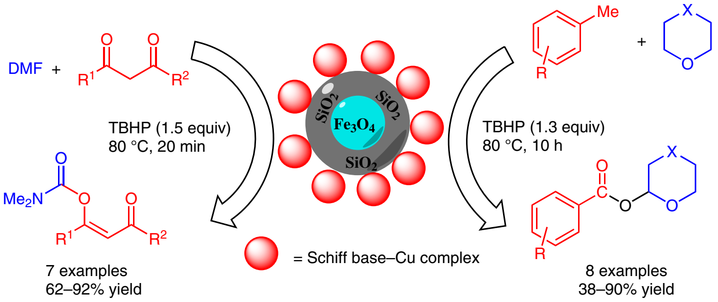
Anchoring of a Copper(II)–Schiff Base Complex onto Silica-Coated Ferrite Nanoparticles: A Magnetically Separable Catalyst for Oxidative C–O Coupling by Direct C(sp^2)–H and C(sp^3)–H Bond Activation

Rashid Ghanbaripour*[a]
Marjaneh Samadizadeh*[b]
Golnaz Honarpisheh[b]
Majid Abdolmohammadi[b]

[a] Young Researchers and Elite Club, Central Tehran Branch, Islamic Azad University, Tehran 19379-58814, Iran
r.ghanbaripour@gmail.com
[b] Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran 19379-58814, Iran
mar.samadizadeh@iauctb.ac.ir



Received: 01.06.2015
Accepted after revision: 04.07.2015

DOI: 10.1055/s-0035-1560067; Art ID: st-2015-d0408-l

Abstract A novel catalyst consisting of a Schiff base–copper complex on surface-modified silica-coated ferrite nanoparticles was been prepared and used for oxidative C–O cross-coupling reactions of 1,3-dicarbonyl compounds with formamides for the synthesis of enol carbamates. The new catalyst has also been used for esterification of alkylbenzenes with cyclic ethers.

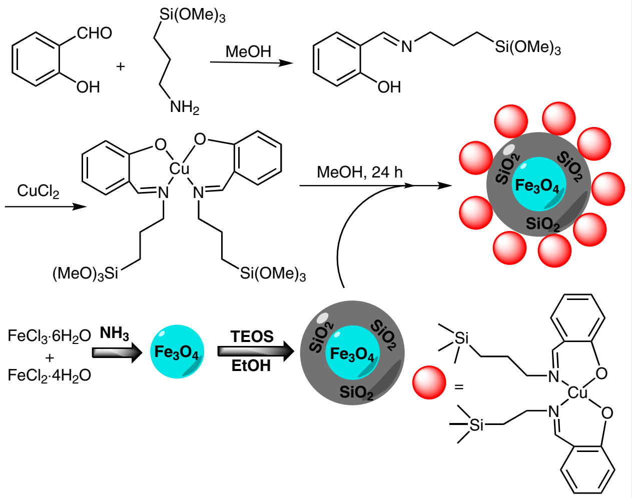
Key words catalysis, bond activations, Schiff bases, oxidative coupling, green chemistry, carbamates

In recent years, the heterogenization of homogeneous catalysts has attracted immense attention.[1] Although many homogeneous catalysts demonstrate high selectivity and can be used to control the stereochemistry and regiochemistry of the reaction products, it can be difficult to separate soluble catalysts from the reaction products.[2] Recovery and reusability of catalysts are highly desirable from both economic and environmental standpoints. As a result, several methods have been explored for the recovery of homogeneous catalysts. These include the use of organic and/or inorganic supports for heterogenized homogeneous catalysts.[3] In this regard, magnetic nanoparticles have a prominent rule because of their good stability and ease of separation by using a magnetic field.[4] The surface of the magnetic nanoparticles is usually coated with a layer of silica to prevent aggregation. Because of the importance of magnetic catalysts, the synthesis and characterization of these types of catalyst are of interest, and there have been many reports dealing with this area.[5]

In the past decade, transition-metal-catalyzed C–H functionalization has been developed as an attractive and powerful strategy, because this method permits more-efficient synthesis of functionalized molecules by minimizing the number of synthetic steps.[6] Although various transition-metal catalyst systems have been developed for C–H activation reactions,[7] copper remains one of the most important metal catalysts for this purpose because of the ability of the copper atom to act as a single-electron and/or a two-electron mediator and as a Lewis acid. Moreover, copper can act as either an electrophile or nucleophile, depending upon its oxidation state and the reaction conditions. Although copper-mediated transformations have been overshadowed by developments in palladium chemistry, many novel copper-catalyzed processes have recently appeared because of the low cost and ready availability of copper compounds in comparison to palladium or other precious metals, such as ruthenium, rhodium, and gold.[8] Oxidative C–O cross-coupling is one of the most important methods for the synthesis of various oxygen-bearing organic compound, such as ethers, esters, oxazoles, or carbamates.[9]

In a continuation of our work on heterogeneous catalysts and C–O coupling reactions,[3c,8f,10] we examined the synthesis of a copper–Schiff base complex covalently supported on magnetic nano particles, and its application in oxidative C–O reactions for the synthesis of esters and carbamates.

Initially, silica-coated ferrite nanoparticles ($Fe_3O_4@SiO_2$) were prepared from iron(III) chloride, iron(II) chloride, and tetraethyl orthosilicate, according to a reported procedure.[11] A copper (II)–Schiff base complex was prepared by the reported procedure[12] then treated with the silica-coated ferrite nanoparticles in methanol to give the new copper catalyst (Scheme 1).



Scheme 1 Preparation of a copper(II)–Schiff base complex covalently anchored on silica-coated ferrite nanoparticles

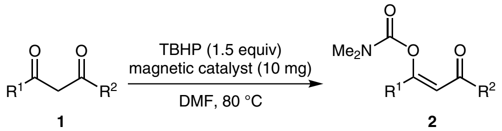
The new magnetic catalyst was characterized by X-ray diffraction, Fourier-transform IR spectroscopy, scanning electron microscopy, vibrating sample magnetometry (VSM), and inductively coupled plasma techniques (ICP) (see Supplementary Information). In the IR spectrum, absorption bands at 2925, 2852, 1664, and 1097 cm^{-1}, related to symmetric and asymmetric vibrations of CH_2, C=N, and Si–O–Si groups, clearly indicated the incorporation of the Schiff base complex onto the surface of the silica-coated ferrite nanoparticles. VSM analysis showed that the magnetic saturation value of the copper-containing catalyst was less than that of the silica-coated ferrite nanoparticles; this can be explained by a shielding effect of the functional copper complex on the magnetic nanoparticles. Finally, elemental analysis indicated a loading of 1.1 mmol g^{-1}.

After characterizing the catalyst, we decided to examine its activity in oxidative C–O coupling reactions for the synthesis of enol carbamates[13] and esters.[14]

First, we examined the oxidative coupling of methyl acetoacetate with *N*,*N*-dimethylformamide in the presence of a subequivalent amount of the catalyst with *tert*-butyl hydroperoxide as an oxidant. To optimize the reaction conditions, we investigated various parameters, such as the amount of catalyst, the temperature, and the nature and quantity of the oxidant. Optimal results were obtained for the reaction in the presence of 10 mg catalyst (containing 0.011 mmol copper) and *tert*-butyl hydroperoxide (1.5 equiv) at 80 °C for 20 minutes, which gave a 92% yield of methyl (2*Z*)-3-{[(dimethylamino)carbonyl]oxy}but-2-enoate (**2a**).[15] In addition, the pure silica-coated nanoparticles were tested for catalytic activity in this reaction, and no product was obtained under these conditions.

With the optimized reaction conditions in hand, we extended our study to various 1,3-dicarbonyl compounds. The reactions were generally clean, and gave the desired products **2a**–**g** in good to excellent yields (Table 1).

Table 1 Synthesis of Enol Carbamate Derivatives



Entry	R^1	R^2	Product	Yield (%)
1	Me	OMe	**2a**	92
2	Me	OEt	**2b**	90
3	Me	OBn	**2c**	85
4	Me	Me	**2d**	78
5	Ph	OEt	**2e**	76
6	Pr	OEt	**2f**	62
7	Me	OAll	**2g**	75

A plausible mechanism for the oxidative C–O coupling reaction between 1,3-dicarbonyl compounds and *N*,*N*-dimethylformamide has been proposed in the literature.[13]

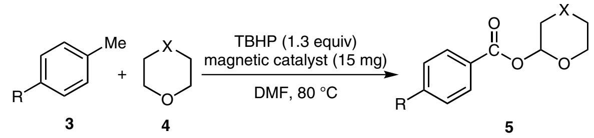
Having successfully synthesized the enol carbamates **2a**–**g**, we decided to evaluate the effect of this new catalyst system in an oxidative esterification reaction between alkylbenzenes and cyclic ethers. For this purpose, our initial studies focused on determining the optimal conditions for the reaction of toluene with 1,4-dioxane. The best results were obtained in the presence of 15 mg of the catalyst (containing 0.016 mmol of copper) and 1.3 equivalent of *tert*-butyl hydroperoxide at 80 °C for 10 hours, which gave an 83% yield of the ester **5a**.[16] When the reaction was attempted in the absence of the catalyst and/or the oxidizing agent, the desired product was not obtained. To explore the generality of the reaction, we extended our study to various alkylbenzenes **3** and cyclic ethers **4** (Table 2).

This protocol tolerates a variety of alkylbenzenes containing electron-withdrawing or electron-donating substituents. The electron-donating groups increased the yield of the reaction, because the electron-rich compounds are more easily oxidized than the electron-deficient compounds.

A plausible mechanism for the oxidative esterification reaction between alkylbenzenes and cyclic ethers has been proposed in the literature.[14g]

Next, we examined the reusability of the catalyst in both reactions. After completion of a first reaction by either protocol, the catalyst was recovered by using an external magnet, washed with ethanol and diethyl ether, and oven-

Table 2 Synthesis of Benzoate Derivatives



Entry	R	X	Product	Yield (%)
1	H	O	**5a**	83
2	Me	O	**5b**	85
3	Cl	O	**5c**	55
4	OMe	O	**5d**	90
5	Br	O	**5e**	64
6	H	CH_2	**5f**	49
7	Me	CH_2	**5g**	51
8	Cl	CH_2	**5h**	38

dried at 100 °C overnight. The recovered catalyst could be used at least five times without significant loss in yield. To examine whether there was any leaching of the copper complex, we removed the catalyst by using a magnet 10 minutes after the beginning of the reaction, and we observed that the reaction did not reach completion, even after 24 hours. This clearly confirmed that the active species does not leach into the solvent. Furthermore, ICP analysis showed that there was no copper in solution

In summary, we have developed a novel magnetic catalyst functionalized with a Schiff base–copper complex. The new catalyst was characterized by a range of physical techniques and its catalytic activity was successfully demonstrated in oxidative C(sp^2)–O and C(sp^3)–O coupling reactions. The recyclability of the catalyst, ease of manipulation, shorter reaction times in comparison with other reported catalysts, and good yields are the main advantages of this protocol.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560067.

References and Notes

(1) Minakata, S.; Komatsu, M. *Chem. Rev.* **2009**, *109*, 711.
(2) (a) Hagen, J. *Industrial Catalysis: A Practical Approach*; Wiley-VCH: Weinheim, **1999**. (b) Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702.
(3) (a) Zhang, Y.; Riduana, S. N. *Chem. Soc. Rev.* **2012**, *41*, 2083. (b) Du, X.; Sun, Y.; Tan, B.; Teng, Q.; Yao, X.; Su, C.; Wang, W. *Chem. Commun.* **2010**, *46*, 970. (c) Ghanbaripour, R.; Mohammadpoor-Baltork, I.; Moghadam, M.; Khosropour, A. R.; Tangestaninejad, S.; Mirkhani, V. *Polyhedron* **2012**, *31*, 721.
(4) (a) Reddy, L. H.; Arias, J. L.; Nicolas, J.; Couvreur, P. *Chem. Rev.* **2012**, *112*, 5818. (b) Panella, B.; Vargas, A.; Baiker, A. *J. Catal.* **2009**, *261*, 88. (c) Shin, J.; Kim, H.; Lee, I. S. *Chem. Commun.* **2008**, 5553. (d) Abu-Reziq, R.; Alper, H.; Wang, D.; Post, M. L. *J. Am. Chem. Soc.* **2006**, *128*, 5279. (e) Rossi, L. M.; Silva, F. P.; Vono, L. L. R.; Kiyohara, P. K.; Duarte, E. L.; Itri, R.; Landers, R.; Machado, G. *Green Chem.* **2007**, *9*, 379.
(5) (a) Wang, S.; Zhang, Z.; Liu, B.; Li, J. *Catal. Sci. Technol.* **2013**, *3*, 2104. (b) Stevens, P. D.; Li, G.; Fan, J.; Yen, M.; Gao, Y. *Chem. Commun.* **2005**, 4435. (c) Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Vander Elst, L.; Muller, R. N. *Chem. Rev.* **2008**, *108*, 2064.
(6) (a) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 8960. (b) Xie, J.; Pan, C.; Abdukader, A.; Zhu, C. *Chem. Soc. Rev.* **2014**, *43*, 5245. (c) Haines, B. E.; Musaev, D. G. *ACS Catal.* **2015**, *5*, 830. (d) Zheng, C.; You, S. L. *RSC Adv.* **2014**, *4*, 6173. (e) He, Y.-P.; Zhang, C.; Fan, M.; Wu, Z.; Ma, D. *Org. Lett.* **2015**, *17*, 496. (f) Li, B.; Wang, S.-Q.; Liu, B.; Shi, B.-F. *Org. Lett.* **2015**, *17*, 1200. (g) Wu, X.; Zhao, Y.; Ge, H. *J. Am. Chem. Soc.* **2015**, *137*, 4924.
(7) (a) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (b) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584. (c) Baggett, A. W.; Vasiliu, M.; Li, B. *Dixon D. A., Liu S. Y.* **2015**, *137*, 5536. (d) Dateer, R. B.; Chang, S. *J. Am. Chem. Soc.* **2015**, *137*, 4908. (e) Li, M.; Yang, Y.; Zhou, D.; Wan, D.; You, J. *Org. Lett.* **2015**, *17*, 2546.
(8) (a) Klapars, A.; Antilla, J. C.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 7727. (b) Klapars, A.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7421. (c) Sequeira, F. C.; Turnpenny, B. W.; Chemler, S. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 6365. (d) Xiong, T.; Li, Y.; Bi, X.; Lv, Y.; Zhang, Q. *Angew. Chem. Int. Ed.* **2011**, *50*, 7140. (e) Neumann, J. J.; Suri, M.; Glorius, F. *Angew. Chem. Int. Ed.* **2010**, *49*, 7790. (f) Alizadeh, A.; Ghanbaripour, R. *Synlett* **2014**, *25*, 2777.
(9) (a) Ke, Q.; Zhang, B.; Hu, B.; Jin, Y.; Lu, G. *Chem. Commun.* **2015**, *51*, 1012. (b) Wang, C. Y.; Song, R. J.; Wei, W. T.; Fan, J. H.; Li, J. H. *Chem. Commun.* **2015**, *51*, 2361. (c) Sarkar, R.; Mukhopadhyay, C. *Tetrahedron Lett.* **2015**, *56*, 3872. (d) Shang, X.-J.; Liu, Z.-Q. *Tetrahedron Lett.* **2015**, *56*, 482. (e) Xu, W.; Nachtsheim, B. J. *Org. Lett.* **2015**, *17*, 1585.
(10) Ghanbaripour, R.; Mohammadpoor-Baltork, I.; Moghadam, M.; Khosropour, A. R.; Tangestaninejad, S.; Mirkhani, V. *J. Iran. Chem. Soc.* **2012**, *9*, 791.
(11) Liu, Z. L.; Ding, Z. H.; Yao, K. L.; Tao, J.; Du, G. H.; Lu, Q. H.; Wang, X.; Gong, F. L.; Chen, X. *J. Magn. Magn. Mater.* **2003**, *265*, 98.
(12) Lim, M. H.; Stein, A. *Chem. Mater.* **1999**, *11*, 3285.
(13) (a) Kumar, G. S.; Maheswari, C. U.; Kumar, R. A.; Kantam, M. L.; Reddy, K. R. *Angew. Chem. Int. Ed.* **2011**, *50*, 11748. (b) Saberi, D.; Heydari, A. *Tetrahedron Lett.* **2013**, *54*, 4178. (c) Azizi, K.; Karimi, M.; Heydari, A. *Tetrahedron Lett.* **2015**, *56*, 812.
(14) (a) Yoo, W.-J.; Li, C.-J. *Tetrahedron Lett.* **2007**, *48*, 1033. (b) Rout, S. K.; Guin, S.; Chara, K. K.; Banerjee, A.; Patel, B. K. *Org. Lett.* **2012**, *14*, 3982. (c) Yoo, W.-J.; Li, C.-J. *J. Org. Chem.* **2006**, *71*, 6266. (d) Xu, X.; Ding, W.; Lin, Y.; Song, Q. *Org. Lett.* **2015**, *17*, 516. (e) Li, W.; Duan, Z.; Jiang, R.; Lei, A. *Org. Lett.* **2015**, *17*, 1397. (f) Zhou, J.; Jin, C.; Li, X.; Su, W. *RSC Adv.* **2015**, *5*, 7232. (g) Rout, S. K.; Guin, S.; Ali, W.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2014**, *16*, 3086.
(15) **Enol Carbamates 2a–g; General Procedure**
A 70% aq solution of TBHP (0.193 g, 1.5 equiv) was added dropwise to a mixture of the appropriate 1,3-dicarbonyl compound **1** (1 mmol), the magnetic catalyst (10 mg), and DMF (2 mL). The mixture was heated to 80 °C, stirred for 20 min, and then cooled

to r.t. The catalyst was removed by using an external magnet, and the residue was extracted with EtOAc (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by column chromatography.

Allyl (2*Z*)-3-{[(Dimethylamino)carbonyl]oxy}but-2-enoate (2g)

Yellow oil; yield: 160 mg (75%); IR (KBr): 1725, 1669, 1382, 1320, 1271, 1211, 1145, 1035, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, CH_3), 2.97 (s, 3 H, CH_3N), 3.02 (s, 3 H, CH_3N), 4.57 (dd, $^{3}J_{HH}$ = 5.6 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2 H, CH_2O), 5.18–5.34 (m, 2 H, CH_2=CH), 5.58 (s, 1 H, $CHCO_2$), 5.82–5.97 (m, 1 H, CH_2=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.21, 36.59, 64.62, 107.61, 118.03, 132.31, 152.99, 161.33, 163.66.

(16) **Aryl Esters 5a–5h; General Procedure**

In a round-bottomed flask, a mixture of alkylbenzene **3** (1 mmol), magnetic catalyst (15 mg), and 70% aq TBHP (0.167 g, 1.3 equiv) in 1,4-dioxane (2 mL) was stirred at 80 °C for 10 h, then cooled to r.t. The catalyst was removed by using an external magnet and the residue was extracted with EtOAc (2 × 10 mL). The extracts were washed with 5% aq $NaHCO_3$ (15 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by column chromatography.

1,4-Dioxan-2-yl Benzoate (5a)

Pale yellow oil; yield: 156 mg (75%); IR (KBr): 3071, 2970, 2861, 1718, 1529, 1455, 1402, 1276, 1014, 911, 879, 715 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64–3.69 (m, 1 H), 3.80–3.83 (m, 2 H), 3.85–3.89 (m, 2 H), 4.16–4.23 (m, 1 H), 6.08 (t, $^{3}J_{HH}$ = 2.1 Hz, 1 H), 7.42–7.46 (m, 2 H), 7.55–7.57 (m, 1 H), 8.09–8.11 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 61.9, 66.4, 68.1, 90.0, 128.6, 129.9, 130.2, 133.56, 165.4.