サイエンス〈特別〉セミナー

New Ruthenium(II) Thiolate Complexes: Cooperative Activation of E–H Bonds (E = H, Si, B) and Catalytic Applications

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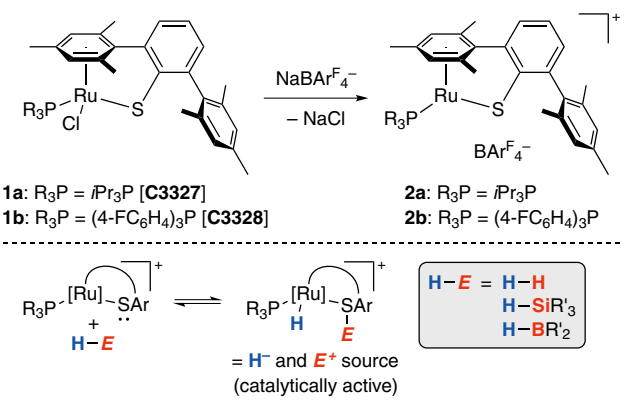
Introduction

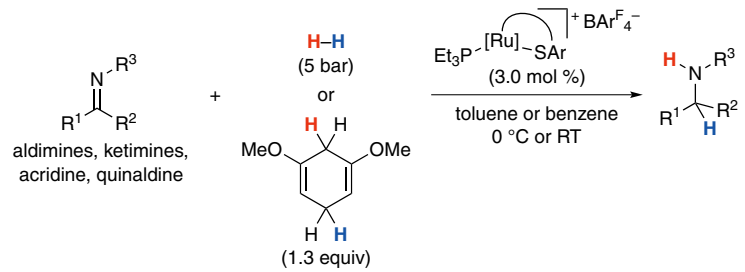
Ruthenium(II) thiolate complexes of type [(DmpS)RuCl(PR$_3$)] (**1a**: R = *i*-Pr; **1b**: R = *p*-FC$_6$H$_4$), introduced by Ohki, Tatsumi, and Oestreich, serve as air-stable precursors for cationic ruthenium(II) thiolate complexes **2** (Scheme 1, top). These (formally) 16-valence-electron complexes are highly active bifunctional catalysts for the cooperative activation of H–H,[1,2] Si–H[3–12] as well as B–H[13] bonds. For catalytic applications, the air-sensitive catalysts **2** can either be preformed or generated in situ by treatment of the corresponding ruthenium(II) chloride complex **1** with NaBAr$^F_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl). The tethered coordination mode of the bulky 2,6-dimesitylphenyl thiolate (DmpS) ligand is crucial, stabilizing the coordinatively unsaturated ruthenium atom in **2** and also preventing formation of binuclear sulfur-bridged complexes. The polar Ru–S bond of these complexes combines Lewis acidity at the metal center and Lewis basicity at the adjacent sulfur atom. This structural motif allows for reversible heterolytic splitting of E–H bonds (E = H, Si, and B) across the polar Ru–S bond, generating a metal hydride and a sulfur-stabilized E$^+$ cation (Scheme 1, bottom).[3] After transfer of the electrophile to a Lewis-basic substrate, the resulting neutral ruthenium(II) hydride can either act as a hydride donor (reductant) or as a proton acceptor (Brønsted base), thereby releasing dihydrogen. On the basis of this approach, complexes **2** emerged as broadly applicable catalysts for chemoselective reductions (hydrogenation and transfer hydrogenation,[1,2] as well as hydrosilylation[10,11]), dehydrogenative couplings (Si–C(sp^2),[4–6] Si–O,[7] Si–N,[8,9] and B–C(sp^2)[13]), as well as hydrodefluorination reactions.[12]



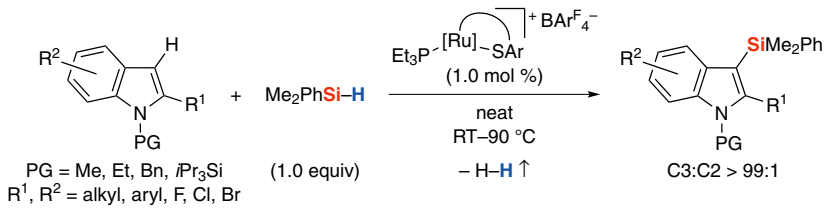
Scheme 1. Preparation of catalytically active ruthenium(II) thiolate complexes for cooperative E–H bond activation (E = H, Si, and B).

Scope

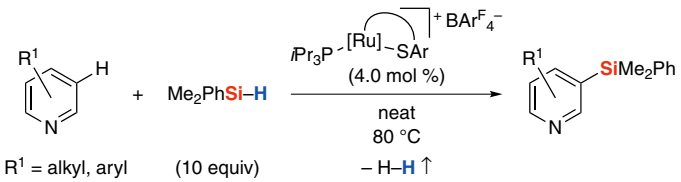
1 - Hydrogenation and transfer hydrogenation of imines:[2]



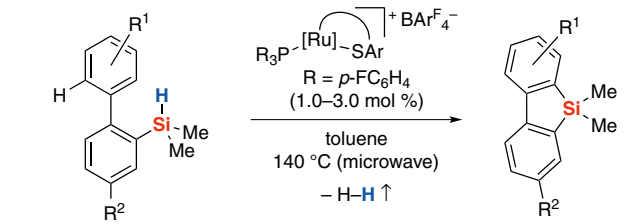
2 - Regioselective electrophilic C–H silylation of indoles:[4]



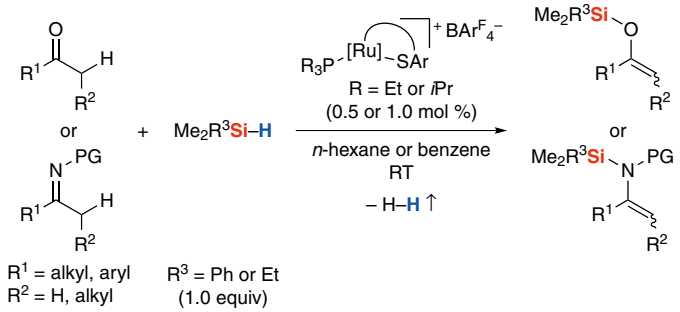
3 – Regioselective electrophilic C–H silylation of pyridines:[5]



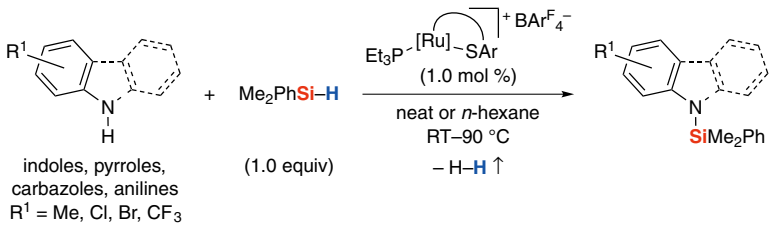
4 - Preparation of dibenzosiloles by intramolecular electrophilic C–H silylation:[6]



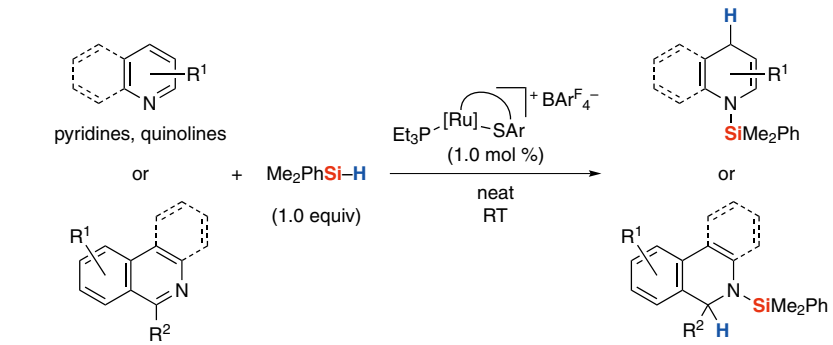
5 - Direct formation of silyl enol ethers[7] *and N-silylated enamines*[8] *by dehydrogenative coupling of enolizable ketones and ketimines with hydrosilanes:*



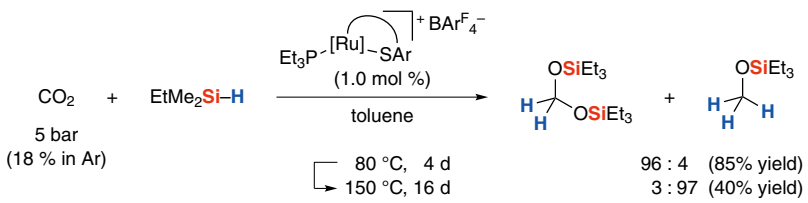
6 - Dehydrogenative silylation of the N–H bond of indoles, pyrroles, carbazoles, and anilines:[9]



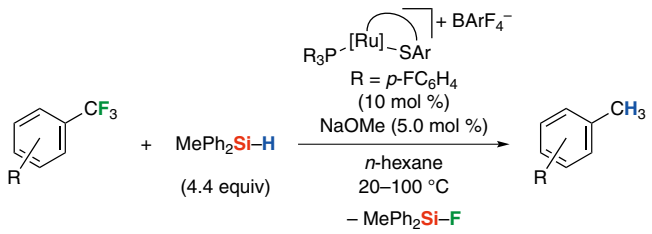
7 - Regioselective hydrosilylation of pyridines and benzannulated congeners:[10]



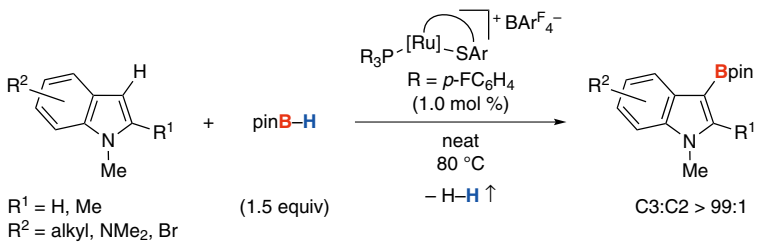
8 - Chemoselective hydrosilylation of carbon dioxide:[11]



9 - Hydrodefluorination of CF_3-substitued anilines:[12]



10 - Regioselective electrophilic C–H borylation of nitrogen-containing heterocycles:[13]



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Martin Oestreich (born in 1971 in Pforzheim/Germany) received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe (Münster, 1999). After a two-year postdoctoral stint with Larry E. Overman (Irvine, 1999–2001), he completed his habilitation with Reinhard Brückner (Freiburg, 2001–2005) and was appointed as Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster (2006–2011). He also held visiting positions at Cardiff University (Wales) and at The Australian National University in Canberra. He has been Professor of Organic Chemistry at the Technische Universität Berlin since 2011.
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