}N NMR[c]	^{119}Sn NMR	^{183}W NMR	elemental analysis found (calcd)
$Q_3HSnClPW_{11}O_{39}$		−11.48		−578.7	−76.2, −90.7 −107.6, −113.8 −129.8, 174.1	C, 22.24 (22.19) H, 4.07 (4.06) N, 1.06 (1.08)
$Q_3HSnClPW_{11}O_{39}-PhNH_2$	7.20−7.46	−12.18	50.9	−583.5	−76.5, −90.9 −107.7, −113.9 −129.9, −174.3	C, 23.53 (23.48) H, 4.14 (4.14) N, 1.40 (1.40)
$PhNH_2$	6.44−7.02		59.7			

[a] The details for the measurements are given in the Experimental Section. [b] The shifts refer only to the hydrogen atoms of aniline. [c] The ^{15}N NMR spectra were measured on 98% ^{15}N-labeled aniline compounds.

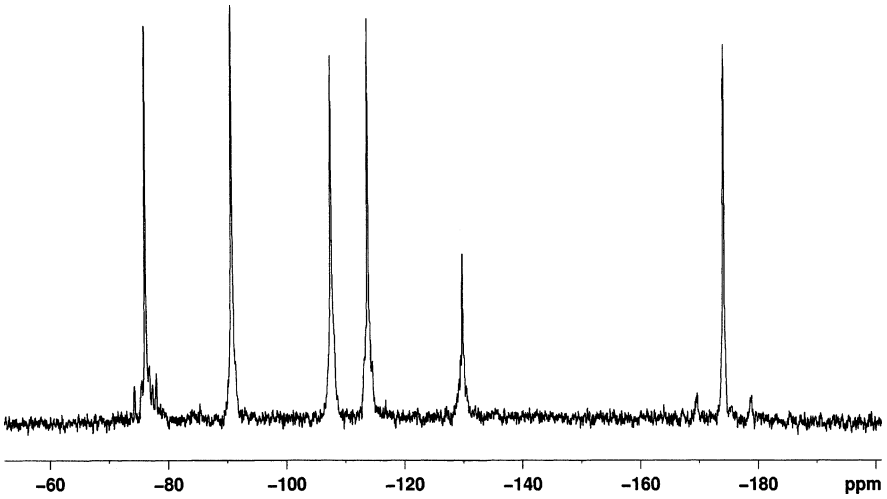


Figure 3. ^{183}W NMR of $Q_3HSn(Cl)W_{11}PO_{39}-PhNH_2$.

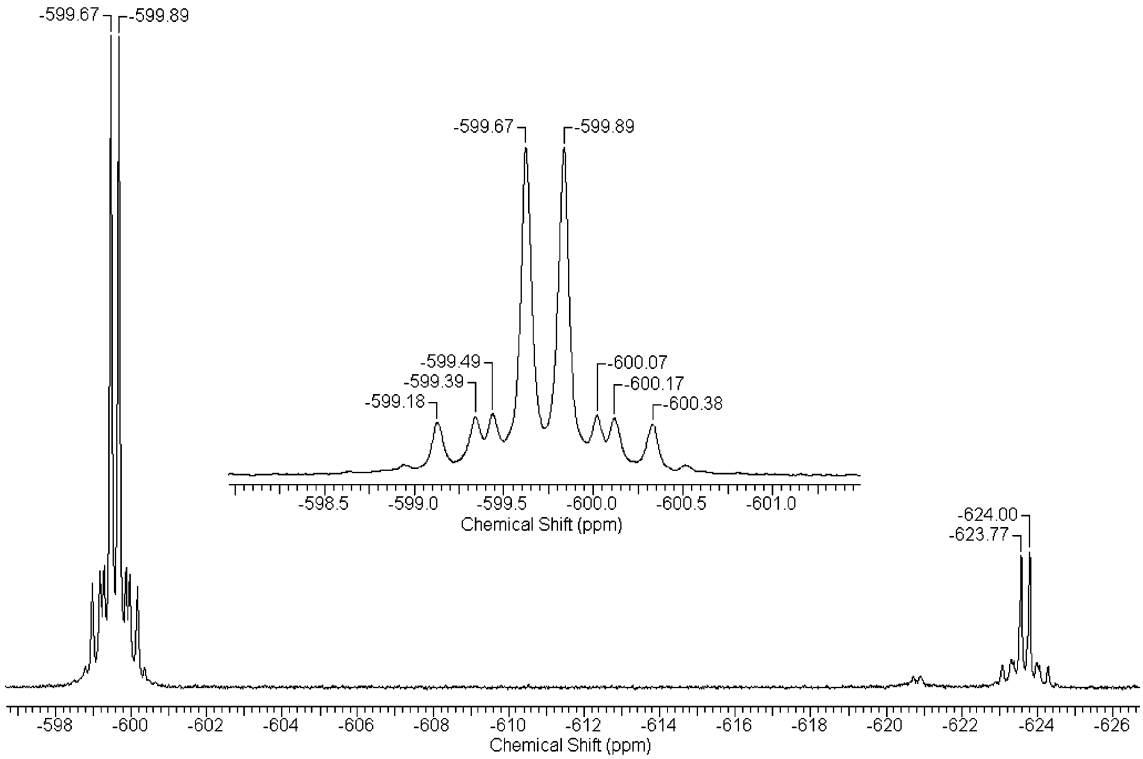


Figure 4. ^{119}Sn NMR spectrum in DMSO-d_6 for $Q_3HPSn(Cl)W_{11}O_{39}$−diisopropylamine indicating two different Sn−N bonding modes.

with the formation of *two* different hybrid compounds. Upon heating the solution, the peak at −12.03 ppm grows at the expense of the peak at −12.19 ppm. Furthermore, ^{119}Sn NMR measurements (Figure 4) supported the results obtained by ^{31}P NMR; two sets of peaks were detected at −599.78 (85%) and at −623.89 (15%) ppm for the hybrid compounds. The satellite peaks are due to coupling, that is, $^{2}J(^{119}Sn-^{31}P) = 38$ Hz and $^{2}J(^{119}Sn-^{183}W) = 30$ Hz.

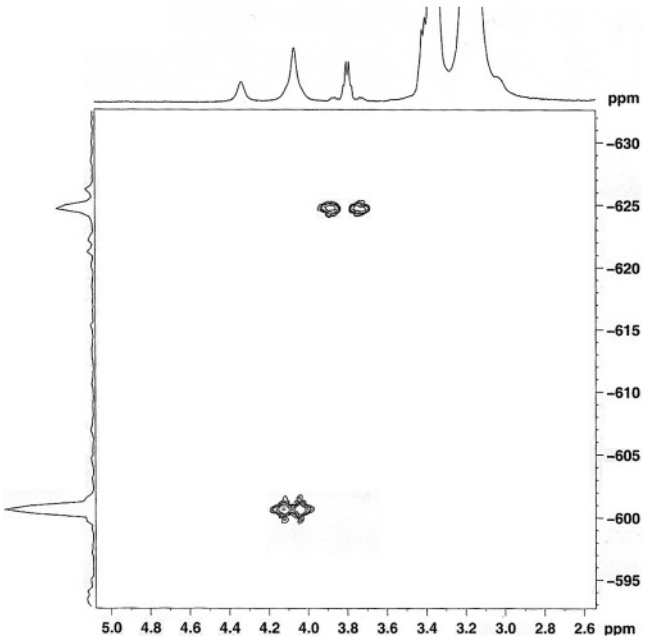


Figure 5. 2D ^{119}Sn−^{1}H HMBC NMR spectrum upon the reaction of $Q_3HPSn(Cl)W_{11}O_{39}$ with diisopropylamine.

Perhaps most importantly, a two-dimensional (2D) ^{119}Sn−^{1}H heteronuclear multiple-bond correlation (HMBC) NMR measurement for the polyoxometalate−diisopropylamine hybrid compounds[10] (Figure 5) showed *direct* proof for both the formation Sn−N bonds and for the existence of two *different* Sn−N bonding modes. The ^{3}J Sn−H couplings (Sn from the polyoxometalate cluster and H from the isopropyl organic moiety) show a ^{3}J Sn−H coupling constant of 42 Hz (for the major peak at −599.78 ppm) and a ^{3}J Sn−H coupling constant of 72 Hz (for the minor peak at −623.89 ppm). The different values of the coupling constants can be correlated with different Sn−N bond lengths. We interpret this result as meaning that the major and initially formed compound is a $Q_3HSn(Cl)PW_{11}O_{39}$−$NH[CH(CH_3)_2]_2$ Lewis acid−base adduct hybrid compound whereas the minor and subsequently formed product is likely the result of further nucleophilic substitution at the Sn atom to yield an amide, $Q_3HSnN[CH(CH_3)_2]_2PW_{11}O_{39}$, via the formation of a covalent bond. The assignment of the second product as $Q_3HSnN[CH(CH_3)_2]_2PW_{11}O_{39}$ is suggested also by the absence of the peak associated to the original N−H bond in the ^{1}H NMR spectrum; however, in the other cases, chemical exchange phenomena with the polar solvents along with longer Sn−N bonds also caused the desired coherences to vanish.[11]

The formation of polyoxometalate−amine adducts ($Q_3HSn(Cl)PW_{11}O_{39}$−NHR_1R_2; $R_1 = R_2 =$ *i*-propyl and $R_1 =$ H, $R_2 =$ Ph) was further supported by their ESI-MS results. Although the molecular peaks were not observed and thus apparently not sufficiently stable to this ionization technique, it is important to note that in the negative ion mode, the spectra of $Q_3HSn(Cl)PW_{11}O_{39}$−NHR_1R_2were identical to the spectrum observed for $Q_3HSn(Cl)PW_{11}O_{39}$ (Figure 1). Importantly, the absence of fragment peaks showing loss of tetrahexylammonium but retaining the $Q_2(R_1R_2NH_2^+)$ combination supports the hypothesis that the polyoxometalate−amine adducts are formed via a SnCl−amine reaction rather than by the protonation of the amine. In the positive anion mode, low-intensity peaks (2−5%) of the amine are observed along with the tetrahexylammonium fragment (100%).

The formation of various additional organopolyoxometalate hybrid compounds using the reaction of $Q_3HPSn(Cl)W_{11}O_{39}$ with *n*-nucleophiles (amines and triphenylphosphine) was surveyed, and the results are summarized in Table 2. As can be observed from Table 2, the formation of the adducts is a generally applicable method for primary, secondary, and tertiary amines and also tertiary phosphines.

An example of the usefulness of this synthetic method is the formation of polyoxometalate−amino acid hybrid compounds. An ongoing important theme in polyoxometalate chemistry is their introduction into biological/medicinal applications.[12] In this context, recently, the combined Malacria and Gouzerh groups have demonstrated the attachment of amino acids to a polyoxometalate through an alkyl tin spacer group functionalized with a carboxylic group.[4a] It has also been suggested in the past by Xin and Pope that such attachment may be possible also with tin-substituted polyoxometalates.[13] The synthetic pathway presented above in Scheme 1 presents an alternative procedure for the formation of such hybrid compounds. Thus, soluble *tert*-butyloxycarbonyl (*t*-BOC) derivatives of a few amino acids (L-phenylalanine and L-tyrosine esters were chosen due to their easily detectable aromatic ring by ^{1}H NMR) were reacted in acetonitrile with $Q_3HSn(Cl)PW_{11}O_{39}$ to yield the hybrid $Q_3HSn(Cl)PW_{11}O_{39}$−L-Phe ester and the $Q_3HSn(Cl)PW_{11}O_{39}$−L-Tyr ester. Valuably, the controlled removal of the *t*-BOC during the reaction leads to high yields of the hybrid compounds. The ^{1}H NMR spectrum of $Q_3HSnClPW_{11}O_{39}$−L-Phe ester prepared in an exemplary reaction is shown in Figure 6.

Conclusions

A new and relatively simple method for the preparation of organopolyoxometalate hybrid compounds with readily available amines has been developed. Although crystals suitable for X-ray diffraction analysis were not available or did not yield conclusive results due to disorder, solution methods relying on mass spectrometry and multinuclear NMR made possible the identification of these hybrid compounds as adducts formed upon the interaction of the amine with the Sn−Cl center of the polyoxometalate. Hopefully this methodology will make possible the selective inclusion of polyoxometalates in a variety of systems in fields ranging from proteins to dendrimers and especially in binary catalytic systems.

(10) Elemental Analysis: Found (Calcd) C, 23.76 (23.90); H, 4.38 (4.54); N, 1.42 (1.40).

(11) (a) Martins, J. C.; Biesemans, R.; Willem, R. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 271−322. (b) Cavanagh, J.; Fairbrother, W. J.; Palmer, A. G.; Skelton, N. J. *Protein NMR Spectroscopy, Principle and Practice*; Academic Press: New York, 1996.

(12) Rhule, J. T.; Hill, C. L.; Judd, D. A.; Schinazi, R. F. *Chem. Rev.* **1998**, *98*, 327.

(13) Xin, F. B.; Pope, M. T. *J. Am. Chem. Soc.* **1996**, *118*, 7731.

Table 2. Analytical Data for Various $Q_3HPSn(Cl)W_{11}O_{39}$−*n*-nucleophile Hybrid Compounds

compound	^{1}H NMR[a]	^{31}P NMR[b]	elemental analysis found (calcd)
POM−2-aminoanthracene	7.25 (dd, 2H); 7.35−7.55 (m, 3H); 7.92−8.11 (m, 2H); 8.41 (s, 1H); 8.50 (s, 1H)	−11.59	C, 25.08 (25.26); H, 4.11 (4.14); N, 1.47 (1.37)
POM−*sec*-butylamine	1.14 (d, CHCH_3); 1.42 (m, NH_2 and CH_2CH_3); 3.05 (m, C*H*)	−11.82	C, 23.74 (23.00); H, 4.50 (4.27); N, 1.81 (1.41)
POM−4-bromoaniline	6.86 (d, 2H); 7.38 (d, 2H)	−11.48	C, 23.91 (23.03); H, 4.48 (4.04); N, 1.38 (1.38)
POM−*N*-methylbenzylamine	2.52 (s, CH_3); 4.06 (s, CH_2); 7.42 (m, 5H aryl)	−11.82	C, 23.67 (23.44); H, 4.38 (4.54); N, 1.42 (1.40)
POM−2-aminopyridine	6.82 (d, 1H); 6.90 (d, 1H); 7.86 (d, 1H); 7.91 (d, 1H)	−12.07	C, 23.25 (23.18); H, 4.12 (4.08); N, 1.69 (1.76)
POM−isopropylamine	1.20 (d, CHCH_3), 3.85 (m, *CH*CH_3), 4.07 (m, *CH*CH_3)[c]	−12.19 −12.03	C, 23.51 (23.42); H, 4.33 (4.38); N, 1.41 (1.40)
POM−triethylamine	1.20 (t, CH_3); 3.14 (q, CH_2)	−12.20	C, 23.55 (23.44); H, 4.28 (4.34); N, 1.42 (1.40)
POM−triphenylphosphine		−12.59; 21.72[d]	

[a] The peaks of the POM-amine adducts are all shifted upfield compared with the peaks of the amine. In some cases, peaks in the aliphatic region are poorly resolved due to their overlap with peaks of the tetrahexylammonium moiety. The peaks of the tetrahexylammonium moiety have not been noted for clarity; they appear at (δ) 0.86 (t, CH_3), 1.28 (m, $CH_2CH_2CH_2$), 1.56 (m, *CH*$_2CH_2N^+$), and 3.16 (t, CH_2N^+). [b] Satellite peaks from ^{119}Sn are observed. [c] The peak at 3.85 ppm is for the minor compound and that at 4.07 is for the major compound. [d] The peak at 21.72 ppm is from the attached Ph_3P moiety. Note the strong upfield shift from −6.28 ppm for Ph_3P alone.

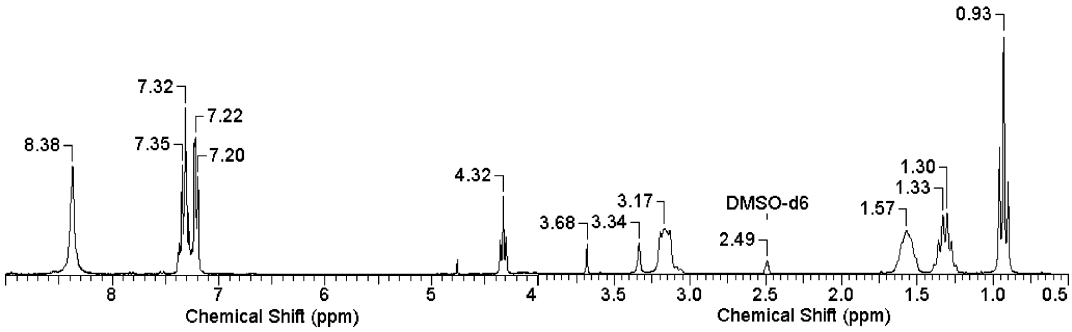


Figure 6. ^{1}H NMR spectrum of $Q_3HSn(Cl)PW_{11}O_{39}$−L-phemethyl ester. The peaks at >4 ppm are enlarged to aid in the visualization of the spectrum. The true integration shows the formation of a 1:1 adduct.

Experimental Section

Instruments and Techniques of Measurement. The ^{1}H NMR (400 MHz), ^{13}C NMR (100.613 MHz), ^{31}P NMR (101.271 MHz), ^{119}Sn NMR (149.211 MHz), ^{15}N NMR (40.545 MHz), and ^{183}W NMR (16.671 MHz) spectra were measured on a Bruker Avance 400 spectrometer in DMSO-d_6. The 2D HMBC NMR (^3J ^{119}Sn−^{1}H) (186.388 and 500.132 MHz) spectrum was measured on a Bruker AV- 500 spectrometer. The chemical shifts are reported with tetramethylsilane as the reference for ^{1}H NMR and ^{13}C NMR, 85% H_3PO_4 in D_2O as the external reference for ^{31}P NMR, 50% $Sn(CH_3)_4$ in $CDCl_3$ for as the external reference for ^{119}Sn NMR, liquid ammonia and nitromethane as the external reference for ^{15}N NMR, and 1 M Na_2WO_4 in D_2O as the external reference for ^{183}W NMR. The IR spectra were measured on a Nicolet Protegé 460 FTIR; solid samples were prepared as ∼3−5 wt % KBr-based pellets.

Materials and Synthesis. The commercial reagents (Aldrich, Fluka, Strem) used were of the highest available purity. **$Q_3H_4PW_{11}O_{39}$.** The tetrahexyl (Q = (*n*-hexyl)$_4N^+$) ammonium salt of the polyoxometalate, $Q_3H_4PW_{11}O_{39}$, was synthesized based on a known procedure.[6] Thus, 13.31 g (4 mmol) of the commercially available phosphotungstic acid, $H_3PW_{12}O_{40}{\cdot}xH_2O$, was dissolved in a beaker containing 40 mL of deionized water and equipped with a stirring bar and pH meter. The pH was adjusted to 4.80 by slowly adding a suspension of Li_2CO_3 in water and waiting for the solution to clear. Stirring was continued for another hour at room temperature. After 18 g (41.5 mmol) of tetrahexyl ammonium bromide salt was added in one portion, a separate oily phase formed immediately. The stirring was stopped, and the oily phase was extracted and washed several times with deionized water. Acetonitrile was added to the beaker, and the clear solution was then evaporated to dryness; 21 g of highly viscous oil was obtained. ^{1}H NMR at 400 MHz (DMSO-d_6): δ 0.85 (t, 48H, CH_3), 1.27 (m, 96H, $CH_2CH_2CH_2$), 1.56 (m, 32H, CH_2), 3.18 (t, 32H, CH_2N^+). ^{31}P NMR at 101.271 MHz (DMSO-d_6): δ −11.68. IR (cm^{-1}): 503, 514, 593, 658, 704, 727, 805, 886, 966, 1056, 1080, 1383, 1467, 1482, 2860, 2929, 2956. Elemental Analysis: Found (Calcd) C, 22.97 (23.09); H, 4.30 (4.31); N, 1.17 (1.12).

$Q_3HSn(Cl)PW_{11}O_{39}$. The tin chloride-substituted polyoxometalate, $Q_3HSnClPW_{11}O_{39}$, was obtained based on a known procedure.[7] The highly viscous oil, $Q_3H_4PW_{11}O_{39}$ (21 g, 4 mmol) was dissolved in 150 mL of acetonitrile, and 4.5 mL of $SnCl_4$ (38.5 mmol) was added and the solution was stirred for 2 h. Deionized water (5 mL) was added, and then the solution was concentrated to approximately to $^1/_{10}$ of its volume. The crystalline precipitate was filtered and washed with ethanol and diethylether before drying in a desiccator. Twelve grams of dry product was obtained (71% yield). ^{1}H NMR at 400 MHz (DMSO-d_6): δ 0.85 (t, 48H, CH_3), 1.27 (m, 96H, CH_2-

CH_2CH_2), 1.56 (m, 32H, CH_2), 3.18 (t, 32H, CH_2N^+). ^{31}P NMR at 101.271 MHz (DMSO-d_6): δ −12.58 [$^2J(^{119}Sn-^{31}P) = 36.8$ Hz)]. ^{119}Sn NMR at 149.211 MHz (DMSO-d_6): δ −578.74 [$^2J(^{31}P-^{119}Sn) = 38$ Hz, $^2J(^{183}W-^{119}Sn) = 30$ Hz]. IR (cm^{-1}): 503, 510, 593, 730, 751, 810, 889, 955, 1052, 1091, 1144, 1381, 1467, 1484, 2857, 2934, 2958. Elemental Analysis: Found (Calcd) C, 23.76 (23.90); H, 4.38 (4.54); N, 1.42 (1.40).

General Procedure for the Reaction of $Q_3HSn(Cl)PW_{11}O_{39}$ with Amines. $Q_3HSn(Cl)PW_{11}O_{39}$ (0.5 g, 0.12 mmol) was dissolved in 20 mL of THF, 1.2 mmol (10 equiv) of the amine was added, and the turbid solution was stirred for few hours at room temperature before filtration. The filtered product was washed with THF, water, ethanol, and ether before drying in a desiccator. The isolating yields were in a range of 70−90%. In the reaction of $Q_3HSn(Cl)W_{11}PO_{39}$ with triphenylphosphine to obtain $Q_3HSn(Cl)W_{11}PO_{39}-PPh_3$, the yield was only 30%. The analytical results are presented in Tables 1 and 2 above.

General Procedure for the Reaction of $Q_3HSn(Cl)PW_{11}O_{39}$ with Amino Acid Derivatives. $Q_3HSn(Cl)PW_{11}O_{39}$ (0.25 g, 0.06 mmol) was dissolved in 2 mL of acetonitrile, and 0.6 mmol of the *t*-BOC amino acid derivative also dissolved in acetonitrile was then added to the solution that was stirred for 4 h at 70 °C. The solvent was then evaporated, and the product was washed with ethanol and ether before drying in a desiccator. The isolated yields of the polyoxometalate/amino acid were in a range of 70−90%.

$Q_3HSn(Cl)W_{11}PO_{39}$−L-Phenyalanine-Methyl Ester. This compound was prepared by reacting $Q_3HSn(Cl)PW_{11}O_{39}$ with L-*t*-BOC−NHCH(CH_2Ph)COOMe. ^1H NMR at 400 MHz (DMSO-d_6): δ 0.92 (t, 48H, CH_3), 1.28 (m, 32H, CH_2CH_3), 1.56 (m, 32H, CH_2), 3.06 (m, 2H, CH_2Ph), 3.16 (t, 32H, CH_2N^+), 3.68 (s, 3H, $COOCH_3$), 4.32 (t, 1H, CH), 7.20−7.35 (m, 5H, Ph), 8.38 (NH). ^{31}P NMR at 101.271 MHz (DMSO-d_6): δ −12.54.

$Q_3HSn(Cl)W_{11}PO_{39}$−L-Tyrosine-Benzyl Ester. This compound was prepared by reacting $^4Q_4SnClPW_{11}O_{39}$ with L-*t*-BOC−NHCH($CH_2$4-OHPh)$COOCH_2$Ph. ^1H NMR at 400 MHz (DMSO-d_6): δ 0.92 (t, 48H, CH_3), 1.28 (m, 32H, CH_2CH_3), 1.56 (m, 32H, CH_2), 2.90 (m, 2H, CH_2Ph), 3.16 (t, 32H, CH_2N^+), 4.1 (s, 3H, $COOCH_2$-Ph), 4.32 (t, 1H, CH), 5.11 (s, 1H, OH), 6.97, 7.15, 7.33−7.45 (10H, aromatics). ^{31}P NMR at 101.271 MHz (DMSO-d_6): δ −12.54.

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Supporting Information Available: CIF file of the crystal structure of $Q_3HSnClPW_{11}O_{39}-PhNH_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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