## Cobalt Polyoxometalate, [CoW<sub>12</sub>O<sub>40</sub>]<sup>5-</sup>, as a New Reusable Catalyst for Addition of Trimethylsilyl Cyanide to Carbonyl Compounds

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Cyanohydrin trimethylsilyl ethers are versatile intermediates for the synthesis of cyanohydrins,  $\alpha$ -hydroxycarboxylic acids,  $\alpha$ -hydroxyaldehydes,  $\alpha,\beta$ -unsaturated nitriles and  $\beta$ aminoalcohols.<sup>1</sup> They are useful for protection of carbonyl groups,<sup>2</sup> and also excellent precursors for ferroelectric liquid crystals<sup>3</sup> and components of commercially important compounds such as the pyrethroid insecticides cypermethrin and fluvalinate.<sup>4</sup> A variety of Lewis acids and Lewis bases have been employed successfully as promoters in cyanosilylation of carbonyl compounds.<sup>5</sup> In recent years, several chiral catalysts have been used for asymmetric synthesis of cyanohydrin trimethylsilyl ethers.<sup>6</sup> However, many of these methods suffer from one or more of the following disadvantages: long reaction times, vigorous reaction conditions, tedious work up procedures and a need for relatively expensive reagents such as titanium complexes and Schiff bases. These limitations were the motivation for further investigation of a new inexpensive and non-corrosive heterogeneous catalyst for this transformation.

Continuing our studies on the application of polyoxometalates in organic synthesis,<sup>7</sup> here the use of potassium dodecatungstocobaltate  $(K_5CoW_{12}O_{40}\cdot 3H_2O)^{7a}$  is reported as a cheap and easily prepared catalyst for cyanosilylation of carbonyl compounds (Scheme 1).

Benzaldehyde was used to optimize the temperature, and molar ratio of the catalyst to substrate and solvent. Different solvents were compared and CH<sub>3</sub>CN was chosen (Table 1). The other solvents including benzene showed lower selectivity.

The reaction was extended to other aryl and alkyl aldehydes and ketones as substrate under the optimum conditions. The reaction of aldehydes and ketones (1.0 mmol) with TMSCN (1.2 mmol) in the presence of  $K_5$ CoW<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O (0.05 mmol) proceeded at room

Table 1. Cyanosilylation of Benzaldehyde in Different Solvents

Solvent	Yield <sup>a</sup> %	Selectivity <sup><math>b</math></sup> %
CH <sub>3</sub> CN	82	93
CHCl <sub>3</sub>	33	39
Benzene	70	89
CH <sub>3</sub> COCH <sub>3</sub>	5	60

<sup>*a*</sup>GC yield of cyanohydrin trimethylsilyl ethers. <sup>*b*</sup>Ratio of the cyanohydrin trimethylsilyl ethers product to the total products.

temperature with good yields of the expected cyanohydrin trimethylsilyl ethers. Table 2 clearly shows that aromatic and aliphatic aldehydes and ketones with different electrondonating and withdrawing groups gave good yields of expected cyanohydrin trimethylsilyl ethers. Acid sensitive aldehydes such as furfuraldehyde and cinnamaldehyde worked well without any decomposition or polymerization under the reaction conditions. The possibility of a concerted electron transfer mechanism was strongly supported by a large decrease of the reaction rate upon addition of a small amount of acrylonitrile and 2,6-di-tert-butylphenol as a radical scavenger.

In addition,  $K_5CoW_{12}O_{40}$ ' $3H_2O$  was found to be reusable several times without loss of activity. Simply the catalyst should be filtered, washed with acetone, dried and immediately reused. After reusing the catalyst for four times, the yield of trimethylsilyl ethers produced from the reaction of benzaldehyde with trimethylsilyl cyanide was 80% and the selectivity was 92%. In order to prove that this is truly heterogeneous, first the reaction solution was filtered at the stage of *ca*. 50% conversion and then the reaction was continued. No further conversion was observed from the filtered solution upon stirring. Also, the filtered solution was checked by ICP analysis and no amount of W was observed.

$$R = aryl or alkyl R' = H o$$

Scheme 1

Table 2. Cyanosilylation of aldehydes and ketones catalyzed by  $K_5 CoW_{12} O_{40}.3 H_2 O$ 

Entry	Compound	Time (h)	Yield <sup>a</sup> (%)	Selectivity <sup>b</sup> %
1		3	88	93
2	мео-	1	94	100
3		4	84	100
4	<b>◯</b> =₀	2	96	96
5		4	76	100
6		2	89	95
7		2	95	96
8		4.5	70	100
9	ме	4	81	98
10	⟨NO2_H	5	72	100
11	Содин	4.5	88	100
12		1.5	93	100
13	Me	1.4	95	100
14		4	54	100
15		1.5	76	100
16	ССС <sup>О</sup> н	7	78	100
17	H OMe	7	85	100
18		3	82	94

<sup>a</sup>GC yield of cyanohydrin trimethylsilyl ethers, Products characterized by <sup>1</sup>H NMR and IR.<sup>8</sup> <sup>b</sup>Ratio of cyanohydrin trimethylsilyl ethers product to total products.

## **Experimental Section**

 $K_5CoW_{12}O_{40}$ ·3H<sub>2</sub>O was prepared according to literature<sup>7a</sup>. Typical experimental procedure: A mixture of carbonyl compound (1.0 mmol),  $K_5CoW_{12}O_{40}$ ·3H<sub>2</sub>O (0.05 mmol) and TMSCN (1.2 mmol) in dried acetonitrile (4 mL) was stirred at room temperature for the time indicated in Table 1. The reaction was monitored by GC with decane as a gas chromatography internal standrad. After completion of the reaction, the catalyst was filtered off and further purification was done by silica gel chromatography. The products were characterised from their IR and NMR spectral data.<sup>8</sup>

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  Some Spectral Data:
- 2-Hydroxyphenyl acetonitril (Table 1, Entry 1): IR (neat),  $\nu$  (cm<sup>-1</sup>): 3417.7 (OH), 2249 (CN). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 2.90 (bs, 1H), 5.55 (s, 1H), 7.40-7.60 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 63.5, 118.8, 126.6, 129.1, 129.8, 135.2.
  - 2-Hydroxy(4-methoxyphenyl) acetonitril (Table 1, Entry 2): IR (neat),  $\nu$  (cm<sup>-1</sup>): 3417.66 (OH), 2250.80 (CN). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 3.08 (d, J = 6.8 Hz, 1H), 3.83 (s, 3H), 5.47 (d, J = 6.8 Hz, 1H), 6.95 (m, 2H), 7.44 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 55.04, 63.2, 114.5, 118.9, 127.5, 128.3, 160.6.

Notes

2-Hydroxy(2-chlorophenyl) acetonitril (Table 1, Entry 3): IR (neat),  $\nu$  (cm<sup>-1</sup>): 3504.5 (OH), 2232.2 (CN). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 2.75 (s, 1H), 5.46 (s, 1H), 7.33 (m, 3H), 7.46 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 63.5, 118.8, 126.6, 129.1, 129.8, 135.2.

1-Hydroxy-1-cyanocyclohexane (Table 1, Entry 4): <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 1.03-1.45 (m, 5H), 1.61-1.95 (m, 6H), 2.86 (d, J = 6.4 Hz, 1H), 4.27 (t, J = 6.3 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 25.3, 25.4, 25.9, 27.8, 28.1, 42.1, 66.2, 119.3.

2-Hydroxy(4-nitrophenyl) acetonitril (Table 1, Entry 5): <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 3.42 (s, 1H), 5.54 (s, 1H), 7.70 (m, 2H), 7.75 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 63.26, 116.54, 116.76, 119.14, 129.10, 131.51, 162.59, 165.07.

2-Hydroxy(4-cyanophenyl) acetonitril (Table 1, Entry 8): <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 3.70(d, J = 6.5 Hz, 1H), 5.64 (d, J = 6.5 Hz, 1H), 7.73 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 62.5, 113.3,

117.9, 118.0, 127.2, 132.9, 140.1.

2-Hydroxy(4-methylphenyl) acetonitril (Table 1, Entry 9): IR (neat),  $\nu$  (cm<sup>-1</sup>): 3415.7 (OH), 2246.9 (CN). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 2.38 (s, 3H), 3.28 (bs, 1H), 5.48 (s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.41 (2H, d, J = 8.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 21.2, 63.3, 119.0, 126.6, 129.8, 132.3, 139.9.

2-Hydroxy(2,4-methoxyphenyl) acetonitril (Table 1, Entry 12): <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 3.73 (d, J = 7.0 Hz, 1H), 3.94 (s, 3H), 5.59 (d, J = 7.0 Hz, 1H), 6.90 (m, 2H), 7.40 (m, 2H).

2-Hydroxy(1-naphtyl) acetonitril (Table 1, Entry 15): <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 3.41 (d, J = 6.9 Hz, 1H), 6.15 (d, J = 6.9 Hz, 1H), 8.20-7.40 (m, 7H).

2-Hydroxy(2-naphtyl) acetonitril (Table 1, Entry 16): <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 2.97 (bs, 1H), 5.72 (bs, 1H), 7.50 (m, 3H), 7.90 (m, 4H).