[2] a) W.-Q. Fan, A. R. Katritzky in *Comprehensive Heterocyclic Chemistry II*, *Vol. 4* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 101–126; b) R. N. Butler in *Comprehensive Heterocyclic Chemistry II*, *Vol. 4* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 621–678; c) K. Banert, *Chem. Ber.* **1989**, *122*, 911–918.

[3] a) R. Huisgen, *Pure Appl. Chem.* **1989**, *61*, 613–628; b) R. Huisgen, G. Szeimies, L. Moebius, *Chem. Ber.* **1967**, *100*, 2494–2507; c) W. Lwowski in *1,3-Dipolar Cycloaddition Chemistry*, *Vol. 1* (Ed.: A. Padwa), Wiley, New York, **1984**, chap. 5; d) J. Bastide, J. Hamelin, F. Texier, V. Q. Ven, *Bull. Soc. Chim. Fr.* **1973**, 2555–2579; J. Bastide, J. Hamelin, F. Texier, V. Q. Ven, *Bull. Soc. Chim. Fr.* **1973**, 2871–2887.

[4] Although applications which utilize the unique reactivity offered by the azide group itself are rare, delightful exceptions can be found the following works: a) P. Desai, K. Schildknegt, K. A. Agrios, C. Mossman, G. Milligan, J. Aube, *J. Am. Chem. Soc.* **2000**, *122*, 7226–7232; b) K. Banert, *Targets Heterocycl. Syst.* **1999**, *3*, 1–32; K. Banert, *Liebigs Ann./Recl.* **1997**, 2005–2018; c) W. H. Pearson, W.-K. Fang, *Isr. J. Chem.* **1997**, *37*, 39–46; d) J. Cao, M. C. T. Fyfe, J. F. Stoddart, *J. Org. Chem.* **2000**, *65*, 1937–1946; e) B. Carboni, A. Benali, M. Vaultier, *J. Org. Chem.* **1993**, *58*, 3736–3741, and references therein.

[5] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 1198–1220; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[6] Organic azides, particularly in the aliphatic series, are exceptionally stable toward the common reactive chemicals on the Earth's surface, which range from dioxygen and water to the aqueous solutions of highly functionalized organic molecules which make up living cells: E. Saxon, C. R. Bertozzi, *Science* **2000**, *287*, 2007–2010; K. L. Kiick, E. Saxon, D. A. Tirrel, C. R. Bertozzi, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 19–24.

[7] In fact, it was the razor sharp reactivity window for this cycloaddition process which spawned our "in situ click chemistry" ideas—an approach which recently resulted in the discovery of the most potent noncovalent inhibitor of acetylcholinesterase known to date: W. G. Lewis, L. G. Green, F. Grynszpan, Z. Radic, P. R. Carlier, P. Taylor, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 1095–1099; *Angew. Chem. Int. Ed.* **2002**, *41*, 1053–1057.

[8] Unless the acetylene component is attached to an electron-withdrawing group such as a carbonyl or perfluoroalkyl group: J. Bastide, O. Henri-Rousseau, *Bull. Chim. Soc. Fr.* **1973**, 2294–2296; N. P. Stepanova, N. A. Orlova, V. A. Galishev, E. S. Turbanova, A. A. Petrov, *Zh. Org. Khim.* **1985**, *21*, 979–983; N. P. Stepanova, V. A. Galishev, E. S. Turbanova, A. V. Maleev, K. A. Potekhin, E. N. Kurkutova, Yu. T. Struchkov, A. A. Petrov, *Zh. Org. Khim.* **1989**, *25*, 1613–1618; D. Clarke, R. W. Mares, H. McNab, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1799–1804.

[9] P. Zanirato, *J. Chem. Soc. Perkin Trans. 1* **1991**, 2789–2796; D. J. Hlasta, J. A. Ackerman *J. Org. Chem.* **1994**, *59*, 6184–6189; C. A. Booth, D. Philp, *Tetrahedron Lett.* **1998**, *39*, 6987–6990; S. J. Howell, N. Spencer, D. Philp, *Tetrahedron* **2001**, *57*, 4945–4954; W. L. Mock, T. A. Irra, J. P. Wepsiec, M. Adhya, *J. Org. Chem.* **1989**, *54*, 5302–5308; W. L. Mock, *Top. Curr. Chem.* **1995**, *175*, 1–24; J. Chen, J. Rebek, Jr., *Org. Lett.* **2002**, *4*, 327–329; J. W. Wijnen, R. A. Steiner, J. B. F. N. Engberts, *Tetrahedron Lett.* **1995**, *36*, 5389–5392; M. P. Repasky, W. L. Jorgensen, *Faraday Discuss.* **1998**, *110*, 379–389.

[10] While this manuscript was in preparation, an independent account of copper-catalyzed synthesis of 1,4-triazoles from azides and terminal acetylenes on solid support was reported: C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057.

[11] For a review of reactions of L-ascorbic acid with transition metals, see M. B. Davies, *Polyhedron* **1992**, *11*, 285–321, and references therein; redox properties of ascorbic acid are summarized in C. Creutz, *Inorg. Chem.* **1981**, *20*, 4449.

[12] The starting materials do not need to be dissolved in the reaction solvent. The reaction seems to proceed just as efficiently as long as adequate stirring is maintained.

[13] Amazingly, even Cu^0 can be used as a source of the catalytic species. Although these reactions may take longer to proceed to completion, the experimental procedure is exceedingly simple. For example, bistriazole shown in entry 2 (Table 1) was obtained in quantitative yield after stirring the corresponding azide and acetylene components for 24 h with about 1 g of coiled copper metal turnings. The turnings were removed at the end of the reaction, and the pure white product was collected by simple filtration.

[14] CCDC 186236 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[15] For a recent summary of the reactions of copper(I) complexes with dioxygen, see S. Schindler, *Eur. J. Inorg. Chem.* **2000**, 2311–2326 and A. G. Blackman, W. B. Tolman in *Structure and Bonding, Vol. 97* (Ed: B. Meunier), Springer, Berlin, **2000**, pp. 179–211.

[16] For example, ethyl propiolate and benzylazide furnished the corresponding 1,4-triazole in 55% yield when this procedure was used, but only a trace amount of the product was obtained with one equivalent of triethylamine and without exclusion of oxygen.

[17] G. van Koten, J. G. Noltes in *Comprehensive Organometallic Chemistry*, *Vol. 2* (Ed.: G. Wilkinson), Pergamon, Oxford, **1982**, chap. 14, p. 720.

[18] F. Himo, T. Lovell, V. Rostovtsev, V. V. Fokin, K. B. Sharpless, L. Noodleman, unpublished results.

[19] M. P. Doyle, M. A. McKervey, T. Ye in *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1997**, pp. 163–248.

[20] The reaction proceeded equally well even in human plasma (protein loading 65–85 mg mL^{-1}, $C_{\text{azide}} = C_{\text{alkyne}} = 5$ mM; $C_{\text{Cu}^+} = 100$ μM), which indicates that the copper species remained available for the catalysis despite being heavily bound to plasma proteins.

Electronic and Steric Effects on Catalysts for CO_2/Epoxide Polymerization: Subtle Modifications Resulting in Superior Activities[**]

David R. Moore, Ming Cheng, Emil B. Lobkovsky, and Geoffrey W. Coates[*]

Carbon dioxide is an attractive chemical feedstock. In addition to the fact that CO_2 is an inexpensive substance of practically inexhaustible supply, it is also nonflammable and exhibits low toxicity.[1–3] Since CO_2 is believed to contribute significantly to global warming, its removal from the atmosphere has added environmental benefits. Consequently, the alternating copolymerization of carbon dioxide with epoxides to aliphatic polycarbonates has been a topic of increasing

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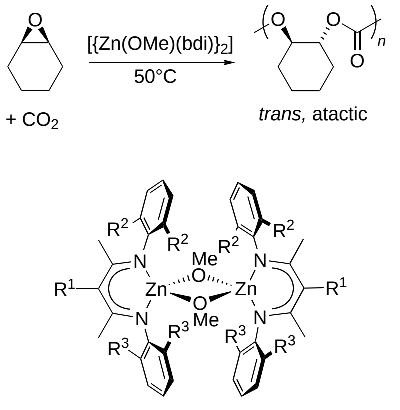
[**] This work was generously supported by the NSF (Career Award CHE-9875261). We thank the Cornell University Center for Biotechnology and Eastman Chemicals for partial support of this research. This work made use of the Cornell Center for Materials Research Shared Experimental Facilities, supported through the NSF Materials Research Science and Engineering Centers program (DMR-0079992). G.W.C. gratefully acknowledges a Packard Foundation Fellowship in Science and Engineering, an Alfred P. Sloan Research Fellowship, an Arnold and Mabel Beckman Foundation Young Investigator Award, and a Camille Dreyfus Teacher-Scholar Award. D.R.M. is grateful for a Corning Foundation Science Fellowship.

interest over the past decade.[4] Not only do these polymers exhibit interesting material properties, but they have the additional environmental advantage that they biodegrade under composting conditions.[5, 6] Thus the development of efficient and versatile catalysts that can enchain CO_2 with a range of epoxides remains a significant scientific goal.

In 1969, Inoue first reported that $ZnEt_2/H_2O$ mixtures catalyzed the copolymerization of propylene oxide and CO_2.[7] Although these original catalysts exhibited extremely low activities, requiring days to make appreciable amounts of polymer, they represent a truly remarkable achievement in the field of CO_2 utilization. Detailed information of the active species is not available owing to the heterogeneous nature of the catalyst, but propagation sites are generally thought to consist of zinc alkoxide and carbonate propagating species. In the ensuing two decades, a substantial amount of work was reported regarding the development of related heterogeneous catalyst mixtures for epoxide/CO_2 polymerization.[4, 8, 9] In the past decade, significantly improved catalysts for cyclohexene oxide (CHO)/CO_2 copolymerization were reported, including chromium porphyrins,[10–12] discrete zinc phenoxides,[13–17] and ZnO/fluorinated carboxylic acids.[18] We recently discovered β-diiminate zinc alkoxides ($[\{Zn(OMe)(bdi)\}_2]$; Scheme 1), as well as zinc carboxylates, that exhibit unprecedented rates for CHO/CO_2 polymerization under mild reaction conditions.[19, 20] In addition, these were the first catalysts reported for the living synthesis of high molecular weight polymers from epoxides and CO_2. Subsequent work centered on the development of chiral imine/oxazoline ligated complexes for the enantioselective copolymerization of epoxides with CO_2.[21] One of the key design features of these complexes is a permanent ligand set that remains bound to the active zinc center throughout the polymerization and thus improves its catalytic behavior.



	R^1	R^2	R^3
$[\{Zn(OMe)(bdi\text{-}\mathbf{1})\}_2]$	H	Et	Et
$[\{Zn(OMe)(bdi\text{-}\mathbf{2})\}_2]$	CN	Et	Et
$[\{Zn(OMe)(bdi\text{-}\mathbf{3})\}_2]$	CN	Et	*i*Pr
$[\{Zn(OMe)(bdi\text{-}\mathbf{4})\}_2]$	CN	Me	*i*Pr

Scheme 1. Epoxide/CO_2 copolymerization with $[\{Zn(OMe)(bdi)\}_2]$ catalysts.

Mechanistic studies involving $[\{Zn(OR)(bdi)\}_2]$ complexes revealed that subtle ligand modifications led to dramatic differences in catalytic activity. For example, the 2,6-substituents of the aryl group have a profound effect on activity; small methyl and large *n*-propyl groups result in inactivity, while ethyl and isopropyl groups result in excellent activity.[20] Preliminary kinetic studies have revealed that the polymerizations are second order in $[Zn(OR)(bdi)]$ which suggests a bimetallic enchainment of monomer. Therefore, we interpret the inactivity of complexes bearing *ortho*-methyl groups to result from a strongly bound dimer, while the inactivity of complexes bearing *ortho*-*n*-propyl groups stems from the high energy of the bimetallic transition state required for enchainment. Given the fact that extremely subtle steric effects produced such dramatically different catalytic activities, we embarked on the investigation of unsymmetrically substituted complexes in search of improved activities. In addition, we sought to understand the effect of electronic perturbation of the ligand on polymerization rate.[22, 23] Herein, we report a significantly improved class of single-site catalysts for CHO/CO_2 polymerization as a result of these studies.

Under the premise that a more electron-deficient zinc center would increase the reaction rate due to more efficient epoxide coordination, we investigated the addition of an electron-withdrawing cyano group to the β-diiminate ligand (Scheme 1). Ligand (bdi-**2**)H was synthesized by the deprotonation of (bdi-**1**)H followed by reaction with *p*-toluenesulfonylcyanide.[24] The complexes $[\{Zn(\mu\text{-}OMe)(bdi\text{-}\mathbf{1})\}_2]$[20] and $[\{Zn(\mu\text{-}OMe)(bdi\text{-}\mathbf{2})\}_2]$ were made by reaction of the ligand with $ZnEt_2$ followed by reaction with methanol.[25] In Table 1, we report the data for alternating copolymerization of CHO and CO_2 with $[\{Zn(\mu\text{-}OMe)(bdi)\}_2]$, with ligands (bdi-**1**)H and (bdi-**2**)H. Reactions were

Table 1. Combined ligand effects on CHO/CO_2 copolymerization.[a]

Complex	*t* [min]	CO_2 pressure [psi/MPa]	TON[b]	TOF[c] [h^{-1}]	$g_{poly}\, g_M^{-1}$ [h^{-1}]	Carbonate linkages [%][d]	M_n [$kg\,mol^{-1}$][e]	M_w/M_n[e]
$[\{Zn(\mu\text{-}OMe)(bdi\text{-}\mathbf{1})\}_2]$	120	100/0.69	478	239	518	96	23.7	1.14
$[\{Zn(\mu\text{-}OMe)(bdi\text{-}\mathbf{2})\}_2]$	10	100/0.69	282	1690	3670	93	17.8	1.08
$[\{Zn(\mu\text{-}OMe)(bdi\text{-}\mathbf{3})\}_2]$	10	100/0.69	362	2170	4710	89	22.8	1.11
$[\{Zn(\mu\text{-}OMe)(bdi\text{-}\mathbf{4})\}_2]$	10	100/0.69	382	2290	4980	90	22.9	1.09
[CrCl(tfpp)]/DMAP[f]	1080	3300/23	3120	173	472	97	3.9	1.16
$[Zn(O\text{-}2,6\text{-}F_2C_6H_3)_2\cdot THF]_2$[g]	2880	800/5.5	365	8	17	> 99	42.0	6.0
$HO_2CCH{=}CHCO_2(CH_2)_2C_6F_{13}/ZnO$[h]	1440	2000/14	216	4	9	93	17.0	6.4

[a] All of the $[\{Zn(\mu\text{-}OMe)(bdi)\}_2]$ polymerizations were performed in neat cyclohexene oxide with [monomer]/[Zn] = 1000 at 50°C. [b] Turnover number; moles of CHO consumed per mole of metal. [c] Turnover frequency; moles of CHO consumed per mole of metal per hour. [d] Calculated by integration of methine resonances in the ^1H NMR spectrum of polymer ($CDCl_3$, 300 MHz). [e] Determined by gel permeation chromatography, calibrated with polystyrene standards in tetrahydrofuran. [f] tfpp = tetraperfluorophenylporphyrin, DMAP = 4-dimethylaminopyridine; data from ref. [11] ($T = 110\,°C$). [g] Data from ref. [16] ($T = 80\,°C$). [h] Data from ref. [18] ($T = 100\,°C$).

run to moderate conversions ($\approx$40%) in neat epoxide to emphasize differences in reactivity, although reactions in THF and toluene at longer reaction times proceed to near quantitative conversion. [{Zn(μ-OMe)(bdi-**1**)}$_2$] is an adequate catalyst over the course of 2 hours and produces monodisperse carbonate polymer with a turnover frequency of 239 h^{-1}. In a short 10-minute reaction, [{Zn(μ-OMe)(bdi-**1**)}$_2$] produces only a trace amount of polymer. In contrast, [{Zn(μ-OMe)(bdi-**2**)}$_2$] exhibits substantially higher activity for the polymerization, with a turnover frequency of 1690 h^{-1}. Although the polymer is still monodisperse, the percentage of carbonate linkages is slightly lower (93%).

During our prior copolymerization studies of CHO and CO$_2$, we found that the [{Zn(OMe)(bdi)}$_2$] complex containing 2-ethyl-6-isopropylphenyl groups exhibits superior activity to those with either 2,6-diisopropylphenyl or 2,6-diethylphenyl groups.[20] We therefore believed that further modification of the ligand geometry could provide an optimal active site for monomer enchainment to result in dramatically improved activities. To probe this we decided to synthesize complexes with ligands bearing different aryl groups. Unsymmetrical ligands were synthesized by refluxing two different anilines (one equivalent of each) plus one equivalent of 2,4-pentanedione in acidic ethanol. Isolation of the unsymmetrical ligands was accomplished through repeated crystallization from ethanol. Cyanation of the ligands and complex synthesis was performed as previously described to give the complexes [{Zn(μ-OMe)(bdi-**3**)}$_2$] and [{Zn(μ-OMe)(bdi-**4**)}$_2$] in 25% and 18% yield, respectively (Scheme 1). The unsymmetrical ligand allows for two potential dimeric complex structures, where the diisopropylphenyl substituents are either *syn* or *anti* to each other. A steric argument would suggest the molecules would rather crystallize to alleviate unnecessary repulsions. A single-crystal X-ray diffraction study[26] was performed on [{Zn(μ-OMe)(bdi-**4**)}$_2$] and interestingly, the dimeric zinc methoxide aligns the more bulky isopropyl groups adjacent to one another causing minor distortion of the dimer versus symmetrical complexes (Figure 1). The Zn–Zn separation is 2.98 Å, and each zinc atom adopts a distorted tetrahedral geometry. The six-membered chelate is fairly planar (a slight boat-shaped conformation is achieved) with a Zn deviation of 0.64 Å from the plane defined by N(1)-N(2)-C(4). The Zn–O bond lengths are 1.94 and 1.98 Å, and the bond angles of N(1)-Zn(1)-N(2) and O(1)-Zn(1)-O(1A) are 94.19° and 80.89°, respectively. It is unclear why {Zn(OMe)(bdi-**4**)} dimerizes and then crystallizes in this fashion, although ^{1}H NMR spectra of both [{Zn(μ-OMe)(bdi-**3**)}$_2$] and [{Zn(μ-OMe)(bdi-**4**)}$_2$] show a mixture of the two dimeric structures in C_6D_6 solution. We therefore propose that the sterically disfavored dimeric structure is merely more crystalline.

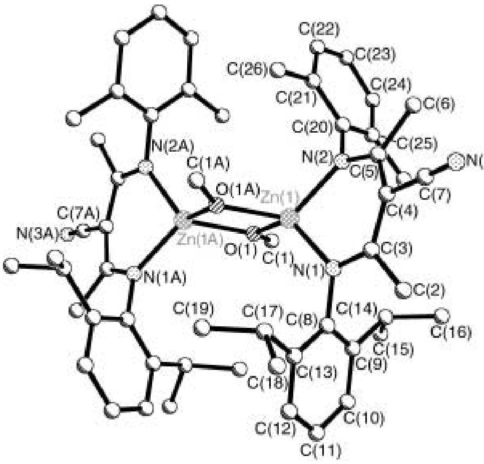


Figure 1. X-ray crystal structure of [{Zn(μ-OMe)(bdi-**4**)}$_2$]. Selected bond lengths [Å] and bond angles [°]: Zn(1)-N(1) 2.003(2), Zn(1)-N(2) 1.997(2), Zn(1)-O(1) 1.9427(17), Zn(1)-O(1A) 1.9780(17), O(1)-C(1) 1.408(3); O(1)-Zn(1)-O(1A) 80.89(7), N(1)-Zn(1)-N(2) 94.19(8), N(1)-Zn(1)-O(1A) 116.38(8), N(2)-Zn(1)-O(1) 119.85(8) Zn(1)-O(1)-Zn(1A) 99.11(7), C(1)-O(1)-Zn(1) 131.5(2), C(1)-O(1)-Zn(1A) 128.2(2).

To the best of our knowledge, [{Zn(μ-OMe)(bdi-**3**)}$_2$] and [{Zn(μ-OMe)(bdi-**4**)}$_2$] exhibit the highest reported activity for CHO/CO$_2$ copolymerization. Table 1 gives polymerization data for these compounds, as well as literature data for competing catalysts. At 50 °C and 100 psi (0.69 MPa) of CO$_2$ the catalysts exhibit turnover frequencies of 2170 and 2290 h^{-1}. The polymers produced are nearly identical with $\approx$90% carbonate linkages, $M_n = 23000$ Da, and molecular weight distributions of $\approx$1.1. Despite the small presence of polyether linkages, these complexes are inactive for the homopolymerization of CHO over one day. We are currently investigating the mechanistic issues as to why polyether linkages are observed, while CHO homopolymer is not synthesized.

In conclusion, we have systematically improved the activity of β-diiminate zinc methoxide complexes for CHO/CO$_2$ copolymerization. [{Zn(μ-OMe)(bdi-**4**)}$_2$] exhibits the highest reported activity for this reaction. In addition, these complexes offer new opportunities for control of molecular weights and block copolymer synthesis owing to the living nature of the copolymerizations. The well-defined nature of the complexes provides excellent opportunities to probe the mechanism of the polymerization steps in detail, and these studies are currently underway. Work is also centered on employing these catalysts for the polymerization of new classes of epoxides with CO$_2$, as well as other monomers.

Received: March 4, 2002 [Z18816]

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[1] H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953–996.

[2] W. Leitner, *Angew. Chem.* **1995**, *107*, 2391–2405; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207–2221.

[3] W. Leitner, *Coord. Chem. Rev.* **1996**, *153*, 257–284.

[4] For reviews on epoxide/CO$_2$ copolymerizations, see: a) D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155–174; b) M. S. Super, E. J. Beckman, *Trends Polym. Sci.* **1997**, *5*, 236–240; c) A. Rokicki, W. Kuran, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1981**, *C21*, 135–186.

[5] M. Okada, *Prog. Polym. Sci.* **2002**, *27*, 87–133.

[6] S. Y. Yang, X. G. Fang, L. B. Chen, *Polym. Adv. Technol.* **1996**, *7*, 605–608.

[7] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. Part B: Polym. Lett.* **1969**, *7*, 287–292.

[8] M. Ree, J. Y. Bae, J. H. Jung, T. J. Shin, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 1863–1876.
[9] L. B. Chen, *Macromol. Symp.* **1992**, *59*, 75–82.
[10] W. J. Kruper, D. V. Dellar, *J. Org. Chem.* **1995**, *60*, 725–727.
[11] S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan, A. B. Holmes, *Macromolecules* **2000**, *33*, 303–308.
[12] L. M. Stamp, S. A. Mang, A. B. Holmes, K. A. Knights, Y. R. de Miguel, I. F. McConvey, *Chem. Commun.* **2001**, 2502–2503.
[13] D. J. Darensbourg, M. W. Holtcamp, *Macromolecules* **1995**, *28*, 7577–7579.
[14] D. J. Darensbourg, S. A. Niezgoda, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1998**, *120*, 4690–4698.
[15] D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1999**, *121*, 107–116.
[16] D. J. Darensbourg, J. R. Wildeson, J. C. Yarbrough, J. H. Reibenspies, *J. Am. Chem. Soc.* **2000**, *122*, 12487–12496.
[17] M. B. Dinger, M. J. Scott, *Inorg. Chem.* **2001**, *40*, 1029–1036.
[18] M. S. Super, E. Berluche, C. Costello, E. J. Beckman, *Macromolecules* **1997**, *30*, 368–372.
[19] M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019.
[20] M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749.
[21] M. Cheng, N. A. Darling, E. B. Lobkovsky, G. W. Coates, *Chem. Commun.* **2000**, 2007–2008. For a prior system, see: K. Nozaki, K. Nakano, T. Hiyama, *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009.
[22] G. W. Coates, M. Cheng, PCT Int. Appl. WO 2000008088, **2000** [*Chem Abstr.* **2000**, *132*, 152332].
[23] M. Cheng, Ph. D. Thesis, Cornell University, August 2000.
[24] E. J. Corey, Z. Wang, *Tetrahedron Lett.* **1993**, *34*, 4001–4004.
[25] The syntheses and detailed characterization of complexes reported in this paper will be reported separately (manuscript in preparation).
[26] CCDC 180471 ($[\{Zn(\mu\text{-OMe})(bdi\text{-}\mathbf{4})\}_2]$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

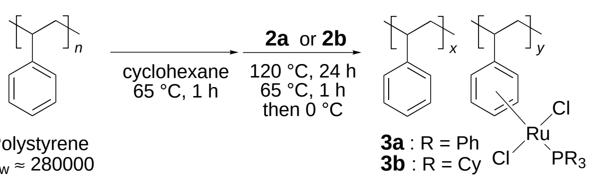
A Novel Polymer-Supported Arene–Ruthenium Complex for Ring-Closing Olefin Metathesis**

Ryo Akiyama and Shū Kobayashi*

Arene–ruthenium complexes are very useful precatalysts for several organic reactions, such as transfer hydrogenation,[1] Diels–Alder reaction,[2] olefin cyclopropanation,[3] enol formate formation,[4] cyclization of dienylalkyne,[5] and olefin metathesis.[6] While the catalysts prepared from the arene–ruthenium complexes are air- and moisture-sensitive, expensive, and cannot be recovered in many cases, immobilized catalysts are expected to solve these problems. Although several polymer-supported ruthenium complexes have been reported,[7] however, these are not without problems, such as tedious procedures for the preparation of the complexes, low activity compared with the original catalysts, and difficulty of applying the catalysts to other reactions. Therefore, development of more versatile polymer-supported ruthenium complexes is strongly demanded. Herein, we describe a novel polymer-supported arene–ruthenium complex that is recovered quantitatively and reused for ring-closing olefin metathesis and other reactions.

Our idea is to utilize the benzene rings of polystyrene as ligands to immobilize arene–metal complexes. However, it is known that arene-displacement reactions at Ru^{II} centers are often sluggish.[8] Thus, we carefully chose $[\{Ru(\eta^6\text{-}C_6H_5CO_2Et)Cl_2\}_2]$ (**1**) as the starting material, because it was reported that an intramolecular arene exchange proceeded in good yield using **1** instead of $[\{Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$.[9] Dimer **1** was easily prepared according to the literature procedure,[8, 9] and treatment of **1** with triphenylphosphane or tricyclohexylphosphane gave $[Ru(\eta^6\text{-}C_6H_5CO_2Et)(PR_3)Cl_2]$ (**2a**: R = Ph, **2b**: R = Cy) quantitatively.

Preparation of the polymer-supported arene–ruthenium complexes using **2** was successfully performed based on a procedure which is similar in part to that of formation of microcapsules (Scheme 1).[10, 11] All other methods we tested did not give satisfactory results. The structure of the polymer-supported arene–ruthenium complexes was confirmed by NMR spectroscopic analysis. We measured the ^{31}P swollen-resin magic-angle spinning (SR-MAS) NMR spectra[12] of the catalysts, and only one peak arising from PR_3 (**3a** R = Ph: δ = 25.7 ppm, **3b** R = Cy: δ = 28.5 ppm) coordinating to the ruthenium was observed.[13] From these results, we concluded that the catalyst was supported as $[(arene)RuCl_2(PR_3)]$ (polymer-supported $[(arene)RuCl_2(PR_3)]$ (**3**; PS-RuCl$_2$(PR$_3$))). To our knowledge, this is the first example of a polymer-supported ruthenium catalyst, in which the benzene rings of the polymer coordinated to the ruthenium to immobilize the catalyst onto the polymer.



Scheme 1. Synthesis of polymer-supported $[(arene)RuCl_2(PR_3)]$ (**3**).

PS-RuCl$_2$(PR$_3$) was used in the ring-closing olefin metathesis (RCM). We prepared a polymer-supported cationic ruthenium–allenylidene complex according to the Dixneuf and Fürstner method.[6b,c] PS-RuCl$_2$(PPh$_3$) (**3a**), tricyclohexylphosphane (PCy$_3$), 1,1-diphenyl-2-propynol (**4**), and sodium hexafluorophosphate (NaPF$_6$) were mixed in several solvents, and the mixture was stirred for 1 h under reflux. Signals of the

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[**] This work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society of the Promotion of Science (JSPS). R.A. thanks the JSPS fellowship for Japanese Junior Scientist.

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