Polyoxometalates

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Cyanosilylation of Carbonyl Compounds with Trimethylsilyl Cyanide Catalyzed by an Yttrium-Pillared Silicotungstate Dimer**

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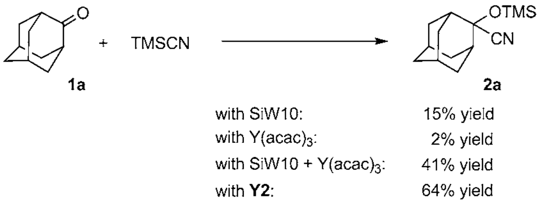
Cyanohydrins are a very important class of compounds in chemistry as well as biology, and have been widely utilized as important synthetic intermediates for organic compounds, such as α-hydroxy acids, α-hydroxy aldehydes, and β-amino alcohols.[1] For the synthesis of cyanohydrins, various cyanating reagents have been employed, and trimethylsilyl cyanide (TMSCN) is one of the most useful and safe cyanating reagents for nucleophilic addition to carbonyl compounds to give cyanohydrin trimethylsilyl ether.[1] Hence, the development of efficient catalysts for cyanosilylation of carbonyl compounds with TMSCN is a very important subject in current research, and several efficient catalysts have been developed so far.[2–4] Lewis acid catalysts can act as electrophilic catalysts to activate carbonyl compounds and have been extensively investigated for cyanosilylation (see Table S1 in the Supporting Information).[2,3] Several nucleophilic catalysts, such as amines, phosphines, phosphazanes, and alkaline-earth metal oxides, can activate TMSCN and promote cyanosilylation (Table S1).[2,3] Asymmetric cyanosilylations have also been successfully developed by employing customly designed chiral ligands.[4]

Polyoxometalates (POMs) are a large family of anionic metal–oxygen clusters that consist of Group V and VI metals in their highest oxidation states, and are thermally and oxidatively stable in comparison with commonly utilized organometallic catalysts and organocatalysts.[5] The chemical properties of POMs, for example, redox potentials, (multi)-electron-transfer properties, acidities, and solubilities, and negative charges, can be finely tuned by choosing the constituent anion and countercations, and diverse structures can be synthesized.[5] In addition to the above-mentioned properties, the important feature of POMs is the presence of bare nucleophilic surfaces as a result of external oxygen atoms (M−O−M and M=O species, M = W or Mo), which might act as nucleophilic sites as well as stabilizers of cationic intermediates.[5,6] In particular, it is expected that POMs with large negative charges can nucleophilically activate TMSCN, thus resulting in promotion of cyanosilylations, as observed for Lewis base catalyzed cyanosilylations.[2h,3h]

Initially, the cyanosilylation of 2-adamantanone (**1a**) with TMSCN was carried out with the −8-charged POM $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ (SiW10, TBA = tetra-*n*-butylammonium) in 1,2-dichloroethane at 30 °C. SiW10 promoted the cyanosilylation, giving the corresponding cyanohydrin trimethylsilyl ether **2a** in 15 % yield after 20 minutes (Scheme 1).[7] In the case of $TBA_4H_4[\alpha\text{-}SiW_{11}O_{39}]$ (SiW11), **2a** was also obtained in 16 % yield (Table S2). In the absence of the catalysts, cyanosilylation was not observed under the present conditions.



Scheme 1. Cyanosilylation of 2-adamantanone (**1a**) with TMSCN. Reaction conditions: catalyst (1 mol% for SiW10 and $Y(acac)_3$; 0.5 mol% for **Y2**), **1a** (0.5 mmol), TMSCN (molar ratio TMSCN/**1a** = 1.5:1), 1,2-dichloroethane (3 mL), 30 °C, 20 min.

The ^{13}C NMR spectrum of TMSCN in $[D_4]$1,2-dichloroethane (50 mM) showed a methyl signal at −1.95 ppm. Upon addition of one equivalent of SiW10 to the solution, the signal almost disappeared, and a new signal was observed at 1.01 ppm and assigned to the methyl groups of trimethylsilanol,[8] thus suggesting that SiW10 can nucleophilically activate TMSCN; trimethylsilanol is probably produced through the nucleophilic activation of TMSCN by SiW10, followed by the reaction with water (including in SiW10 and/or the solvent).[9] In addition, the positive-ion cold-spray ionization mass spectrometry (CSI-MS) analysis of a solution of SiW10 and TMSCN (molar ratio = 1:200) in 1,2-dichloroethane showed a set of signals centered at $m/z = 3947$ and corresponding to $[TBA_5TMS_4SiW_{10}O_{36}]^+$ (TMS = trimethylsilyl cation, Figure S1), also supporting the idea.

Although SiW10 could activate TMSCN and promote the cyanosilylation of **1a**, the activity was still very low. If carbonyl compounds are simultaneously activated at the neighboring electrophilic Lewis acid centers, reaction rates for cyanosilylation are increased by the synergetic effect. In

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order to investigate the simultaneous activation of both TMSCN and carbonyl compounds, we carried out the SiW10-catalyzed cyanosilylation of **1a** in the presence of various Al^{3+}, Sc^{3+}, Zn^{2+}, Y^{3+}, Zr^{4+}, Sn^{4+}, La^{3+}, Yb^{3+}, and Hf^{4+} salts as Lewis acids (Table S2).[10] Several rare-earth-metal salts were found to promote the cyanosilylation of **1a** effectively (Table S2). For example, addition of $Y(acac)_3$ (acac = acetylacetonato) to SiW10 increased the yield of **2a** from 15 % to 41 %, while the activity of $Y(acac)_3$ was almost negligible (2 % yield; Scheme 1). In contrast, such a positive effect of $Y(acac)_3$ was not observed for the SiW11-catalyzed cyanosilylation (Table S2). The positive-ion CSI-MS spectrum of a mixture of SiW10 and $Y(acac)_3$ in 1,2-dichloroethane exhibited several sets of signals. Among them, two main sets of signals centered at $m/z = 3745$ and 7283 were assignable to $[TBA_{10}H_2(SiYW_{10}O_{36})_2]^{2+}$ and $[TBA_9H_2(SiYW_{10}O_{36})_2(H_2O)_2]^{+}$, respectively (Figure S2 a). This result suggests that SiW10 reacts with $Y(acac)_3$ in situ to form an yttrium-containing POM $[(SiYW_{10}O_{36})_2]^{10-}$,[11] which would simultaneously activate both TMSCN and carbonyl compounds. These results led us to synthesize the yttrium-containing POM by employing $Y(acac)_3$ (as an yttrium source) and SiW10 (as an inorganic ligand).

The yttrium-containing POM **Y2** was successfully synthesized by the reaction of SiW10 with $Y(acac)_3$ (molar ratio = 1:1) in acetone (85 % yield based on SiW10, see the Supporting Information). The positive-ion CSI-MS spectrum of **Y2** in 1,2-dichloroethane exhibited only the set of signals that corresponds to the POM $[(SiYW_{10}O_{36})_2]^{10-}$ (Figure S2 b). The ^{29}Si NMR spectrum of a solution of **Y2** in $[D_4]$1,2-dichloroethane showed a signal at −82.1 ppm (Figure S3 a), thus suggesting that **Y2** is a single species in 1,2-dichloroethane. From the results of elemental analysis and thermogravimetry, the formula of **Y2** was determined to be $TBA_8H_2[(SiYW_{10}O_{36})_2]\cdot 7\,H_2O$.[12] Fortunately, single crystals of the yttrium-containing POM with the formula $TBA_6H_4[(SiYW_{10}O_{36})_2]\cdot 3\,(acetone)\cdot 6\,H_2O$ (**Y2′**)[12] suitable for X-ray crystallographic analysis were successfully obtained by recrystallization in a mixture of acetone and acetonitrile (see the Supporting Information). The ORTEP representation of the anion of **Y2′** is shown in Figure 1.[13]

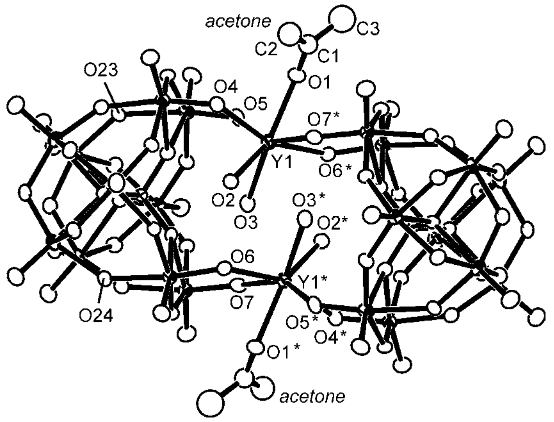


Figure 1. ORTEP representation of the anion part of **Y2′**. The thermal ellipsoids are shown at 50 % probability.

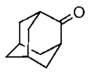
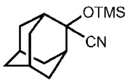
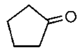
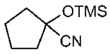
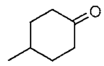
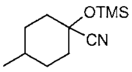
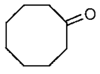
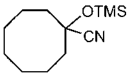
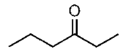
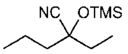
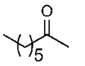
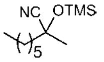
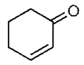
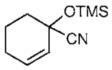
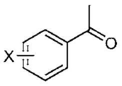
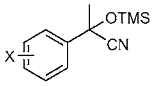
The bond-valence sum (BVS) values of silicon (3.85), tungsten (5.92–6.09), and yttrium (3.11) atoms in **Y2′** indicate that the respective valences are +4, +6, and +3. In addition, the oxygen atoms with relatively lower BVS values (1.13 and 1.14 for O23 and O24, respectively) were found in the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ framework, thus suggesting that protons are likely located on these oxygen atoms. The O2 (BVS = 0.36) and O3 (BVS = 0.39) atoms were oxygen atoms of water molecules (aqua ligands).

Yttrium-containing POM **Y2′** is a dimer of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ pillared by two yttrium atoms (Figure 1). Each yttrium atom in **Y2′** is heptacoordinated by one acetone molecule, two aqua ligands, and four terminal oxygen atoms of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ subunits. Most importantly, acetone molecules are coordinated to the yttrium centers in **Y2′**, thus suggesting that these sites might act as Lewis acidic centers to activate carbonyl compounds.[14] Each yttrium atom is located “out-of-pocket” without direct interaction with the internal SiO_4 tetrahedrons. The distances between oxygen atoms that are connected to yttrium atoms (O2 and O3) and nearest-neighbor oxygen atoms of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ framework are in the range of 2.71–2.96 Å (Table S3), thus suggesting the existence of hydrogen-bonding networks between these oxygen atoms.[15] Thus, the unique local structure around yttrium atoms is likely stabilized by the hydrogen-bonding networks. The slipped configuration of the dimer of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ is probably a result of the steric bulk of four aqua ligands located in the interior.[16]

To date, various yttrium-containing POMs have been reported,[17] e.g., $[YW_{10}O_{36}]^{9-}$, $[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]^{17-}$, $[\{Y(H_2O)\}_3(\beta\text{-}XW_9O_{34})CO_3]^{n-}$ (X = Ge, Si, As, and P, $n = 13$ and 12), $[Y(GeW_{11}O_{39})(H_2O)_2]^{5-}$, $[Y_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$, $[(PY_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$, $[Y(H_2O)P_5W_{30}O_{110}]^{12-}$, and $[\{Y_4(\mu_3\text{-}OH)_4(H_2O)_8\}(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$. To the best of our knowledge, yttrium-containing POMs with γ-Keggin frameworks have not been reported to date.

Finally, we investigated the catalytic property of **Y2** for cyanosilylation of carbonyl compounds with TMSCN.[18] The catalytic performance of **Y2** was higher than those of SiW10, $Y(acac)_3$, and a mixture of SiW10 and $Y(acac)_3$ (Scheme 1). In the presence of **Y2** (using only 1 mol %), several structurally diverse ketones could be converted into the corresponding cyanohydrin trimethylsilyl ethers, and desilylated products (cyanohydrins) were not formed in any of these cases (Table 1). The cyanosilylation of linear aliphatic ketones **1e** and **1f** proceeded smoothly and gave the corresponding cyanohydrin trimethylsilyl ethers in high yields. Sterically hindered aliphatic cyclic ketones, such as 2-adamantanone (**1a**) and cyclooctanone (**1d**), also reacted with TMSCN to afford the corresponding products in high yields, although the steric effect was very significant. Compound **2b** was selectively obtained in 89 % yield along with a small amount of **2d** (8 % yield) when the **Y2**-catalyzed competitive cyanosilylation of **1b** (C5, 0.25 mmol) and **1d** (C8, 0.25 mmol) with TMSCN (0.375 mmol) was carried out for 0.3 hours under the conditions shown in Table 1. Such a size-selective cyanosilylation might be caused by the steric hindrance around the active site(s).[19]

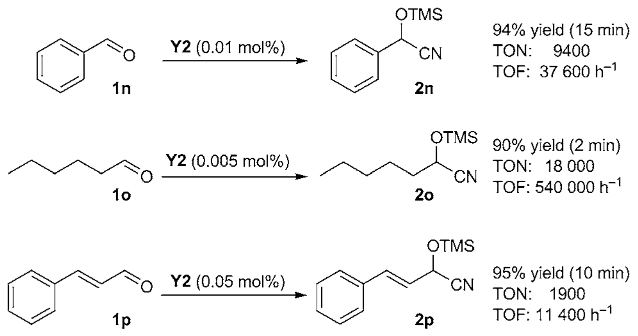
Table 1: Scope of the **Y2**-catalyzed cyanosilylation of ketones.[a]

Entry	Substrate		t [h]	Product		Yield [%]
1		**1a**	1.5		**2a**	91
2		**1b**	0.3		**2b**	90
3		**1c**	0.5		**2c**	97
4		**1d**	8		**2d**	80
5		**1e**	2		**2e**	83
6		**1f**	2		**2f**	93
7		**1g**	10		**2g**	59[b]
						
8	X=*p*-H	**1h**	3	X=*p*-H	**2h**	80
9	X=*p*-Me	**1i**	10	X=*p*-Me	**2i**	79
10	X=*o*-Me	**1j**	10	X=*o*-Me	**2j**	80
11	X=*p*-OMe	**1k**	20	X=*p*-OMe	**2k**	61
12	X=*p*-Cl	**1l**	2	X=*p*-Cl	**2l**	92
13	X=*p*-CN	**1m**	1	X=*p*-CN	**2m**	90

[a] Reaction conditions: **Y2** (1 mol%), ketone (0.25 mmol), TMSCN (molar ratio TMSCN/ketone = 1.5:1), 1,2-dichloroethane (1.5 mL), 30 °C. Yields were determined by GC analysis using naphthalene as an internal standard. [b] 1,4-Addition product (5% yield).

In the case of the α,β-unsaturated ketone 2-cyclohexen-1-one (**1g**), the 1,2-addition of TMSCN mainly took place to give 1-cyano-1-trimethylsilyl-2-cyclohexene (**2g**) in 59% yield along with a small amount of the 1,4-addition product (5% yield; Michael addition). Not only aliphatic ketones but also less reactive acetophenone derivatives (**1h**–**1m**) could be converted into the corresponding cyanohydrin trimethylsilyl ethers. The cyanosilylation of acetophenone derivatives with electron-withdrawing substituents (**1l** and **1m**) proceeded smoothly. In contrast, acetophenone derivatives with electron-donating substituents (**1i**–**1k**) required longer reaction times. The Hammett plot for the competitive cyanosilylation of *para*-substituted acetophenone derivatives gave the positive ρ value of $+1.92$ (Figure S4), thus suggesting that the nucleophilic attack of CN^- species to a carbonyl carbon atom is part of the rate-limiting step.

Notably, **Y2** showed extremely high catalytic activities for cyanosilylation of sterically less hindered aldehydes (in comparison with ketones). The cyanosilylation of benzaldehyde (**1n**) with 0.01 mol% of **Y2** gave **2n** in 94% yield after 15 minutes. In the case of *n*-hexanal (**1o**), the cyanosilylation proceeded very efficiently with only 0.005 mol% of **Y2**, the turnover frequency (TOF) was 540000 h^{-1}, and the turnover number (TON) reached 18000. The α,β-unsaturated aldehyde *trans*-cinnamaldehyde (**1p**) also selectively gave the corresponding cyanohydrin trimethylsilyl ether without formation of the 1,4-addition product. The TOF value for the **Y2**-catalyzed cyanosilylation of **1o** was the highest among previously reported values (Table S1).[2–4] Notably, when the **Y2**-catalyzed competitive cyanosilylation of aldehyde **1n** (0.25 mmol) and ketone **1h** (0.25 mmol) with TMSCN (0.375 mmol) and **Y2** (0.05 mol%) was carried out under the conditions shown in Scheme 2, **2n** was chemoselectively obtained in 97% yield in just one minute without formation of **2h**.



Scheme 2. Cyanosilylation of aldehydes. Reaction conditions: aldehyde (0.5 mmol for **1n** and **1o**, 0.25 mmol for **1p**), TMSCN (molar ratio TMSCN/aldehyde = 1.5:1), 1,2-dichloroetnane (0.5 mL), 25 °C.

A CSI-MS analysis showed that the structure of **Y2** was preserved after cyanosilylation (Figure S5). The isolation of the product and the recovery of the catalyst were very easy (see the Supporting Information). The IR spectrum of the recovered **Y2** was identical to that of the freshly prepared **Y2** (Figure S6). In addition, the recovered **Y2** could be reused for cyanosilylation without an appreciable loss of its high catalytic performance; for example, **2b** was obtained in 97% yield when recovered **Y2** was used.

The CSI-MS spectrum of a solution of **Y2** and TMSCN in 1,2-dichloroethane (molar ratio = 1:200) showed sets of signals centered at $m/z = 3834$, 7355, and 7427, which were assigned to $[TBA_{10}TMS_2(SiYW_{10}O_{36})_2(H_2O)_2]^{2+}$, $[TBA_9TMSH(SiYW_{10}O_{36})_2(H_2O)_2]^+$, and $[TBA_9TMS_2(SiYW_{10}O_{36})_2(H_2O)_2]^+$, respectively (Figure S7). In addition, the yttrium centers might act as Lewis acids to activate carbonyl compounds (Figure 1).[14] Therefore, it is likely that both TMSCN and carbonyl compounds are activated by surface oxygen atoms (nucleophilically) and the yttrium centers (electrophilically), respectively, thus resulting in coexistence of activated coupling partners on the same **Y2** molecules. Cyanosilylation would therefore be efficiently promoted by the presence of **Y2**. The above-mentioned size- and chemoselectivity of the cyanosilylation resulting from steric interactions also supports the hypothesis.

In conclusion, we successfully synthesized a novel yttrium-pillared silicotungstate dimer by the reaction of SiW10 with $Y(acac)_3$ in an organic medium (acetone). In the presence of **Y2**, cyanosilylation of several structurally diverse ketones and aldehydes with TMSCN selectively proceeded to afford the corresponding cyanohydrin trimethylsilyl ethers. In particular, the catalytic performance for aldehydes was very significant; for example, TON = 18000 and TOF = 540000 h^{-1} were observed for *n*-hexanal.

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Keywords: carbonyl compounds · cyanosilylation · polyoxometalate · trimethylsilyl cyanide · yttrium

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[7] The cyanosilylation of **1a** hardly proceeded in the presence of a −4-charged POM $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$ (Table S2).

[8] The formation of trimethylsilanol was also confirmed by GC-MS analysis of the solution.

[9] The formation of trimethylsilanol was hardly observed in the presence of excess amounts of carbonyl compounds (catalytic turnover conditions).

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[11] We have reported similar in situ prepared catalysts, such as $TBA_8[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2(\gamma\text{-}HSiW_{10}O_{36})_2]\cdot 9\,H_2O$ $(Zn(acac)_2 + SiW10)$[11a] and $TBA_8[Ag_4(DMSO)_2(\gamma\text{-}H_2SiW_{10}O_{36})_2]\cdot 2\,DMSO\cdot 2\,H_2O$ (AgOAc + SiW10) (DMSO = dimethyl sulfoxide, OAc = acetate):[11b] a) Y. Kikukawa, K. Yamaguchi, N. Mizuno, *Angew. Chem.* **2010**, *122*, 6232; *Angew. Chem. Int. Ed.* **2010**, *49*, 6096; b) Y. Kikukawa, Y. Kuroda, K. Yamaguchi, N. Mizuno, *Angew. Chem.* **2012**, DOI: 10.1002/ange.201108371; *Angew. Chem. Int. Ed.* **2012**, DOI: 10.1002/anie.201108371.

[12] The IR spectrum of **Y2** was very similar to that of **Y2’** (Figure S8). Although the complete structural determination of **Y2** by X-ray crystallographic analysis has so far been unsuccessful because of the severe disorder around the yttrium centers and TBA molecules, **Y2** was determined to be a dimer of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ pillared by two yttrium atoms, and the structure was almost identical to that of **Y2′**. In addition, the positive-ion CSI-MS analysis of **Y2′** in acetonitrile showed only the sets of signals resulting from the POM $[(SiYW_{10}O_{36})_2]^{10-}$ (Figure S9). All these results show that the anion structures of **Y2** and **Y2′** are intrinsically identical, and the difference between them is the number of TBA cations.

[13] CCDC 860121 (compound **Y2′**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] The stretching vibration of the C=O bond of coordinated acetone molecules on the yttrium centers was observed at 1696 cm^{-1} (that of non-coordinated acetone: 1715 cm^{-1}), thus suggesting that acetone is electrophilically activated on the yttrium centers.

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[18] The scope of cyanosilylation of various ketones was examined with **Y2** (Table 1) because of the very low solubility of **Y2′** in 1,2-dichloroethane (below 0.05 mM). The cyanosilylation of aldehyde **1o** was carried out with **Y2′** (0.005 mol %) in 1,2-dichloro-

ethane under the conditions described in Scheme 2. Although **Y2′** was partially insoluble under this conditions, **2o** was obtained in 78% yield.

[19] Competitive cyanosilylations of **1b** and **1d** with Sc(OTf)$_3$ (OTf = triflate) and MgO were carried out under the same reaction conditions. In the case of Sc(OTf)$_3$, **2b** and **2d** were obtained in 70% and 27% yields, respectively. MgO selectively gave **2b** in 79% yield along with a small amount of **2d** (2% yield). The ratio of the yields of **2b** and **2d** with **Y2** (89/9) was much higher than that with the homogeneous catalyst Sc(OTf)$_3$ (70/27) and comparable to that with the heterogeneous catalyst MgO (79/2).