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The catalytic activity of Zn(II) and Mn(II) organometallic complexes

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Abstract Zn(II) and Mn(II) organometallic complexes **I** and **II** were first used to catalyze the cyanosilylation reaction, and good catalytic results (24–99 %) were achieved. The catalytic activity of the complexes was determined by ^{1}H NMR.

Keywords Zn(II) and Mn(II) organometallic complexes · Catalyze · The cyanosilylation reaction · Catalytic activity

Introduction

Organometallic complexes such as Zn(II) and Mn(II) complexes have been widely used in catalyzing organic and polymer synthesis [1–7]. For example, generation of geminal dimetallic species of zinc for the Wittig-type olefination, Mn(III) salen catalysts and their application in asymmetric epoxidation, Mn(III)-salphen complex for catalytic epoxidation, etc., and they have all shown good catalytic activity (46–99 % ee) and the yield (60–99 %). Cyanosilylation reactions have attracted chemists' interests, because the products, cyanohydrins, are intermediates for the synthesis of pharmaceuticals. The Shibasaki group, the Corey, Deng, Jacobsen group and the Feng group [8–18] have devised many excellent catalysts for this reaction, with catalytic activity up to 99 % ee and 99 % yield. Encouraged by this pioneer work, our group has also attempted the Lewis acidic catalysts involving the ethylenediamine zinc acetate complex and DMF·$MnCl_2$ complexes in the cyanosilylation reaction.

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Experimental

Materials and instruments

All cyanosilylation reactions were performed using chloroform as solvent, and reactions were monitored by thin layer chromatography using 0.25 mm Merck silica gel-coated glass plates (60F-254) and UV light to visualize the course of reaction. Flash column chromatography was performed using Merck silica gel (60, particle size 0.02–0.03 mm). Yield % was obtained by ^{1}H NMR, while ^{1}H spectra was obtained using a Bruker AM-300 spectrometer. The following abbreviations were used to designate chemical shiftmutiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 Spectrometer. 1,2-ethylenediamine, *o*-phenylendiamine, $Zn(OAc)_2{\cdot}2H_2O$, $MnCl_2{\cdot}4H_2O$, TMSCN, aldehydes were purchased from Aldrich.

Preparation of 1,2-ethylenediamine zinc complexes ***I***

Amounts of 0.66 mL (0.01 mmol) of 1,2-ethylenediamine, and 2.19 g (0.01 mmol) of $Zn(OAc)_2{\cdot}2H_2O$ were added under anhydrous and oxygen-free conditions to a dry 100-mL Schlenk flask. They were dissolved in 15 mL of dry alcohol, and the reaction mixture was refluxed for 14 h. The solvent was filtrated to give the white crystals (0.38 g, yield 15 %). m.p.: 78–80 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ (ppm) = 2.85(s, 4H), 2.43 (s, 6H), 1.96 (s, 4H). IR (KBr): 3,494, 3,103, 2,319, 1,651, 1,647, 1,565, 1,470, 1,428, 1,418, 1,405, 1,377, 1,338, 1,179, 1,025, 978, 932, 727, 684, 616, 600, 509. Elemental analysis: Anal. Calcd. For $Zn[C_6H_{14}N_2O_4]$: C, 29.63 %; H, 5.76 %, N, 11.52 %; found, % C: 29.24 %; H: 6.06 %; N: 11.89 %.

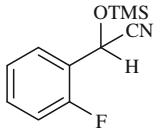
Synthesis of complex ***II***

Amounts of 1.4162 g (4.9 mmol) of *o*-Phenylendiamine and 1.1186 g (10 mmol) were added to 30 ml THF and 0.9768 g (5 mmol) $MnCl_2{\cdot}4H_2O$ in a dry 100-mL Schlenk flask. The reaction mixture was refluxed for 24 h. After hot filtration, the residue was recrystallized from DMF and ether, and colorless crystals were obtained. m.p.: 110–112 °C; Anal. Calcd. % for $C_6H_{14}\ N_2O_2MnCl_2$, C: 26.49; H: 5.19; N: 10.30; found, % C: 26.42; H: 5.493; N: 9.96. IR (KBr, νcm^{-1}): 2,923, 2,810, 1,658, 1,576, 1,496, 1,434, 1,388, 1,250, 1,105, 677.

General procedure of complexes ***I*** *and* ***II****-catalyzed addition of TMSCN to benzaldehyde*

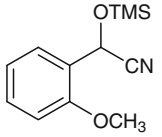
Complexes **I** and **II** 0.15 mmol were dissolved in 2 mL toluene, and benzaldehyde 0.1 mL (1 mmol) and TMSCN 0.3 ml (3.3 mmol) were successively added at room temperature. After 8 h, yield % was obtained by 1H NMR. 1H NMR (300 MHz, CDCl3) 7.56–7.59 (m, 0.9 Hz, 2H), 7.31–7.34 (m, 3H), 5.43 (s, 1H), 0.16 (s, 9H). 13C NMR (75 MHz, CDCl3) 136.1, 128.8 (×2), 126.2 (×2), 119.1, 63.5, −0.39 (×3).

2-(2-Furyl-phenyl)-2-(trimethylsilyloxy)acetonitrile



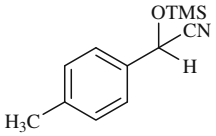
Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 7.56–7.57 (m, 0.9 Hz, 1H), 7.29–7.31 (m, 1H), 7.14–7.15 (m, 1H), 6.99–7.03 (m, 1H), 5.69 (s, 1H), 0.16 (s, 9H), yield (%): >99 %, 91 %.

2-(2-Methyloxyphenyl)-2-(trimethylsilyloxy) acetonitrile



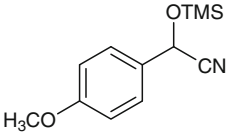
Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 7.52–7.54 (d, J = 7.5 Hz, 1H), 7.20–7.30 (m, 3H), 5.57 (s, 1H), 2.44 (s, 3H), 0.22 (s,9H), yield (%): >99 %, 85 %.

2-(4-Methylphenyl)-2-(trimethylsilyloxy)acetonitrile



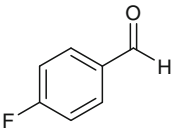
Following the procedure described 3,^{1}H NMR (300 MHz, $CDCl_3$) 7.37–7.39 (m, 2H), 7.21–7.24 (m, 2H), 5.48 (s, 1H), 2.38 (s, 3H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 139.3, 133.5, 129.6, 126.4, 63.6, 31.6, 22.6, 21.2, 14.1, −0.23 (×3), yield (%): 63 %, 73 %.

2-(4-Methyloxyphenyl)-2-(trimethylsilyloxy)acetonitrile



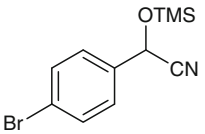
Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 7.61–7.63 (m, 1H), 7.37–7.40 (m, 1H), 7.04–7.07 (m, 1H), 6.92–6.94 (m, 1H), 5.82 (s, 1H), 3.91 (s, 3H), 0.25 (s, 9H), yield (%): 84 %, 24 %.

2-(4-Furylphenyl)-2-(trimethylsilyloxy)acetonitrile



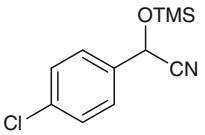
Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 7.40–7.41 (m, 4H), 5.46 (s, 1H), 0.24 (s, 9H), yield (%): 76 %, 49 %.

2-(4-Bromophenyl)-2-(trimethylsilyloxy)acetonitrile



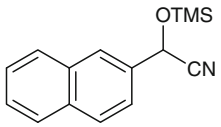
Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 7.53–7.55 (m, 2H), 7.33–7.36 (m, 2H), 5.44 (s, 1H), 0.24 (s, 9H), yield (%): 94 %, >99 %.

2-(4-Chlorophenyl)-2-(trimethylsilyloxy)acetonitrile



Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 7.40–7.41 (m, 4H), 5.46 (s, 1H), 0.23 (s, 9H), yield (%): 82 %, 45 %.

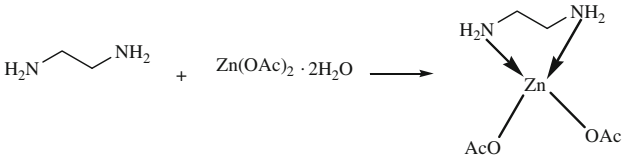
α-(Trimethylsilyoxyl)-1-naphthylacetonitrile



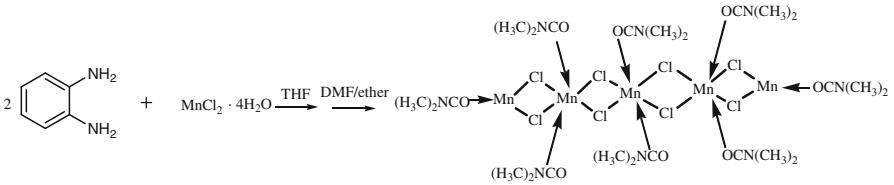
Following the procedure described 3, ^{1}H NMR (300 MHz, $CDCl_3$) 8.16–8.18 (m, 1H), 7.88–7.91 (m, 2H), 7.69–7.71 (m, 1H), 7.25–7.61 (m, 4H), yield (%): 88 %, 76 %.

Results and discussion

Following treatment of the ligands 1,2-ethylenediamine with $Zn(OAc)_2{\cdot}2H_2O$ in ethanol, the corresponding complex was obtained after refluxing for 14 h. The crystals of complex **I** were obtained.

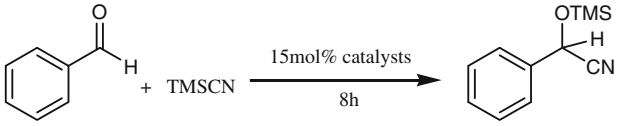


Scheme I The synthetic route to complex **I**



Scheme II The synthetic route to complex **II**

Table 1 The effect of different solvents[a]



Solvents	Yield %[b] (complex **I**)	Yield %[b] (complex **II**)
THF	28	68
CH_2Cl_2	23	67
Toluene	96	99
Ether	94	5
Hexane	96	91

[a] Reactions were carried out with 1 mL PhCHO and 0.3 mL TMSCN in 2 mL CH3OH using 15 mol % of catalyst I, II and III at room temperature (30–40 °C) for 120 h

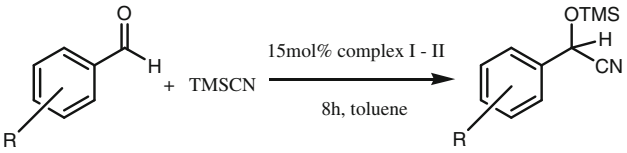
[b] Yield % was determined by NMR analysis

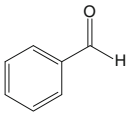
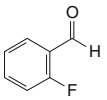
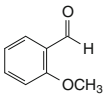
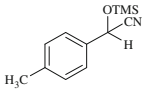
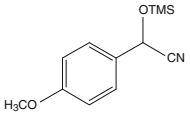
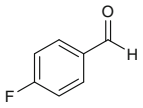
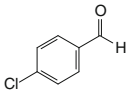
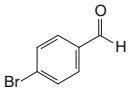
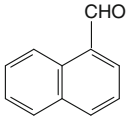
The complex **II** was synthesized from the reaction of *o*-phenylenediamine with $MnCl_2{\cdot}4H_2O$, and, unexpectedly, the colorless crystal structure was obtained by recrystallization of the residue from DMF and ether (Schemes I, II).

In the catalytic process, under the equal condition, if reaction time for 8 h, different solvents such as ether, toluene, THF, and dichloromethane were attempted at room temperature, and the results can be seen in Table 1. Because the catalysts were easily soluble in toluene, and insoluble in ether, toluene was the solvent of best choice. Then, the scope of the catalysts to cyanosilylation of prochiral aldehydes was explored (Table 2).

From the Table 2, we got the conclusion as follows:

Table 2 Cyanosilylation of different aldehydes



Entry	Substrate	Time (h)	Yield %[a, b] (complex **I**)	Yield %[a, b] (complex **II**)
1		8	96	>99
2		8	>99	91
4		8	85	>99
5		8	73	63
6		8	84	24
7		8	76	49
8		8	82	45
9		8	94	>99
10		8	88	76

[a] Reactions were carried out with 1 mL PhCHO and 0.3 mL TMSCN in 2 mL toluene using 15 mol % of catalyst I and II at room temperature (30–40 °C) for 8 h

[b] Yield % was determined by NMR analysis

(i) Aldehydes bearing the electron-donor group and electron-withdrawing group tended to give the lower yield compared with benzaldehyde (entries 1–10, except entry 2).
(ii) Aldehydes substituted in the ortho-position afforded higher yields than in the para position substituted aldehydes (entries 2–10, except entry 9)

All in all, no matter what the kind of substituted group, the stereoscopic effect occupied an important factor in determining the reactivities.

The mechanism can be proposed that the metal ions (Zn^{2+}, Mn^{2+}) could activate the C=O, affording products with high activity.

Conclusion

In summary, Zn(II) and Mn(II) organometallic complexes **I** and **II** were first used to catalyze the cyanosilylation reaction, and achieved good catalytic results (24–99 %). Further efforts towards the other catalytic applications of the complexes such as the Henry reaction, Baylis–Hillman reaction, Allylation reaction, etc.

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