Ce^{3+}-Exchanged Montmorillonite (Ce^{3+}-Mont) as a Useful Substrate-Selective Acetalization Catalyst

Jun-ichi Tateiwa, Hiroki Horiuchi, and Sakae Uemura*

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Received February 7, 1995[⊗]

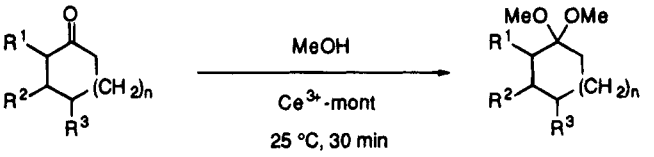
The acetalization of carbonyl compounds with methanol was investigated in the presence of a cation-exchanged montmorillonite (M^{n+}-mont; M^{n+} = Ce^{3+}, Zr^{4+}, Fe^{3+}, Al^{3+}, Zn^{2+}, H^+, and Na^+). Ce^{3+}-mont was found to be the most effective catalyst for substrate-selective acetalization. Cyclohexanones, benzaldehydes, and acid-sensitive 2-furancarboxaldehyde were converted nearly quantitatively to the corresponding acetals in methanol at 25 °C in the presence of Ce^{3+}-mont. The substrates were activated by a Lewis acidic Ce^{3+} cation in the interlayer space on the order of 1 kJ mol^{-1} as measured by FT-IR. The turnover number was estimated to be up to 2.6×10^3 based on the number of active acid sites in Ce^{3+}-mont.

Introduction

We are currently interested in the catalytic use of a cation-exchanged montmorillonite (abbreviated as M^{n+}-mont) in organic syntheses under mild conditions.[1] M^{n+}-monts have many advantages over other catalysts such as ease of handling, noncorrosiveness, low cost, elimination of metal wastes such as aluminum (an environmentally-friendly catalyst[2]), regeneration, and facile modification of acidity by exchange of cations in the interlayer space.[3,4]

One of the most useful protecting methods for carbonyl compounds is acetalization and thioacetalization.[5] Acetalization in the presence of solid catalysts has been carried out successfully with trialkyl orthoformate using a modified natural clay,[6] resin,[7] or zeolite.[8] However, the acetalization with an alcohol did not occur well.[9] For example, the acetalization of cyclohexanone with methanol in the presence of Al^{3+}-bentonite has been performed (room temperature for 30 min), but with incomplete conversion (33% yield).[9e] We attempted the acetalization of several carbonyl compounds with methanol in the presence of various M^{n+}-mont catalysts and found that a lanthanide metal ion, Ce^{3+}-mont, shows high reactivity for the substrate-selective acetalization.

Scheme 1



	n	R^1	R^2	R^3
1a;	1	H	H	H
1b;	1	Me	H	H
1c;	1	H	Me	H
1d;	1	H	H	Me
1e;	1	H	H	Et
1f;	1	H	H	Pr^i
1g;	1	H	H	Bu^t
1h;	1	H	H	Ph
1i;	1	Cl	H	H
1j;	0	H	H	H
1k;	2	H	H	H
1l;	3	H	H	H

Results and Discussion

A variety of M^{n+}-mont catalysts showed catalytic activity for the acetalization of cyclohexanone (**1a**) to cyclohexanone dimethyl acetal (**2a**) with methanol at 25 °C for 30 min (Scheme 1; Table 1, runs 1–4, 8–11). Ce^{3+}-mont proved to be the most effective for this acetalization, and the reaction proceeded almost quantitatively with complete conversion of the cyclohexanone. The order of catalytic efficiency of the M^{n+}-monts is $Ce^{3+} > Fe^{3+}$, Al^{3+}, $Zr^{4+} \gg Zn^{2+}$, Na^+, H^+-mont. The acetal **2a** could be isolated after simple filtration and washing of the catalyst with dichloromethane, followed by evaporation of the solvent. No side products were detected by GLC and ^1H NMR analyses. The proper acidity as well as the drying ability of Ce^{3+}-mont seems to work well in shifting the equilibrium to the product side. It is worth noting

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

(1) (a) Tateiwa, J.; Horiuchi, H.; Hashimoto, K.; Yamauchi, T.; Uemura, S. *J. Org. Chem.* **1994**, *59*, 5901. (b) Tateiwa, J.; Horiuchi, H.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2883. (c) Tateiwa, J.; Nishimura, T.; Horiuchi, H.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3367.

(2) Clark, J. H.; Kybett, A. P.; Macquarrie, D. J.; Barlow, S. J.; Landon, P. *J. Chem. Soc., Chem. Commun.* **1989**, 1353. Barlow, S. J.; Clark, J. H.; Darby, M. R.; Kybett, A. P.; Landon, P.; Martin, K. *J. Chem. Res. (S)* **1991**, 74.

(3) For recent reviews on the reactions in the presence of clay, see: Balogh, M.; Laszlo, P. In *Organic Chemistry Using Clays*; Springer-Verlag: New York, 1993. Izumi, Y.; Urabe, K.; Onaka, M. In *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*; VCH: Weinheim, 1992; Chapter 1, pp 21–44. Kellendonk, F. J. A.; Heinerman, J. J. L.; van Santen, R. A.; McKillop, A.; Clissold, D. W.; Pinnavaia, T. J.; Foucaud, A.; Adams, J. M. In *Preparative Chemistry Using Supported Reagents*; Laszlo, P., Ed.; Academic Press: New York, 1987; Part 8, pp 453–528.

(4) Technical Information Bulletin AL-143, Aldrich Chemical Co., Inc., 1987.

(5) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991; Chapter 4, pp 175–210.

(6) Thuy, V. M.; Maitte, P. *Bull. Soc. Chim. Fr.* **1975**, 2558. Taylor, E. C.; Chiang, C.-S. *Synthesis* **1977**, 467.

(7) Patwardhan, S. A.; Dev, S. *Synthesis* **1974**, 348. Olah, G. A.; Narang, S. C.; Meidar, D.; Salem, G. F. *Synthesis* **1981**, 282.

(8) Corma, A.; Climent, M. J.; Carcia, H.; Primo, J. *Appl. Catal.* **1990**, *59*, 333.

(9) (a) Balogh, M.; Laszlo, P. In *Organic Chemistry Using Clays*; Springer-Verlag: New York, 1993, Chapter 14, pp 140–143. (b) Heinemann, H. U.S. Patent 2,451,949, **1948**; *Chem. Abstr.* **1949**, *43*, 2222c. (c) Lorette, N. B.; Howard, W. L.; Brown, J. H., Jr. *J. Org. Chem.* **1959**, *24*, 1731. (d) Lambert, P. *Ind. Chim. Belge* **1961**, *26*, 1012. (e) Ballantine, J. A.; Purnell, J. H.; Thomas, J. M. *Clay Miner.* **1983**, *18*, 347. (f) Joshi, M. V.; Narasimhan, C. S. *J. Catal.* **1989**, *120*, 282.

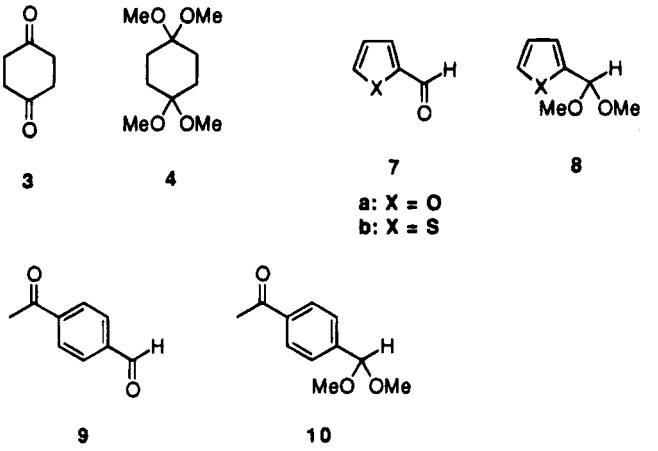
0022-3263/95/1960-4039$09.00/0

Table 1. Reaction Conditions and Acetal Yields in M^{n+}-Mont-Catalyzed Acetalization[a]

run	reactant	M^{n+}-mont (mg, mmol[b])	product	reaction time (h)	isolated yield (%)[c]	turnover number[d]
1	**1a**	Zr^{4+}-mont (55, 0.0404[e])	**2a**	0.5	13[f]	3.3×10
2	**1a**	Al^{3+}-mont (55, 0.0292[e])	**2a**	0.5	39[f]	1.4×10^2
3	**1a**	Fe^{3+}-mont (55, 0.0192[e])	**2a**	0.5	65[f]	3.4×10^2
4	**1a**	Ce^{3+}-mont (55, 0.0078)	**2a**	0.5	94	1.2×10^3
5	**1a**	Ce^{3+}-mont (65, 0.0092, 1st)	**2a**	0.5	94	1.1×10^3
6	**1a**	Ce^{3+}-mont (65, 0.0092, 2nd)[g]	**2a**	0.5	94	1.1×10^3
7	**1a**	Ce^{3+}-mont (65, 0.0092, 3rd)[g]	**2a**	0.5	94	1.1×10^3
8	**1a**	Zn^{2+}-mont (55, 0.0204[e])	**2a**	0.5	0	0
9	**1a**	Na^{+}-mont (55, 0)[h]	**2a**	0.5	0	–
10	**1a**	H^{+}-mont (55)[i]	**2a**	0.5	0	0
11	**1a**	–	**2a**	0.5	0	–
12	**1b**	Ce^{3+}-mont (55, 0.0078)	**2b**	0.5	24[f]	3.1×10^2
13	**1c**	Ce^{3+}-mont (55, 0.0078)	**2c**	0.5	95	1.2×10^3
14	**1d**	Ce^{3+}-mont (55, 0.0078)	**2d**	0.5	95	1.2×10^3
15	**1e**	Ce^{3+}-mont (55, 0.0078)	**2e**	0.5	95	1.2×10^3
16	**1f**	Ce^{3+}-mont (55, 0.0078)	**2f**	0.5	95	1.2×10^3
17	**1g**	Ce^{3+}-mont (55, 0.0078)	**2g**	0.5	95	1.2×10^3
18	**1j**	Ce^{3+}-mont (55, 0.0078)	**2j**	0.5	20[f]	2.6×10^2
19	**3**	Ce^{3+}-mont (55, 0.0078)	**4**	0.5	96	2.6×10^3
20	**5a**	Ce^{3+}-mont (55, 0.0078)	**6a**	12	97	1.3×10^3
21	**5b**	Ce^{3+}-mont (55, 0.0078)	**6b**	12	18[f]	2.3×10^2
22	**5c**	Ce^{3+}-mont (55, 0.0078)	**6c**	12	62[f]	8.1×10^2
23	**5d**	Ce^{3+}-mont (55, 0.0078)	**6d**	12	96	1.3×10^3
24	**5e**	Ce^{3+}-mont (55, 0.0078)	**6e**	12	97	1.3×10^3
25	**5f**	Ce^{3+}-mont (55, 0.0078)	**6f**	12	99	1.3×10^3
26	**5g**	Ce^{3+}-mont (55, 0.0078)	**6g**	12	99	1.3×10^3
27	**5h**	Ce^{3+}-mont (55, 0.0078)	**6h**	12	99	1.3×10^3
28	**5i**	Ce^{3+}-mont (55, 0.0078)	**6i**	12	99	1.3×10^3
29	**7a**	Ce^{3+}-mont (55, 0.0078)	**8a**	0.5	76	9.9×10^2
30	**7b**	Ce^{3+}-mont (55, 0.0078)	**8b**	12	83[f]	1.1×10^3
31	**9**[j]	Ce^{3+}-mont (6.5, 0.00092)	**10**	0.5	98	1.1×10^3

[a] Reactant (5.09 mmol), methanol (16 mL) at 25 °C. [b] The number of active acid sites. [c] Based on reactant. [d] Based on the number of active acid sites. [e] Estimated by NH_3-TPD analysis. [f] By ^1H NMR. [g] Recycled Ce^{3+}-mont was dried again at 120 °C in an oven for 24 h before use. [h] Kunipia G, Kunimine Industries Co., Ltd. [i] Montmorillonite K10, Aldrich Chemical Co., Inc. [j] Reactant (0.50 mmol), methanol (1.6 mL) at 25 °C.

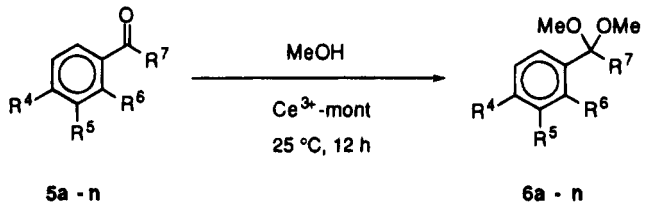
that, although the recovered Ce^{3+}-mont did not show any activity for acetalization, it was regenerated and reused after drying at 120 °C for 24 h (Table 1, runs 5–7). The Ce^{3+}-mont-catalyzed acetalization was applied to a variety of ketones and aldehydes, and the results are shown in Table 1. 3-Methylcyclohexanone (**1c**), 4-methylcyclohexanone (**1d**), 4-ethylcyclohexanone (**1e**), 4-isopropylcyclohexanone (**1f**), and 4-*tert*-butylcyclohexanone (**1g**) reacted smoothly to give the corresponding acetals **2c–g** (runs 13–17). On the other hand, 2-methylcyclohexanone (**1b**) and cyclopentanone (**1j**) reacted slowly (runs 12 and 18), while 4-phenylcyclohexanone (**1h**), 2-chlorocyclohexanone (**1i**), cycloheptanone (**1k**), and cyclooctanone (**1l**) did not react at all. 1,4-Cyclohexanedione (**3**) was converted to 1,1,4,4-tetramethoxycyclohexane (**4**) quantitatively under the same conditions (run 19). A variety of substituted benzaldehydes such as benzaldehyde (**5a**), 2-methylbenzaldehyde (**5d**), 3-methylbenzaldehyde (**5e**), 4-methylbenzaldehyde (**5f**), 4-bromobenzaldehyde (**5g**), 4-chlorobenzaldehyde (**5h**), and 4-nitrobenzaldehyde (**5i**) (except for 4-(dimethylamino)benzaldehyde (**5b**) and 4-methoxybenzaldehyde (**5c**)) were completely converted to the corresponding acetals by reaction at 25 °C for 12 h (Scheme 2; runs 20–28), while aromatic ketones such as acetophenone (**5j**), propiophenone (**5k**), butyrophenone (**5l**), valerophenone (**5m**), and benzophenone (**5n**) did not react at all. An acid-sensitive 2-furancarboxaldehyde (**7a**) was converted to the corresponding acetal **8a** almost quantitatively in methanol at 25 °C for 30 min in the presence of Ce^{3+}-mont, while acetalization of an acid-sensitive 2-thiophenecarboxaldehyde (**7b**) was slow and gave acetal **8b** after 12 h (runs 29 and 30). On the other hand, 2-pyridinecarboxaldehyde did not react



at all. The acetalization of 4-acetylbenzaldehyde (**9**) occurred only at the formyl group to give acetal **10** chemoselectively and nearly quantitatively (run 31). Linear ketones and aldehydes such as 2-pentanone, 2-heptanone, 2-octanone, 2-decanone, pentanal, heptanal, and octanal were converted to the corresponding acetals incompletely (conversion of 18–30%) under these conditions, and the products could not be isolated in a pure form. As described above, the reactivity of carbonyl compounds depends very much upon their structure. However, we do not have a reasonable explanation for the difference in reactivities at present.

We estimated the number of active acid sites in Ce^{3+}-mont by poisoning the acetalization system with triethylamine.[1b,10] In the acetalization of **1a** in the presence of Ce^{3+}-mont (65 mg), the addition of 0.0092 mmol of triethylamine stopped the reaction completely.

Scheme 2



5a - n 6a - n

	R^4	R^5	R^6	R^7
5a;	H	H	H	H
5b;	NMe_2	H	H	H
5c;	OMe	H	H	H
5d;	H	H	Me	H
5e;	H	Me	H	H
5f;	Me	H	H	H
5g;	Br	H	H	H
5h;	Cl	H	H	H
5i;	NO_2	H	H	H
5j;	H	H	H	Me
5k;	H	H	H	Et
5l;	H	H	H	Pr^n
5m;	H	H	H	Bu^n
5n;	H	H	H	Ph

Table 2. Low Frequency Shift of IR Absorption of Carbonyl Compounds Activated on M^{n+}-Mont

run	substrate	adsorbent	IR shift / cm^{-1} (kJ mol^{-1})[a]
1	**1a**	Ce^{3+}-mont	−27.8 (0.33), −85.6 (1.03)
2	**1a**	Al^{3+}-mont	−29.7 (0.36)
3[b]	**1a**	$CeCl_3$	−79.9 (0.96)
4	**1b**	Ce^{3+}-mont	0 (0)
5	**1c**	Ce^{3+}-mont	−22.0 (0.26), −91.4 (1.10)
6	**1d**	Ce^{3+}-mont	−34.8 (0.42), −83.0 (1.00)
7	**5a**	Ce^{3+}-mont	0 (0)
8[c]	**5a**	Ce^{3+}-mont	−50.1 (0.60)
9	**5j**	Ce^{3+}-mont	0 (0)
10[c]	**5j**	Ce^{3+}-mont	0 (0)

[a] Difference between IR adsorption of the substrate on the adsorbent (KBr disk method) and that of the substrate (liquid film method). [b] Mineral oil mull method. [c] Preparation time, 24 h in place of 0.5 h.

This result indicates that the number of active acid sites in Ce^{3+}-mont is 0.14 mmol g^{-1}. Thus, in the cases of **1a**, **3**, and **7a** the turnover numbers were estimated to be 1.3×10^3, 2.6×10^3, and 9.9×10^2, respectively, based on the active acid sites. The number of acid sites in Ce^{3+}-mont was also estimated from the amount of adsorbed ammonia gas at 100 °C by the temperature-programmed desorption of ammonia gas (NH_3-TPD) and was again found to be 0.14 mmol g^{-1}.[1b] Although the number of acid sites in the M^{n+}-mont determined by NH_3-TPD analyses may not accurately represent the active acid sites available for reaction, it provides a reference for M^{n+}-mont acidity and is used tentatively for Zr^{4+}-, Fe^{3+}-, Al^{3+}-, and Zn^{2+}-mont.[1a]

In order to investigate the interaction of the M^{n+} cation and/or the Lewis acid site of the M^{n+}-mont catalyst with carbonyl compounds, FT-IR analysis of the compounds was carried out by treating either Ce^{3+}- or Al^{3+}-mont with **1a** at 25 °C for 30 min (see Experimental Section). New peaks due to low frequency shifts of the carbonyl stretching absorptions were observed as shown in Table 2, *i.e.*, 27.8 and 85.6 cm^{-1} in the case of Ce^{3+}-mont and 29.7 cm^{-1} in the case of Al^{3+}-mont. It was confirmed separately that a new peak at a low frequency shift of 79.9 cm^{-1} was observed in the interaction between **1a** and anhydrous $CeCl_3$ besides the normal carbonyl stretching peak of **1a** (Table 2). Therefore, in the case of Ce^{3+}-mont, the carbonyl oxygen presumably coordinates to a Ce^{3+} cation in the interlayer space as well as to an aluminum atom (a Lewis acid site) in the framework of clay, while in the case of Al^{3+}-mont, the carbonyl oxygen coordinates to an aluminum atom in the framework of clay and/or a Al^{3+} cation in the interlayer space. These low frequency shifts mean that the activation energy of **1a** by coordination to a Ce^{3+} cation and to a Al^{3+} cation or an aluminum atom (a Lewis acid site) is 1.03 and 0.33−0.36 kJ mol^{-1}, respectively. It has been known[11] that the carbonyl oxygen of acetone coordinated to the exchangeable cations (Al^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, and Na^+) in the corresponding M^{n+}-mont either directly or through water as detected in the low frequency shifts of the carbonyl stretching absorptions in IR. It is clear from these results that a M^{n+} cation (in this case, Ce^{3+}) in the interlayer space acts as a Lewis acid site in this reaction system. It is worth noting that, in the cyanosilylation and Mukaiyama aldol reaction, the carbonyl group was activated by a strong Brönsted acid site induced by exchangeable cations (Sn^{4+}, Fe^{3+}, and Al^{3+}) in the interlayer space.[10]

In agreement with the acetalization results, a similar coordination was observed in the cases of **1c** and **1d**, but not in the case of **1b** as shown in Table 2. The acetalization of benzaldehydes was slow. Consistent with this observation, the adsorption of benzaldehyde (**5a**) to the interlayer space of Ce^{3+}-mont was slow and no carbonyl absorption was observed in the FT-IR spectra from compounds treated for 30 min, while those treated for 24 h showed a broad new peak at a low frequency shift of 50.1 cm^{-1} probably due to the coordination of the carbonyl to the metal. On the other hand, no new peaks appeared in the case of acetophenone (**5j**), even after prolonged treatment with Ce^{3+}-mont.

The basal spacing value of Ce^{3+}-mont swollen with **1a** or **5a** was shown to be the same as that of pure Ce^{3+}-mont (d_{001} = 15.2 Å[1b]) by X-ray powder diffraction (XRD) analyses. This value is large enough that reactants can be included in the interlayer space.

Conclusion

Ce^{3+}-mont was revealed to be an efficient catalyst for the acetalization of some ketones and aldehydes with methanol. The characteristic features of Ce^{3+}-mont are as follows: (1) Ce^{3+}-mont is a reusable solid acid catalyst that offers easy handling and a ready workup, (2) Ce^{3+}-mont has both the proper acidity and drying ability, which drive the acetalization, and the equilibrium of the reaction in the presence of Ce^{3+}-mont shifts to the acetal side with complete conversion of some carbonyl compounds, and (3) a Ce^{3+} cation acts as a Lewis acid site and activates the carbonyl group by coordination, on the order of 1 kJ mol^{-1}. Cyclohexanones **1a−g** and **3** reacted smoothly in methanol at 25 °C for 30 min in the presence of Ce^{3+}-mont (turnover number, $1.1-1.2 \times 10^3$), but **1h−l** did not react. A variety of substituted benzaldehydes **5a−i** except for **5b** and **5c** were completely converted to the corresponding dimethyl acetals after 12 h (turnover number, 1.3×10^3), while aromatic ketones **5j−n** did not react at all. A cyclic dione **3** and an acid-sensitive aldehyde **7a** were converted readily to the corresponding dimethyl acetals **4** and **8a** (turnover number, 2.6×10^3

(10) Kawai, M.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1237. Higuchi, K.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2016.

and 9.9×10^2), respectively. Compound **9** under the same conditions produced dimethyl acetal **10** chemoselectively.

Experimental Section

General. FT-IR spectra were measured as thin films, KBr disks or mineral oil mulls. GC-MS spectra were measured with a CBP10-M25-025 column (Shimadzu, fused silica capillary column, 25 m × 0.20 mm, 2.5-μm film thickness) by the electron-impact method (the ionizing voltage, 70 eV) for ionization. GLC analyses were carried out on a CBP10-S25-050 column (Shimadzu, fused silica capillary column, 25 m × 0.33 mm, 5.0-μm film thickness). X-ray powder diffraction (XRD) data were obtained using Cu Kα radiation and an energy dispersive detector. Combustion analyses were performed at the Microanalytical Center of Kyoto University.

All commercially available organic and inorganic compounds were used without further purification except for the solvent, which was dried and distilled by the known method before use.[12] Kunipia G, namely Na^+-mont, was obtained from Kunimine Industries Co., Ltd. Montmorillonite K10, namely H^+-mont, was commercially available from Aldrich Chemical Co., Inc. M^{n+}-mont (M^{n+} = Ce^{3+}, Zr^{4+}, Fe^{3+}, Al^{3+}, and Zn^{2+}) was prepared by treatment of Na^+-mont with the corresponding metal oxychloride or nitrate in aqueous acetone as described previously.[1a,b] 4-Acetylbenzaldehyde (**9**) was synthesized by the reported method.[13] Benzaldehyde dimethyl acetal (**6a**) is commercially available and identified by ^{13}C NMR[14] and MS.[15]

General Procedure for the Acetalization and the Product Isolation. The example of acetalization of cyclohexanone (**1a**) is shown (Table 1, run 4). To a mixture of **1a** (500 mg, 5.09 mmol) and dry methanol (16 mL) was added Ce^{3+}-mont (55 mg, 0.0078 mmol as active acid sites) in one portion at 25 °C with a magnetic stirring. The mixture was stirred at the temperature for 30 min. The catalyst was filtered with suction (Whatman quantitative filter paper no. 5 or Gelman Ekikurodisk 3CR) and washed with dichloromethane (20 mL). The solvent in a mixture of the filtrate and dichloromethane washings was removed by distillation (a Vigroux condenser) at normal pressure to leave a colorless oil of the acetal **2a** (689.9 mg, 4.78 mmol, 94% isolated yield). The complete conversion of **1a** was confirmed by GLC, ^1H NMR, and ^{13}C NMR analyses. The acetal **2a** is commercially available and also identified by ^1H NMR, ^{13}C NMR,[14,16] and MS[15] after isolation (>99% purity). The acetals **2c-g**, **4**, **6d-i**, and **8a** are known compounds and characterized by their spectral data. The acetal **10** is a new compound. As to the acetals **2b**, **2j**, **6b**, **6c**, and **8b**, they were determined by ^1H NMR, ^{13}C NMR, and MS from a mixture with a starting carbonyl compound, respectively. New spectral data of the compounds are shown below.

2-Methylcyclohexanone Dimethyl Acetal (2b). The acetal **2b** was isolated as a mixture (colorless oil) with the ketone **1b** and determined by ^1H NMR, ^{13}C NMR,[14,17] and MS[15] (24% yield, **2b**:**1b** = 25:75 by ^1H NMR). ^1H NMR δ 0.95 (d, J = 7.3, 3H), 1.41 (m, 9H), 3.16 (s, 3H), 3.17 (s, 3H); MS m/z (relative intensity) 158 (M^+, 8), 127 (25), 115 (20), 101 (100), 55 (25), 41 (25).

3-Methylcyclohexanone Dimethyl Acetal (2c). The acetal **2c** was isolated as a colorless oil and identified by ^{13}C NMR[14,17] and MS.[15] ^1H NMR δ 0.77-2.02 (m, 9H), 0.90 (d, J = 6.6, 3H), 3.14 (s, 3H), 3.20 (s, 3H); MS m/z (relative intensity) 158 (M^+, 2), 127 (58), 115 (100), 101 (81), 95 (41), 55 (37), 41 (39).

4-Methylcyclohexanone Dimethyl Acetal (2d). The acetal **2d** was isolated as a colorless oil and identified by ^{13}C NMR[14,17] and MS.[15] ^1H NMR δ 0.91 (d, J = 6.6, 3H), 1.13 (td, J = 12.6, 3.3, 2H), 1.34 (td, J = 13.0, 3.9, 2H), 1.42 (m, 1H), 1.57 (d, J = 13, 2H), 1.97 (d, J = 13, 2H), 3.15 (s, 3H), 3.20 (s, 3H); MS m/z (relative intensity) 158 (M^+, 1), 127 (25), 101 (100), 55 (22), 43 (22).

4-Ethylcyclohexanone Dimethyl Acetal (2e). A colorless oil; ^1H NMR δ 0.88 (t, J = 7.3, 3H), 1.08 (qd, J = 13, 3, 2H), 1.13-1.18 (m, 1H), 1.24 (q, J = 7.3, 2H), 1.32 (td, J = 12.9, 3.9, 2H), 1.63 (d, J = 12, 2H), 1.99 (d, J = 12, 2H), 3.15 (s, 3H), 3.20 (s, 3H); ^{13}C NMR δ 11.7 (q), 28.8 (t), 29.0 (t), 32.2 (t), 38.6 (d), 47.4 (q), 47.5 (q), 100.3 (s); MS m/z (relative intensity) 172 (M^+, 1), 101 (100).

4-Isopropylcyclohexanone Dimethyl Acetal (2f). A colorless oil; ^1H NMR δ 0.87 (d, J = 6.8, 6H), 1.00-1.09 (m, 1H), 1.16 (qd, J = 12, 3, 2H), 1.30 (td, J = 13, 4, 2H), 1.44 (septet, J = 6.8, 1H), 1.63 (d, J = 12, 2H), 2.03 (d, J = 12, 2H), 3.15 (s, 3H), 3.20 (s, 3H); ^{13}C NMR δ 20.1 (q), 26.0 (t), 32.3 (d), 32.4 (t), 43.4 (d), 47.4 (q), 47.5 (q), 100.1 (s); MS m/z (relative intensity) 186 (M^+, 0.1), 101 (100).

***tert*-Butylcyclohexanone Dimethyl Acetal (2g).** A colorless oil; ^1H NMR δ 0.86 (s, 9H), 1.00 (t, J = 12, 1H), 1.23 (sextet, J = 12, 4H), 1.65 (d, J = 12, 2H), 2.06 (d, J = 12, 2H), 3.15 (s, 3H), 3.20 (s, 3H); ^{13}C NMR δ 23.7 (t), 27.7 (q), 32.3 (s), 32.8 (t), 47.4 (q), 47.6 (d), 47.6 (q), 99.9 (s); MS m/z (relative intensity) 200 (M^+, 0.1), 101(100).

Cyclopentanone Dimethyl Acetal (2j). The acetal **2j** was isolated as a mixture (colorless oil) with the ketone **1j** and determined by ^1H NMR,[18] ^{13}C NMR,[19] and MS (20% yield, **2j**:**1j** = 39:61 by ^1H NMR). MS m/z (relative intensity) 130 (M^+, 0.7), 101 (100), 67 (45), 57 (34), 41 (27).

1,1,4,4-Tetramethoxycyclohexane (4). A colorless granular crystal; mp 77.0 °C (lit.[20] 81 °C); ^1H NMR δ 1.71 (s, 8H), 3.19 (s, 12H); ^{13}C NMR δ 28.8 (t), 47.8 (q), 99.7 (s); MS m/z (relative intensity) 204 (M^+, 0.1), 141 (32), 109 (81), 103 (100), 88 (43), 55 (25), 43 (45).

4-(Dimethylamino)benzaldehyde Dimethyl Acetal (6b). The acetal **6b** was isolated as a mixture (colorless oil) with the ketone **5b** and determined by ^1H NMR[21] and MS (18% yield, **6b**:**5b** = 18:82 by ^1H NMR). MS m/z (relative intensity) 195 (M^+, 13), 164 (61), 149 (100).

4-Methoxybenzaldehyde Dimethyl Acetal (6c). The acetal **6c** was isolated as a mixture (colorless oil) with the ketone **5c** and determined by ^1H NMR,[22] ^{13}C NMR, and MS (62% yield, **6c**:**5c** = 75:25 by ^1H NMR). ^{13}C NMR δ 52.6 (q), 55.2 (q), 103.1 (d), 113.5 (d), 127.9 (d), 130.4 (s), 159.7 (s); MS m/z (relative intensity) 182 (M^+, 8), 151 (100), 135 (65).

2-Methylbenzaldehyde Dimethyl Acetal (6d). The acetal **6d** was isolated as a colorless oil and identified by MS.[23] ^1H NMR δ 2.36 (s, 3H), 3.31 (s, 6H), 5.45 (s, 1H), 7.14 (dd, J = 7, 2, 1H), 7.20 (td, J = 7, 2, 2H), 7.53 (dd, J = 7, 2, 1H); ^{13}C NMR δ 18.9 (q), 52.9 (q), 101.7 (d), 125.4 (d), 126.6 (d), 128.4 (d), 130.5 (d), 135.6 (s), 136.2 (s).

3-Methylbenzaldehyde Dimethyl Acetal (6e). The acetal **6e** was isolated as a colorless oil and identified by MS.[24] ^1H NMR δ 2.36 (s, 3H), 3.33 (s, 6H), 5.35 (s, 1H), 7.12-7.27 (m, 4H); ^{13}C NMR δ 21.5 (q), 52.8 (q), 103.3 (d), 123.8 (d), 127.3 (d), 128.1 (d), 129.2 (d), 137.9 (s), 138.0 (s).

4-Methylbenzaldehyde Dimethyl Acetal (6f). The acetal **6f** was isolated as a colorless oil and identified by ^1H NMR and MS.[25] ^1H NMR δ 2.21 (s, 3H), 3.18 (s, 6H), 5.23 (s, 1H),

(11) Theng, B. K. G. In *The Chemistry of Clay-Organic Reactions*; Adam Hilger: London, 1974; Chapter 3, pp 63-84.
(12) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.
(13) Kauffmann, T.; Kieper, H.; Pieper, H. *Chem. Ber.* **1992**, *125*, 899.
(14) Bremser, W.; Ernst, L.; Franke, B.; Gerhards, R.; Hardt, A. In *Carbon-13 NMR Spectral Data*; Springer-Verlag: New York, 1979 (microfiche).
(15) McLafferty, F. W.; Stauffer, D. B. In *The Wiley/NBS Registry of Mass Spectral Data*; Wiley: New York, 1989.
(16) Duddeck, H.; Wolff, P. *Org. Magn. Reson.* **1976**, *8*, 593.
(17) Borsdorf, R.; Kleinpeter, E.; Agurakis, S. *J. Prakt. Chem.* **1978**, *320*, 309.
(18) Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907.
(19) Wiering, P. G.; Steinberg, H. *J. Org. Chem.* **1981**, *46*, 1663.
(20) Konz, E.; Pistorius, R. *Synthesis* **1979**, 603.
(21) Fleming, I.; Iqbal, J.; Krebs, E.-P. *Tetrahedron* **1983**, *39*, 841.
(22) Martin, C. W.; Lund, P. R.; Rapp, E.; Landgrebe, J. A. *J. Org. Chem.* **1978**, *43*, 1071.
(23) Barba, F.; Guirado, A.; Barba, I. *J. Chem. Res. (S)* **1986**, 228.
(24) Barba, I.; Alonso, F.; Florencio, F. *J. Org. Chem.* **1989**, *54*, 4365.
(25) Barba, F.; Guirado, A.; Barba, I. *J. Org. Chem.* **1984**, *49*, 3022.

7.03 (d, J = 8.3, 2H), 7.19 (d, J = 8.3, 2H); ^{13}C NMR δ 21.2 (q), 52.6 (q), 103.2 (d), 126.6 (d), 128.9 (d), 135.1 (s), 138.1 (s).

4-Bromobenzaldehyde Dimethyl Acetal (6g). The acetal **6g** was isolated as a colorless oil and identified by ^1H NMR and ^{13}C NMR.[26] MS, m/z (relative intensity) 232 (4), 230 (M^+, 4), 201 (98), 199 (100), 91 (26), 75 (29), 51 (21).

4-Chlorobenzaldehyde Dimethyl Acetal (6h). The acetal **6h** was isolated as a colorless oil and identified by ^1H NMR.[27] ^{13}C NMR δ 52.5 (q), 102.3 (d), 128.2 (d), 128.4 (d), 134.3 (s), 136.6 (s); MS, m/z (relative intensity) 186 (M^+, 2), 155 (100), 109 (81), 91 (30), 75 (20).

4-Nitrobenzaldehyde Dimethyl Acetal (6i). The acetal **6i** was isolated as a colorless oil and identified by ^1H NMR.[27] ^1H NMR δ 3.34 (s, 6H), 5.48 (s, 1H), 7.65 (d, J = 8.3, 2H), 8.22 (d, J = 8.3, 2H); ^{13}C NMR δ 52.7 (q), 101.6 (d), 123.4 (d), 127.9 (d), 145.1 (s), 148.0 (s); MS, m/z (relative intensity) 197 (M^+, 4), 166 (100), 120 (67).

2-Furancarboxaldehyde Dimethyl Acetal (8a). The acetal **8a** was isolated as a colorless oil and identified by ^1H NMR, ^{13}C NMR, and MS.[28]

2-Thiophenecarboxaldehyde Dimethyl Acetal (8b). The acetal **8b** was isolated as a mixture (colorless oil) with the ketone **7b** and determined by ^1H NMR, ^{13}C NMR, and MS (83% yield, **8b**:**7b** = 91:9 by ^1H NMR). ^1H NMR δ 3.36 (s, 6H), 5.64 (s, 1H), 7.01 (dd, J = 4.9, 3.9, 1H), 7.08 (d, J = 3.9, 1H), 7.30 (d, J = 4.9, 1H); ^{13}C NMR δ 52.6 (q), 100.1 (d), 125.4 (d), 125.7 (d), 126.7 (d), 141.5 (s); MS m/z (relative intensity) 158 (M^+, 4), 127 (100), 111 (19), 65 (24).

4-Acetylbenzaldehyde (9). The compound **9** was synthesized by the previously reported method[13] and identified by ^1H NMR.[29] A white solid; mp 34 °C (lit.[13] 34 °C); ^{13}C NMR δ 27.0 (q), 128.8 (d), 129.8 (d), 139.0 (s), 141.2 (s), 191.6 (d), 197.4 (s); MS m/z (relative intensity) 148 (M^+, 18), 133 (100), 105 (43), 77 (37), 43 (63).

1-[4-(Dimethoxymethyl)phenyl]ethanone (10). A colorless oil; ^1H NMR δ 2.61 (s, 3H), 3.33 (s, 6H), 5.44 (s, 1H), 7.56 (d, J = 8.3, 2H), 7.97 (d, J = 8.3, 2H); ^{13}C NMR δ 26.7 (q), 52.7 (q), 102.3 (d), 127.0 (d), 128.3 (d), 137.1 (s), 143.1 (s), 197.9 (s); MS m/z (relative intensity) 194 (M^+, 0.6), 163 (100), 75 (21), 43 (50). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.93; H, 7.46.

Estimation of the Number of Active Acid Sites on Ce^{3+}-Mont with Triethylamine-Doped Methanol. By following a literature method,[1b,10] a mixture of a variety amount of triethylamine-doped methanol (15.0 mL) and Ce^{3+}-mont (65.0 mg) was stirred magnetically at 25 °C for 30 min. The compound **1a** (500.0 mg, 5.09 mmol) was added to the mixture and stirred at the temperature for 30 min. Biphenyl (100.0 mg, an internal standard) was added to the reaction mixture and the mixture was stirred for 5 min. After filtration of the catalyst through a Gelman Ekikurodisk 3CR, the acetal **2a** and the recovered **1a** in the filtrate were analyzed by GLC.

IR Analysis of Coordination of Carbonyl Compounds to M^{n+}-Mont and Anhydrous $CeCl_3$ (Table 2). A mixture of a carbonyl compound (2 mL) and Ce^{3+}-mont (100 mg) was stirred magnetically at 25 °C for 30 min. The catalyst Ce^{3+}-mont, coordinated with the carbonyl compound, was filtered by suction (Whatman quantitative filter paper no. 5) and washed with diethyl ether (1 mL). IR spectra were recorded on a KBr disk which was prepared from an equal amount (weight) of the catalyst and KBr powder. In anhydrous $CeCl_3$ case IR spectrum was measured on a mixture of cyclohexanone (500 mg) and anhydrous $CeCl_3$[30] (500 mg) in mineral oil (1 mL).

Acknowledgment. We thank Kunimine Industries Co., Ltd. for the gift of Kunipia G.

JO950236Z

(26) Creary, X.; Aldridge, T. *J. Org. Chem.* **1991**, *56*, 4280.
(27) Kwart, H.; Silver, P. A. *J. Org. Chem.* **1975**, *40*, 3019.
(28) Otera, J.; Dan-oh, N.; Nozaki, H. *Tetrahedron* **1992**, *48*, 1449.
(29) Milstein, D.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 1613.
(30) Mine, N.; Fujiwara, Y.; Taniguchi, H. *Chem. Lett.* **1986**, 357.