

令和元年6月10日現在

機関番号：11301

研究種目：基盤研究(C) (一般)

研究期間：2016～2018

課題番号：16K05714

研究課題名(和文) シリル配位子部分を含むキレート錯体を触媒とした不活性結合変換反応の開発

研究課題名(英文) Development of Transformations of Inert Bonds Catalyzed by Chelate Complexes Involving Silyl Coordinating Moieties

研究代表者

小室 貴士 (Komuro, Takashi)

東北大学・理学研究科・助教

研究者番号：20396419

交付決定額(研究期間全体)：(直接経費) 3,700,000円

研究成果の概要(和文)：炭素-水素(C-H)結合などの不活性な結合を温和な条件下で変換する触媒の開発を目指し、ケイ素で金属に結合するシリル配位子部分を導入したキレート配位子を持つ金属錯体を設計・合成し、それらの触媒作用を調べた。主な成果として、後周期遷移金属(イリジウムおよびルテニウム)のシリルキレート錯体が、(1) ベンゼン-d<sub>6</sub>の炭素-重水素(C-D)結合活性化を経るトリアルキルシランのSi-H重水素化、(2) 芳香族化合物のC-Hボリル化、(3) 二酸化炭素のヒドロシリル化、および(4) ベンゼン-d<sub>6</sub>とのH/D交換によるトリアルキルホスフィンのC-H重水素化、の触媒となることを明らかにした。

研究成果の学術的意義や社会的意義

本研究では、新しいシリルキレート配位子を持つ金属錯体の合成手法を確立するとともに、それら錯体が不活性なC-H結合や二酸化炭素分子を温和な条件下(室温～60℃)で変換する高性能な触媒として働くことを実証したことで、学術的に独自性と新規性の高い成果が得られたといえる。特に有機化合物のC-H結合を直接変換する反応は、医薬品や化成品などの有用物質の製造手法に活用できると期待されているため、その反応を促進する触媒を開発する意義が大きい。

研究成果の概要(英文)：To develop catalysts for transformations of inert bonds such as carbon-hydrogen (C-H) bonds under mild conditions, we investigated synthesis and catalysis of newly-designed metal complexes bearing chelate ligands involving silyl coordinating moieties bound to metals via silicon. As representative results, silyl chelate complexes of late transition metals (iridium and ruthenium) were found to catalyze the following reactions: (1) Si-H deuteration of trialkylsilanes with benzene-d<sub>6</sub> via activation of its carbon-deuterium (C-D) bonds, (2) C-H borylation of aromatic compounds, (3) hydrosilylation of carbon dioxide, and (4) C-H deuteration of trialkylphosphine via H/D exchange with benzene-d<sub>6</sub>.

研究分野：有機金属化学，金属錯体化学

キーワード：金属錯体 シリル配位子 キレート配位子 配位子設計 触媒 C-H結合活性化 官能基化 小分子活性化



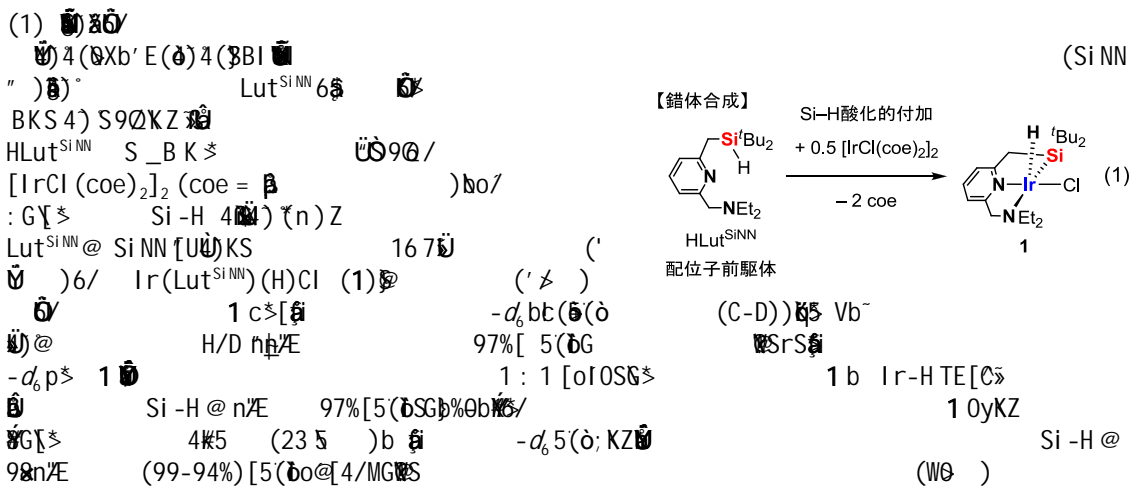


図2 イリジウム錯体1を触媒とした室温での芳香環C-D結合活性化を経るトリアルキルシランのSi-H重水素化

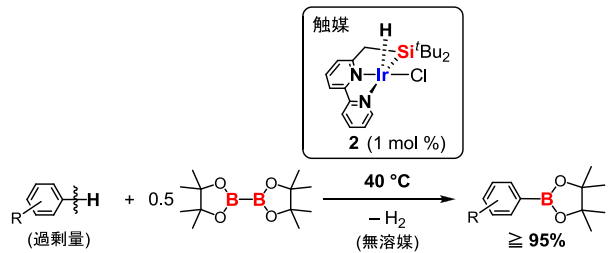
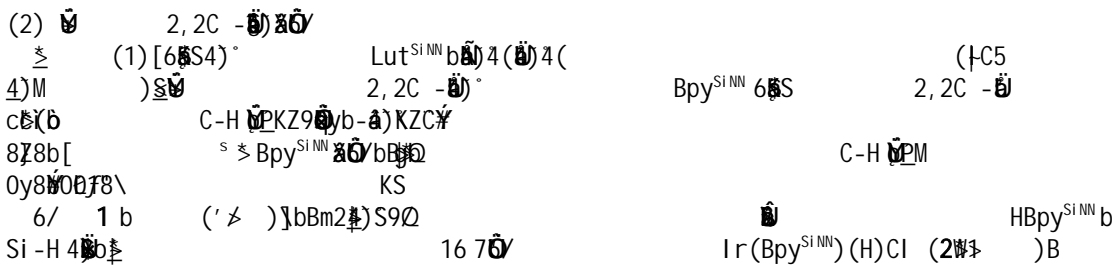
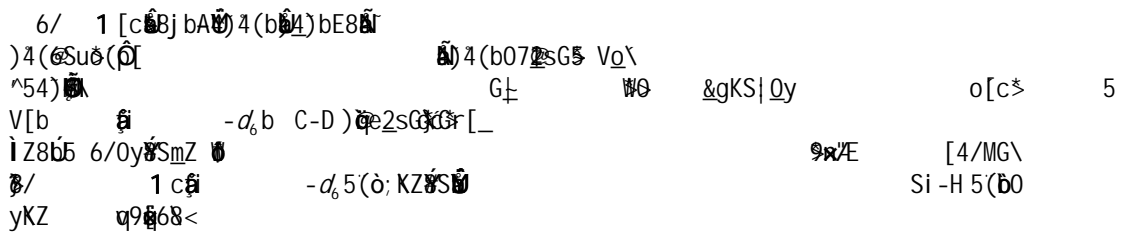
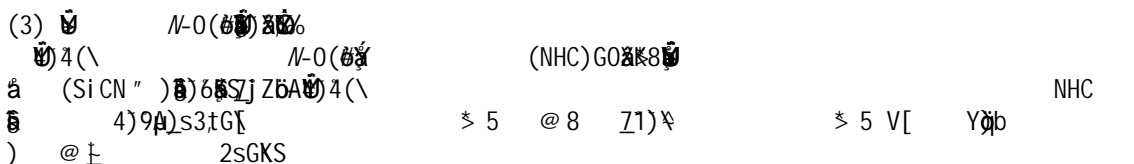


図3 シリル-2,2'-ビピリジンイリジウム錯体2を触媒とした芳香族化合物のC-Hボリル化





Fang, Y.-K. Choe, Y. Li, S. Shimada, *Chem. Asian J.*, **6**, 2512-2521 (2011); (c) C.-I Lee, J. Zhou, O. V. Ozerov, *J. Am. Chem. Soc.*, **135**, 3560-3566 (2013); (d) B. Ghaffari, S. M. Preshlock, D. L. Plattner, R. J. Staples, P. E. Maligres, S. W. Krska, R. E. Maleczka, Jr., M. R. Smith, III, *J. Am. Chem. Soc.*, **136**, 14345-14348 (2014); (e) Y. Sunada, H. Soejima, H. Nagashima, *Organometallics*, **33**, 5936-5939 (2014); (f) J. Takaya, S. Ito, H. Nomoto, N. Saito, N. Kirai, N. Iwasawa, *Chem. Commun.*, **51**, 17662-17665 (2015)  
 r H. Tobita, N. Yamahira, K. Ohta, T. Komuro, M. Okazaki, *Pure Appl. Chem.*, **80**, 1155-1160 (2008)  
 s (a) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaoura, N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc.*, **124**, 390-391 (2002); (b) I. A. I. Mkhaliid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.*, **110**, 890-931 (2010)  
 t M. Grellier, S. A. Mason, A. Albinati, S. C. Capelli, S. Rizzato, C. Bijani, Y. Coppel, S. Sabo-Etienne, *Inorg. Chem.*, **52**, 7329-7337 (2013)

3 >z\$1=e ' ...  
 7\$1=80E 5 6

q Takashi Komuro, Tomohiro Osawa, Ryuju Suzuki, Dai ki Mochi zuki, Hi ronori Higashi, Hi romi Tobita, Silyl-pyridine-amine pincer-ligated iridium complexes for catalytic silane deuteration via room temperature C-D bond activation of benzene-d<sub>6</sub>, *Chem. Commun.*, **1w**, **55**, 957-960 (2019)  
 DOI: 10.1039/c8cc09178a

r Takeo Kitano, Takashi Komuro, Hiromi Tobita, Double and Single Hydroboration of Nitriles Catalyzed by a Ruthenium-Bis(silyl)xanthene Complex: Application to One-Pot Synthesis of Diaryl amines and *N*-Aryl imines, *Organometallics*, **1w**, **38**, 1417-1420 (2019)  
 DOI: 10.1021/acs.organomet.9b00064

s 2, 80 \$ , 4) IS 6/  
 bB10y87 , wPU , **1w**, **76**, 1301-1309 (2018)  
 DOI: 10.5059/yuki gosei kyokai shi . 76. 1301

t Indra Kusuma, Takashi Komuro, Hiromi Tobita, Diruthenium Complexes with a 1,8-Naphthyridine-based Bis(silyl) Supporting Ligand: Synthesis and Structures of Complexes Containing Ru<sup>II</sup><sub>2</sub>(# -H)<sub>2</sub> and Ru<sub>2</sub> Cores, *Chem. Lett.*, **1w**, **47**, 400-403 (2018)  
 DOI: 10.1246/cl.171099

u Takeo Kitano, Takashi Komuro, Rikima Ono, Hiromi Tobita, Tandem Hydro-silylation/*o*-C-H Silylation of Arylalkynes Catalyzed by Ruthenium Bis(silyl) Aminophosphine Complexes, *Organometallics*, **1w**, **36**, 2710-2713 (2017)  
 DOI: 10.1021/acs.organomet.7b00528

v 2, 85 6/0y8S C-H)g(bn  
 6Mab6a , *Bull. Jpn. Soc. Coord. Chem.*, **1w**, **70**, 36-39 (2017)

w Takashi Komuro, Takeo Kitano, Nobukazu Yamahira, Keisuke Ohta, Satoshi Okawara, Nathalie Mager, Masaaki Okazaki, Hiromi Tobita, Directed *ortho*-C-H Silylation Coupled with *trans*-Selective Hydrogenation of Arylalkynes Catalyzed by Ruthenium Complexes of a Xanthene-Based *Si, O, Si*-&KHODWH/LJDF; D/WLOG , *Organometallics*, **1w**, **35**, 1209-1217 (2016)  
 DOI: 10.1021/acs.organomet.5b01013

80E 0x 6  
 q P z , 2, 80 \$ , V -NHC 80/b  
 BS49oö , 99 0 (2019) (2019)

r Takashi Komuro, Takeo Kitano, Hi ronori Higashi, Junpei Asagami, Hi romi Tobita, Metal Complexes with a Bis(silyl)xanthene Supporting Ligand: Catalysis for Hydroboration of Nitriles and C-H Deuteration of Trialkylphosphine, International Congress on Pure & Applied Chemistry Langkawi (ICPAC Langkawi) 2018 (2018)

s Takashi Komuro, Dai ki Mochi zuki, Tomohiro Osawa, Hi romi Tobita, Silyl-Pyridine-Amine/Pyridine Pincer Ligated Iridium Complexes as Catalysts for C-H/C-D Bond Activation, 43rd International Conference on Coordination Chemistry (ICCC2018) (2018)

t 3/4 0 , ;P β , 2, 80 \$ , 2 (V ) 8U  
 6/0yNA (4E# C-H5(0 , 6/Ü 68G0f=  
 (2018)

u v 3d , 2, 80 \$ , V (2,2'-Ü ) 8U  
 6/bB9oö , 98 0 (2018) (2018)

v 90 96 , 2 80 \$ , V (N-8) 8U  
 6/bBS492A , 98 0 (2018) (2018)

Takashi Komuro, Dai-ichi Mochizuki, Hiromi Tobita, Transition-Metal Complexes with  
SLOOC -Bipyridine) Pincer Ligands: Synthesis and Catalysis for Functionalization  
of C-H/C=D Bonds, International Congress on Pure & Applied Chemistry (ICPAC) 2018 (2018)  
x 5 pe, ' 2, 8 \$, 16 7 ( ) %yKS%

y ' 2, ; 3, 8 \$, Iridium complexes having a bis(silyl) chelate  
ligand: synthesis and catalysis for C-H deuteration, 29 (2017)

z v 3d, ' 2, 8 \$, Arene C-H borylation catalyzed by iridium complexes  
bearing a silyl-bipyridine pincer ligand, 29 (2017)

{ 90 96, ' 2, 8 \$, Synthesis of precursors of silyl-carbene chelate  
ligand and their reactions with ruthenium complexes, 29 (2017)

| Takashi Komuro, Takeo Kitano, Hiromi Tobita, *ortho*-C-H Silylation/Hydrosilylation of  
Diarylalkynes Catalyzed by Ruthenium Complexes Bearing a Bis(silyl) Chelate Ligand, 18th  
International Symposium on Silicon Chemistry (ISOS-18) (2017)

} v 3d, ' 2, 8 \$, Si NN 9  
5 6/bB 30y\$ C-H (b) 97 (2017)

~ ; 3, ' 2, 8 \$, 8P& ( ) (2017)

5 pe, 5 1, ' 2, 8 \$, 16 7 ( ) (2017)

' 2, 8 \$, 20 G (2016)

v 3d, ' 2, 8 \$, 20 G (2016)

Indra Kusuma, ' 2, 8 \$, Synthesis and Structures of Dinuclear  
Late-Transition-Metal Complexes Supported by a Naphthyridine-Based Bis(silyl) Chelate  
Ligand, 6/ (2016)

5 pe, ' 2, 8 \$, Unusual Double-Silylation of Arylalkynes Catalyzed  
by Ruthenium Bis(silyl) Complexes: Development and Mechanistic Studies, 28 (2016)

Takashi Komuro, Takeo Kitano, Hiromi Tobita, Ruthenium Catalysts Supported by a  
Xanthene-Based Bis(silyl) Chelate Ligand for C-H Silylation of Diarylalkynes,  
International Symposium on Pure & Applied Chemistry (ISPAC) (2016)

& ' 2, 8 \$, 33 G (2016)

4>% ' 2 ) )

(1)% ' 2 (\* K

d&E2 ↓ % ' 2 c % ' 2\* b 0 \ 2i 8Z Mvb[MSu % ' 2 b x % ' 2BY b 1f... \_  
X8Zc \ b 0[13' ... ö YCvb[c00 % ' 2BY \_ 6iM 0b0 x 2i c % ' 2f \_ IrM