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Heterogeneous catalysis of a coordination network: cyanosilylation of imines catalyzed by a Cd(II)-(4,4′-bipyridine) square grid complex

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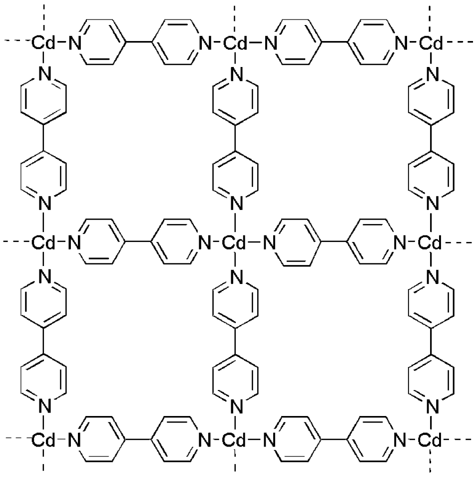
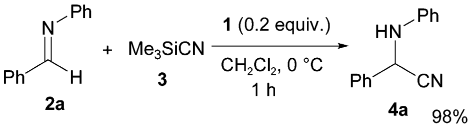
A coordination network prepared from $Cd(NO_3)_2$ and 4,4′-bipyridine (4,4′-bpy) catalyzed the cyanosilylation of imines under heterogeneous conditions.

The zeolite-like function of coordination networks with cavities and channels is most actively studied in recent years.[1] Organic enclathration,[2] ion exchange,[3] and reversible gas absorption,[4] which are often accompanied by study of the dynamic properties[5] of the networks, have been rapidly explored. Although catalysis by these zeolite-mimic materials is to be expected, there have appeared only a few reports on catalysis by coordination networks.[1a,6,7] In 1994, we reported that a Cd(II)-(4,4′-bipyridine) square grid complex catalyses cyanosilylation of aldehydes.[1a] However, the mechanistic aspect of this reaction remains unclear. Here we extend this reaction to cyanosilylation of imines to discuss some mechanistic insights of the heterogeneous catalysis by the network complex. Synthetic utility is also emphasized.

The grid complex employed here has the composition of $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2](NO_3)_2\cdot 4H_2O\}_n$ (**1**).[1a,8] This complex is easily prepared as colorless crystals from $Cd(NO_3)_2$ and 4,4′-bpy (bpy = bipyridine) in a high yield. When powdered **1** (0.1 mmol) was suspended in CH_2Cl_2 solution (1.5 mL) of imine **2a** (0.5 mmol) and trimethylsilyl cyanide (**3**, 0.75 mmol) at 0 °C for 1 h, a smooth reaction took place and, after workup, aminonitrile **4a** was formed quantitatively (98% isolated yield) (eqn. (1)).



1 (NO_3^- counter ions omitted.)



(1)

The heterogeneous catalysis of **1** is evidenced by the following experiments. The cyanosilylation of CF_3-substituted imine (**2b**) was relatively slow due to the electronic effect of CF_3 group (as discussed later). Therefore, the conversion of this reaction was easily monitored by NMR. The solid line in Fig. 1 shows that the reaction completes in several hours. In a control experiment, the whole suspension was filtrated at 1 h (59% conversion) to remove solid **1**. Then the reaction was not promoted any more (Fig. 1, dashed line). The filtration of solid **1** at earlier stage (0.25 h, 21% conversion) also stopped the reaction (Fig. 1, dotted line). These results clearly show that soluble and catalytically active species are not eluted at all from the complex under the reaction conditions. Thus the reaction does proceed by the heterogeneous catalysis of the grid complexes.

In the crystal structure of **1**, the grid layers stack on each other in such a way that each Cd(II) center is located *ca.* 4.8 Å above the square cavity of the next layer [Fig. 2]. Thus the substrate, once accommodated in the square cavity, can easily coordinate to the Cd^{2+} center of the next layer. However, the complex took up no detectable amount of imines into the channels when the crystals of **1** were immersed in CH_2Cl_2 solution of the imines. We therefore suggest that active sites exist mainly around the surface of the solid **1**. We note that, given a surface-promoted reaction, the catalytic activity of **1** is remarkably high.

For comparison, we also examined organic soluble $Cd(Py_4)\cdot(NO_3)_2$ complex (**5**, Py = pyridine) that has the partial structure of **1** but does not possess an infinite framework. Surprisingly, despite moderate solubility in CH_2Cl_2, complex **5**

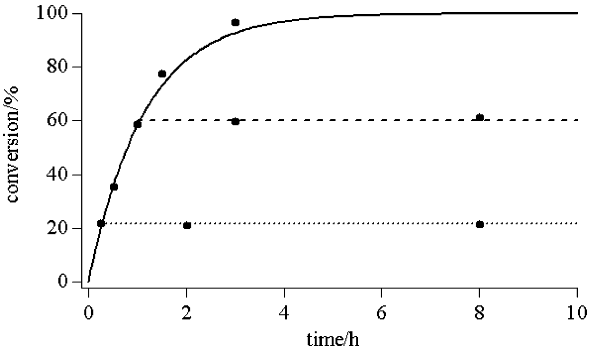


Fig. 1 The conversion of the cyanosilylation of CF_3-substituted imine (**2b**) determined by NMR: dot and dashed lines indicate the conversion after filtration of solid **1** at 0.25 h and 1 h, respectively.

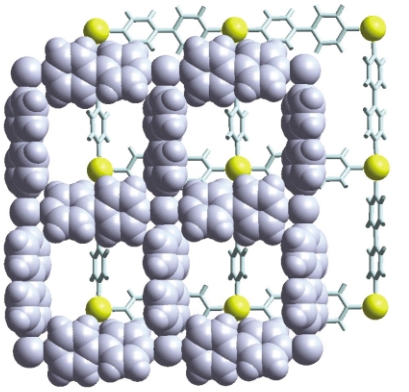


Fig. 2 Geometrical relationship between the two adjacent layers of **1**. Substrates accommodated in the square cavity of the first layer (space-filling) can interact with Lewis acidic Cd(II) center of the second layer (ball and stick) that locates 4.8 Å below (and above) the square cavities.

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promoted the reaction less effectively (85% at 1 h). This result suggests that hydrophobic grid cavities of **1** bind the substrate very efficiently to promote the rapid reaction.

Interestingly, $Cd(NO_3)_2 \cdot 4H_2O$ (suspension) poorly promoted the reaction under the same conditions. The difference in the catalytic activity is explained by comparing the crystal structures of **1**[8] and $Cd(NO_3)_2 \cdot 4H_2O$.[9] In **1**, the Cd(II) atom has hexacoordinate environment with pyridyl groups at the equatorial positions and two water molecules at the apical positions [Fig. 3(a)] and nitrate ions exist in the grid. Meanwhile, the Cd(II) atom in $Cd(NO_3)_2 \cdot 4H_2O$ has an octacoordinate environment with four water molecules at the equatorial positions and two nitrate ions at the apical positions [Fig. 3(b)]. As a result, the Cd(II) center of **1** is more cationic than that of $Cd(NO_3)_2 \cdot 4H_2O$ and the Lewis acidity increases.

The imine addition was compared with aldehyde addition to obtain some mechanistic insight. We found that the cyanosilylation of **2a** was much faster than that of benzaldehyde: the latter required higher temperature (30 °C) and prolonged reaction time (24 h) to obtain the adduct in 77% yield. A competition experiment sharply contrasted the difference in the reactivity of these substrates: when a 1:1 mixture of **2a** and benzaldehyde was treated with **3** at 0 °C for 24 h, only **4a** was formed and benzaldehyde remained unchanged. The higher reactivity of an imine over an aldehyde does not agree with the general understanding that a nucleophile preferentially attacks a more polar C=O group rather than a less polar C=N group under strong Lewis acidic conditions. In fact, **4a** adds aldehydes selectively in solution in the presence of $SnCl_4$ (a strong Lewis acid).[10] In the literature, the imine-selective addition of Me_3SiCN takes place only if the reaction is mediated by a lanthanoid Lewis acid such as $Yb(OTf)_3$ (catalytic amount) because the metal is selectively coordinated by the more electron-donating imino nitrogen. Thus, we conclude that the present heterogeneous reaction should involve the selective activation of imino nitrogen by the weak Lewis acidic Cd(II) center.

The present reaction is applicable to a variety of imine substrates (Table 1). Taking the advantage of the heterogeneous catalysis, the products are in most cases isolated quantitatively only by filtrating the catalyst. The reaction proceeds in 1–2 h at 0 °C except for the reaction of **2b** where the substrate is electron deficient. In this case, the electron-withdrawing CF_3 group weakens the Cd coordination of imino nitrogen in consistent with our proposed mechanism.

In summary, we found the heterogeneous catalysis of infinite grid complex **1** for cyanosilylation of imines. The incorporation of catalytic active metal centers in network complexes, particularly in porous complexes, provides a new strategy for designing solid catalyst at molecular level.

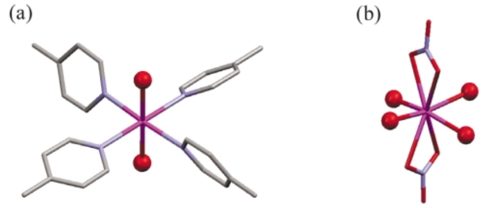

Fig. 3 Environment around Cd(II) ion in crystal structures of the square grid complex **1** and $Cd(NO_3)_2 \cdot 4H_2O$ (a) View around the Cd(II) ion of **1**. (b) View around the Cd(II) ion of $Cd(NO_3)_2 \cdot 4H_2O$ (Cd = purple, O = red, N = blue, C = grey).

Table 1 Reaction of imines with Me_3SiCN catalyzed by **1**

$R^1CH=NR^2$	Reaction time/h	Yield (%)[a]
PhCH=NPh (**2a**)	1	97
m-CH_3–C_6H_4CH=NPh	1	98
o-CH_3–C_6H_4CH=NPh	1.5	99
p-CH_3–C_6H_4CH=NPh	1	96
p-CF_3–C_6H_4CH=NPh (**2b**)	14	98
c-$C_6H_{11}CH$=NPh	2	86
1-$C_{10}H_7CH$=NPh	1.5	96
PhCH=NCH_2Ph	1	70

[a] Trimethylsilyl was hydrized during the workup and the products were isolated as corresponding aminonitriles. Isolated yields are given. 1- $C_{10}H_7$ = 1-naphthyl.

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