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## Letter

# Lewis Acid Rather than Brønsted Acid Sites of Montmorillonite K10 Act as a Powerful and Reusable Green Heterogeneous Catalyst for Rapid Cyanosilylation of Ketones

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Xiao Huang\* Lin Chen Fengying Ren Chen Yang Jianghong Li Kejin Shi Xiaojun Gou Wei Wang\*

Antibiotics Research and Reevaluation Key Laboratory of Sichuan Province, Sichuan Industrial Institute of Antibiotics, Chengdu University, 168 Huaguan Road, 610052, Chengdu, P. R. of China huangxiao@cdu.edu.cn wildwang\_5@hotmail.com

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**Abstract** A practical green protocol was developed for highly efficient cyanosilylation of various ketones catalyzed by commercial montmorillonite K10, with excellent isolated yields (91–99%). The catalyst can be used as received, and its catalytic strength can be easily restored without loss of activity. Investigations of catalyst recycling and of the active catalytic sites indicated that Lewis acid sites were mainly responsible for the cyanosilylation of ketones.

**Key words** montmorillonite, heterogeneous catalysis, cyanosilylation, ketones, green chemistry

Montmorillonite (MMT), a naturally abundant clay, is composed of stacked, negatively charged, two-dimensional layers of aluminosilicate, with exchangeable cationic species in the interlayers.<sup>1</sup> MMT has been widely used as a heterogeneous catalyst for many organic reactions,<sup>2</sup> because of its favorable properties, such as low cost, thermal stability, the presence of Lewis and Brønsted acid sites, large surface area, and ease of separation; furthermore, it is environmentally benign.

The cyanosilylation of carbonyls with TMSCN is a powerful protocol for forming new C–C bonds, as well as simultaneously protecting an alcohol with a trimethylsilyl group. The resulting cyanohydrin silyl ethers can be further converted into other important organic building blocks,<sup>3</sup> such as  $\alpha$ -hydroxy acids,  $\alpha$ -amino acids, or  $\beta$ -amino alcohols. Many efficient catalytic systems have been reported for cyanosilylation of various carbonyl compounds, including alkali metal salts,<sup>4</sup> salen complexes,<sup>5</sup> metal organic frame-



works (MOFs),<sup>6</sup> ionic liquids or phase-transfer catalysts,<sup>7</sup> Nheterocyclic carbenes,<sup>8</sup> thiourea catalysts,<sup>9</sup> Lewis acids,<sup>10</sup> base catalysts,<sup>11</sup> dual-activation catalysts,<sup>5c,12</sup> and supported catalysts.<sup>13</sup> In particular, modified MMTs, such as Sn-MMT<sup>14</sup> and Fe-MMT,<sup>15</sup> have been developed as solid-acid catalysts for cyanosilylation of carbonyls. However, the use of unmodified commercial MMT (generally known as MMT K10) has not been well documented for this type of reaction.<sup>16</sup> Here, we report the use of commercial MMT K10 as a green, powerful, reusable, heterogeneous, solid-acid catalyst for the cyanosilylation of various ketones.

Initially, we examined the cyanosilylation of acetophenone (1a) by using commercial MMT K10 (Sigma-Aldrich; surface area 220–270 m<sup>2</sup>/g) as a catalyst. Acetophenone reacted efficiently with TMSCN in the presence of unmodified MMT K10 as a catalyst (Table 1, entry 1). To our delight, the reactivity was improved by increasing the concentration of the substrate or by carrying out the reaction under solventless conditions (entries 2-4). Among the solvents tested, hydrocarbon solvents (entries 3 and 5) produced a high reactivity, whereas moderately or strongly polar solvents gave relatively poor results (entries 9-11). This might be explained in terms of masking of acid sites on the catalyst by the weak Lewis base sites of the solvent (typically oxygen atoms in these cases). On the other hand, hydrocarbons cannot act as acceptors in which the leaving carbonyl group can be smoothly activated by the acid sites on the catalyst. As a result of a steric effect, the lone pair of electrons of diisopropyl ether (entry 8) is almost embraced by the methyl side-arms, preventing it from acting as an acid acceptor; consequently, this solvent also gave good results. Although chloride atoms attached to a carbon can serve as weak acid

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acceptors, they are too weak to compete with the carbonyl oxygen atom. Consequently, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> also gave good results in the reaction (entries 6 and 7).

Table 1	<b>1</b> Cyanosilylation of Acetophenone ( <b>1a</b> ) under Various Conditions				
Entry	Catalyst	Solvent <sup>b</sup>	<b>1a</b> [mmol/m	Time L] (min)	Yield <sup>c</sup> (%)
1	MMT K10	PhMe	1	60	90
2	MMT K10	PhMe	2	6	>98
3	MMT K10	PhMe	4	5	>98
4	MMT K10	none	neat <sup>d</sup>	4	>98
5	MMT K10	hexane	2	6	>98
6	MMT K10	$CH_2Cl_2$	2	6	>98
7	MMT K10	CHCl₃	2	6	>98
8	MMT K10	<i>i</i> -Pr <sub>2</sub> O	2	6	>98
9	MMT K10	Et <sub>2</sub> O	2	30	45 <sup>e</sup>
10	MMT K10	t-BuOMe	2	30	30 <sup>e</sup>
11	MMT K10	THF	2	30	12 <sup>e</sup>
12	Sn <sup>4+</sup> -MMT <sup>f</sup>	PhMe	2	20	>98
13	Fe <sup>3+</sup> -MMT <sup>f</sup>	PhMe	2	7	>98
14	Al <sup>3+</sup> -MMT <sup>f</sup>	PhMe	2	5	>98

<sup>a</sup> Reaction conditions: **1a** (1 mmol substrate), MMT K10 (20 mg), TMSCN (1.5 equiv) solvent (0.5 ml) r.t.

All solvents were of analytical grade and used as received.

<sup>c</sup> Isolated vield.

<sup>d</sup> TMSCN (1.2 equiv) was used.

<sup>e</sup> Acetophenone (**1a**) was recovered. <sup>f</sup> Prepared from MMT K10 by a reported procedure.<sup>14c</sup>

Various cation-exchanged MMTs were also effective catalysts for the cyanosilylation, including Sn<sup>4+</sup>-, Fe<sup>3+</sup>-, and Al<sup>3+</sup>-exchanged MMTs (Table 1, entries 12-14). Fe<sup>3+</sup>- and Al<sup>3+</sup>-MMT had similar catalytic activities relative to unmodified MMT, whereas Sn<sup>4+</sup>-MMT showed a slightly lower activity.15b

Inspired by the above results, we treated various ketones under the optimized catalytic conditions (Table 2). Generally, most of the tested ketones were converted into the corresponding cyanohydrin silvl ethers within 15 minutes; these included aliphatic ketones (Table 2, entries 11-14), aromatic ketones substituted with electron-donating or electron-withdrawing groups (entries 1–9),  $\alpha$ , $\beta$ -unsaturated ketones (entry 10; the 1,2-adduct was cleanly obtained), and sterically hindered ketones (entries 15 and 16). For 2-acetylpyridine (1s; entry 19), however, the catalytic system failed, probably because the active acid sites were immediately quenched by the basic nitrogen atom of the pyridine ring. Other ketones bearing heteroatoms (entries 17 and 18) required slightly longer reaction times. In the case of ethyl acetoacetate (1t; entry 20), the prolonged reaction time might be explained by the presence of an extra acid acceptor, which reduces the activity of the catalyst, and also by stabilization of the enol form of the substrate through conjugation with the adjacent carboxylate group, decreasing the concentration of the ketone form.

The turnover frequencies (TOFs) of the substrates were also calculated and are listed in Table 2. The quantity of active acid sites on MMT K10 is about 0.0495 mmol per 100 mg catalyst, as estimated by a poisoning method<sup>14c</sup> using 2-acetylpyridine as a base probe.

The recyclability under the standard conditions was then investigated. As shown in Figure 1, the catalytic strength of MMT K10 gradually decreased with successive cvanosilvlation cvcles (Figure 1, runs 2–5): at the fifth run. it was almost completely lost. To our delight, however, the catalytic strength was restored simply by washing the spent catalyst with a dilute hydrochloric acid solution (runs 6.9. and 12). When the regenerated catalyst was reused, the pattern of loss and subsequent restoration of activity repeated itself (runs 6–12). In addition, when the spent catalyst was washed after each use, its activity was fully regenerated (runs 13 and 14). Consequently, by applying this restoration method, the catalyst can reused more times than were tested.17

Table 2 Cyanosilylation of Various Ketones 1 Catalyzed by MMT K10<sup>a</sup>

Ŷ	cat. MMT K10	TMSO CN
$R^1 + R^2$	TMSCN, PhMe, RT	$R^1 \times R^2$
1		2

Entry	Substrate	Time (min)	Product	Yield <sup>b</sup> (%)	TOF <sup>c</sup> (min <sup>-1</sup> )
1	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	6	2a	99	17
2	<b>1b</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Et	6	2b	99	17
3	<b>1c</b> , R <sup>1</sup> = 4-FC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	8	2c	99	13
4	<b>1d</b> , R <sup>1</sup> = 4-ClC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	10	2d	99	11
5	<b>1e</b> , R <sup>1</sup> = 4-BrC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	15	2e	99	7
6	<b>1f</b> , R <sup>1</sup> = 4-HOC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	10	2f	96	11
7	<b>1g</b> , R <sup>1</sup> = 4-MeOC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	15	2g	98	7
8	<b>1h</b> , R <sup>1</sup> = 2-HOC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	10	2h	97	11
9	<b>1i</b> , R <sup>1</sup> = 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ; R <sup>2</sup> = Me	15	2i	96	7
10	<b>1j</b> , R <sup>1</sup> = PhCH=CH; R <sup>2</sup> = Me	10	2j	97 <sup>d</sup>	11
11	<b>1k</b> , $R^1 = 4$ -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> $R^2 = Me$	10	2k	96	11
12	<b>11</b> , $R^1 - R^2 = (CH_2)_5$	5	21	98	20
13	<b>1m</b> , R <sup>1</sup> = <i>i</i> -Bu; R <sup>2</sup> = Me	5	2m	98	20
14	<b>1n</b> , R <sup>1</sup> = <i>n</i> -Pent; R <sup>2</sup> = Me	5	2n	98	20
	10,				
15		8	20	99	13
16	<b>1p</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Ph	15	2р	99	7
17	<b>1q</b> , R <sup>1</sup> = 2-furyl; R <sup>2</sup> = Me	50	2q	91	2

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Table 2 (continued)

Entry	Substrate	Time (min)	Product	Yield <sup>ь</sup> (%)	TOF <sup>c</sup> (min <sup>-1</sup>
18	<b>1r</b> , R <sup>1</sup> = 2-thienyl; R <sup>2</sup> = Me	50	2r	93	2
19	<b>1s</b> , R <sup>1</sup> = 2-pyridyl; R <sup>2</sup> = Me	180		_e	-
20	<b>1t</b> , R <sup>1</sup> = EtO <sub>2</sub> CCH <sub>2</sub> ; R <sup>2</sup> = Me	180	2t	92	<1
21 <sup>f</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	300	2a	12	-
22 <sup>g</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	300	2a	46	-
23 <sup>h</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	300		_d	-
24 <sup>i</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	300 (60 h)	2a	18 (93)	-
25 <sup>j</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	300	2a	21	-
26 <sup>k</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	5	2a	99	20
27 <sup>1</sup>	<b>1a</b> , R <sup>1</sup> = Ph; R <sup>2</sup> = Me	4	2a	99	25

<sup>a</sup> Reaction conditions: **1** (1.0 mmol), MMT K10 (20 mg), PhMe (0.5 mL), TMSCN (1.5 mmol), r.t.

<sup>b</sup> Isolated yield.

<sup>c</sup> TOF = turnover frequency (number of ketone molecules converted per active acid site per min).

<sup>d</sup> The 1,2-adduct was obtained.

<sup>e</sup> No product was detected by TLC, and the substrate was recovered.

<sup>f</sup> MMT K10 (20 mg) was pretreated with TMSCN (1.5 mmol) in PhMe (0.5 mL) for 6h, then **1a** (1.0 mmol) was added.

<sup>g</sup> TfOH (20 mg) was used as the catalyst.

<sup>h</sup> Concd H<sub>2</sub>SO<sub>4</sub> (20 mg) was used as the catalyst.

<sup>i</sup> TMSCN-pretreated MMT K10 was used as the catalyst;<sup>17</sup> the yield in parentheses is for a reaction time of 60 h.

<sup>j</sup> Wet MMT K10 (20 mg containing 20 mg H<sub>2</sub>O) was used as the catalyst.

<sup>k</sup> MMT K10 was dried in a vacuum at 120 °C for 1 h before use.

<sup>1</sup> MMT K10 was calcined at 400 °C for 1 h before use.



MMT K10, as a heterogeneous catalyst that contains both Brønsted and Lewis acid sites, has a relatively high acid strength, and its Hammett acidity constant ( $H_0$ ) is similar to that of concentrated HNO<sub>3</sub> (MMT K10;  $H_0 = -5.5$  to -5.9;<sup>18a</sup> HNO<sub>3</sub>:  $H_0 = -6.3$ <sup>18b</sup>). Its relatively high surface area and variable intercalated space make MMT K10 an active acid catalyst. The typical structure of MMT (Figure 2) consists of aluminosilicate layers in the form of a sandwich in which central Al<sup>3+</sup> ions occupy an octahedral sheet that is symmetrically embedded between Si<sup>4+</sup> ions in two tetrahedral sheets. In these layers, a small fraction of the tetrahedral Si<sup>4+</sup> ions are isomorphously replaced by other trivalent metal cations, such as Al<sup>3+</sup>, and a proportion of the octahedral  $Al^{3+}$  ions are replaced by divalent cations, such as  $Mg^{2+}$ , which leads to a charge deficiency. To balance this charge deficiency, hydrated cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, H<sub>3</sub>O<sup>+</sup>, etc.) occupy the interlayer space of MMT. Accordingly, Brønsted acidity arises from the presence of terminal hydroxy groups on the external surface and from the hydrated cations in the interlamellar space of MMT. Lewis acidity stems from central metal ions such as Al<sup>3+</sup>, Mg<sup>2+</sup>, and Fe<sup>3+</sup> in the lattice and from other metallic cations in the interlamellar space. Normally, the central metal ions are fully bonded to adjacent oxygen atoms to form typical octahedra; consequently, these intact octahedra within the crystal arrays are incapable of providing much Lewis acidity. However, the small particle size of MMT K10 (typically 5–10 µm) means that the sandwich layers are crushed to a remarkable extent, creating many broken edges of stacked lavers, which contribute to both Brønsted and Lewis acidity. In particular, these surface imperfections with many coordinated metal ions, which are poised to trap external ligands, should be the main source of the Lewis acidity of unmodified MMT K10.



Although details of the reaction mechanism are not clear, both Brønsted and Lewis acid sites might act as active catalytic sites for the cyanosilylation of ketones. A precedent has been reported in which TMSCN is suggested to react with protic sites of acidic MMT to release HCN, possibly with generation of the TMS cationic Lewis acid, in a manner similar to that of the TfOH-catalyzed cyanosilylation of heptanal.<sup>14c</sup> The TMS cationic Lewis acid then activates the carbonyl group to produce a carbenium and another TMSCN molecule that attacks the carbenium intermediate to afford the product and regenerate the TMS cationic Lewis site.<sup>14c</sup> In the case of the ketone, however, concentrated H<sub>2</sub>SO<sub>4</sub> (~96%) showed no reactivity (Table 2, entry 23), despite its stronger acidity ( $H_0 = -9.9^{18c}$ ). TfOH, as a much stronger Brønsted acid ( $H_0 = -14.1^{18b}$ ), did catalyze the cyanosilylation (Table 2, entry 22), although its activity was not comparable to that of MMT K10. It is probable, therefore, that the Brønsted acid sites on MMT K10 contribute little to its catalytic activity.

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When MMT K10 was merely exposed to TMSCN for six hours before addition of the substrate (Table 2, entry 21), only 12% of the product was isolated after five hours, and a large amount of the ketone was recovered. This suggested TMSCN was adsorbed onto the catalyst, blocking its catalytic ability. It has been reported that MMT can efficiently adsorb HCN,<sup>19</sup> so it is reasonable to infer that TMSCN might also be gradually adsorbed physically and chemically onto MMT.

On the basis of the above observations, the Lewis acid sites on MMT K10 appear to be mainly responsible for its catalytic activity. As shown in Figure 3, the carbonyl group of the ketone is activated by a Lewis site to generate a highly reactive carbenium species that is simultaneously attacked by TMSCN to afford a cvanohydrin silvl ether. It is known that cyanide has a high affinity for metals, and therefore it adsorbs onto the Lewis acid sites of MMT K10, not only physically, but also chemically, thereby reducing the Lewis acidity of the MMT. The results for TMSCN-pretreated MMT K10 (Table 2, entry 21) and the fifth run in catalyst recycling (Figure 1) confirm this catalyst-activitydiminishing effect. Interestingly, when methanol-washed MMT K10 pretreated with TMSCN was used in the cyanosilylation of acetophenone (Table 2, entry 24), a poor result was nevertheless obtained. Cyanide anion was detected in the methanol eluate by a rapid colorimetric technique using ninhydrin;<sup>20</sup> further cyanide was detected in the diluted HCl washing eluate by the same technique. We therefore inferred that methanol, as a weak ligand, can wash off weakly adsorbed cyanides, but leaves strongly coordinated cyanides nearly intact; at this stage, Lewis acidity is not fully restored. Consequently, a long time was required for completion of the reaction [Table 2, entry 24 (parentheses)]. Further washing with dilute hydrochloric acid breaks the coordinating bond of the cyanides to release HCN and restore Lewis acid sites on the MMT (Figure 2); however, these sites might not have the same structure as the original ones, as the color in solution of the catalyst at this stage was dark green, rather than the original earth yellow. Furthermore, the catalytic strength was similar to the original value. Additionally, when wet MMT K10 was used as a catalyst (Table 2, entry 25), the active Lewis acid sites were probably coordinated to water instead of carbonyl groups, resulting in poor performance. When MMT K10 was predried in a vacuum at 120 °C for one hour to remove surfaceabsorbed and interlamellar water, a slightly higher catalytic activity was observed (Table 2, entry 26). However, precalcination of the MMT K10 at 400 °C for one hour resulted in a collapse of the interlayer structure, as all the water was driven out, leading to a decrease in the Brønsted acidity but an increase in the Lewis acidity.<sup>21</sup> The calcined MMT K10 exhibited an even better catalytic activity (Table 2, entry 27), strongly suggesting that Lewis acid sites are mainly responsible for the catalytic activity of MMT.



In conclusion, commercially unmodified MMT K10, as a heterogeneous solid acid, proved to be a powerful, green, low-cost, and recyclable catalyst for cyanosilylation of various ketones<sup>22</sup> (except 2-1-pyridin-2-ylethanone). In addition, an investigation of catalyst recyclability suggested that MMT can be used repeatedly without loss of activity if it is subjected to a simple acid wash between cycles. Further evidence has been found to confirm that adsorption of TMSCN and coordination of cyanides occur at Lewis acid sites on MMT K10,<sup>23</sup> implying that Lewis acid sites, rather than Brønsted acid sites, play a critical role in the cyanosilylation of ketones. Further studies on various types of MMT-catalyzed organic reactions are in progress.

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- (22) 2-Phenyl-2-(trimethylsiloxy)propanenitrile (2a); Typical Procedure

A test tube was charged with PhCOMe (**1a**; 120 mg, 1.0 mmol), MMT K10 (20 mg), and PhMe (0.5 mL). TMSCN (190  $\mu$ L, 1.5 mmol) was added dropwise with stirring at r.t. After 6 min, TLC indicated that the reaction was complete, and the mixture was filtered, washed with PhMe, and concentrated under reduced pressure to afford **2a** as a colourless oil; yield: 218 mg (99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 0.18 (s, 9 H), 1.87 (s, 3 H), 7.33–7.40 (m, 3 H), 7.53–7.57 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 1.1, 33.6, 71.6, 121.6, 124.6, 128.5, 128.6, 141.6.

## 1,3,3-Trimethyl-2-(trimethylsiloxy)bicyclo[2.2.1]heptane-2carbonitrile (20)

colorless oil; yield: 250 mg (99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 0.26 (s, 9 H), 0.91 (s, 3 H), 0.99 (s, 3 H), 1.02 (s, 3 H), 1.12–1.25 (m, 1 H), 1.60–1.88 (m, 4 H), 2.06 (d, *J* = 14.1 Hz, 1 H), 2.23 (ddd, *J* = 14.1, 3.4, 3.0 Hz, 1 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 1.0, 10.5, 20.4, 21.1, 26.5, 31.7, 45.1, 47.8, 48.8, 54.1, 78.4, 121.8.

# 2,2-Diphenyl-2-(trimethylsiloxy)acetonitrile (2p)

colourless oil; yield: 281 mg (99%).  $^1\mathrm{H}$  NMR (300 MHz,

CDCl<sub>3</sub>,TMS):  $\delta$  = 0.12 (s, 9 H), 7.31–7.39 (m, 6 H), 7.47–7.51 (m, 4 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 1.0, 76.2, 120.5, 125.7, 128.3, 128.5, 141.7.

(23) Rapid Colorimetric Ninhydrin Detection of Cyanide (see also ref. 18)

MMT K10 (100 mg) was treated with TMSCN (400  $\mu$ L) for 6 h, collected by filtration, washed thoroughly with PhMe, and suction-dried under air for a few minutes. The filtrate was discarded. The resulting catalyst was washed slowly with anhyd MeOH (10 mL), while the filtrate was trapped simultaneously in 1 M aq NaOH (5 mL). Active charcoal (100 mg) was added to the resulting solution, and the mixture was agitated for 10 min then filtered. To the filtrate was added 1 wt% aq ninhydrin solution (1 mL) with stirring. The color of the solution gradually became blue within 2 min, indicating the presence of cyanide anion.

The MeOH-washed catalyst was further rinsed thoroughly with an additional 20 mL of anhydrous MeOH to ensure a negative response to ninhydrin (the resulting catalyst was used in Table 2, entry 24, after washing with PhMe and suction-drying under air). The catalyst was washed again with 5 mL of dilute HCI solution, prepared by adding 1 volume of concd HCI to 20 volumes of MeOH, and the filtrate was trapped in 2 M aq NaOH (5 mL). Active charcoal (100 mg) was added to the resulting solution, and the mixture was agitated for 10 min then filtered. The final filtrate was subjected to colorimetric ninhydrin cyanide detection, as described above. The positive blue color obtained within 2 min proved that cyanide anion was present in this solution, showing that cyanide anions had been coordinated by Lewis sites and washed off with the dilute HCI.