the other hand, the angular systems are best described by invoking varying (and diminishing) degrees of bond alternation. Thus, **5** contains an internal "cyclohexatriene",[7b] maximizing the "aromaticity" of the flanking two benzene rings. Bond localization is increasingly attenuated along the series **5**, **6**, **7**, as more and more ($4n + 2$) circuits contribute to the π-structure. Support for this notion is found in the steadily increasing coupling constants between the hydrogens of the internal rings, e.g., **5**, J(H5–H6) = 6.53 Hz; **6**, J(H5–H6) = 6.68 Hz; **7**, J(H5–H6) = 6.80 Hz, J(H7–H8) = 7.00 Hz.

We are actively seeking corroborative evidence for these hypotheses by the continuing investigation of the structural and chemical properties of these unusual molecules.

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1,2-Asymmetric Induction in the Sn–H Bond Insertion Reaction of Aliphatic Fischer Carbene Complex

Eiichi Nakamura,* Koichi Tanaka, and Satoshi Aoki

Department of Chemistry
Tokyo Institute of Technology
Meguro, Tokyo 152, Japan

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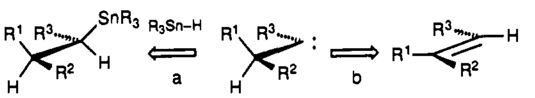
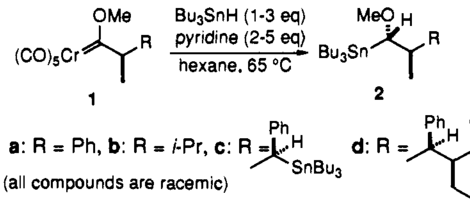
We report herein a case of a novel intermolecular carbene insertion reaction, wherein stereochemical information is effectively transmitted from an adjacent stereogenic center to the reacting carbene carbon (eq 1a). Examples of such 1,2-asymmetric inductions have not been reported previously, perhaps due to the propensity of aliphatic carbenes to undergo 1,2-hydrogen migration (eq 1b) faster than intermolecular insertion.[1]



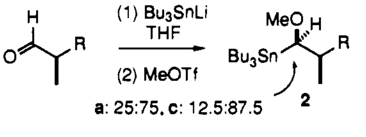
(1)

Aliphatic Fischer carbene complexes readily undergo 1,2-hydrogen migration upon heating with a base.[2] We have found, however, that intermolecular insertion into an Sn–H σ-bond[3] can effectively compete with the intramolecular reaction and that it proceeds with considerable diastereoselectivity for a carbene complex bearing an α-stereogenic center (eq 2). The following example illustrates the experimental procedure, which is very simple. A mixture of carbene complex **1d** (single isomer; 0.147 g, 0.33 mmol), Bu_3SnH (0.26 mL, 0.98 mmol), and pyridine (0.16 mL, 2.0 mmol) was heated in 5 mL of hexane for 8 h at 60 °C. Removal of the yellow precipitate of chromium(0)/pyridine complexes[3] by filtration followed by silica gel chromatography (hexane) gave 145 mg of the α-alkoxytin compound **2d** (81%) as a 93:7 diastereomeric mixture. The reaction gave only a trace amount of an olefin due to 1,2-hydrogen migration.[4]



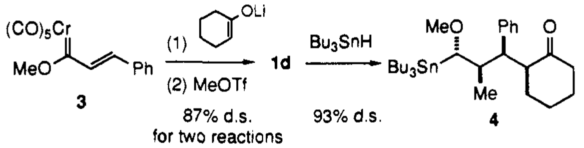
(2)

Inspection of the data in Table I reveals several notable features of the reaction. First, the reaction proceeds with a synthetically useful level (4:1–13:1) of asymmetric induction. Comparison of **1a** and **1c** (entries 1 and 5) with authentic samples (eq 3) indicated that the stereochemistry of these compounds is different from that obtained by Cram addition of Bu_3SnLi to the structurally comparable aldehyde and that the Sn–H insertion and the SnLi addition showed virtually the same level of diastereoselectivity.[5]



(3)

Upon combination with the stereoselective Michael addition/trapping sequence,[6] the insertion reaction stereoselectively creates the four chiral centers in **4** in two steps from **3** (eq 4). The reaction conditions are mild enough not to affect ketone and stannyl groups or to cause epimerization at the carbon adjacent to a ketone group (entries 5 and 6). It is well-known that the conversion of the Sn–C bond in an (α-alkoxyalkyl)stannane to a C–C bond can be carried out with retention of stereochemistry via an (α-alkoxyalkyl)lithium.[7]



(4)

Notably, the diastereoselectivity was little influenced either by the added basic ligand or by the nature of the group 14 metal. Thus, the selectivities of the reaction of **1b** with Bu_3SnH in the presence of pyridine, DABCO, DMAP, Ph_3P, $(PhO)_3P$, and $(MeO)_3P$ fell in a small range, 79, 76, 75, 71, 74, and 74% ds, respectively (40–80%), and the reaction rate remained qualitatively unchanged. In addition, neither the selectivity nor the rate of the reaction changed much for Bu_3SnH and Ph_3SnH (entries 1 and 3), in spite of the apparent difference in their steric demand.[8] The reaction of Bu_3SnD (99% deuterium) with the complex **1a** resulted in complete deuterium incorporation to the carbene center (entry 2),[9] proceeding with selectivity identical with that of the Bu_3SnH reaction. Among other group 14 metals, Ph_3GeH, which was much less reactive (6% yield), also showed a 7:3 selectivity, and $PhMe_2SiH$ gave a complex mixture of products.

While at this time there is insufficient data to discuss the details of the reaction mechanism, Scheme I illustrates some factors relevant to the origin of the diastereoselectivity. In an insertion reaction of a carbene-type reactive intermediate, the stereocontrol is a complex issue, since two new σ-bonds are formed on the forming chiral center in a single reaction. The likely conformation of the 1-phenylethyl complex **1a** is based on the steric bulk of the $Cr(CO)_5$ moiety as supported by MMX calculations.[10] The

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(1) For the discussion of this issue, see: Taber, D. F.; Hennessy, M. J.; Louey, J. D. *J. Org. Chem.* **1992**, *57*, 436. Guzman, A.; Pinedo, A.; Saldana, A.; Torre, D.; Muchowski, J. M. *Can. J. Chem.* **1983**, *61*, 454. Cama, L. D.; Cheristensen, B. G. *Tetrahedron Lett.* **1978**, 4233. Padwa, A.; Kulkarni, Y. S.; Zhang, Z. *J. Org. Chem.* **1990**, *55*, 4144.

(2) (a) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. Soderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951. (b) General reviews of Fischer carbene chemistry: Wulff, W. D. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, Chapter 9.2.

(3) (a) The insertion reaction of arylcarbene complexes to group 14 hydrides: Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organomet. Chem.* **1973**, *55*, 111. (b) Mechanistic studies: Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 108. Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 283.

(4) Side reactions involve intramolecular C–H insertion and carbene dimerization, which became dominant for unreactive substrates and metal hydrides (e.g., R_3GeH and R_3SiH).

(5) Further correlation[7] of **2a** to the known diastereomers of 2-phenyl-3-pentanol (EtMgBr + 2-phenylpropanal) confirmed the stereochemistry of **2a** as indicated in eq 3 (see supplementary material).

(6) Cf. Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985. For diastereoselective aldol chemistry of carbene complexes: Wulff, W. D.; Anderson, B. A.; Toole, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5485. Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(7) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201.

(8) These are consistent with the assumptions made for Scheme I.

(9) There was very small deuterium isotope effect (k_H/k_D = ca. 1.1, competition with 10 equiv each of the hydride and deuteride).

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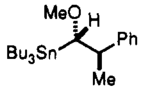
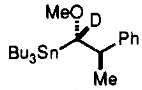
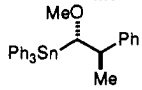
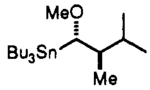
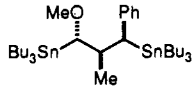
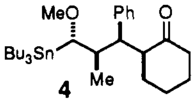
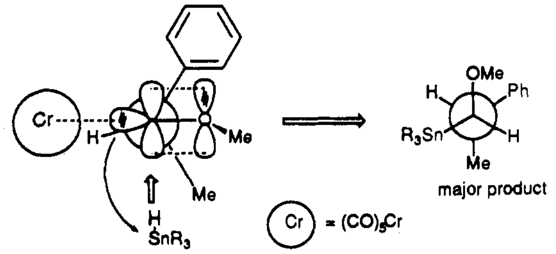
Table I. Stereoselective Sn-H Insertion Reaction[a]

entry	1	diastereo ratio[b]	% yield	major product
1	**1a**	77:23	69	
2	**1a**	77:23	66	
3	**1a**	74:26	73	
4	**1b**	79:21	82	
5	**1c**	88:12	43	
6	**1d**	93:7	81	 **4**

[a] The reaction was carried out with 1.5-3 equiv of a tin hydride and 2-5 equiv of pyridine in hexane at 60 °C for 5-10 h. Tin hydride reagents: Bu_3SnH in entries 1 and 4-6; Bu_3SnD in entry 2; Ph_3SnH in entry 3. [b] The ratios were determined by ^1H NMR analysis (e.g., of MeO signals).

Scheme I



crucial feature is that the bulky $Cr(CO)_5$ group severely restricts the conformation of the 1-phenylethyl side chain and allows only a hydrogen atom to be located (approximately) in the plane defined by O-C(carbene)-C(α). The selectivity of the reaction can thus be rationalized on the basis of the following three assumptions: (1) the approach of the tin hydride reagent takes place from the less hindered bottom side; (2) the reagent approaches with hydride projecting toward the carbene;[3b,8] and (3) the Cr-carbene bond is cleaved with retention of configuration to form a tin-carbon bond as indicated by the arrow.

Despite the accumulated knowledge on face-selective trigonal-to-tetrahedral transformations,[11] there is little information on digonal-to-tetrahedral conversions. The present results shed the first light on the potential utility of the latter type of transformation, which will be the subject of future studies in our laboratory.

Acknowledgment. We thank the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid 04217207) and the Nissan Foundation for financial support.

Supplementary Material Available: Listings of physical data for the insertion products (4 pages). Ordering information is given on any current masthead page.

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(10) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Adv. Mol. Model.* **1990**, *2*, 65. While parameterization is poor for Cr, the steric bulk of the $Cr(CO)_5$ may be reasonably estimated.

(11) For other aspects of this problem, see: Arai, M.; Nemoto, T.; Ohashi, Y.; Nakamura, E. *Synlett* **1992**, 309. Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1990**, *112*, 7428. Nakamura, E. *Synlett* **1991**, 539.

Synthesis and Characterization of μ_2-η^2- and μ_2-η^3-CO_2 Complexes of Iron and Rhenium

Dorothy H. Gibson,* Ming Ye, and John F. Richardson

Department of Chemistry
University of Louisville
Louisville, Kentucky 40292

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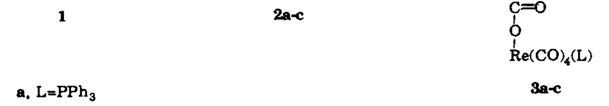
There is current interest in finding ways to activate CO_2 and to use it as a building block for organic synthesis.[1] The possibility for thermal activation of CO_2 was outlined by Floriani,[2] who suggested that bifunctional systems, having a highly basic metal to bind carbon and an acidic one to bind one or both oxygens, might be effective in sequestering CO_2 and in activating it. Floriani characterized a cobalt metallocarboxylate anion with a potassium counterion.[2] Since then, several μ_2-η^2- and μ_2-η^3-CO_2-bridged complexes have been reported[3] and a few other μ_2-η^3 complexes have been structurally characterized. We report here the synthesis of three μ_2-η^2-CO_2 complexes, the structural characterization of one, and the conversion of all to the corresponding μ_2-η^3-CO_2 complexes.

We reported the characterization of **1**, $CpFe(CO)(PPh_3)CO_2^-K^+$ (Cp = η^5-C_5H_5), previously.[3i,r] Reactions of **1** with a series of rhenium cations[4,5] having a weakly coordinated BF_4 anion yield μ_2-η^2-CO_2 complexes as shown below:



$$\underset{\mathbf{1}}{CpFe(CO)(PPh_3)CO_2^-K^+} + \underset{\mathbf{2a\text{-}c}}{Re(CO)_4(L)(F{-}BF_3)} \xrightarrow{-KBF_4} \underset{\mathbf{3a\text{-}c}}{\begin{array}{l}CpFe(CO)(PPh_3)\\ \quad | \\ \quad C{=}O\\ \quad | \\ \quad O\\ \quad | \\ \quad Re(CO)_4(L)\end{array}}$$

a, L=PPh_3
b, L=$P(OPh)_3$
c, L=CO

Compound **3a** is the most stable and has been fully characterized;[6,7]

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(1) (a) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. (b) Behr, A. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel Publ. Co.: Dordrecht, 1988; Vol. 6, p 59. (c) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (d) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (e) *Carbon Dioxide Activation by Metal Complexes*; Behr, A., Ed.; VCH Publishers: Weinheim, Federal Republic of Germany, 1988. (f) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.

(2) (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(3) (a) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. (b) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797. (c) Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352. (d) Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121. (e) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794. (f) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478. (g) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069. (h) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. (i) Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* **1987**, *109*, 7191. (j) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956. (k) Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737. (l) Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasinghe, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 7098. (m) Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1287. (n) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333. (o) Gibson, D. H.; Richardson, J. F.; Ong, T.-S. *Acta. Crystallogr.* **1991**, *C47*, 259. (p) Torreson, I.; Michelin, R. A.; Marsella, A.; Zanardo, A.; Pinna, F.; Strukul, G. *Organometallics* **1991**, *10*, 623. (q) Vites, J. C.; Steffey, B. D.; Giuseppetti-Dery, M. E.; Cutler, A. R. *Organometallics* **1991**, *10*, 2827. (r) Gibson, D. H.; Ong, T.-S.; Ye, M. *Organometallics* **1991**, *10*, 1811.

(4) Reactions were done in an argon-filled glovebox at -40 °C in dry CH_2Cl_2 (**3a**,**b**) or dry THF (**3c**). Compounds **2a**,**c** have been prepared previously by Beck.[5] Compound **2b** was prepared in the same way; acceptable elemental analyses have been obtained for **2a**,**b**.

(5) (a) See: Beck, W. *Inorg. Synth.* **1990**, *28*, 1 and references cited therein. (b) Schweiger, M.; Beck, W. *Z. Anorg. Allg. Chem.* **1991**, *595*, 203.

(6) **3a**: IR ν_{OCO} (neat, DRIFTS) 1505 (m) and 1135 (m) cm^{-1}; ^{13}C NMR (carbonyl and carboxyl only; CD_2Cl_2, -10 °C) δ 221.54 (d, J_{PC} = 33.0 Hz), 211.91 (dd, J_{PC} = 32.6 Hz, 3.9 Hz), 190.33 (d, J_{PC} = 9.9 Hz), 190.13 (d, J_{PC} = 9.0 Hz), 188.65 (d, J_{PC} = 4.6 Hz), 186.79 (d, J_{PC} = 61.2 Hz); ^{31}P NMR (THF, -35 °C) δ 80.37 (s) and 8.61 (s).

(7) Characterization data are contained in the supplementary material.

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