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Oxidative Addition of a Strained C–C Bond onto Electron-Rich Rhodium(I) at Room Temperature

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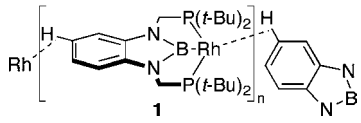
Supporting Information

ABSTRACT: The C–C bond of cyclobutanones undergoes oxidative addition to a T-shape rhodium(I) complex possessing a PBP pincer ligand at room temperature. The remarkable propensity of the rhodium complex for oxidative addition is attributed to the highly electron-donating nature of the boron ligand as well as the unsaturation on the rhodium center.

Selective activation of nonpolar σ-bonds between two elements of similar electronegativities, like C–H[1] and C–C[2] bonds, has gained increasing attention in organic chemistry. Whereas a wide variety of transition metal-mediated or -catalyzed reactions cleaving C–H bonds have been developed in the past decade, examples of C–C bond cleavage with transition metal complexes are much fewer, probably due to the kinetic inertness of C–C bonds. Considerably harsh reaction conditions are generally required for their cleavage. Herein, we report a striking example of oxidative addition of a C–C bond to rhodium(I) that occurs even at room temperature.

We recently reported the synthesis of an infinitely networked T-shape 14-electron rhodium(I) complex **1** possessing a PBP pincer ligand (Figure 1).[3] It showed a remarkable reactivity at

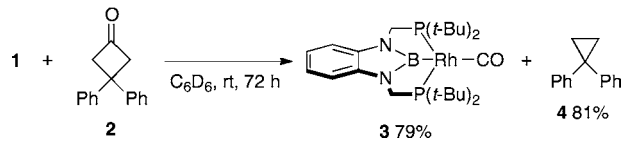


1

Figure 1. Structure of rhodium complex **1**.

the rhodium center to insert into O–H bonds of phenols and primary alcohols through a rapid dissociation of its polymeric form into the corresponding monomeric form of T-shape complex. This reactivity suggested that the strongly electron-donating boryl ligand[4] enhanced the electron density on the rhodium center to facilitate its insertion into the polar O–H bonds. We next examined the reactivity toward nonpolar strained C–C bonds. Thus, [PBP]Rh(H)(OTf) complex was initially treated with Me_3SiCH_2Li in C_6D_6 under an argon atmosphere. The resulting [PBP]Rh(I) complex **1** was treated with cyclobutanone **2**, and the mixture was stirred at room

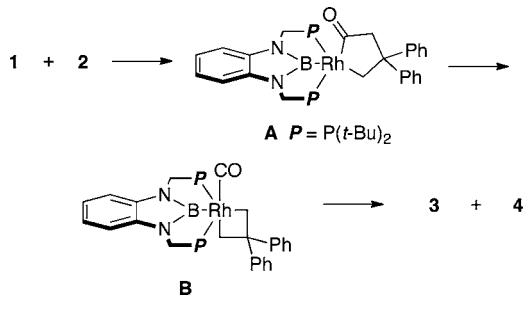
Scheme 1. Reaction of Cyclobutanone 2 with 1



temperature for 72 h (Scheme 1). Rhodium carbonyl complex **3** (79% NMR yield) was generated along with cyclopropane **4** (81% NMR yield). No intermediary complexes—except for the starting rhodium complex **1** and the resulting carbonyl complex **3**—were observed by ^{31}P NMR analysis during the course of the decarbonylation reaction.

The formation of **3** and **4** from **1** and **2** is explained by assuming a stepwise mechanism depicted in Scheme 2. The

Scheme 2. Plausible Mechanism for the Formation of 3 and 4 from 1 and 2



carbonyl group of **2** initially coordinates to the electron-rich and coordinatively unsaturated rhodium center of **1**. The σ-bond between the carbonyl carbon and its α-carbon undergoes oxidative addition onto the rhodium(I) center to generate the five-membered ring acylrhodium(III) species **A**. The CH_2 group of **A** migrates onto rhodium with a carbonyl ligand left out to form four-membered ring rhodacyclobutane **B**. Reductive elimination gives rise to rhodium carbonyl complex **3** and cyclopropane **4**. The oxidative addition is suggested to be

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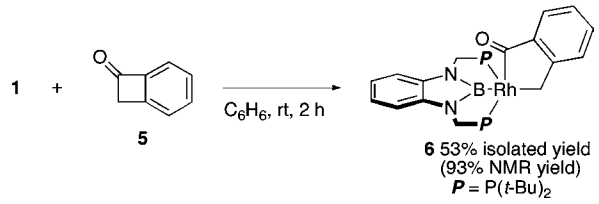
the rate-determining step, and the ensuing steps would follow spontaneously. The hexa-coordinated complex **B** would be thermodynamically unstable due to the repulsive force which the four *t*-Bu groups extend to the other ligands. In contrast, the tetra-coordinated complex **3** is less congested and gain stabilization due to π-back-donation from Rh to CO ligand, and therefore, would be thermodynamically far more stable. This would provide a major driving force for reductive elimination of cyclopropane.

An analogous decarbonylation reaction of cyclobutanones is mediated by various rhodium(I) complexes bearing PPh_3 or NHC ligands.[5,6] It generally requires refluxing in toluene or in xylene, even when a stoichiometric amount of a rhodium(I) complex is used. The [PBP]Rh complex **1** is apparently more active. We assume that the strongly σ-donating nature of the boryl ligand[7] as well as the unsaturation on the metal center[8] facilitates the intrinsically sluggish oxidative addition of the C−C σ-bond.

We next examined the reaction of **1** with benzocyclobutenone **5**. Again, oxidative addition occurred at room temperature and single crystals of the resulting complex were successfully obtained using a benzene/hexane solution for recrystallization. An X-ray crystallographic analysis revealed that the bond between the carbonyl carbon and the sp^3 α-carbon was site-selectively cleaved to afford five-membered acylrhodium(III) complex **6** (Scheme 3, Figure 2). Although an analogous

Scheme 3. Stoichiometric Reaction of Rhodium Complex 1 with Benzocyclobutenone 5



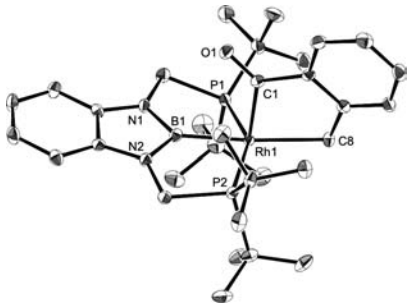


Figure 2. ORTEP drawing of **6** (50% thermal ellipsoid, hydrogen atoms and one of two independent molecules are omitted for clarity) Selected bond lengths (Å) and angles (°) as averages: B−Rh 2.044, Rh−C(acyl) 1.955, C(acyl)=O 1.212, Rh−C(benzyl) 2.213, Rh−P 2.3588, B−N 1.430, B−Rh−C(benzyl) 174.89, P−Rh−P 151.10, N−B−N 105.4.

reaction of benzocyclobutenone with $ClRh(PPh_3)_3$ has been reported by Liebeskind et al.,[9] the reaction requires heating at 130 °C, and oxidative addition occurs with both the C(CO)−$C(sp^3)$ and C(CO)−$C(sp^2)$ bonds to afford a mixture of isomeric products. Thus, the PBP pincer ligand not only accelerates the C−C oxidative addition but also confers the site-selectivity probably due to the bulky $P(t\text{-Bu})_2$ groups. Whereas the assumed intermediate **A** underwent elimination of CO and reductive elimination in the reaction of **2**, the complex **6** failed to go through those steps. We presume that this difference arose because the possible reductive elimination product resulting from the complex **6** is energetically too high.

Two independent molecules of complex **6** with almost identical structure were contained in the asymmetric unit. The acyl ligand is located on the apical position of a distorted square pyramidal structure. A vacant coordination site located trans to the acyl ligand is effectively blocked by the two bulky *t*-Bu groups in the pseudoaxial positions. The Rh−B [av. 2.044 Å] and Rh−P [av. 2.3588 Å] bonds of **6** are slightly longer than those of **1** [Rh−B, 1.948(3) Å; Rh−P, av. 2.2958 Å],[3a] probably due to the steric repulsion between the rhodabenzocyclopentenone moiety and PBP ligand. Whereas the C=O (av. 1.212 Å) and Rh−C(benzoyl) (av. 1.995 Å) lengths are within their typical values,[9,10] the Rh−(η^1-benzyl) bond (av. 2.213 Å) located trans to boron is considerably longer than typical Rh−(η^1-benzyl) bonds,[9,11] clearly indicating a strong trans influence of the boryl ligand.

The ^{1}H NMR spectrum in C_6D_6 showed two signals of the *t*-Bu groups. This magnetic inequivalency is consistent with its C_s-symmetrical structure in the solid state. The ^{13}C NMR spectrum exhibits a resonance assigned to the carbonyl carbon at δ_C 211.6 with two distinct couplings of $^1J_{RhC}$ (d, 33 Hz) and $^2J_{PC}$ (t, 5 Hz). The signal of the methylene carbon derived from benzocyclobutenone was observed at δ_C 23.5 with couplings of $^1J_{RhC}$ (d, 26 Hz) and $^2J_{PC}$ (t, 6 Hz). In the ^{31}P NMR spectrum, a doublet signal (δ_P 93.7) with $^1J_{RhP}$ of 139 Hz was observed. The coupling constant is smaller than that of **1** ($^1J_{RhP}$ = 192 Hz), which reflects weaker π-back-donation from the Rh(III) center than that from Rh(I). The ^{11}B nucleus resonated at around 53 ppm. This value is similar to those of [PBP]Rh(CO) and [PBP]Rh(CH_2=CH_2) rather than those of [PBP]Rh(H)(Cl) and [PBP]Rh(H)(OTf), which possess interaction between boron and hydride atoms.[3a] The strong signal observed at 1639 cm^{-1} in the IR spectrum was similar to those of the related acylrhodium complexes, in accordance with ν_{CO} values predicted by DFT calculation.[12]

The reactivity of various alcohols toward the rhodium complex **1** was examined in our previous study.[3a] Whereas primary alcohols underwent oxidative addition, secondary alcohols such as cyclohexanol and 2-propanol failed to react with **1**. Much to our surprise, 3,3-diphenylcyclobutanol **7**, slightly smaller than cyclohexanol because of the strained four-membered ring, facilely reacted with **1** in C_6D_6 at room temperature to generate the new rhodium hydride complex **9** together with unidentified byproducts (Scheme 4). This is the first example of oxidative addition of the O−H linkage of secondary alcohols to **1**. Furthermore, the ring-opened alkane **11** (10%) was generated together with rhodium carbonyl complex **3** (16%) upon heating at 80 °C.[13] It is assumed that the rhodium(III) hydride complex **9** undergoes β-hydride elimination to form rhodium(I) dihydrogen complex **C**.[14] Subsequent oxidative addition affords (dihydrogen)-rhodacyclopentanone intermediate **D**. The carbon−rhodium bond of **D** is hydrogenolyzed to produce **E**. Migratory elimination of a carbonyl group forms **F** and subsequent reductive elimination gives **3** and **11**. The reaction with *N*-toluenesulfonyl azetidinol proceeded more cleanly to afford carbonyl complex **3** (75%) and dimethylamide **12** (65%).

In summary, we disclose that a thermally stable C−C bond of cyclobutanones was cleaved, even at room temperature, by oxidative addition onto T-shape [PBP]Rh complex **1**. Crystallo-

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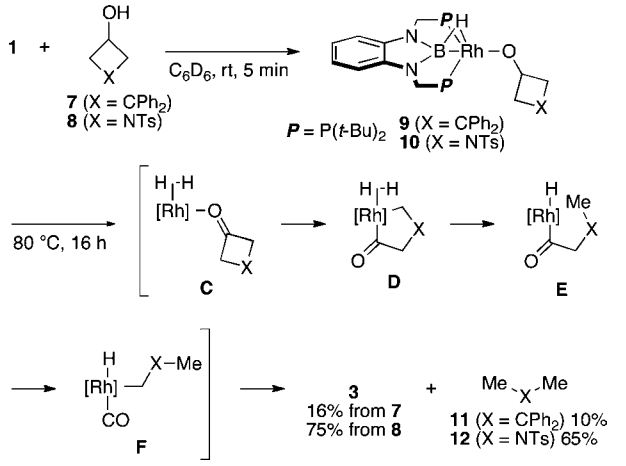
Scheme 4. Reaction of 1 with *sec*-Alcohols 7 and 8



graphic analysis of the C−C cleaved product revealed its distorted square pyramidal structure with the acyl ligand on the apical position in the solid state. This work demonstrates that T-shape [PBP]Rh complex **1** possesses a high propensity for oxidative addition of nonpolar C−C σ-bonds as well as polar O−H bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, physical and spectroscopic data, crystallographic data, and theoretical study for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(4) Ref 3b showed that the boryl ligand in PBP pincer could be considered as σ-donor according to the long Ir−Cl bond length in [PBP]Ir(H)(CO)(Cl), where Cl located at trans to boryl ligand, while CO stretch of [PBP]Rh-CO (**3**) in ref 3a was 1933 cm^{-1}, similar to that of benzene-based PCP system (1925 cm^{-1}, see: Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton* **1976**, 1020−1024.). However, it was difficult to estimate the difference in donor ability of X ligand in PXP system (X = B, C) from CO stretch, because the Rh−C bond lengths in these system were different [**3**, 1.908(3) Å; PCP, 1.848(16) Å]. It may lead to difference in orbital overlapping between d-orbital of Rh and π*-orbital of CO ligand. That is, it may cancel the lower wavenumber shift come from electron richness at Rh center by strong σ-donor ability of boryl ligand.

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(7) The IR absorption for CO stretching of **3** appeared at lower wavenumber (1933 cm^{-1}) compared to that of $ClRh(PPh_3)_2CO$ (1960 cm^{-1}), and [7a] even the Rh−CO bond length of **3** [1.908(3) Å][3a] was longer than that of $ClRh(PPh_3)_2CO$ [1.821(5) Å].[7b] This suggests that the rhodium center in **3** is considerably more electron-rich, perhaps due to the strongly electron-donating nature of the boryl ligand. The strong donation accelerates the formation of the low-coordinate species, which would be a key elementary step for the C−C cleavage. (a) Serp, P.; Hernandez, M.; Richard, B.; Kalck, P. *Eur. J.*

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(8) DFT calculation was carried out on the monomeric **1** and $(Ph_3P)_2RhCl$, tri-coordinated species possibly generated from $(Ph_3P)_3RhCl$, in order to compare the sterics of their vacant coordination sites. The two phosphine arms of **1** are pulled back toward boron to leave the vacant site more widely open for an incoming substrate, whereas the two phenyl rings of $(Ph_3P)_2RhCl$ hang over the vacant site. See Supporting Information for their calculated structures.

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(11) CCDC database showed known Rh-(η^1-benzyl) bonds are in the range of 2.045−2.172 Å as of Apr 6, 2013. The upper end of previously reported Rh−(η^1-benzyl) bond [2.172(3) Å] is found in the following reference: Mitchell, G. P.; Tilley, T. D. *Organometallics* **1998**, *17*, 2912−2916.

(12) Geometrical optimization of **6** (B3LYP//LanL2DZ/cc-pVDZ) from crystal structure could reproduce the experimentally obtained structure with no imaginary frequency. The vibrational analysis showed the CO stretch at 1672 cm^{-1}.

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(14) When the reaction was conducted in the presence of 3,3-dimethylbut-1-ene (2 equiv), cyclopropane **4** (46%) was obtained together with rhodium carbonyl complex **3** (51%) and ring-opened product **11** (38%). This result indicates that β-hydride elimination takes place to generate the dihydrogen complex **C**, which partially reacts with the alkene.