Communication

Catalytic cleavage of C(sp2)-C(sp2) bonds with Rh-carbynoids

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Catalytic cleavage of C(sp^2)–C(sp^2) bonds with Rh-carbynoids

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Supporting Information Placeholder

ABSTRACT: We report a catalytic strategy that generates rhodium-carbynoids by selective diazo activation of designed carbyne sources. We found that rhodium-carbynoid species provoke C(sp^2)–C(sp^2) bond scission in alkenes by inserting a monovalent carbon unit between both sp^2-hybridized carbons. This skeletal remodeling process access synthetically useful allyl cation intermediates that conduct to valuable allylic building blocks upon nucleophile attack. Our results rely on the formation of cyclopropyl-I(III) intermediates able to undergo electrocyclic ring-opening, following the Woodward-Hoffmann-DePuy rules.

For more than half a century, the discovery of new metal-carbon bond-forming strategies has been cornerstone in the development of transition-metal catalysis.[1] The catalytic generation of organometallic species with metal-carbon single/double bonds, such as metal−L (L = alkyl, alkenyl, alkynyl, aryl) or metal-carbene (metal=L) is widely used in reaction discovery and development. However, while metal-carbynes – the organometallic species with a metal-carbon triple bond (metal≡L) –,[2] have been key catalysts in alkyne metathesis,[3] their catalytic generation and general application in catalytic carbyne transfer has been largely unexplored, mainly due to the lack of suitable monovalent carbon sources (Figure 1A).[4] *Surprisingly, methodologies circumventing this problem by generating metal-carbynoids as equivalent reactive species of metal-carbynes, have not been reported.*

Recently, our group demonstrated the first catalytic generation of diazomethyl radicals [N_2=C(•)–R] as carbyne equivalents by means of photoredox catalysis.[5,6] This work highlighted the under-appreciated ability of neutral carbynes to form three new bonds[7] and provided the fundaments of an "assembly-point" coupling for chiral center construction, through a C–H bond diazomethylation reaction in aromatic feedstocks and drug molecules. Key on this work was the use of stable carbyne sources decorated with a hypervalent iodine moiety [I(III)(Ar)(OTf)] and a diazo functionality (=N_2).[8] We recently questioned whether well-known dirhodium catalysts in diazo activation,[9] might generate Rh-carbynoids as I(III)–substituted Rh-carbenes (Figure 1B). Considering the outstanding leaving group ability of the I(III) moiety[10] and weakness of the hypervalent bond, we anticipated that the electrophilic carbon center of the Rh-carbynoid would emulate the carbene/carbocation behavior of a monovalent cationic carbyne (:+C–R), and enable a novel route to allylic cations from alkenes, by the insertion of the monovalent carbon unit in the C(sp^2)–C(sp^2) bond (Figure 1B).

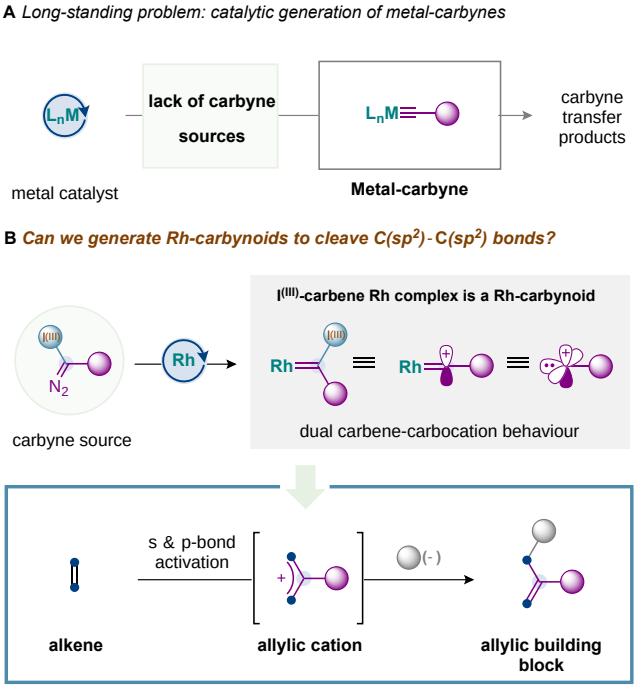


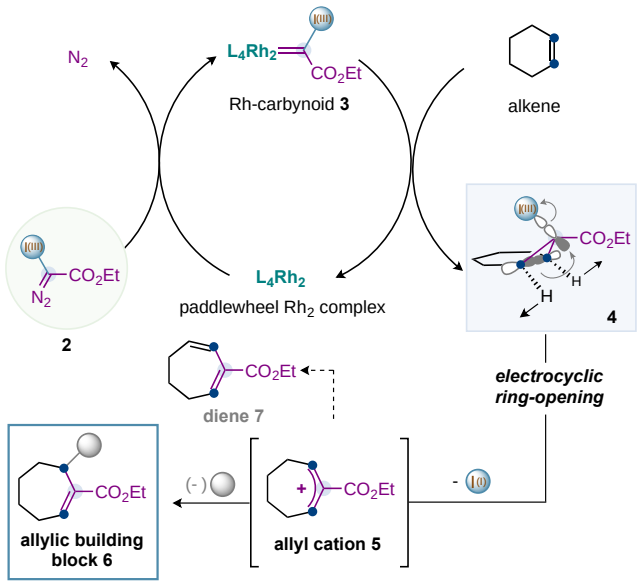
Figure 1. Catalytic cleavage of C(sp^2)–C(sp^2) with Rh-carbynoids

Such process, that involves a σ- & π-bond activation of the alkene double bond and uses both sp^2-hybridized carbons as functional groups, would be a rare example of a catalytic cleavage of strong double C–C bonds (BDE, H_2C=CH_2 = 174.1 kcal/mol), besides processes of metathesis[11,12] or rearrangements.[13] It would also

represent a new way for catalytic skeletal remodeling, complementing "cut and sew" and deconstructive transformations based on single C–C bond functionalization.[14] Notably, accessing allyl intermediates by C(sp^2)–C(sp^2) bond cleavage would represent a complementary, but clearly different strategy, to the well-established transition-metal-catalyzed allylations[15] or allylic C–H bond functionalizations.[16] Herein, we disclose the successful development of a Rh-catalyzed carbyne transfer platform for the catalytic cleavage of C(sp^2)–C(sp^2) bonds that provides a novel route to allylic building blocks.

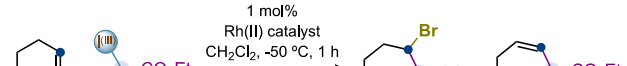
We envisioned that the selective diazo activation of reagent **2** with a paddlewheel dirhodium complex L_4Rh_2 would conduct to a highly electrophilic Rh-carbynoid **3** (Scheme 1). The latter species would cyclopropanate an alkene and generate a transient cyclopropyl–$I_{(III)}$ intermediate **4**. In analogy to the well-known ring-opening of cyclopropyl tosylates or cyclopropyl bromides with silver salts,[17] **4** would open in concert with the departure of the $I_{(III)}$ leaving group through a disrotatory mode, following the Woodward-Hoffmann-DePuy rules.[18] This process would lead to a putative allylic cation **5** able to provide the desired allylic product **6** by nucleophile attack, or diene **7** by proton elimination.

Scheme 1. Mechanistic hypothesis

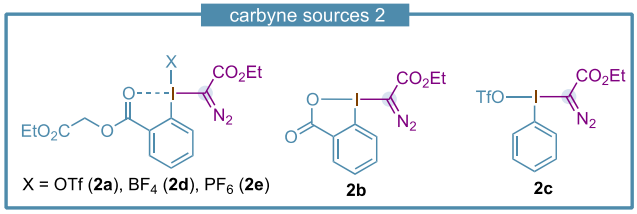


Initial successful results were found when a solution of **2a** in dichloromethane was added to cyclohexene (5 equivalents) and $Rh_2(Oct)_4$ (1 mol%) at –50 ºC during 1 hour. Then, Bu_4NBr (3 equiv.) was added at –50 ºC and the resulting mixture stirred for 60 min. With this protocol allyl bromide **7a** was obtained in a promising 18% yield (Table 1, entry 1). The use of the more sterically demanding catalysts $Rh_2(Adc)_2$ or $Rh_2(esp)_2$ (Du Bois catalyst)[19] provided significantly superior levels of efficiency of **7a** (30-48 % yield, respectively) and the formation of diene **7a** in less than 10% yield (entry 2,3). After identifying $Rh_2(esp)_2$ as the most promising catalyst, we questioned whether the nature of reagent **2** could have a substantial impact in the efficiency of the process. Firstly, we realized that the pseudocyclic structure of reagent **2a** was crucial for enabling the synthesis of allylic bromide **7a**. No conversion to **7a** was observed for cyclic reagent **2b** (entry 4) and very poor yields were obtained for the linear analogue **2b** (entry 5). Finally, we were pleased to find that pseudocyclic reagents **2d,e** with BF_4 and PF_6 counterions, dramatically improved the efficiency of the C(sp^2)–C(sp^2) cleaving process (entry 6,7). We also appreciated that excess of alkene **1a** was needed to reach good efficiency. A experiment carried out with equimolecular ratio of **1a** and **2e**, showed a poorer yield for **6a**/**7a** (entry 8, 45/7% yield) and 30% of cyclohexene was detected. This might suggests that such excess ensures full conversion in the ligand transfer event between the corresponding Rh-carbynoid **3** and cyclohexene (the cyclopropanation), preventing the evolution of **3** through undesired pathways.[20] The use of Bu_4PBr or TMSBr as bromide source did not provide better results (entry 9,10).[21]

Table 1. Optimization studies



entry	Rh catalyst[b]	reagent **2**	nucleophile	yield **6a** (**7a**) [%][c]
1	$Rh_2(oct)_4$	**2a**	Bu_4NBr	17
2	$Rh_2(Adc)_4$	**2a**	Bu_4NBr	30 (8)
3	$Rh_2(esp)_2$	**2a**	Bu_4NBr	48 (10)
4	$Rh_2(esp)_2$	**2b**	Bu_4NBr	0 (0)
5	$Rh_2(esp)_2$	**2c**	Bu_4NBr	12 (11)
6	$Rh_2(esp)_2$	**2d**	Bu_4NBr	62 (11)
7	$Rh_2(esp)_2$	**2e**	Bu_4NBr	76 (13)
8	$Rh_2(esp)_2$	**2e**	Bu_4NBr	45 (7)[d]
9	$Rh_2(esp)_2$	**2e**	Bu_4PBr	74 (13)
10	$Rh_2(esp)_2$	**2e**	Me_3SiBr	19 (5)

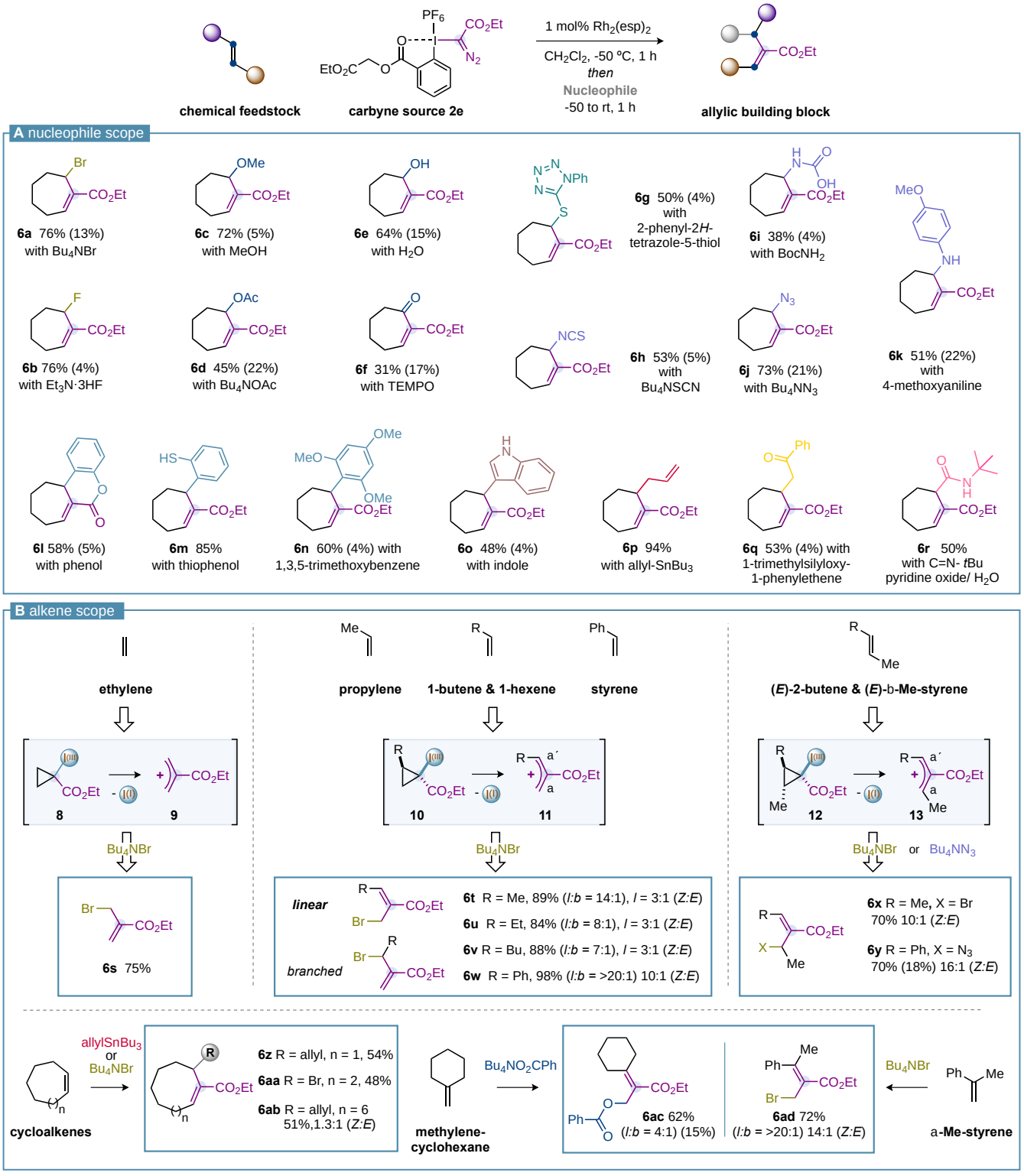


[a] Perfomed with cyclohexene (0.5 mmol, 5 equiv.), reagent **2a** (0.1 mmol, 1 equiv.), CH_2Cl_2 (0.1 M) and nucleophile (3 equiv). [b] oct = octanoate. Adc = 1-adamantylcarboxylate. esp = α,α,α',α'-tetramethyl-1,3-benzenedipropanoate. [c] Yields are reported on the basis of ^1H NMR analysis using anisole as internal standard. [d] Reaction carried out with 1 equiv. of **1a**. 30% of **1a** was detected.

Having the optimized conditions in hand, we evaluated the nucleophile scope by using cyclohexene and reagent **2e** (Table 2A). We were delighted to see that our methodology worked well for a broad and diverse range of simple nucleophiles that created: (i) carbon-halogen bonds with Bu_4NBr (**6a**), and $Et_3N{\cdot}3HF$ (**6b**); (ii) carbon-oxygen bonds with methanol (**6c**), tetrabutylammonium acetate (**6d**), water (**6e**), and TEMPO (**6f**); (iii) carbon-sulfur bonds with thiols (**6g**);

and (iv) carbon-nitrogen bonds with Bu_4NSCN (**6h**), *tert*-butyl carbamate (**6i**), Bu_4NN_3 (**6j**), and 4-methoxyaniline (**6k**). Moreover, our strategy permitted the use of a diverse range of carbon nucleophiles, enabling C–H arylation processes with electron-rich arenes (**6l–n**) or heterocycles (**6o**), allylation with allyl-$SnBu_3$ (**6p**), alkylation with the trimethylsilyl enol ether derived from acetophenone (**6q**), or amidation with the combination of *tert*-butylisocyanide, pyridine oxide and water (**6r**). It is noteworthy the high degree of complexity introduced into both C(sp_2)–C(sp_2) carbons in the constructive cleaving process: one new single C–C bond and one new double C–C bond are created, in addition to the formation of a chiral center at one of the sp_2-hybridized carbons of cyclohexene using some of the most simple and abundant nucleophiles.

Table 2. Scope of the catalytic cleavage of C(sp_2)–C(sp_2) bonds for allylic building block synthesis[a]



[a] Perfomed with alkene (1.0 mmol, 5 equiv.), reagent **2e** (0.2 mmol, 1 equiv.), CH_2Cl_2 (0.1 M) and nucleophile (3-20 equiv). Yield in parenthesis of the diene **7**. See supporting information for experimental details.

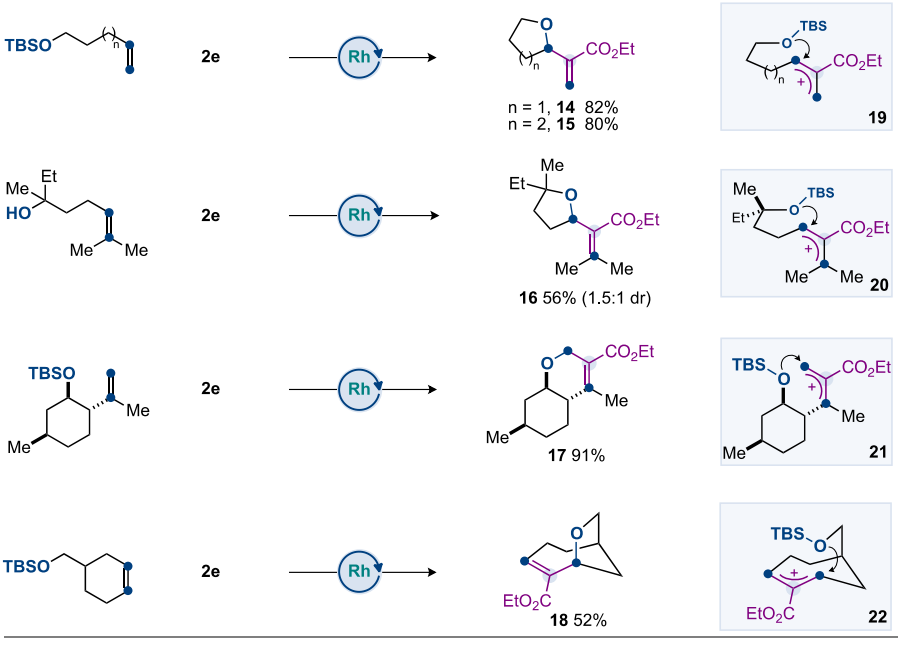
Next, we wondered whether we could convert olefin petrochemical feedstocks and styrenes into allylic building blocks. We embarked on this journey by firstly evaluating ethylene, the most widely produced chemical feedstock by the petrochemical industry with an annual global production above 134 million tones. We were glad to find that our methodology was able to convert ethylene into allyl bromide **6s** with high efficiency (Table 2B). To the best of our knowledge, this is the first example of a catalytic constructive scission in ethylene that provokes the conversion to an allyl bromide. This result can be explained by the initial formation of

intermediate **8**, subsequent electrocyclic ring-opening and bromide attack to the resulting allyl cation **9**. Also, our process worked well with propylene, the most important feedstock of the α-olefin family. In this case, allyl bromide **6t** was obtained with a 14:1 linear/branched selectivity and in 89% yield (Table 2B). The 4:1 selectivity observed in favor for the *Z* isomer in the linear isomer, is suggesting the preferential formation of **10**, where substituent R and $I_{(III)}$ moiety are in relative *syn* disposition. Subsequently, the electrocyclic ring-opening by disrotatory mode would conduct to **11** – the R group rotates inwardly– which undergo bromide attack at the less hindered electrophilic carbon site (α position). Moreover, while similar efficiencies and selectivities were obtained for 1-butene (**6u**) and 1-hexene (**6v**), the reaction with styrene provided excellent yield and selectivities in favor of the linear isomer **6w.** On the other hand, we anticipated that 1,2-disubstituted alkenes such as (*E*)-2-butene and *β*-methyl-styrene would potentially challenge our methodology: the formation of **12** and subsequent electrocyclic ring-opening, would provide a trisubstituted allyl cation **13** with two similar electrophilic sites (α & α′ position), and mixtures of allyl bromides could be formed (Table 2B). However, we were delighted to find that the reaction gave allyl bromides **6x** and **6y** with a high regio- and stereoselectivity. Furthermore, our insertion reaction enabled ring expansion in larger rings, including cycloheptene (**6z**), cyclooctene (**6aa**) and cyclododecene (**6ab**).

An important feature of our C(sp_2)–C(sp_2) cleavage process is the ability to transform alkenes into others with a higher substitution. We believed that we could provide a new approach for the synthesis of synthetic challenging tetrasubstituted olefins, which lack a general synthesis approach and are present in drug molecules and molecular motors.[22] Based on previous results, we anticipated that 1,1-disubstituted olefins, which are commercially available or easy to make from ketones by ylide olefination, could be suitable substrates to reach the tetrasubstituted olefin core. We were pleased to find that commercial methylenecyclohexane and α-methylstyrene could be efficiently converted into tetra-substituted olefins **6ac** and **6ad** by using Bu_4NO_2CPh and Bu_4NN_3 as nucleophile, respectively (Table 2B). It is noteworthy the high degree of stereoselectivity observed for **6ad** (14:1, *Z:E*), which can be rationalized based on the preferential formation of an analogue of **10** having both Ph ring and $I_{(III)}$ moiety in *syn* disposition.

The strategic advantage of inserting a monovalent carbon unit into a C(sp_2)–C(sp_2) bond was further exploited to induce cyclization reactions (Scheme 2). Simple alkenes with a remote alcohol nucleophile and natural product derivatives were selectively cyclized with moderate to excellent yields (**14–18,** 52-91% yield). Based on the previous results, we believe that the cyclization reactions involve the selective catalytic generation of carbocations **19–21** that selectively evolve to the heterocyclic products through *exo* (**19,20,22**) and *endo* cyclizations (**21**).

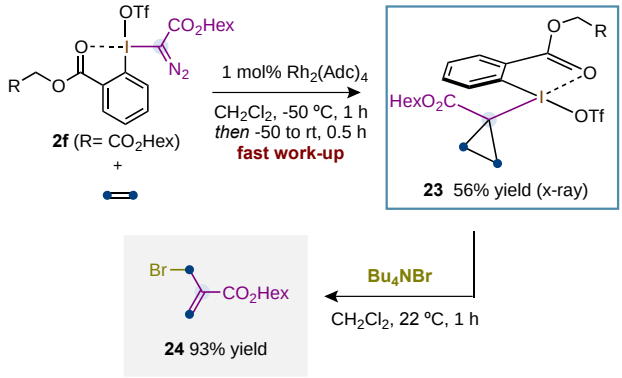
Scheme 2. C(sp_2)–C(sp_2) bond cleavage enables cyclizations[a]



[a] Reaction conditions: 1 mol % $Rh_2(esp)_2$, -50 °C, 1 h *then* -50 to rt, 3 h, CH_2Cl_2.

Finally, we wanted to provide evidence of cyclopropyl hypervalent iodine intermediates **4**, despite the well-known thermodynamic instability of alkyl-I(III) species.[23] Initial efforts towards the isolation of cyclopropyl–I(III) intermediates from mono (styrene) and di-substituted olefins (cyclohexene) at –50 ºC were unsuccessful. It is known that the electrocyclic ring-opening in substituted cyclopropyl tosylates is kinetically favored over the non-substituted derivatives.[17a] With this information, we hoped that trapping the corresponding cyclopropyl–I(III) intermediate derived from ethylene could be more feasible. By using reagent **2f** and $Rh_2(Adc)_4$ as catalyst, we were glad to isolate at room temperature cyclopropyl–I(III) compound **23** as a relative stable white solid in 56% yield, whose structure was confirmed by single-crystal x-ray diffraction analysis (Scheme 3). To the best of our knowledge, this is the first isolable alkyl–I(III) compound of this class, and we believe this result may inspire future endeavors for the design of novel hypervalent alkyl–I(III) reagents. As a control experiment, we demonstrated that the treatment of **23** with Bu_4NBr gave the expected allyl bromide **24** with high efficiency (Scheme 3).

Scheme 3. Synthesis of cyclopropyl–I(III) compound 23



In summary, we have developed a Rh-catalyzed carbyne transfer platform for the catalytic cleavage of C(sp^2)–C(sp^2) bonds. We have demonstrated that this process is able to convert feedstock alkenes, styrenes and a broad diversity of simple nucleophiles into valuable allylic building blocks. The value of the constructive scission of C(sp^2)–C(sp^2) bonds in alkenes for the synthesis of more substituted ones is remarkable and is well exemplified with the synthesis of all-carbon tetrasubstituted alkenes from readily available starting materials. The isolation of a cyclopropyl-I(III) compound, which opens following the Woodward-Hoffmann-DePuy rules, clearly proves the involvement of these species as intermediates in the reaction. We believe that the insertion of a monovalent carbon unit in C(sp^2)–C(sp^2) bonds underscores an opportunity as tool in skeletal editing that will be relevant to reach previously unattainable chemical space in drug discovery.[24]

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: Experimental procedures and spectral data (PDF)
x-ray crystallographic data for **6g**
x-ray crystallographic data for **6n**
x-ray crystallographic data for **23**

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Notes

The authors declare no competing interest

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