

Figure 1. (a) A structure of the twin complex, $[\text{Co}(\text{tren})_2(\text{tae})]^{4+}$. (b) The side view of tren parts from the right-hand side of (a). (c) The mirror image of (b).

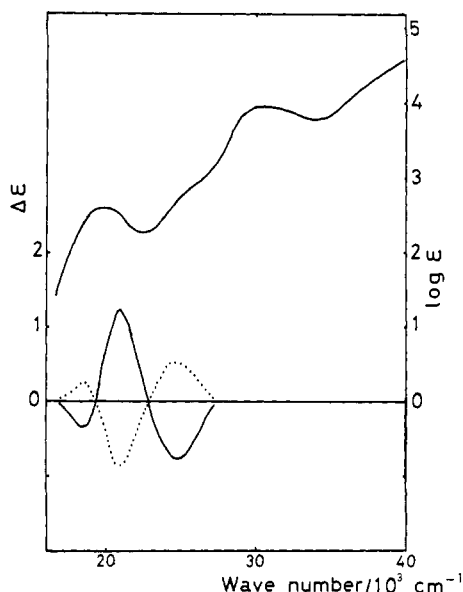


Figure 2. Absorption and circular dichroism spectra of partially resolved complexes.

coordination compounds. We have selected the $\text{Co}(\text{tren})$ system as the partner of 1,1,2,2-tetraacetylacetonate anion (tae). Molecular model of the resulting twin complex (see Figure 1) shows a novel structure in which the two units of $[\text{Co}(\text{acac})(\text{tren})]^{2+}$ types are bound to tae at right angles to each other. Although the unit itself has a symmetry plane neglecting the conformational structure of a chelate ring, the symmetry is invalidated in the twin complex. Therefore it is expected that the twin complex can be resolved into optically active isomers.

The complex was prepared analogously to β -diketonato complexes and gave compatible IR, ^1H NMR, ^{13}C NMR, and absorption spectra and elemental analysis data with the expected twin structure. The red complex was subjected to recycling chromatography on an SP-Sephadex (C-25, ϕ 4.4 \times 90 cm) column using an aqueous 0.25 M sodium (+)₅₈₉-tartrate solution as eluent. The flow rate of the elution was about 80 mL per hour. After the 20th recycling the adsorbed complex could not be separated into two bands, but the circular dichroism spectrum of the initial part (solid line shown in Figure 2) of the elution curve showed the mirror image of that of the last part (dotted line). The rotatory strength of the latter fraction is significantly weaker than that of the former, indicating partial resolution. Success in resolution confirms that the complex has the expected structure

(4) Schaefer, J. P.; Wheatly, P. J. *J. Chem. Soc. A* 1966, 528.

(5) Circular dichroism spectra of the series will be published elsewhere.

as shown in Figure 1, and the two units of $[\text{Co}(\text{acac})(\text{tren})]^{2+}$ types cannot rotate freely around the central C-C bond of tae.

Since the two units of $[\text{Co}(\text{acac})(\text{tren})]^{2+}$ types are bound perpendicularly and two acetylacetonato-ring units cannot conjugate to each other, the absorptivity of the twin complex must be 2 times that of $[\text{Co}(\text{acac})(\text{tren})]^{2+}$. Comparing the obtained CD spectrum to that of naphthyl derivative, we can assign the two peaks, 18 500 and 20 800 cm^{-1} , to $B_1 \leftarrow A_1$ and $B_2 + A_2 \leftarrow A_1$ transitions, respectively. Complete CD spectra and the other detailed characterizations will be reported on later.

Registry No. $[\text{Co}(\text{tren})_2(\text{tae})]^{4+}$, 88211-16-9.

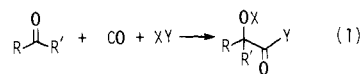
Catalytic Incorporation of Carbon Monoxide into a Ketonic Carbon. Conversion of Cyclobutanones to Disiloxycyclopentenones with Hydrosilane and Carbon Monoxide in the Presence of Cobalt Carbonyl¹

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Carbonylation of carbon-carbon double bonds with the aid of transition-metal complexes is a popular catalytic reaction,² which finds fruitful application in industry, hydroformylation of olefins being a representative example.^{2,3} In contrast, catalytic carbonylation of carbon-oxygen double bonds (i.e., carbonyl group) with carbon monoxide remains almost unexplored. Of the two available reaction sites in a carbon-oxygen double bond, C-carbonylation (eq 1) is more important than O-carbonylation,⁴



since the former could bring about carbon-chain extension.⁵ Investigation devoted to finding effective catalyst systems that would enable the conversion of formaldehyde to glycolaldehyde (eq 1, $\text{R} = \text{R}' = \text{X} = \text{Y} = \text{H}$), or to ethylene glycol, via C-carbonylation have been made.⁶ Few examples are known of the transition-metal catalyst system that is effective for C-carbonylation of higher aldehydes^{7,8} (eq 1, $\text{R} = \text{alkyl}$; $\text{R}' = \text{H}$).

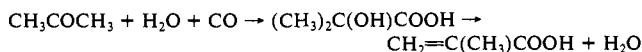
(1) For previous papers of this series: (a) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* 1983, 105, 1370. (b) Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N. *Organometallics* 1983, 2, 1883.

(2) Wender, I.; Pino, P. "Organic Syntheses via Metal Carbonyls"; Wiley: New York, 1977; Vol. II. Farbe, J. "New Syntheses with Carbon Monoxide"; Springer-Verlag: New York, 1980.

(3) Prueft, R. L. *Adv. Organomet. Chem.* 1979, 17, 1. Siegel, H.; Mimmelle, W. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 178.

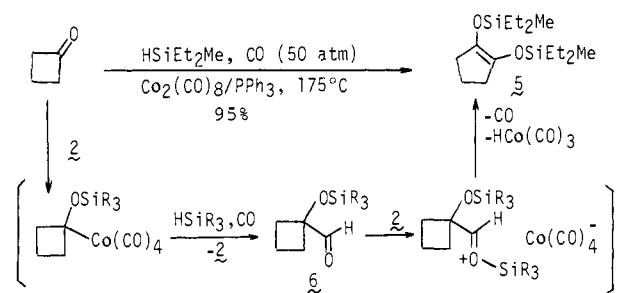
(4) Marko, L.; Szabo, P. *Chem. Tech. (Berlin)* 1961, 13, 482; *Chem. Abstr.* 1962, 56, 7102. Marko, L. *Proc. Chem. Soc.* 1962, 67. Polievka, M.; Mistrík, E. *J. Chem. Zvesti* 1972, 26, 149; *Chem. Abstr.* 1972, 77, 113388. Weil, T. A.; Metlin, S.; Wender, I. *J. Organomet. Chem.* 1973, 49, 227. Orchin, M. *Acc. Chem. Res.* 1981, 14, 259.

(5) The following unknown reaction may illustrate the importance of C-carbonylation:



(6) Yukawa, T.; Wakamatsu, H. Brit. Pat. 1 408 857, 1974. Spencer, A. *J. Organomet. Chem.* 1980, 194, 113. Fahey, D. R. *J. Am. Chem. Soc.* 1981, 103, 136. Parker, D. G.; Pearce, R.; Prest, D. W. *J. Chem. Soc., Chem. Commun.* 1982, 1193. Suzuki, T.; Kudo, K.; Sugita, N. *Nippon Kagaku Kaishi* 1982, 1357; *Chem. Abstr.* 1982, 97, 144126. Chan, A. S. C.; Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* 1983, 19, 377. See also: *Chem. Eng. News* 1983, 61, 41.

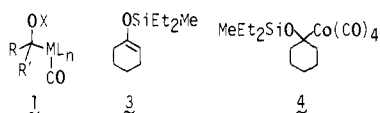
Scheme I



To the best of our knowledge, no example of C-carbonylation of a ketone (eq 1, R = R' = alkyl) has been reported.

Herein we wish to report a novel cobalt carbonyl catalyzed ring enlargement of cyclobutanones with a hydrosilane and carbon monoxide (vide infra, Scheme I). This reaction represents the first example for the catalytic incorporation of carbon monoxide into a ketonic carbon. Moreover, the transformation is potentially of high synthetic utility. The starting cyclobutanones are readily obtained from olefins and ketenes.⁹ The products are disiloxycyclopentenes, which contain the enediol disilyl ether moiety that is known to be a versatile synthon.¹⁰

The difficulty in achieving reaction 1 lies mainly in the correct selection of a suitable catalyst that undergoes the regioselective addition that affords an α -oxyalkyl transition-metal intermediate 1.¹¹ Intermediate 1 is required for the successive insertion of



carbon monoxide and hence for C-carbonylation. The use of $R_3SiCo(CO)_4$ (2), which can be generated in situ in $HSiR_3/CO/Co_2(CO)_8$ system,^{1,12} seemed promising. The addition of 2 across the carbon-oxygen double bond was expected to take place in the desired direction because of the high oxygenphilicity of silicon.¹³ We attempted the carbonylation of several ketones such as acetone, acetophenone, and cyclohexanone, using $HSiEt_2Me/CO/Co_2(CO)_8-PPh_3$ (a system to give 2) at 1–80 atm and 25–180 °C, but only in vain. For example, the only product obtained from cyclohexanone was an enol silyl ether 3.¹⁴ The result suggests that an α -oxyalkylmetal carbonyl 4, if it is formed from cyclohexanone and 2, would undergo β -hydride elimination to give $HCo(CO)_3$ and 3 rather than carbon monoxide insertion. Consequently, adamantanone (10 mmol), which might not give the corresponding enol silyl ether because of the ring strain, was reacted with $HSiEt_2Me$ (30 mmol) and CO (50 atm) in the

(7) Bhattacharyya, S. K.; Palit, S. K.; Das, A. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1970**, *9*, 92.

(8) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 199. Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Ibid.* **1979**, *18*, 393.

(9) (a) Ghosez, L.; Montaigne, M.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615. (b) Jeffs, P. W.; Molina, G.; Cass, M. W.; Cortese, N. A. *J. Org. Chem.* **1982**, *47*, 3871.

(10) For reviews, see: Ruhlmann, K. *Synthesis* **1971**, 236. Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 228, 279, 267–273. A literature survey of useful transformations via disiloxalkenes is given in the supplementary material.

(11) (a) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27. (b) Dombeck, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466. (c) Johnson, D. L.; Gladysz, J. A. *Ibid.* **1979**, *101*, 6433; *Inorg. Chem.* **1981**, *20*, 2508. (d) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056. (e) DePoorter, C. K. R. *Chem. Rev.* **1981**, *81*, 477. (f) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(12) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(13) This has been suggested in the catalytic formylation of aldehydes.^{8,12} For the stoichiometric reaction of $(CH_3)_3SiMn(CO)_5$ with aldehydes, see ref 11c.

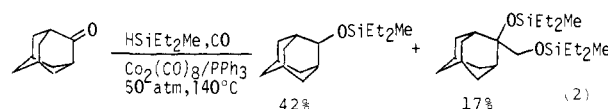
(14) The $Co_2(CO)_8$ -catalyzed conversion of ketones to enol silyl ethers with hydrosilane (without using CO) has been reported. Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2671. See also ref 11c.

Table I. Synthesis of Disiloxycyclopentenes^a

cyclobutanone	reaction temp, °C	product ^b	yield, % ^c
	120		88
	100		73 ^d
	110		100 (80)
	110		94 (80)

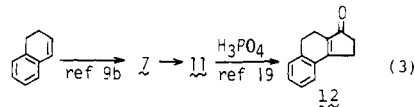
^a Reaction conditions: cyclobutanone (2.5 mmol), $HSiEt_2Me$ (7.5 mmol), CO (50 atm), $Co_2(CO)_8$ (0.1 mmol), PPh_3 (0.1 mmol), C_6H_6 (5 mL), 20 h. ^b For structural assignment, see supplementary material. ^c GLC yields based on cyclobutanones. Isolated yields are in parentheses. ^d Compound 9 was contaminated with a small amount (3% GLC yield) of 8.

presence of $Co_2(CO)_8/PPh_3$ (0.4 mmol/0.4 mmol) in benzene (10 mL) at 140 °C for 20 h. Although simple hydrosilylation predominated, incorporation of carbon monoxide did take place (eq 2).¹⁵



Encouraged by these observations, the reaction of cyclobutanone whose ring strain might also suppress the competitive enol ether formation was studied. The result of the experiment carried out under similar conditions as above (175 °C, 50 atm) was somewhat surprising. The product formed was disiloxycyclopentene 5, which showed the clean incorporation of carbon monoxide (Scheme I). The result would imply that C-formylation and cationic ring enlargement¹⁶ took place in the sequence outlined in Scheme I.¹⁷

Importantly, from the viewpoint of organic synthesis, the present catalytic reaction provides a novel method for the formation of five-membered rings containing a useful functional group (i.e., disiloxalkene¹⁰). This new chemistry has been found applicable to the synthesis of polycyclopentanoids, an important class of compounds.¹⁸ The results are presented in Table I. An example of the usefulness of these products is shown in eq 3. The overall



transformation illustrated in eq 3¹⁹ shows a new method of cy-

(15) All new compounds had satisfactory spectral data and elemental analyses. The data are given in the supplementary material.

(16) The four- to five-membered ring enlargement via cationic intermediates has ample precedents. Roberts, J. D.; Gorham, W. F. *J. Am. Chem. Soc.* **1952**, *74*, 2278. Cohen, T.; Kuhn, D.; Falck, J. R. *Ibid.* **1975**, *97*, 4749. Greene, A. E.; Depress, J.-P. *Ibid.* **1979**, *101*, 4003. Knapp, S.; Trope, A. F.; Orna, R. M. *Tetrahedron Lett.* **1980**, *21*, 4301. Ogura, K.; Yamashita, M.; Suzuki, M.; Tsuchihashi, G. *Chem. Lett.* **1982**, 93. Yamashita, M.; Onozuka, J.; Tsuchihashi, G.; Ogura, K. *Tetrahedron Lett.* **1983**, *24*, 79.

(17) The reaction without PPh_3 resulted in decreased yield of 5. Mechanistically, the role of PPh_3 is not clear at present time. For regeneration of 2 from $HCo(CO)_3$, CO, and $HSiR_3$ in the catalytic cycle, see ref 1a. An alternative and less likely mechanism leading to 6 involves carbonylation by the reaction of uncoordinated carbon monoxide with 1-siloxycyclobut-1-yl cation formed from cyclobutanone and 2.

(18) The strong interest on this subject is evident from a recent Symposium-in-Print, edited by: Paquette, L. A. *Tetrahedron* **1981**, *37*, 4357–4559.

clopentenone annulation at an olefinic linkage.

The present methodology for C-carbonylation of a carbonyl compound (i.e., the use of Lewis-acidic silicon to bind unshared electrons of the carbonyl oxygen) could be broader than mononuclear catalyst system. A cluster or a heterogenous surface, having a metal center and a Lewis-acid center located at a suitable distance, might also be envisaged as a potentially effective catalyst.

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Supplementary Material Available: Characterization of new products and a literature survey of synthetic transformations via disiloxyalkenes (8 pages). Ordering information is given on any current masthead page.

(19) A mixture of **11** (0.5 mmol, 0.20 g) and 60% phosphoric acid (2.3 mL) was heated at 90 °C for 5 h, extracted with benzene, and dried. Chromatography (silica gel, *n*-hexane/Et₂O = 8/2) gave **12** (61 mg, 66%). Cf.: Hirano, S.; Takagi, S.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 169.

Synthesis of Neutral Ruthenium Formyls by Hydride Transfer from [Ph₃PCuH]₆. Evidence for a Radical-Initiated Decomposition of Neutral Formyl Complexes

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In recent years increased importance has been placed on the understanding of mechanistic routes involved in the reduction of carbon monoxide by transition-metal complexes.¹ During the course of these studies, metal formyl and metal hydroxyalkyl complexes have been proposed as viable intermediates in the reduction of carbon monoxide.^{1,2} We report here the reaction of a transition-metal hydride cluster, [Ph₃PCuH]₆,³ with (η-C₅Me₅)Ru(CO)₃⁺BF₄⁻ (**1**)⁴ and (η-C₅Me₅)Ru(CO)₂(PMe₂Ph)⁺I⁻ (**2**) to produce the new neutral formyl complexes (η-C₅Me₅)Ru(CO)₂CHO (**3**) and (η-C₅Me₅)Ru(CO)(PMe₂Ph)CHO (**4**).⁵ In

(1) (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *23*, 1-38. (b) Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *17*-38. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103. (d) Muettterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479-490. (e) Henrici-Olive, G.; Olive, S. *Angew. Chem.* **1976**, *88*, 144-150; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136-141.

(2) (a) Dombbeck, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6855-6857. (b) Fahey, D. R. *Ibid.* **1981**, *103*, 136-141.

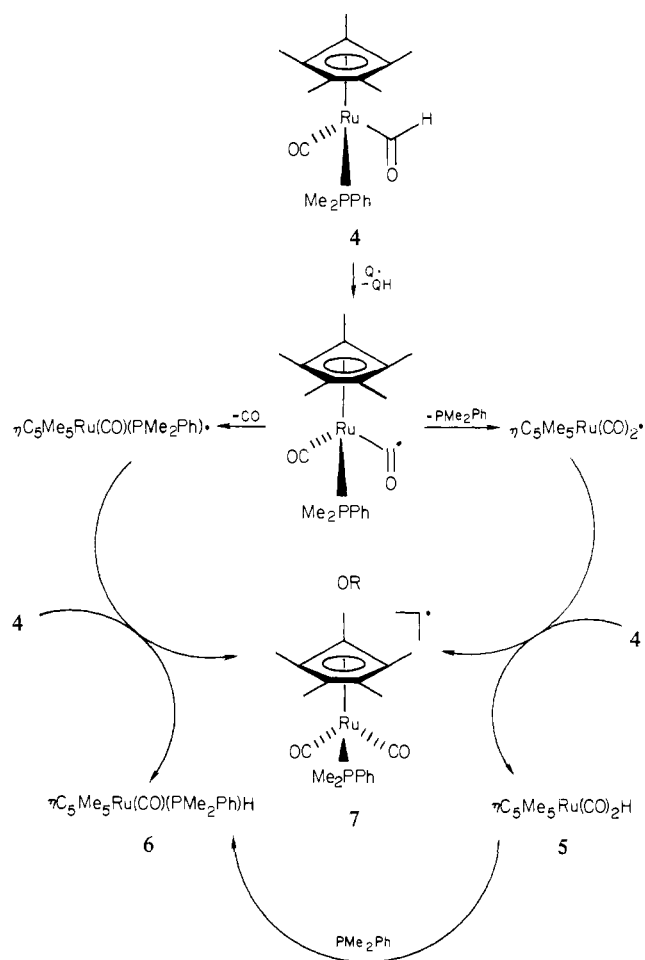
(3) Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818.

(4) Nelson, G. O. *Organometallics* **1983**, *2*, 1474.

(5) (a) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9-C12. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927-1933. (c) Bodnar, T.; Coman, G.; LaCroe, S.; Lambert, C.; Menard, K.; Cutter, A. *Ibid.* **1981**, *103*, 2471-2472. (d) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49-C51.

(e) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811-2815. (f) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275-1277. (g) Tam, W.; Wong, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589-1591. (h) Tam, W.; Lin, G.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525-529. (i) Davies, S. G.; Simpson, S. J. *J. Organomet. Chem.* **1982**, *240*, C48-C50. (j) Tam, W.; Lin, G.; Wong, W.; Kiel, W.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141-152. (k) The synthesis and -90 °C decomposition of the related complex (η-C₅H₅)Ru(CO)₂CHO has been reported: Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43-59.

Scheme I



addition, we disclose data that indicate that neutral formyl complexes can decompose by a radical chain mechanism and are, therefore, stabilized in the presence of radical scavengers.

When 1 equiv of red [Ph₃PCuH]₆³ (238 mg, 0.12 mmol) dissolved in 2 mL of degassed THF (tetrahydrofuran) is added to a THF (2 mL) slurry of (η-C₅Me₅)Ru(CO)₃⁺BF₄⁻ (50 mg, 0.12 mmol), the resulting solution almost immediately turns pale yellow with concomitant precipitation of a yellow, copper-containing solid. IR and ¹H NMR show that this solution contains approximately a 1:1 mixture of (η-C₅Me₅)Ru(CO)₂H (**5**) and (η-C₅Me₅)Ru(CO)₂CHO (**3**). The hydride complex **5** is known,⁴ and **3** is clearly identified by its carbonyl stretches [ν_{CO} (THF) = 2020, 1665, 1642 cm⁻¹] and its ¹H NMR (C₆D₆), which shows singlets at δ 14.0 (CHO) and 1.50 (C₅Me₅). Interestingly, **3** shows varying degrees of stability, which range from decomposing rapidly to **5** to persisting for several hours. This behavior is reminiscent of radical-initiated organometallic reactions,⁶ and in fact, the presence of radical scavengers causes a marked change in the copper hydride reduction just described. When the reduction is performed in the presence of 5 equiv of 9,10-dihydroanthracene, a known hydrogen atom donor,⁷ the formyl complex is quantitatively formed by IR and NMR. Complex **3** still decomposes over several hours, and attempts to isolate it always give a mixture of **3** and **5**. Extremely brief exposure of **3** to air causes the complete transformation of **3** to **5**.

A deeper probe of the radical character of the decomposition of neutral formyl complexes is possible with the stable phosphine-substituted complex (η-C₅Me₅)Ru(CO)(PMe₂Ph)CHO (**4**). Although **4** can be synthesized from cation **2** by using

(6) See, for instance: Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527-2532.

(7) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082-4090.