

Reactive N-Protonated Isocyanate Species Stabilized by Bis(μ -hydroxo)divanadium(IV)-Substituted Polyoxometalate**

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Polyoxometalates (POMs) are anionic nanosized metal oxide clusters that consist of early transition metals, and stimulate many current research activities in broad fields of science, such as catalysis, materials, and medicine, because their chemical properties, such as acidity and redox potential, can be finely tuned by constituent elements and counteranions.^[1] Especially, acidic forms of POMs are active catalysts in various reactions, and some of them have been industrially used.^[1b,i] Spectroscopic data indicate that POMs induce unique activities by stabilizing reaction intermediates, such as onium and carbenium ions.^[1c,h,i,2] However, to the best of our knowledge, isolated unstable organic cationic intermediates stabilized by POMs that exhibit catalytic activity have never been reported, and only one structurally determined O-alkylated POM has been reported.^[3]

Carbocations play an important role as highly reactive intermediates for electrophilic C–C bond-forming reactions, such as Friedel–Crafts alkylation and acylation, Mukaiyama aldol reaction, and Tsuji–Trost reaction.^[4,5] Isolation of such reactive species is quite difficult because of the instability, and their existence is usually confirmed by NMR and IR spectroscopy.^[6] π Conjugation and hyperconjugation contribute to stabilization of the reactive species. Bulky conjugated bases of superacids, such as trifluoromethane sulfonate (CF_3SO_3^-), tetrafluoroborate (BF_4^-), and carborate, can also stabilize carbocations with electrostatic and hydrogen-bonding interaction between the anionic and cationic moieties, thus enabling the determination of their structures by X-ray crystallography.^[4c,f,7]

Isocyanates are reactive heterocumulenes that show a variety of reactivities for dehydration, deoxygenation, insertion, oligomerization, and polymerization.^[8] Especially the N-protonated isocyanate cation is energetically favorable by theoretical calculation,^[8] whereas the O-protonated one has been proposed as an intermediate for Friedel–Crafts

acylation.^[8b] With regard to the protonated isocyanate cations, their isolation and structural determination have never been realized. Herein, we report the formation and isolation of the putative “N-protonated phenyl isocyanate species” by the reaction of a bis(μ -hydroxo)divanadium(IV)-substituted γ -Keggin-type POM, $(\text{TBA})_4[\gamma\text{-SiV}^{\text{IV}}_2\text{W}_{10}\text{O}_{36}(\mu\text{-OH})_4]$, with phenyl isocyanate.

The divanadium(IV)-substituted γ -Keggin-type POM was synthesized by the reaction of VOSO_4 with $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ in water, in which the pH value was adjusted to 4.8 with 0.1 M acetate buffer. Addition of TBABr resulted in formation of reddish brown powders. Recrystallization from a mixed solvent of 1,2-dichloroethane and toluene gave dark brown crystals in 28% yield. The IR spectrum of **1** showed $\nu(\text{O-H})$ vibration bands at 3628 and 3566 cm^{-1} and $\nu(\text{V=O})$ vibration bands at 1007 and 962 cm^{-1} (see Figure S9 in the Supporting Information). Cold-spray ionization mass spectroscopy (CSI-MS) showed the parent signal centered at m/z 3824.22, in agreement with $\{(\text{TBA})_5\text{H}_4[\gamma\text{-SiV}_2\text{W}_{10}\text{O}_{40}]\}^+$ (centered at m/z 3824.62; Figure S11). The ^{29}Si and ^{51}V NMR spectra in CD_3CN did not exhibit any signals, suggesting the paramagnetic $d^1(\text{V}^{\text{IV}})$ - $d^1(\text{V}^{\text{IV}})$ high spin state in **1** (Figure S10). The magnetic susceptibility of **1** was 3.011(4) μ_B at 300 K, thus supporting the idea (Figure S24).

The molecular structure of **1** was successfully determined by single-crystal X-ray crystallography (see Figure 1a, and Tables S1 and S2 in the Supporting Information). Compound **1** was identified as $(\text{TBA})_4[\gamma\text{-SiV}^{\text{IV}}_2\text{W}_{10}\text{O}_{36}(\mu\text{-OH})_4]$, which contains a $\text{V}^{\text{IV}}_2(\mu\text{-OH})_2$ diamond core, in which the γ -Keggin framework was maintained by introduction of vanadium(IV) moieties. Four TBA cations per anion were observed. The bond-valence sum (BVS) values for O(113), O(114), O(126), and O(128) were 1.22, 1.21, 1.25, and 1.25, respectively, suggesting that these oxygen atoms are monoprotonated and two protons are generated on W–O–W bridging oxygen atoms (O(126) and O(128)) on introduction of two V^{IV} atoms (Table S3).^[9] The BVS values for the other bridging and terminal oxygen atoms were 1.70–2.06 and 1.59–2.00, respectively, suggesting that the valences are –2. The BVS values for Si (3.93), V (4.18 and 3.96), and W (5.64–6.42) suggest that the respective valences are +4, +4, and +6. All the data show formation of $(\text{TBA})_4[\gamma\text{-SiV}^{\text{IV}}_2\text{W}_{10}\text{O}_{36}(\mu\text{-OH})_4]$.

The V...V (3.101(5) Å), V=O (1.605(17) and 1.64(2) Å), and V–O(–V) (1.95(2)–2.01(2) Å) distances in **1** were similar to those in the vanadium(V) derivative, $(\text{TBA})_4[\gamma\text{-SiV}^{\text{V}}_2\text{W}_{10}\text{O}_{36}(\mu\text{-OH})_2]$ (**1'**; 3.096(3), 1.631(14), and 1.577(14), and 1.957(13)–1.980(12) Å). On the other hand, the V...O(–Si) distances in **1** were 2.90(1) and 2.91(1) Å and much longer than those in **1'** (2.511(12) and 2.531(11) Å; Table S2).^[10] Therefore, the interaction between the diamond core and

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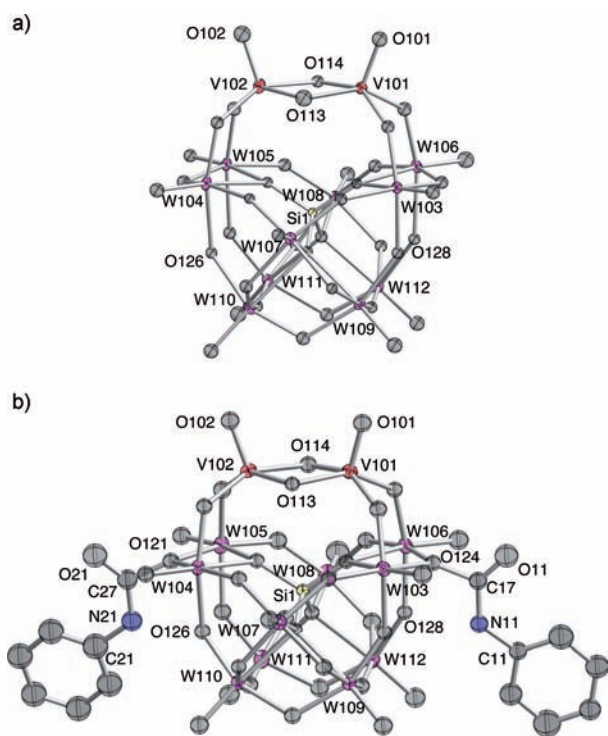


Figure 1. Thermal ellipsoid plots of a) $(\text{TBA})_4[\gamma\text{-SiW}_{10}\text{O}_{36}(\mu\text{-OH})_4]$ **1**, and b) $(\text{TBA})_4[\gamma\text{-SiW}_{10}\text{O}_{38}(\mu\text{-OH})_2(\text{PhNHCO})_2]$ **2**, drawn at 50% probability level (TBA cations were omitted for clarity).

the $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ fragment in **1** is weaker than that in **1'**, probably because of the Jahn–Teller effect, which is characteristic of d^1 transition-metal complexes.^[11] The $\text{W}(104)\text{--O}(126)$ and $\text{W}(106)\text{--O}(128)$ distances were 2.163(13) and 2.185(13) Å, respectively, and thus longer than the others, because of monoprotection at O(126) and O(128).

Next, the reactivity of **1** with phenyl isocyanate was investigated. Compound **1** was dissolved in a mixed solvent of acetone and 1,2-dichloroethane containing an excess amount of phenyl isocyanate. Keeping the reaction solution for one day gave dark brown crystals **2** in 71 % yield. The IR spectrum of **2** showed strong bands at 3335, 1736, 1597, and 1537 cm^{-1} , which are assignable to $\nu(\text{N--H})$,^[12] $\nu(\text{C=O})$, $\nu(\text{C=N})$, and $\nu(\text{C=C})$ vibration modes, respectively, suggesting the existence of a phenyl isocyanate moiety (Figure S12). The ^1H NMR spectrum of **2** was measured (Figure S13). Just after dissolution of **2** in CD_3CN , four broad signals of the phenyl isocyanate species were observed at $\delta = 8.77$, 7.70, 7.40, and 7.03 ppm with the respective integration ratio of 1:2:2:1.^[14] Generally, the protons of alcohols have been observed in the range of $\delta = 4\text{--}5$ ppm, whereas those of imines and amides have been observed in the range of $\delta = 8\text{--}9.5$ ppm. For example, the NH protons of N,N' -diphenylurea were observed at $\delta = 8.66$ ppm in $[\text{D}]_6\text{DMSO}$.^[10] Therefore, the ^1H NMR signal at $\delta = 8.77$ ppm is assignable to the NH moiety and those at $\delta = 7.70$, 7.40, and 7.03 ppm are assignable to the *o*-, *m*-, and *p*- C_6H_5 moieties, respectively. In addition, the $^{13}\text{C}\{^1\text{H}\}$ NMR signals of CO ($\delta = 148.86$ ppm)^[15] and Ph ($\delta = 130.27$, 130.15, 126.76, and 119.38 ppm) were observed (Figure S14). The CSI-MS spectrum of **2** also

showed the parent signal centered at m/z 4062.27, in agreement with $\{(\text{TBA})_5\text{H}_4[\text{SiV}_2\text{W}_{10}\text{O}_{40}(\text{C}_6\text{H}_5\text{NCO})_2]\}^+$ (centered at m/z 4062.70), thus supporting the idea (Figure S16). All these NMR and CSI-MS results support the existence of the phenylisocyanate moiety.

On the other hand, no signals were observed in ^{29}Si and ^{51}V NMR spectra because of the paramagnetic nature of **2** (Figure S15).^[16] The magnetic susceptibility of **2** was 2.527(4) μ_B at 300 K. These results indicate the retention of valence of vanadium centers as +4 (Figure S25).

The molecular structure of **2** was successfully determined by single-crystal X-ray crystallography (see Figure 1 b, and Figure S2 and Tables S1 and S2 in the Supporting Information). Four TBA cations per anion were observed. The BVS values for O(113) (1.30) and O(114) (1.25) indicate that these oxygen atoms are monoprotected. No proton was observed on O(126) and O(128), respectively, thus suggesting the reaction of two protons on O(126) and O(128) in **1** with phenyl isocyanate (Table S4). The BVS values of the other bridging and terminal oxygen atoms were 1.73–2.09 and 1.46–1.86, respectively, suggesting that the valences of these oxygen atoms are -2 . Therefore, the valences of O(126) and O(128) in **2** were decreased to -2 by the deprotection of **1**. The $\text{W}(104)\text{--O}(126)$ (2.010(13) Å), $\text{W}(110)\text{--O}(126)$ (1.873(13) Å), $\text{W}(106)\text{--O}(128)$ (1.996(12) Å), and $\text{W}(112)\text{--O}(128)$ (1.882(12) Å) distances were shortened, thus supporting the idea. The $\text{N}(11)\text{--O}(128)$ and $\text{N}(21)\text{--O}(126)$ distances in **2** were 2.885 and 2.839 Å, respectively, suggesting the hydrogen-bonding interaction between the phenylisocyanate species and the POM.

We next focused on the organic moieties depicted in Figure 2, and Figure S3 in the Supporting Information. The $\text{C}(11)\text{--N}(11)$ distance (1.41(2) Å) and $\text{C}(11)\text{--N}(11)\text{--C}(17)$ angle ($125.9(18)^\circ$) of the N-protonated phenylisocyanate species in **2** show the single bond and bent characters, respectively. The IR band of N–H stretching vibration and ^1H NMR signal of NH of the N-protonated phenylisocyanate species were observed at 3335 cm^{-1} and $\delta = 8.77$ ppm, respec-

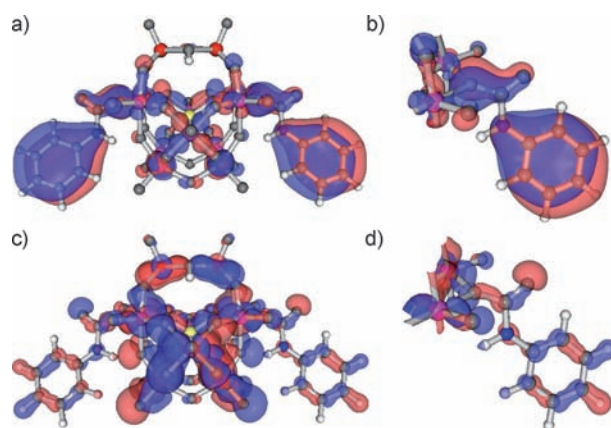


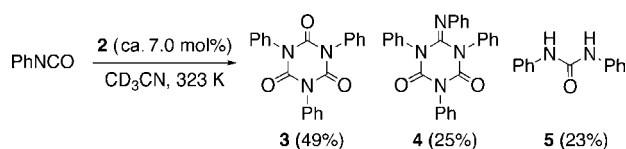
Figure 2. Representative molecular orbitals illustrating interaction between the N-protonated phenyl isocyanate and POM in **2** (isosurface value 0.01), a) $\alpha(212)$ orbital, b) $\alpha(212)$ orbital with emphasis on cationic moiety, c) $\alpha(210)$ orbital, and d) $\alpha(210)$ orbital with emphasis on cationic moiety.^[17]

tively. The DFT calculation showed that the N-protonated cation is by 31.13 kJ mol⁻¹ more stable than the O-protonated one (Figure S8).^[18] All these results show that protonation takes place at the N atom of the phenyl isocyanate. Two protons at O(126) and O(128) in **1** probably transfer to the N atoms of phenyl isocyanates in close proximity to O(126) and O(128) in **2**.

The C(17)–O(11) and C(17)–N(11) distances were 1.20(3) and 1.33(3) Å, respectively, exhibiting double bond characters, whereas the C(17)–O(124) distance was 1.44(3) Å and thus much longer than the C(17)–O(11) distance. DFT calculation of the anionic part of **2** also supports the hypothesis of the interaction between the N-protonated phenyl isocyanate cation and POM. The representative orbitals $\alpha(212)$ and $\alpha(210)$ prove that the C(17)–O(124) bond mainly consists of the polar π interaction (electrostatic attraction; coefficients of p_y orbitals (0.035 for C(17) and 0.113 for O(124)) with slight contribution of the σ bond (coefficients of p_x orbitals (0.047 for C(17) and –0.046 for O(124))).^[19] The Mulliken charge of the carbonyl group (0.809) in the N-protonated phenyl isocyanate species was almost the same as that without the POM (0.827), thus supporting the idea that the interaction between O(124) and C(17) is weak (Table S6). N(11)–C(17)–O(124), O(11)–C(17)–O(124) and O(11)–C(17)–N(11) angles were 111.5(18), 117(2), and 132(2)°, respectively, and the sum of these angles was approximately 360°. The W(103)–O(124) and W(106)–O(124) distances were 2.101(13) and 2.118(13) Å, respectively, and longer than those of the other W–O(W) bonds (1.855(15)–2.010(13) Å). These facts show that N(11), C(11), O(11), and C(17) atoms are placed in the same plane by the localization of the π electrons along the OCNC moiety. In addition, N(11)···O(128) and N(21)···O(126) distances were 2.885 and 2.839 Å, respectively, suggesting the presence of the hydrogen-bonding interaction, which would stabilize the N-protonated phenylisocyanate species. All the results lead to the conclusion that compound **2** is assignable to (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₈(μ -OH)₂(PhNHCO)₂], which is the first example of isolation and stabilization of the N-protonated phenyl isocyanate species by using the bulky POM.^[23]

The reaction of **1** with phenyl isocyanate at room temperature for about three months produced 1,3,5-triphenylisocyanurate (**3**)^[20] and **2**. In addition, compound **1** catalyzed cyclotrimerization of phenyl isocyanate to form **3** in 39% yield at 333 K. Compound **2** catalyzed the same reaction at the lower temperature of 323 K to form **3** and 2-(phenylimino)-1,3,5-triphenylhexahydro-s-triazine-4,6-dione (**4**)^[21] in 49% and 25% yields, respectively (mole of products **3** + **4**/mole of catalyst = 3.3; see Scheme 1, and Figures S17–S23 in the Supporting Information). All these results show that the N-protonated phenyl isocyanate in **2** is the intermediate for the catalysis.^[22]

In conclusion, the novel bis(μ -hydroxo)divanadium(IV)-substituted POM, (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₆(μ -OH)₄] (**1**) was synthesized and fully characterized by IR and CSI-MS spectroscopy and X-ray crystallography. Two protons at W–O–W bridging oxygen reacted with two phenyl isocyanate molecules to form (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₈(μ -OH)₂(PhNHCO)₂] (**2**) with the theoretically proposed N-proton-



Scheme 1. Cyclotrimerization of phenyl isocyanate catalyzed by **2** (yields in parentheses are those of isolated products). *N,N'*-diphenylurea would be formed by hydration and decomposition of phenyl isocyanate.^[8c]

ated phenyl isocyanate species. This species weakly interacted with the bridging oxygen atoms of the POM through the polar π interaction mainly contributing from the POM with small contribution of the σ bond as well as the hydrogen-bonding interaction. Compound **2** catalyzed the cyclotrimerization of phenyl isocyanate to produce 1,3,5-triphenylisocyanurate (**3**) and 2-(phenylimino)-1,3,5-triphenylhexahydro-s-triazine-4,6-dione (**4**).

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- [1] a) Thematic issues on polyoxometalate: *Chem. Rev.* (Ed.: C. L. Hill) **1998**, 98, 1; b) *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T. Yamase, M. T. Pope), Kluwer, Dordrecht, The Netherlands, **2002**; c) *Catalysts for Fine Chemical and Synthesis. Catalysis by Polyoxometalates 2* (Ed.: I. V. Kozhevnikov), Wiley, Chichester, UK, **2002**; d) M. T. Pope, *Comprehensive Coordination Chemistry II*, Vol. 4 (Eds.: A. G. Wedd, J. A. McCleverty, T. J. Meyer), Elsevier, New York, **2004**, pp. 635; e) C. L. Hill, *Comprehensive Coordination Chemistry II*, Vol. 4 (Eds.: A. G. Wedd, J. A. McCleverty, T. J. Meyer), Elsevier, New York, **2004**, p. 679; f) R. Neumann, *Modern Oxidation Methods* (Ed.: J. E. Backvall), Wiley-VCH, Weinheim, **2004**, p. 223; g) B. S. Bassil, U. Kortz, *Dalton Trans.* **2011**, 40, 9649–9661; h) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, 41, 113–252; i) *Zeolite, Clay, and Heteropoly Acid in Organic Reactions* (Eds.: Y. Izumi, K. Urabe, A. Onaka), Kodansha, Tokyo, **1992**.
- [2] a) J. Macht, M. J. Janik, M. Neurock, E. Iglesia, *J. Am. Chem. Soc.* **2008**, 130, 10369–10379; b) J. Macht, M. J. Janik, M. Neurock, E. Iglesia, *Angew. Chem.* **2007**, 119, 8010–8014; *Angew. Chem. Int. Ed.* **2007**, 46, 7864–7868.
- [3] W. H. Knoch, R. L. Harlow, *J. Am. Chem. Soc.* **1981**, 103, 4265–4266.
- [4] a) *Carbocation Chemistry* (Eds.: G. A. Olah, G. K. S. Prakash), Wiley Interscience, New York, **2004**; b) G. A. Olah, *J. Org. Chem.* **2001**, 66, 5944–5957; c) T. Laube, *Chem. Rev.* **1998**, 98, 1277–1312; d) T. Laube, *Acc. Chem. Res.* **1995**, 28, 399–405; e) H. Grützmaier, C. M. Marchand, *Coord. Chem. Rev.* **1997**, 163, 287–344; f) C. A. Reed, *Acc. Chem. Res.* **2010**, 43, 121–128.
- [5] a) M. Bochmann, *Acc. Chem. Res.* **2010**, 43, 1267–1278; b) P. G. Cozzi, F. Benfatti, *Angew. Chem.* **2010**, 122, 264–267; *Angew. Chem. Int. Ed.* **2010**, 49, 256–259; c) T. Laube, *Angew. Chem.*

- 1996, 108, 2939–2940; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 2765–2766.
- [6] a) H. Alvaro Galué, J. Oomens, *Angew. Chem.* **2011**, 123, 7142–7145; *Angew. Chem. Int. Ed.* **2011**, 50, 7004–7007; b) E. Stavitski, E. A. Pidko, M. H. F. Kox, E. J. M. Hensen, R. A. van Santen, B. M. Weckhuysen, *Chem. Eur. J.* **2010**, 16, 9340–9348; c) M. H. F. Kox, E. Stavitski, J. C. Groen, J. Pérez-Rmírez, F. Kapteijn, B. M. Weckhuysen, *Chem. Eur. J.* **2008**, 14, 1718–1725; d) M. J. Truitt, S. S. Toporek, R. Rovira-Truitt, J. L. White, *J. Am. Chem. Soc.* **2006**, 128, 1847–1852; e) M. Winkler, W. Sander, *Angew. Chem.* **2000**, 112, 2091–2094; *Angew. Chem. Int. Ed.* **2000**, 39, 2014–2016; f) R. D. Bolskar, R. S. Mathur, C. A. Reed, *J. Am. Chem. Soc.* **1996**, 118, 13093–13094.
- [7] a) C. Douvris, E. S. Stoyanov, F. S. Tham, C. A. Reed, *Chem. Commun.* **2007**, 1145–1147; b) M. G. Davlieva, S. V. Lindeman, I. S. Neretin, J. K. Kochi, *J. Org. Chem.* **2005**, 70, 4013–4021; c) S. V. Lindeman, I. S. Neretin, M. G. Davlieva, J. K. Kochi, *J. Org. Chem.* **2005**, 70, 3263–3266; d) T. Kato, C. A. Reed, *Angew. Chem.* **2004**, 116, 2968–2971; *Angew. Chem. Int. Ed.* **2004**, 43, 2908–2911; e) H. Kawai, T. Nagasu, T. Takeda, K. Fujiwara, T. Tsuji, M. Ohkita, J. Nishida, T. Suzuki, *Tetrahedron Lett.* **2004**, 45, 4553–4558; f) C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller, P. D. W. Boyd, *J. Am. Chem. Soc.* **2003**, 125, 1796–1804; g) M. Schormann, S. Garratt, D. L. Hughes, J. C. Green, M. Bochmann, *J. Am. Chem. Soc.* **2002**, 124, 11266–11267; h) S. Hollenstein, T. Laube, *J. Am. Chem. Soc.* **1993**, 115, 7240–7245; i) E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Chem. Soc. Chem. Commun.* **1991**, 841–842.
- [8] a) S. Ozaki, *Chem. Rev.* **1972**, 72, 457–496; b) G. A. Olah, J. Nishimura, P. Kreienbühl, *J. Am. Chem. Soc.* **1973**, 95, 7672–7680; c) E. A. Castro, R. D. Moodie, P. J. Sansom, *J. Chem. Soc. Perkin Trans. 2* **1985**, 737–741; d) K. R. Birdwhistell, T. Boucher, M. Ensminger, S. Harris, M. Johnson, S. Toporek, *Organometallics* **1993**, 12, 1023–1025; e) J. Louie, *Curr. Org. Chem.* **2005**, 9, 605–623; f) A. Antiñolo, S. García-Yuste, A. Otero, E. Villaseñor, *J. Organomet. Chem.* **2007**, 692, 4436–4447; g) W. Darwish, E. Seilel, R. Käsmarker, K. Harms, J. Sundermeyer, *Dalton Trans.* **2011**, 40, 1787–1794; h) S. R. Dubberley, A. Friedrich, D. A. Willman, P. Mountford, U. Radius, *Chem. Eur. J.* **2003**, 9, 3634–3654; i) E. B. Brouwer, P. Legzdins, S. J. Rettig, K. Ross, *Organometallics* **1993**, 12, 4234–4240; j) Z. Karpas, W. J. Stevens, T. J. Buckley, R. Metz, *J. Phys. Chem.* **1985**, 89, 5274–5278; k) The *O*-silylated isocyanate cation [(TMS)NCO(TMS)]⁺ has been isolated: A. Schulz, A. Vilinger, *Chem. Eur. J.* **2010**, 16, 7276–7281.
- [9] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, 47, 192–197.
- [10] K. Uehara, N. Mizuno, *J. Am. Chem. Soc.* **2011**, 133, 1622–1625.
- [11] a) A. Ozarowski, D. Reinen, *Inorg. Chem.* **1986**, 25, 1704–1708; b) P. L. W. Tregenna-Piggott, H.-P. Andres, G. J. McIntyre, S. P. Best, C. C. Wilson, J. A. Cowan, *Inorg. Chem.* **2003**, 42, 1350–1365; c) H. Henke, *Z. Kristallogr.* **2003**, 218, 617–625.
- [12] A new IR band appeared at 3335 cm⁻¹ upon transformation from **1** to **2**. Generally, the N–H stretching vibration bands have been observed in the range of 3200–3500 cm⁻¹.^[13] In addition, the frequency calculation of the anionic moiety of **2** also shows that the strong asymmetric and very weak symmetric N–H vibration bands appear at 3410 and 3412 cm⁻¹, respectively (without any corrections). Therefore, the band observed at 3335 cm⁻¹ in **2** is assigned to the N–H stretching vibration mode.
- [13] a) *Spectroscopic Identification of Organic Compounds* (Eds.: R. M. Silverstein, G. C. Bassler, T. C. Morrill), Wiley, New York, **1991**; b) *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Ed: K. Nakamoto), Wiley, New York, **1978**.
- [14] The signals gradually weakened and new signals of phenyl isocyanate (not impurity) appeared. After 6 h, the signal intensity ratio of *N*-protonated phenyl isocyanate species/phenyl isocyanate was 1:9.
- [15] a) G. K. Surya, G. Rasul, G. A. Olah, *J. Phys. Chem.* **1996**, 100, 15805–15809; b) M. G. Davlieva, S. V. Lindeman, I. S. Neretin, J. K. Kochi, *New J. Chem.* **2004**, 28, 1568–1574; c) G. A. Olah, A. M. White, *J. Am. Chem. Soc.* **1967**, 89, 7072–7075.
- [16] The ¹H and ¹³C{H} NMR spectra of TBA in **1** showed peak broadening as a result of the paramagnetic effect by V^{IV} in the POM framework. The ¹H and ¹³C{H} NMR spectra of TBA and phenyl isocyanate species in **2** also showed peak broadening. Since TBA in **1** and TBA and *N*-protonated phenyl isocyanate species in **2** are not included in the paramagnetic POM framework, the effect is weak and their signals are observed. A similar peak broadening was observed for TBA in TBA₄H₂[γ-SiW₁₀O₃₆Cu^{II}(μ-1,1-N₃)₂] (3.15, 1.64, 1.43, 0.99 ppm in CD₃CN), thus supporting the idea.
- [17] Molecular visualization program: U. Varetto, Molekel 5.4, Swiss National Supercomputing Centre (CSCS), Lugano (Switzerland).
- [18] M. J. Frisch, et al., Gaussian 09, Revision B.01 (Gaussian, Inc., Wallingford CT, **2009**).
- [19] a) E. V. Feshina, V. P. Feshin, *Russ. J. Gen. Chem.* **2006**, 76, 970–973; b) V. P. Feshin, E. V. Feshina, *Russ. J. Gen. Chem.* **2006**, 76, 966–969.
- [20] a) M. Roman, B. Andrioletti, M. Lemaire, J.-M. Bernard, J. Schwartz, P. Barbeau, *Tetrahedron* **2011**, 67, 1506–1510; b) F. Paul, S. Moulin, O. Piechaczyk, P. L. Floch, J. A. Osborn, *J. Am. Chem. Soc.* **2007**, 129, 7294–7304; c) Z. Puzsai, G. Vlád, A. Bodor, I. T. Horváth, H. J. Laas, R. Halpaap, F. U. Richter, *Angew. Chem.* **2006**, 118, 113–116; *Angew. Chem. Int. Ed.* **2006**, 45, 107–111; d) Y. Li, H. Matsumura, M. Yamanaka, T. Takahashi, *Tetrahedron* **2004**, 60, 1393–1400; e) H. A. Duong, M. J. Cross, J. Louie, *Org. Lett.* **2004**, 6, 4679–4681; f) S. R. Foley, G. P. A. Yap, D. S. Richeson, *Organometallics* **1999**, 18, 4700–4705; g) J.-S. Tang, J. G. Verkade, *Angew. Chem.* **1993**, 105, 934–936; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 896–898; h) Y. Nambu, T. Endo, *J. Org. Chem.* **1993**, 58, 1932–1934; i) R. J. P. Corriu, G. F. Lanneau, V. D. Mehta, *Heteroat. Chem.* **1991**, 2, 461–463; j) Y. Taguchi, I. Shibuya, M. Yasumoto, T. Tsuchiya, K. Yonemoto, *Bull. Chem. Soc. Jpn.* **1990**, 63, 3486–3489.
- [21] a) F. U. Richter, *Chem. Eur. J.* **2009**, 15, 5200–5202; b) R. Richter, H. Ulrich, *J. Org. Chem.* **1981**, 46, 3011–3015.
- [22] No cyclotrimerization reactions occur using other polyoxometalates that contain protons, such as dry silicododecatungstic acid (H₄[α-SiW₁₂O₄₀]) and bis(μ-hydroxo)divanadium(V)-substituted polyoxometalate ((TBA)₄[γ-SiV₂W₁₀O₃₈(μ-OH)₂]) (**1'**), thus demonstrating the uniqueness of **1**.
- [23] Note added in proof (06.07.2012): We originally formulated the reactive species as a carbocation, however it has since been brought to our attention that certain characteristics of this species, such as the O(124)–C(17) bond length, could also be indicative of the species being a carbamate.