

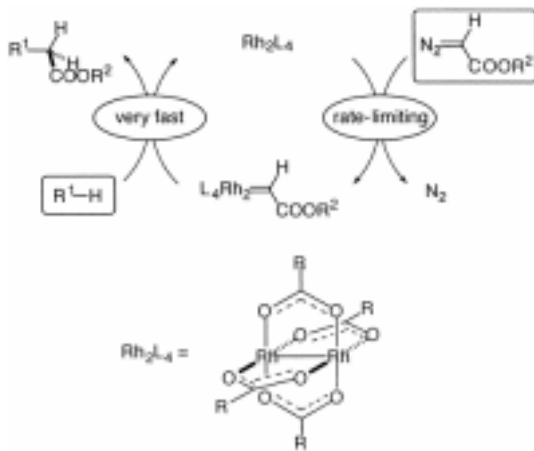
# 物理有機化学研究室

## 研究レビュー

高効率高選択的合成は生命科学，材料科学，またナノ科学・ナノ技術発展の鍵を握る重要分野に成長している．本研究グループでは新規反応開発に関する基礎研究に取り組む中で，反応中間体や遷移状態に関する研究を行い新反応の合理設計の指針を示し，新反応をもって化学及び化学関連分野に強いインパクトを与える新物質の創製することを目的として研究を進めている．

### (1) 複核遷移金属錯体触媒反応の理論研究

飽和炭化水素の炭素-水素結合の触媒的な活性化による炭素-炭素結合形成反応は標準の合成手法になりつつある．中でも二核ロジウム-カルボキシレート錯体を触媒とする飽和炭化水素と  $\alpha$ -ジアゾエステルとの反応は有機合成において幅広く用いられている．我々は密度汎関数法を用いてこの反応の理論研究を行い，反応経路や二核金属構造の役割，重要な中間体や遷移状態を明らかにした．

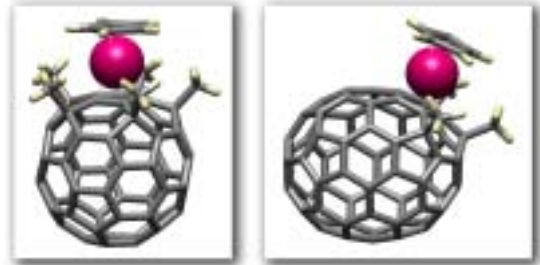


*J. Am. Chem. Soc.*, **124**, 7181-7192 (2002)

### (2) バッキーフェロセン

フラーレンが発見されて以来，2つの重要な歴史的な分子であるフェロセンとフラーレンからなる，“バッキーフェロセン”は科学者の興味の対象であった．しかし，その分子は合成のできない架空の分子となっていた．我々は，メチル5重付加型[60]フラーレンおよびメチル3重付加型[70]フラーレン誘導体を用いることにより，バッキーフェロセンを合成することに成功した．バッキーフェロセンは安定で酸化還元活性な分子であった．この複合分子はフ

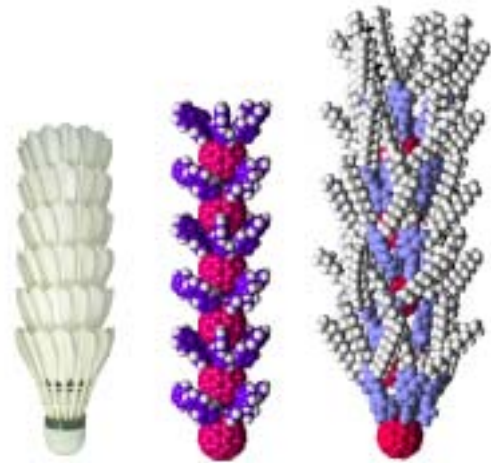
ラーレンの光学的および電子的性質を持ったナノスケールの構造体構築のビルディングブロックとして用いられるであろう．



*J. Am. Chem. Soc.*, **124**, 9354-9355 (2002)

### (3) シャトルコック型液晶分子

極性を示す液晶材料は光学・電子材料への応用が可能であり，最近，極性をもった分子の形状と相互作用を活用して，分子が配向する構造を形成させる戦略に興味もたれてきている．円錐型の分子は極性のあるカラム状集合体を作るはずだが，これまで使われた分子は平べったく，また，反転しやすいため，この手法での極性液晶材料の作製はあまり成功しなかった．我々は，[60]フラーレンを用いて尖った円錐形分子を合成することに成功し，これが積み重なって極性カラム状集合体を作ることを見いだした．柔らかい脂肪族鎖で延長することにより，サーモトロピック液晶とリオトロピック液晶の両方の特性を示す化合物が得られた．我々の設計戦略は他の分子にも適用可能で，新しい極性液晶材料を幅広く生み出すだろう．



*Nature*, **419**, 702-705 (2002)

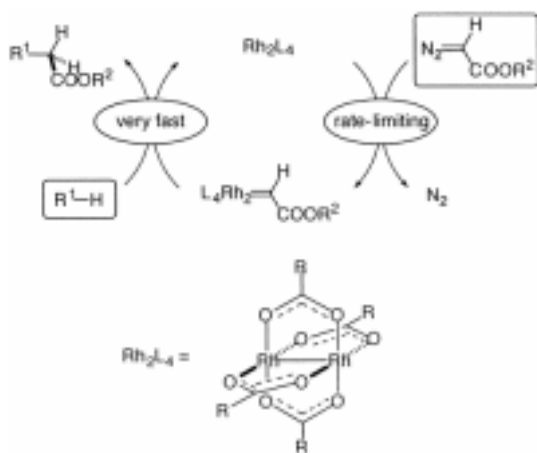
# PHYSICAL ORGANIC CHEMISTRY

## Annual Research Review

High-efficiency and selective synthesis has become important area which serve as the key to development of bio science, materials science, and nano science/technology. On the way of our research in the development of novel reactions, the objective of this research group is the elucidation of reaction mechanism that will generate novel strategies for creation of new functional materials. To this end, we are studying the reaction pathway of the C-C bond formation reaction and the synthesis of organofunctionalized fullerenes.

### (1) "Theoretical study of C-C bond formation reaction catalyzed by dinuclear transition metal complex"

Carbon-carbon bond forming reactions that rely on catalytic activation of the C-H bond in a saturated hydrocarbon have become standard synthetic protocols. Among them, the reaction of an  $\alpha$ -diazoester catalyzed by a dirhodium tetracarboxylate or a related catalyst is the reaction widely utilized as a practical synthetic method. We carried out density functional studies of this reaction, and successfully elucidated the reaction pathway, role of the dimetallic structure, and important intermediates and transition states of this reaction

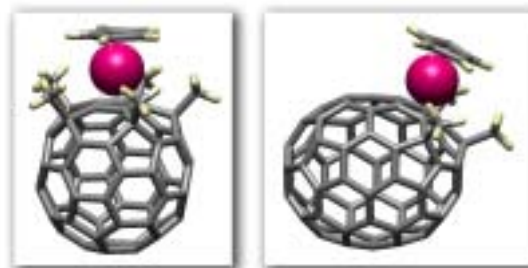


*J. Am. Chem. Soc.*, **124**, 7181-7192 (2002)

### (2) "Bucky ferrocene: hybrid of ferrocene and fullerene"

Since the discovery of fullerene, "bucky ferrocene", which is composed of two quite important historical molecules, ferrocene and fullerene, has attracted considerable interest of scientists. However, the molecule so far remained hypothetical. We successfully synthesized molecular hybrid of

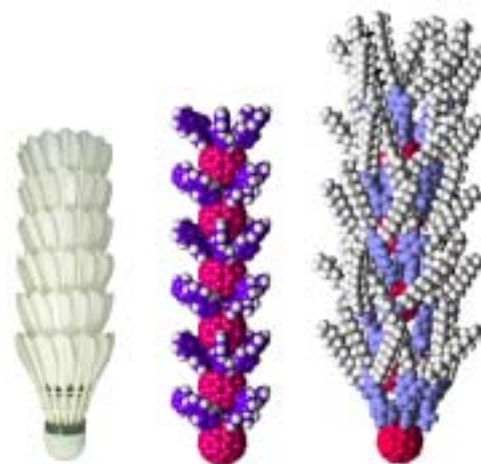
ferrocene and fullerene by using pentamethylated [60]fullerene or trimethylated [70]fullerene derivatives. This hybrid molecule could be used as building blocks to construct other types of nano-structures having useful photonic or electronic properties.



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### (3) "Shuttlecock-shaped liquid crystalline molecules"

Polar liquid crystalline materials can be used in optical and electronic applications, and recent interest has turned to formation strategies that exploit the shape of polar molecules and their interactions to direct molecular alignment. We showed that the attachment of five aromatic groups to one pentagon of a  $C_{60}$  fullerene molecule yields deeply conical molecules that stack into polar columnar assemblies. This packing pattern is maintained when we extended the aromatic groups by attaching flexible aliphatic chains, which yielded compounds with thermotropic and lyotropic liquid crystalline properties. Our design strategy should be applicable to other molecules and yield a range of new polar liquid crystalline materials.



*Nature*, **419**, 702-705 (2002)

## A. Original Papers

- 1) (M. Sawamura), N. Nagahama, M. Toganoh, E. Nakamura: "Regioselective Penta-addition of 1-Alkenyl Copper Reagent to [60]Fullerene Synthesis of Pentaalkenyl FCp Ligand", *J. Organomet. Chem.* (JOM Symposium Issue), **652**, 31-35 (2002).
- 2) M. Nakamura, N. Yoshikai, and E. Nakamura: "Carbozincation of Dipolar Trimethylenemethane. A New Route to Functionalized Organozinc Reagents", *Chem. Lett.*, (Mukaiyama Special Issue), 146-147 (2002).
- 3) H. Isobe, S. Satoh, and E. Nakamura: "Synthesis of Disubstituted Cucurbit[6]uril and Its Rotaxane Derivative", *Org. Lett.* **4**, 1287-1289 (2002).
- 4) E. Nakamura, N. Yoshikai, and (M. Yamanaka): "Mechanism of C-H Bond Activation/C-C Bond Formation Reaction between Diazo Compound and Alkane Catalyzed by Dirhodium Tetracarboxylate", *J. Am. Chem. Soc.*, **124**, 7181-7192 (2002).
- 5) (M. Sawamura), M. Toganoh, (H. Iikura), Y. Matsuo, (A. Hirai), and E. Nakamura: "Cu(I)-Mediated Regioselective Tri-addition of Grignard Reagent to [70]Fullerene. Synthesis of Indenyl-type Metal Ligand Embedded into Graphitic Structure", *J. Mater. Chem.* **12**, 2109-2115 (2002).
- 6) (M. Sawamura), Y. Kuninobu, M. Toganoh, Y. Matsuo, (M. Yamanaka) and E. Nakamura: "Hybrid of Ferrocene and Fullerene", *J. Am. Chem. Soc.*, **124**, 9354-9355 (2002).
- 7) (M. Yamanaka), (S. Mori) and E. Nakamura: "Density Functional Studies on Kinetic Reactivity of "Higher Order" Lipshutz Cuprate in Addition Reaction to Acetylene", *Bull. Chem. Soc. Jpn.* **75**, 1815-1818 (2002).
- 8) (M. Sawamura), (K. Kawai), Y. Matsuo, (K. Kanie), (T. Kato) and E. Nakamura: "Stacking of Conical Mesogens with a Fullerene Apex into Polar Columns in Crystals and Liquid Crystals", *Nature*, **419**, 702-705 (2002).
- 9) Y. Matsuo, (K. Mashima), and (K. Tani): "Intramolecular Coupling Reaction of 1-Aza-1,3-butadiene Ligand and Iminoacyl Ligand Giving Amido-Imido Complexes of Tantalum", *Organometallics* **21**, 138-143 (2002). \*
- 10) Y. Matsuo, (K. Mashima), and (K. Tani), "Half-metallocene 1-Aza-1,3-butadiene Complexes of Tantalum: Auxiliary Ligands on Tantalum Controlling Coordination Modes of the 1-Aza-1,3-butadiene Ligand", *Bull. Chem. Soc. Jpn.* **75**, 1291-1297 (2002). \*

## B. Reviews

- 1) E. Nakamura and (S. Yamago): "Thermal Reactions of Dipolar Trimethylenemethane Species", *Acc. Chem. Res.* **35**, 867-877 (2002).
- 2) (S. Yamago) and E. Nakamura: "[3 + 2] Cycloaddition of Trimethylenemethane and Its Synthetic Equivalents", *Org. React.* **61**, 1-215 (2002).

## D. Books

- 1) E. Nakamura: "Organometallic Chemistry, Method, 2nd edition", Manfred Schlosser Ed. Wiley, Chichester (2002).
- 2) E. Nakamura and (S. Mori): "Organocopper Chemistry", Nobert Krause Ed, Wiley-VCH, Weinheim (2002).
- 3) 中村栄一: "有機合成 創造の軌跡 (My Favorite Organic Synthesis)", 有機合成化学協会編, 化学同人 (2002).

- 4) (K. Mashima), Y. Matsuo, and (K. Tani): "Polymerization of Methyl Methacrylate Initiated by Half-Metallocene Complexes of Tantalum: Ligand Architecture Leading to Living Polymerization" in "Future Technology for Polyolefin and Olefin Polymerization Catalysis" M. Terano and T. Shiono Ed., Technology and Education Publishers, Tokyo, pp98-103 (2002).\*