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Cobalt-catalyzed dimerization of alkenes

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Abstract—In the presence of $CoX_2(PPh_3)_2$/3 PPh_3 and zinc metal conjugated alkenes ($CH_2CHCOOR$, CH_2CHCN, CH_2CHSO_2Ph and $CH_2CHCONEt_2$) undergo reductive tail-to-tail dimerization to yield the corresponding saturated linear products. Under similar reaction conditions, vinylarenes ($ArCHCH_2$) give stereoselective head-to-tail dimerization products, *trans*-1,3-diarylbut-1-ene, in good to excellent yields.
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Transition metal-catalyzed dimerization of olefins is useful for synthesizing important intermediates for fine and industrial chemicals.[1,2] A widely studied example is the dimerization of methyl acrylate catalyzed by Rh, Ru, Pd and Ni complexes.[3,4] This regioselective tail-to-tail dimerization of methyl acrylate coupled with further hydrogenation and hydrolysis has provided an attractive alternative route to adipic acid, one of the monomers used in the production of Nylon-6,6.[5,6] In this work, we wish to report two cobalt-catalyzed reaction modes: (a) reductive dimerization of conjugated alkenes to yield directly the saturated linear diesters, offering a more convenient method to the synthesis of adipic acid (Eq. 1) and, (b) cobalt-catalyzed head-to-tail dimerization of vinylarenes in good yields (Eq. 3). To date, few effective methods in the literature are known on the dimerization of electron-withdrawing alkenes[7,8] and vinylarenes.[9,10]

Butyl acrylate in the presence of $CoI_2(PPh_3)_2$ (5 mol%), PPh_3 (16 mol%), zinc metal powder and water in acetonitrile at 80 °C undergoes tail-to-tail reductive dimerization to give product **2a** (dibutyl adipate) in 90% yield. The reaction is completely regioselective. No isomer other than **2a** was detected in the reaction mixture in the ${}^1H$ NMR spectrum. Control reactions reveal that no reductive dimerization occurred in the absence of a cobalt complex or zinc metal and only a trace of **2a** was

produced if no extra water was added. As shown by Eq. 1, the formation of **2a** requires water and zinc metal as the proton source and as the reducing agent, respectively.
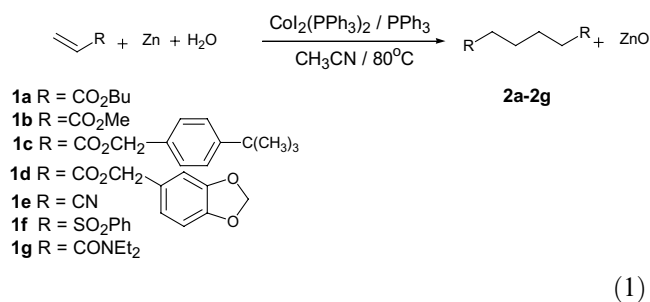
To understand the nature of the present catalytic reaction, the catalytic activities of various metal complexes for the reductive dimerization of butyl acrylate complexes were examined. Both cobalt phosphine complexes $CoI_2(PPh_3)_2$, and $CoCl_2(PPh_3)_2$ show catalytic activities giving dibutyl adipate (**2a**) in 68% and 30% yields, respectively. For cobalt complexes containing bidentate ligands such as $CoI_2(dppe)$, $CoCl_2(dppe)$ and $CoI_2(dppm)$ low activities were observed affording **2b** in 50%, 28% and 22% yields, respectively. The addition of extra PPh_3 to the $CoI_2(PPh_3)_2$ system reveals great influence to the yield of product **2a**. The addition of extra PPh_3 to the $CoI_2(PPh_3)_2$ system first increases the product yield. However, as the amount of PPh_3 increases to more than 3.2 equiv, inhibition of the catalytic activity and decrease of product yield were observed. The most efficient catalyst system for this reaction consists of $CoI_2(PPh_3)_2$ and 3.2 equiv of extra PPh_3 giving the desired product in 90% yield. Nickel and palladium complexes such as $NiBr_2(dppe)$, $NiCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)$ and $Pd(dba)_2$ showed no catalytic activity for the reductive dimerization under similar reaction conditions.

The choice of solvent is also vital to the catalytic reaction. Several common solvents were tested for the catalytic reductive dimerization of butyl acrylate. The most effective solvent is acetonitrile in which the reaction gave
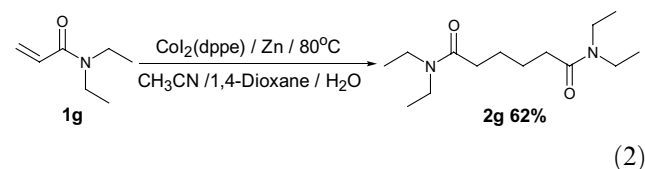
2a in 90% yield. Dichloromethane, THF and DMF are less effective providing **2a** in 63%, 33% and 26% yields, respectively, while toluene is totally ineffective giving no reductive dimerization product. The presence of a stoichiometric amount of water as a proton source is necessary for the catalytic reaction to proceed smoothly. In general, 0.7–1 mol of water was added to the reaction solution to achieve the highest yield of **2a**. However, the presence of a large excess of water led to deactivation of the cobalt complex and the formation of hydrogenation product of butyl acrylate, butyl propionate.

$$\text{R} + \text{Zn} + \text{H}_2\text{O} \xrightarrow[\text{CH}_3\text{CN}/80^{\circ}\text{C}]{\text{CoI}_2(\text{PPh}_3)_2/\text{PPh}_3} \text{R} \diagdown\diagup \text{R} + \text{ZnO}$$

1a R = CO$_2$Bu
1b R = CO$_2$Me
1c R = CO$_2$CH$_2$—C$_6$H$_4$—C(CH$_3$)$_3$
1d R = CO$_2$CH$_2$—
1e R = CN
1f R = SO$_2$Ph
1g R = CONEt$_2$

2a-2g

(1)

Similarly, acrylate **1b**, **1c** and **1d** are also reductively dimerized to give **2b**, **2c** and **2d** in excellent yields. Other electron-withdrawing alkenes also undergo reductive tail-to-tail dimerization in the presence of CoI$_2$(PPh$_3$)$_2$, PPh$_3$, zinc metal powder and water. Thus, acrylonitrile **1e** afforded adiponitrile **2e** and phenyl vinyl sulfone **1f** gave the corresponding reductive dimer **2f** in 89% and 91% isolated yields, respectively. The reductive dimerization can be further extended to N,N-disubstituted acrylamide. Thus, N,N-diethyl acrylamide **1g** in the presence of CoI$_2$(dppe) in a mixture of acetonitrile and 1,4-dioxane (v/v = 1/1) is reductively dimerized to afford product **2g** in 62% yield (Table 1, entry 7 and Eq. 2). For each of these reductive dimerization reactions only one isomer with the structure similar to **2a** was observed.

$$\xrightarrow[\text{CH}_3\text{CN}/1,4\text{-Dioxane}/\text{H}_2\text{O}]{\text{CoI}_2(\text{dppe})/\text{Zn}/80^{\circ}\text{C}}$$

1g   **2g 62%**

(2)

Under similar catalytic reaction conditions, vinylarenes undergo head-to-tail dimerization instead of the tail-to-tail reductive dimerization observed for acrylates. Various reaction conditions for this head-to-tail dimerization were investigated. Suitable catalytic reaction conditions consisted of CoCl$_2$(PPh$_3$)$_2$, PPh$_3$, zinc metal powder and EtOH. A range of vinylarenes (**3a–l**) with different substituents on the aromatic rings were converted to 1,3-diaryl-1-butenes in good to excellent yields under the reaction conditions (Table 2). The catalytic reactions appear insensitive to the substituent on the aromatic ring. Vinylarenes with either an electron-donating or withdrawing substituent on the aromatic ring of vinylarenes were dimerized smoothly.

Table 1. Results of Co-catalyzed reductive dimerization of conjugated alkenes[a]

Entry	Substrate	Yield[b] (%)
1	**1a** R = CO$_2$Bu	**2a** 90
2	**1b** R = CO$_2$Me	**2b** 89
3	**1c** R = CO$_2$CH$_2$Ph-4-^{t}Bu	**2c** 96
4	**1d** R = CO$_2$CH$_2$PhO$_2$CH$_2$	**2d** 97
5	**1e** R = CN	**2e** 89
6	**1f** R = SO$_2$Ph	**2f** 91
7	**1g** R = CONEt$_2$	**2g** 62[c]

[a] Reaction conditions: substrate (2.00 mmol), CoI$_2$(PPh$_3$)$_2$ (5 mol%), Zn (3.0 mmol), H$_2$O (0.7–1.0 mmol), PPh$_3$ (0.16 mmol), CH$_3$CN (2.0 mL), 80 °C and 24 h.
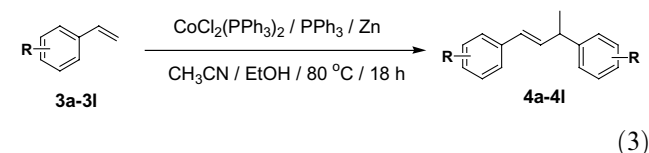[b] Isolated yields.
[c] **1g** (2.00 mmol), CoI$_2$(dppe) (5 mol%), Zn (3.0 mmol), H$_2$O (0.4 mmol), CH$_3$CN (1.0 mL), 1,4-dioxane (1.0 mL), 80 °C and 24 h.

Table 2. Results of Co-catalyzed dimerization of vinylarenes[a]

Entry	Substrate	Yield[b] (%)
1	**3a** R = H	**4a** 88
2	**3b** R = 4-Ph	**4b** 86
3	**3c** R = 2-OMe	**4c** 62
4	**3d** R = 3-OMe	**4d** 94
5	**3e** R = 4-OMe	**4e** 82
6	**3f** R = 4-OAc	**4f** 89
7	**3g** R = 4-NH$_2$	**4g** 91
8	**3h** R = 4-NPh$_2$	**4h** 89
9	**3i** R = 2-F	**4i** 66
10	**3j** R = 3-F	**4j** 74
11	**3k** R = 4-F	**4k** 84
12	**3l** R = 3-Cl	**4l** 79

[a] Reaction conditions: vinylarene (2.00 mmol), CoCl$_2$(PPh$_3$)$_2$ (10 mol%), Zn (3.0 mmol), EtOH (20 mol%), PPh$_3$ (30 mol%), CH$_3$CN (2.0 mL), 80 °C and 18 h.
[b] Isolated yields.

$$\text{R} \xrightarrow[\text{CH}_3\text{CN}/\text{EtOH}/80\,^{\circ}\text{C}/18\,\text{h}]{\text{CoCl}_2(\text{PPh}_3)_2/\text{PPh}_3/\text{Zn}} \text{R}\diagup\diagdown\text{R}$$

3a-3l   **4a-4l**

(3)

To understand the role of water and to help elucidate the mechanism of the present catalytic reaction, an isotope labelling experiment using D$_2$O (99.9%) to replace normal water for the reductive dimerization of vinyl phenyl sulfone **1f** was performed. Analysis of product **2f'** by ^{1}H NMR shows that the two α-protons were 87% deuterated and no deuteration for other protons in this product was observed. The isotope abundance was determined by ^{1}H NMR integration method. In agreement with the ^{1}H NMR results, the ^{13}C NMR spectrum of **2f'** isolated from the above labelling study reveals characteristic deuterium-coupled triplets at 54.9 ppm for the α-carbons.

PhO$_2$S   SO$_2$Ph   **87%**

2 f '
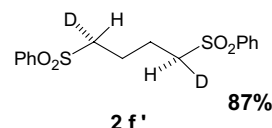
While the mechanism for the reductive dimerization of acrylate is not clear, a possible pathway that can explain

the observed tail-to-tail coupling of the two acrylates and the highly regioselective deuteration by D_2O of the product is based on a cobalt(III) hydride as a key intermediate as shown in Scheme 1. The catalytic reaction is likely initiated by the reduction of the Co(II) complex to a Co(I) species. Protonation of the latter by water generated a cobalt(III) hydride. Insertion of an acrylate molecule into the cobalt-hydride bond gives a five-membered ring species. Further insertion of acrylate molecule and protonation provides the expected reductive dimerization product. A similar pathway involving a Rh(III) or a Co(III) hydride has been proposed to catalyze the tail-to-tail dimerization of acrylate catalyzed by rhodium and cobalt complexes.[3a,7b,11]

The dimerization of vinylarenes can also be explained based on an cobalt(III) hydride as the catalytic intermediate. Insertion of the vinyl group into the Co–H bond with the hydride adding to the terminal carbon gives intermediate **5** as shown in Scheme 2. Further insertion of a vinylarene to the Co–C bond in **5** via the same regiochemistry followed by β-hydrogen elimination affords the dimerization product and regenerates the cobalt(III) hydride (Scheme 2).

Another possible pathway involving cobaltacyclopentanes **I** or **II** as key intermediates (Scheme 3) cannot be ruled out. Coordination of two acrylates (vinylarenes) to the Co(I) centre followed by cyclometallation gives intermediate **I** (or **II**). Successive protonation of this intermediate affords the final product **2**. This mechanism accounts well for the observed regiochemistry of product **2** (or **4**) and also explain nicely the results of the foregoing deuterium-labelling experiment.

In conclusion, we have developed two unique methods for coupling of alkenes. One is the reductive dimerization of electron-withdrawing olefins catalyzed by cobalt complexes. This cobalt-catalyzed reaction yields directly
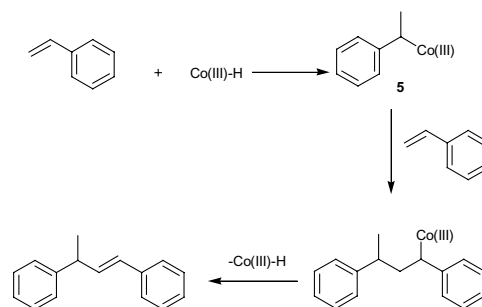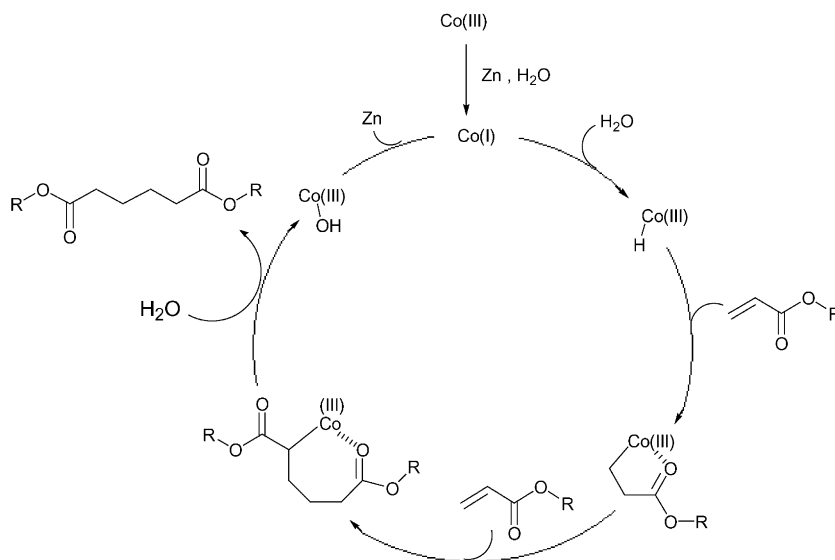

Scheme 2.
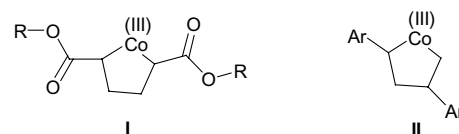
Scheme 3.

the saturated linear diesters, dinitrile and disulfone, offering a convenient alternative method to the synthesis of adipic acid or adiponitrile that are important monomers for the production of Nylon-6,6. Secondly, we have disclosed a very effective regio- and stereoselective cobalt-catalyzed reaction of head-to-tail dimerization of vinylarenes.

Acknowledgements

Scheme 1.

References and notes

1. (a) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W., Eds.; VCH: New York, 1996; Vol. 1, pp 258–268; (b) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613–648.
2. (a) Alderson, T.; Jenner, E.; Lindsey, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 5638–5645; (b) Brookhart, M.; White, P. S.; DiRenzo, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 6225–6234; (c) Small, B. L.; Marcucci, A. J. *Organometallics* **2001**, *20*, 5738–5744; (d) Small, B. L. *Organometallics* **2003**, *22*, 3178–3183; (e) Mitsudo, T.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *J. Am. Chem. Soc.* **1999**, *121*, 1839–1850.
3. (a) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777–2779; (b) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080–1085; (c) Tkatchenko, I.; Neibecker, D.; Grenouillet, P. *Organometallics* **1984**, *3*, 1130–1132; (d) Pertici, P.; Ballantini, V.; Salvadori, P.; Bennett, M. A. *Organometallics* **1995**, *14*, 2565–2569.
4. (a) Barlow, M. G.; Bryant, M. J.; Haszeldine, R. N.; Mackie, A. G. *J. Organomet. Chem.* **1970**, *21*, 215–226; (b) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185–206; (c) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067–2096; (d) Oehme, G.; Pracejus, H. *Tetrahedron Lett.* **1979**, 343–344.
5. (a) Parshall, G. W.; Ittel, S. D. *Applied Homogeneous Catalysis*, 2nd ed.; Wiley-Interscience: New York, 1992, p 242; (b) Weissermel, K.; Arpe, H. J. In *Industrial Organic Chemistry*; 2nd ed.; Verlag Chemie: Weinheim, Germany, 1993; (c) McKinney, R. J. U.S. Patent 4,504,674, 1985.
6. (a) Thomas, J. M.; Raja, R.; Sankar, G.; Bell, R. G. *Acc. Chem. Res.* **2001**, *34*, 191–200; (b) Niu, W.; Draths, K. M.; Frost, J. W. *Biotechnol. Prog.* **2002**, *18*, 201–211; (c) Kiss, G. *Chem. Rev.* **2001**, *101*, 3435–3456.
7. (a) Inanaga, J.; Handa, Y.; Tabuchi, T.; Otsubo, K.; Yamaguchi, M.; Hanamoto, T. *Tetrahedron Lett.* **1991**, *32*, 6557–6558; (b) Kanai, H.; Ishii, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1015–1018; (c) Druliner, J. D.; Blackstone, R. C. *J. Organomet. Chem.* **1982**, *240*, 277–283; (d) Strohmeier, W.; Kaiser, A. *J. Organomet. Chem.* **1976**, *114*, 273–279.
8. (a) Arad, Y.; Levy, M.; Vofsi, D. *J. Org. Chem.* **1969**, *34*, 3709–3710; (b) Chiusoli, G. P.; Agnes, G.; Cometti, G. *Chem. Commun.* **1968**, 1515–1516; (c) Baizer, M. H. *Chemtech* **1980**, 161–164; (d) Danly, D. E. *Chemtech* **1980**, 302–311.
9. (a) Tsuchimoto, T.; Kamiyama, S.; Negoro, R.; Shirakawa, E.; Kawakami, Y. *Chem. Commun.* **2003**, 852–853; (b) Corson, B. B.; Heintzelman, W. J.; Moe, H.; Rousseau, C. R. *J. Org. Chem.* **1962**, *27*, 1636–1640; (c) Matsubara, C.; Kojima, M. *Tetrahedron Lett.* **1999**, *40*, 3439–3442; (d) Waratuke, S. A.; Johnson, E. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1996**, 2617–2618.
10. (a) Fornes, V.; Garcia, H.; Marti, V.; Fernandez, L. *Tetrahedron* **1998**, *54*, 3827–3832; (b) Rao, V. J.; Prevost, N.; Ramamurthy, V.; Kojima, M.; Johnston, L. J. *Chem. Commun.* **1997**, 2209–2210.
11. (a) Schrauzer, G. N.; Weber, J. H.; Beckham, T. M. *J. Am. Chem. Soc.* **1970**, *92*, 7078–7086; (b) Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437–4439; (c) Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, M. J.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038–8060.