

cage should be much slower in ethanol than in benzene.

This solvent cage effect would not only account for the distribution of phenol and aminophenols but would also provide an explanation of formation of biphenyl and diphenylether derivatives. Quenching and emission properties for the detailed mechanism are under investigation.

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## References

- Bungardner, C. L.; Lilly, R. L. *Synthesis* 1962, 559.
- (a) Endo, Y.; Schudo, K.; Okamoto, T. *Synthesis* 1980, 461.  
(b) Endo, Y.; Schudo, K.; Okamoto, T. *Synthesis* 1983, 471.  
(c) Endo, Y.; Schudo, K.; Okamoto, T. *Tetrahedron Lett.* 1986, 27, 4209.
- Haga, N.; Endo, Y.; Kataoka, K.; Yamaguchi, K.; Schudo, K. *J. Amer. Chem. Soc.* 1992, 114, 9795.
- Krause, J. G. *Synthesis* 1972, 140.
- (a) Kalmus, C. E.; Hercules, D. M. *J. Amer. Chem. Soc.* 1974, 96, 449. (b) Meyer, J. W.; Hammond, G. S. *J. Amer. Chem. Soc.* 1972, 94, 2219. (c) Shine, H. J.; Subotkowski, W. *J. Org. Chem.* 1987, 52, 3815.
- The products, phenol and aminophenols were identified by <sup>1</sup>H NMR, IR and Mass spectra comparing with those of authentic samples. Biphenyl and diphenylether derivatives were identified by comparison of GC retention times and Mass spectra with those of authentic samples.

## Synthesis and Characterization of *ortho*-Carborane Substituted Fischer-Type Carbene Complexes 1-[(CO)<sub>5</sub>M=C(OCH<sub>3</sub>)]-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (M=Cr, W; R=CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>)

Young-Joo Lee, Se-Jin Kim, Chang-Hwan Kang, Sijoon Lee<sup>†</sup>,  
Youhyuk Kim<sup>‡</sup>, Jae-Jung Ko, and Sang Ook Kang\*

Department of Chemistry,  
College of Natural Sciences, Korea University,  
Chung-nam 339-700, Korea

<sup>†</sup>Yookong Limited, Taedok R&D Center,  
140-1 Wonchon-dong, Yusung-Gu, Taejeon

<sup>‡</sup>Department of Chemistry,  
College of Natural Sciences, Dankook University,  
Chung-nam 330-714, Korea

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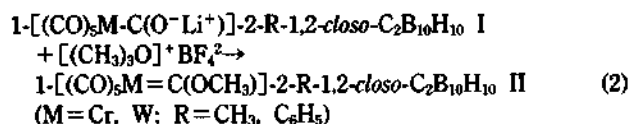
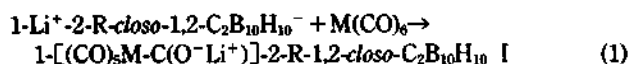
We have studied a series of metal carbene complexes<sup>1</sup> in which the carbene ligand contains a *ortho*-carborane, 1-R-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, group adjacent to the coordinatively unsaturated carbon atom. Cluster complexes of transition-metals in which the metal atoms are not directly bound are of spe-

cial interest for the evidence they provide the ability of cluster to transmit its influence to the metal. Metal carbene complexes of this type in which metal and carborane are separated by one atom, carbene carbon, could show that some metal-carborane interaction occurs in such compounds.

Although numerous electrophilic transition-metal carbene complexes stabilized by alkyl substituents<sup>2</sup> are known, simple complexes possessing sterically bulky inorganic analogue are unknown except for the metal carbene complexes in which the carbene ligand contains a ferrocenyl group.<sup>3</sup>

The addition of organolithium reagents to metal carbonyl complexes is an attractive route metal carbene complexes.<sup>4</sup> Therefore, a number of *ortho*-carborane substituted carbene complexes of chromium and tungsten were prepared by the reaction of metal carbonyls with *ortho*-carborane lithium reagents. We had hope to prepare *ortho*-carborane substituted carbene complexes of chromium and tungsten and we have been able to prepare such compounds.

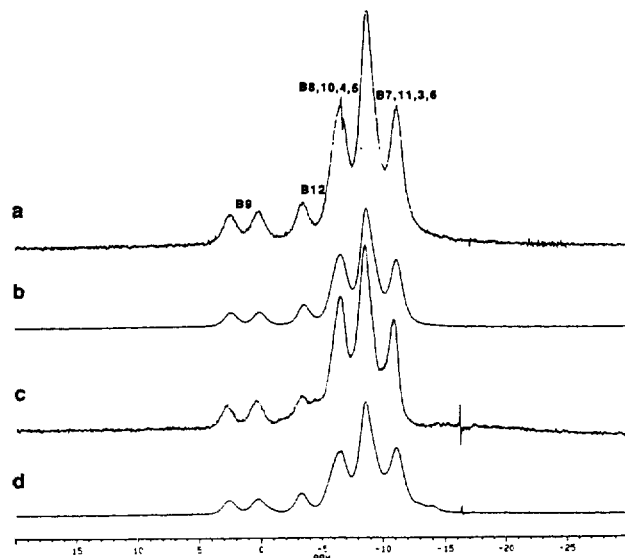
When the anionic *ortho*-carborane was treated with metal carbonyl complexes, *α-ortho*-carboranyl metal complexes 1-[(CO)<sub>5</sub>M-C(O<sup>-</sup>Li<sup>+</sup>)]-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> I were isolated. Subsequent methylation produced desired *ortho*-carboranyl metal-carbene complexes 1-[(CO)<sub>5</sub>M=C(OCH<sub>3</sub>)]-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> II shown in equation 1 and 2.



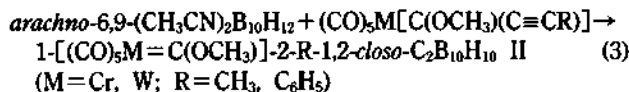
Each of the complexes was prepared by adaptations of the general methods currently available.<sup>4</sup> In a typical experiment, a solution of 1-Li<sup>+</sup>-2-R-closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>-</sup> (R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) was prepared<sup>5,6</sup> by the reaction *in vacuo* of excess *n*-BuLi (4.2 mmol) with 1-R-closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (3.0 mmol) in tetrahydrofuran (~25 mL) at ~-78 °C. To this solution 3.2 mmol of M(CO)<sub>6</sub> (M = Cr, W) in THF was added with warming from -78 °C to room temperature for 2 h. The solution gradually turned dark brown, suggesting the formation of a metal acyl complex. <sup>11</sup>B NMR spectra taken at this point confirmed the exclusive formation of the 1-[(CO)<sub>5</sub>M-C(O<sup>-</sup>Li<sup>+</sup>)]-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> I. Methylation with (CH<sub>3</sub>)<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> followed by extraction with hexane gave yellow solid. Subsequent separation was performed on the flash column of silica with hexane to give complexes 1-[(CO)<sub>5</sub>M=C(OCH<sub>3</sub>)]-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> II; (1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IIa,<sup>7a</sup> 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IIb,<sup>7b</sup> 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IIc,<sup>7c</sup> 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IId.<sup>7d</sup>

The *α-ortho*-carboranyl carbene complexes of chromium and tungsten are all moderately air stable crystalline solids which are readily soluble in all non-polar solvents (hexane, benzene) and sparingly soluble in polar solvents (ether, acetone). All of these complexes are photo-sensitive but show significant thermal stability in the temperature range of room temperature to 80 °C.

The compound II was produced from rather simple manner shown in equation 3.

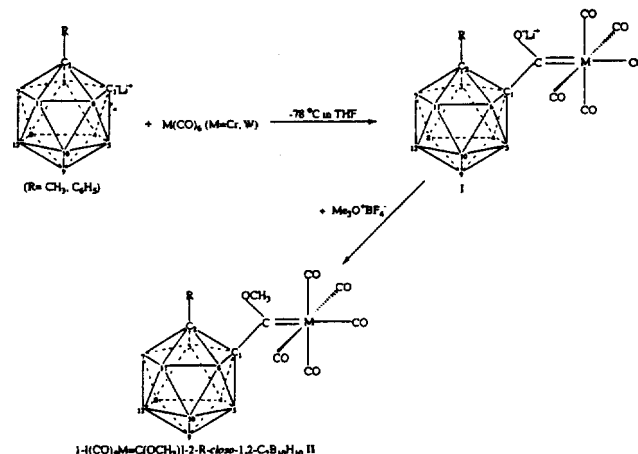


**Figure 1.** The 64.2 MHz  $^{11}\text{B}$  NMR spectra of 1-[(CO) $_5$ Cr=C(OCH $_3$ )]-2-CH $_3$ -1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  IIa (a), 1-[(CO) $_5$ W=C(OCH $_3$ )]-2-CH $_3$ -1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  IIb (b), 1-[(CO) $_5$ Cr=C(OCH $_3$ )]-2-C $_6$ H $_5$ -1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  IIc (c), and 1-[(CO) $_5$ W=C(OCH $_3$ )]-2-C $_6$ H $_5$ -1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  IId (d).



In a typical reaction, 3.0 mmol of *arachno*-6,9-(CH $_3$ CN) $_2$ B $_{10}$ H $_{12}$  and 3.2 mmol of (CO) $_5$ M[C(OCH $_3$ )(C=CR)] (M=Cr, W; R=CH $_3$ , C $_6$ H $_5$ ) were reacted in ~30 mL of benzene *in vacuo*. The reaction mixture was initially warmed to -20 °C where upon solution also gradually turned brown. The reaction was then allowed to react at 0 °C for 1 h. The solution was stirred for another 2 h at reflux temperature, resulting in the formation of a dark brown solution.  $^{11}\text{B}$  NMR spectra taken at this point indicated that the starting material had been completely consumed and that 1-[(CO) $_5$ M=C(OCH $_3$ )]-2-R-1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  II was the sole product. Concentration followed by flash column chromatographic separation of the resulting reaction mixture gave 1-[(CO) $_5$ M=C(OCH $_3$ )]-2-R-1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  II.<sup>9</sup> Although the reaction requires reflux condition in benzene, the high yields and facile product isolation make this route a significant improvement over the synthetic methods based on reactions 1 and 2.

The composition of II was established by both elemental analysis and mass spectral analysis and complexes II show similar spectroscopic data. Thus, the 64.2 MHz  $^{11}\text{B}$  NMR spectra of II (Figure 1) have similar features and support the structures proposed in Scheme 1.  $^{11}\text{B}$  NMR spectra of II consist of a set of overlapping doublets of relative intensities 1 : 1 : 4 : 4. This compares favorably with the 1 : 1 : 2 : 2 : 2 : 2 pattern expected for a 1-R-2-R'-1,2-C $_2$ B $_{10}$ H $_{10}$  derivative possessing a single symmetry plane. The assignment of these resonances to the B9, B12, B8,10,4,5, and B7,11,3,6 borons, respectively, is consistent with those previously made by Hawthorne<sup>10</sup> for the spectrum of complex 1-[(CO) $_5$ Mn=C(OCH $_3$ )]-2-CH $_3$ -1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$ . Thus, the plane of symmetry indicated by the NMR data for complexes II can only be consistent with sub-



**Scheme 1.**

stitution of the carborane at C1 and C2.

The  $^1\text{H}$  NMR data are likewise in agreement with the proposed cage structure,<sup>11</sup> confirming the presence of a methyl (~1.5 ppm) at the cage 2-position and one OCH $_3$  (~4.0 ppm) resonance for carbene substituent of IIa and IIb. The  $^{13}\text{C}$  NMR spectra contain carbene carbon resonance at 363 and 337 ppm, respectively for IIa and IIb. The  $^1\text{H}$  NMR spectra confirm the presence of a phenyl group showing a cage phenyl multiplet at ~7.4 ppm and one methoxy resonances at ~4.0 ppm for a carbene group either at the chromium or tungsten metal of complex IIc and IId. The room temperature proton-spin decoupled  $^{13}\text{C}$  NMR spectra show carbene carbon resonances (~340 ppm) for IIc and IId.

The infrared spectra of II exhibited a strong B-H stretching absorption at ~2590  $\text{cm}^{-1}$  and three sharp strong C=O stretching absorption between ~2100 and ~1900  $\text{cm}^{-1}$ , indicative of a M(CO) $_5$  (M=Cr, W) derivatives possessing local  $C_{4v}$  symmetry.<sup>12</sup> No sharp carborane C-H stretching absorptions around 3060  $\text{cm}^{-1}$  were observed, indicating the product to be a C(1)-substituted derivative.

From this analytical, nmr, and infrared data we proposed the structure in Scheme 1 for these complexes, where the carbene carbon is joined to the icosahedron through a C-C(1) s-bond. Thus, they support the formation of II as a 12-vertex *ortho*-carborane containing Fischer-type carbene complexes.

The presence of a *ortho*-carborane group adjacent to the carbene carbon atom does not lead to significant change in the physical properties of the metal carbene complexes when these are compared with those of carbene complexes containing alkyl substituent. However, IR spectra show the effect of the *ortho*-carborane group in the complexes II. The substitution of a *ortho*-carborane group produces a small increase in carbonyl stretching frequencies from their values in other alkyl-substituted systems,<sup>13</sup> suggesting that ( $d \rightarrow p$ ) $\pi$  donation in the M-C(sp $^2$ ) bond increases in the same manner as ( $d \rightarrow \pi^*$ ) $\pi$  donation in the M-*trans*(CO) bond decreases.

In summary, we provide a reasonable synthetic route to the *ortho*-carborane metal-carbene complexes 1-[(CO) $_5$ M=C(OCH $_3$ )]-2-R-1,2-*closo*-C $_2$ B $_{10}$ H $_{10}$  II. These results demonstrate well for the use of *ortho*-carborane anions as nucleophilic reagents in organometallic chemistry. Further application of these, and related, *ortho*-carborane ligands to organometallic chemistry is being actively pursued.

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### References

- Kim, S.; Lee, S.; Kim, Y.; Ko, J.; Kang, S. O. *Bull. Kor. Chem. Soc.* 1995, 16, 634.
- (a) Brookhart, M.; Tucker, James, R.; Husk, G. R. *J. Am. Chem. Soc.* 1983, 105, 258. (b) Wong, W. K.; Tam, W.; Gladysz, W. A. *J. Am. Chem. Soc.* 1979, 101, 5440. (c) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jesen, J. *J. Am. Chem. Soc.* 1980, 102, 1203. (d) Fischer, E. O.; Clough, R. L.; Best, G.; Dreissl, F. R. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 543.
- Connor, J. A.; Lloyd, P. J. *J. Chem. Soc., Dalton Trans.* 1972, 1470.
- (a) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* 1964, 3, 580. (b) Fischer, E. O.; Maasböl, A. *Chem. Ber.* 1967, 100, 2445. (c) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Muller, J. *J. Organomet. Chem.* 1969, 16, p 29.
- Garrett, P. M.; Smart, J. C.; Hathorne, M. F. *J. Am. Chem. Soc.* 1969, 91, 4707.
- Heying, T. L.; Ager, Jr., J. W.; Clark, S. L.; Alxender, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. *Inorg. Chem.* 1963, 2, 1907.
- (a) The carbene complex 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*cis*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IIa was thus obtained in 37% yield (0.44 g, 1.12 mmol) as a yellow solid. <sup>11</sup>B NMR (64.2 MHz, ppm, C<sub>6</sub>D<sub>6</sub>); 1.3 (d, B<sub>9</sub>, J<sub>BH</sub> = ~150 Hz), -4.6 (d, B<sub>12</sub>, J<sub>BH</sub> = ~200 Hz), -7.9 (d, B<sub>8,10</sub>, B<sub>4,5</sub>, J<sub>BH</sub> = ~140 Hz), -9.9 (d, B<sub>7,11</sub>, B<sub>3,6</sub>, J<sub>BH</sub> = ~180 Hz); <sup>1</sup>H NMR (200.13 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 4.0 (s, OCH<sub>3</sub>), 1.5 (s, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 363 (s, Cr=C), 223 (s, CO), 216 (s, CO), 73 (s, OCH<sub>3</sub>), 28 (s, CH<sub>3</sub>); exact mass calcd for <sup>11</sup>B<sub>10</sub><sup>12</sup>C<sub>10</sub><sup>52</sup>Cr<sub>1</sub><sup>1</sup>H<sub>16</sub><sup>16</sup>O<sub>6</sub> 394.1277, found 394.1296; Anal. Calcd: C, 30.61; H, 4.11. Found: C, 30.75; H, 4.14. R<sub>f</sub> = 0.88 by silica gel TLC analysis (hexane); mp = 78-80 °C (dec); IR spectrum (KBr pallet, cm<sup>-1</sup>) 2970 w, 2940 w, 2880 w, 2600 s, 2070 s, 1985 s, 1940 vs, 1460 w, 1260 m, 1115 w, 1040 w, 950 w, 920 w, 870 w, 850 w, 830 w, 800 w, 730 w, 690 w, 670 m, 660 m, 630 w. (b) The carbene complex 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*cis*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IIb was thus obtained in 40% yield (0.63 g, 1.20 mmol) as a yellow solid. <sup>11</sup>B NMR (64.2 MHz, ppm, C<sub>6</sub>D<sub>6</sub>); 1.4 (d, B<sub>9</sub>, J<sub>BH</sub> = ~150 Hz), -4.6 (d, B<sub>12</sub>, J<sub>BH</sub> = ~200 Hz), -7.8 (d, B<sub>8,10</sub>, B<sub>4,5</sub>, J<sub>BH</sub> = ~140 Hz), -9.9 (d, B<sub>7,11</sub>, B<sub>3,6</sub>, J<sub>BH</sub> = ~180 Hz); <sup>1</sup>H NMR (200.13 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 3.83 (s, OCH<sub>3</sub>), 0.80 (s, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 337 (s, W=C), 204 (s, CO), 198 (s, CO), 69 (s, OCH<sub>3</sub>), 27 (s, CH<sub>3</sub>); exact mass calcd for <sup>11</sup>B<sub>10</sub><sup>12</sup>C<sub>10</sub><sup>184</sup>W<sub>1</sub><sup>1</sup>H<sub>16</sub><sup>16</sup>O<sub>6</sub> 526.1372, found 526.1398; Anal. Calcd: C, 22.91; H, 3.08. Found: C, 22.88; H, 3.04. R<sub>f</sub> = 0.82 by silica gel TLC analysis (hexane); mp = 88-90 °C (dec); IR spectrum (KBr pallet, cm<sup>-1</sup>) 2960 m, 2870 m, 2600 s, 2080 s, 1980 s, 1940 vs, 1470 m, 1450 m, 1400 w, 1370 w, 1260 s, 1110 w, 1055 w, 1035 w, 940 w, 910 w, 860 m, 840 m, 820 s, 800 w, 735 w, 700 w, 680 w, 660 w, 630 w, 600 w, 575 w, 410 w, 385 s, 340 w. (c) The carbene complex 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*cis*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IIc was thus obtained in 35% (0.48 g, 1.05 mmol) yield as a yellow solid. <sup>11</sup>B NMR (64.2 MHz, ppm, C<sub>6</sub>D<sub>6</sub>); 1.7 (d, B<sub>9</sub>, J<sub>BH</sub> = ~150 Hz), -4.5 (d, B<sub>12</sub>, J<sub>BH</sub> = ~200 Hz), -7.5 (d, B<sub>8,10</sub>, B<sub>4,5</sub>, J<sub>BH</sub> = ~140 Hz), -9.4 (d, B<sub>7,11</sub>, B<sub>3,6</sub>, J<sub>BH</sub> = ~180 Hz); <sup>1</sup>H NMR (200.13 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 7.41 (m, C<sub>6</sub>H<sub>5</sub>), 3.89 (s, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 344 (s, Cr=C), 192 (s, CO), 133, 130, 128 (s, C<sub>6</sub>H<sub>5</sub>), 58 (s, OCH<sub>3</sub>); exact mass calcd for <sup>11</sup>B<sub>10</sub><sup>12</sup>C<sub>15</sub><sup>52</sup>Cr<sub>1</sub><sup>1</sup>H<sub>18</sub><sup>16</sup>O<sub>6</sub> 456.1433, found 456.1428; Anal. Calcd: C, 39.65; H, 3.99. Found: C, 39.58; H, 3.95. R<sub>f</sub> = 0.66 by silica gel TLC analysis (benzene/hexane, 50/50); mp = 74-76 °C (dec); IR spectrum (KBr pallet, cm<sup>-1</sup>) 3070 w, 2970 w, 2940 w, 2600 s, 2080 s, 1990 s, m, 1930 vs, m, 1490 w, 1445 w, 1385 w, 1330 m, 1260 w, 1220 w, 1170 w, 995 w, 920 w, 875 w, 810 w, 760 w, 700 w, 665 w, 620 w, 590 w, 565 w, 490 w, 370 m. (d) The carbene complex 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*cis*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> IId was thus obtained in 43% yield (0.76 g, 1.30 mmol) as a yellow solid. <sup>11</sup>B NMR (64.2 MHz, ppm, C<sub>6</sub>D<sub>6</sub>); 1.6 (d, B<sub>9</sub>, J<sub>BH</sub> = ~150 Hz), -4.4 (d, B<sub>12</sub>, J<sub>BH</sub> = ~200 Hz), -7.3 (d, B<sub>8,10</sub>, B<sub>4,5</sub>, J<sub>BH</sub> = ~140 Hz), -10.2 (d, B<sub>7,11</sub>, B<sub>3,6</sub>, J<sub>BH</sub> = ~180 Hz); <sup>1</sup>H NMR (200.13 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 7.40 (m, C<sub>6</sub>H<sub>5</sub>), 3.90 (s, OCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, ppm, C<sub>6</sub>D<sub>6</sub>) 337 (s, W=C), 196 (s, CO), 133, 130, 128 (s, C<sub>6</sub>H<sub>5</sub>), 53 (s, OCH<sub>3</sub>); exact mass calcd for <sup>11</sup>B<sub>10</sub><sup>12</sup>C<sub>15</sub><sup>184</sup>W<sub>1</sub><sup>1</sup>H<sub>18</sub><sup>16</sup>O<sub>6</sub> 588.1528, found 588.1539; Anal. Calcd: C, 30.73; H, 3.09. Found: C, 30.69; H, 3.07. R<sub>f</sub> = 0.79 by silica gel TLC analysis (benzene/hexane, 50/50); mp = 82-94 °C (dec); IR spectrum (KBr pallet, cm<sup>-1</sup>) 3070 w, 2970 w, 2940 w, 2600 s, 2080 s, 1990 s, m, 1930 vs, m, 1445 w, 1385 w, 1330 m, 1260 w, 1220 w, 1170 w, 995 w, 920 w, 810 w, 760 w, 700 w, 590 w, 565 w, 490 w, 370 m.
- (a) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* 1986, 108, 5229. (b) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* 1985, 286, C23. (c) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* 1984, 106, 7565.
- The same procedure was applied for the rest of the *α-ortho*-carboranyl metal carbene complexes II with the following variations in the procedure of purification. IIa. Procedure variation: Evaporation of the benzene solution to dryness and flash chromatography (hexane/CHCl<sub>3</sub>, 98/2) on silica; 45% yield (0.53 g, 1.35 mmol). IIb. Reaction time: 4h. Procedure variation: Evaporation of the benzene solution to dryness and flash chromatography (hexane/CHCl<sub>3</sub>, 98/2) on silica; 48% yield (0.75 g, 1.43 mmol). IIc. Procedure variation: Evaporation of the benzene solution to dryness and flash chromatography (hexane/benzene, 95/5) on silica; 52% yield (0.71 g, 1.56 mmol). IId. Reaction time: 4h. Procedure variation: Evaporation of the benzene solution to dryness and flash chromatography (hexane/benzene, 95/5) on silica; 64% yield (1.13 g, 1.93 mmol). In each case, the mother liquors were evaporated to dryness, and the <sup>11</sup>B and <sup>1</sup>H NMR spectra were studied.
- Owen, D. A.; Smart, J. C.; Garrett, P. P.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1971, 93, 1362.
- Hawthorne, M. F.; Andrews, T. D.; Garrett, P. M.; Reintjes, M.; Tebbe, F. N.; Warren, Jr., L. F.; Wegner, P. A.;

- Young, D. C. *Inorg. Synth.* 1967, 10, 91.  
 12. Edgell, W. F.; Fisher, J. W.; Asato, G.; Risen, Jr., W. M. *Inorg. Chem.* 1969, 8, 1103.  
 13. (a) Graham, W. A. G. *Inorg. Chem.* 1968, 7, 315. (b) Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* 1970, 9, 32.

### A Facile Synthesis of Highly Substituted $\gamma$ -Butyrolactones via Trans-Lactonization of the Baeyer-Villiger Products

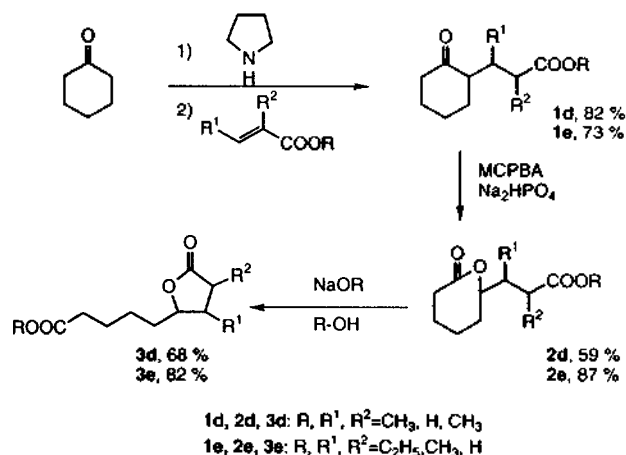
Chang Ho Oh\*, Bun Seang Park, Andre Kim,  
and Yong Ae Park

Department of Chemistry, Inje University,  
Aubang 607, Kimhae 621-749, Korea

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About 10% of all natural products and many synthetic intermediates contain a  $\gamma$ -butyrolactone skeleton.<sup>1</sup> Various synthetic methods to these  $\gamma$ -butyrolactones are present such as intramolecular esterification of  $\gamma$ -hydroxyacids or their derivatives in the presence of acid or base catalyst,<sup>2</sup> halolactonization of  $\gamma,\delta$ -unsaturated acids,<sup>3</sup> palladium-catalyzed lactonization of  $\gamma,\delta$ -unsaturated acids leading to the formation of  $\gamma$ -vinyl substituted  $\gamma$ -lactones<sup>4</sup> and an intramolecular addition of oxycarbonyl radicals to double or triple bonds.<sup>5</sup> Although those methods have been widely applied to the many natural products syntheses, yet  $\gamma$ -butyrolactones, having a labile or reactive functional group such as an ester at the  $\gamma$  position, are limited to access. We wish to describe an easy and convenient synthetic method to regiospecifically substituted  $\gamma$ -lactones. Our strategy involved three steps: alkylation of cyclic ketones,<sup>6</sup> Baeyer-Villiger oxidation for generating the transient  $\gamma$ -hydroxyacid equivalents, and followed by transesterification of the corresponding lactones (Scheme 1).<sup>8</sup>

The pyrrolidine enamine of cyclohexanone smoothly underwent the Michael addition with ethyl acrylate to afford ethyl

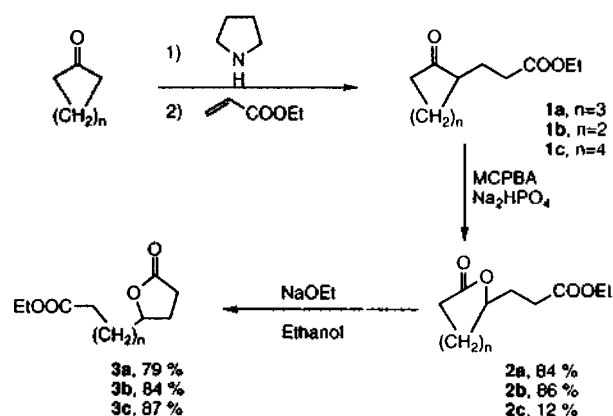


Scheme 2.

3-(2-oxocyclohexyl)propanoate (**1a**) in over 80% yield. When the above 2-alkyl substituted cyclohexanone **1a** was treated with MCPBA and disodium phosphate as a base resulted in clean disappearance of the starting material on analytical TLC plate after 5-6 h at room temperature.<sup>9</sup> The extractive workup and separation on flash chromatography afforded the corresponding 7-membered lactone **2a** in 84% yield. The 7-membered lactone **2a** was then subjected to a catalytic amount of sodium ethoxide in refluxing ethanol and the corresponding  $\gamma$ -lactone **3a** was obtained after purification in 79% yield.

Structural variations from the cyclohexanone to a cyclopentanone and a cycloheptanone were highly operative. When ethyl 3-(2-oxocyclopentyl)propanoate (**1b**) was subjected to the MCPBA oxidation conditions, the corresponding  $\delta$ -lactone **2b** was formed in a few hours. However, the Baeyer-Villiger reaction of ethyl 3-(2-oxocycloheptyl)propanoate (**1c**) with MCPBA was not completed, because the cycloheptanone **1c** is much less reactive than the cyclohexanone or the cyclopentanone. The synthesis of  $\gamma$ -butyrolactones via trans-lactonization of the above 6-, 7-, and 8-membered lactones was more interesting to us. In fact, the eight membered lactone **2c** has been transformed smoothly to the corresponding  $\gamma$ -butyrolactone **3c** in 1 h in refluxing ethanol in the presence of a catalytic amount of sodium ethoxide, while the  $\delta$ -lactone **2b** derived from ethyl 3-(2-oxocyclopentyl)propanoate (**1b**) required longer reaction time (20 h) to complete the trans-lactonization presumably due to the stability of a 6-membered lactone **2b**. It is an important finding that the 6-membered lactone **2b** has been thermodynamically transformed to the 5-membered lactone **3b** in a very high yield. We have also concerned about the Dieckmann cyclization of the two pendant ester groups in the presence of a catalytic amount of a base. Note that no other side product was formed during this trans-lactonization.

Further structural variations in the Michael acceptors have provided the very easy synthesis of more substituted  $\gamma$ -lactones (Scheme 2).<sup>10</sup> The substituent R<sub>1</sub> and R<sub>2</sub> in the Michael acceptors would be eventually ended in the  $\beta$  and  $\alpha$  position in the final  $\gamma$ -lactones, respectively. Although the Michael addition of carbanions to  $\alpha,\beta$ -unsaturated esters has been well-known,<sup>11</sup> several attempts to obtain the addition product



Scheme 1.