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Rhodium-catalyzed silylative carbocyclization on C_{60}

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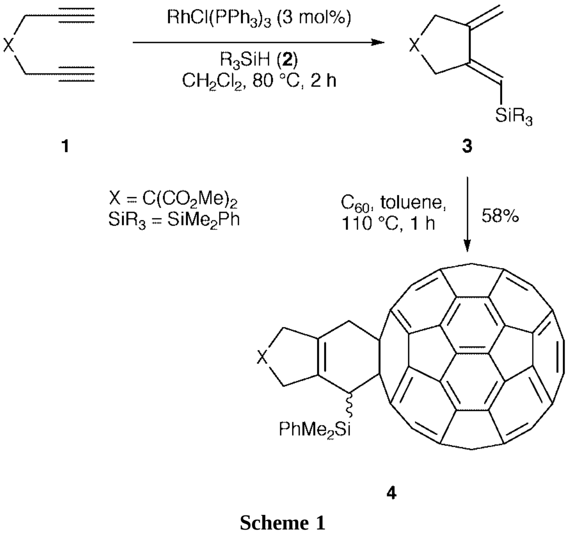
Rhodium-catalyzed three component coupling of hepta-1,6-diyne, hydrosilane and C_{60} proceeded smoothly to give a fullerene derivative in good yield.

Studies on the functionalization of C_{60} fullerene have attracted considerable attention,[1] because fullerene derivatives are expected to be effective precursors for advanced composite materials,[1c] photoconductive thin films,[2] electron transfer dyad,[3] efficient photosensitizers,[4] *etc*. Fullerene derivatives are also anticipated to form materials with stimulating biological properties,[1b,d] such as inhibition of HIV-1 protease,[5] promotion of DNA cleavage,[6] and enzymatic inhibition.[6e,7] In order to prepare a wide range of designed C_{60} derivatives, cycloadditions have proved the most useful method because well-defined mono-adducts can be easily obtained in most cases.[8] The obtained C_{60}-fused carbo- and heterocycles are interesting key molecular components for the construction of the aforementioned functionalized materials, which are often composed of organized molecular aggregates. In particular, the Diels–Alder reaction, employing C_{60} as a dienophile, is a reliable tool to obtain the cyclohexene-fused C_{60} derivatives.[8a] In addition, cycloaddition protocols include the reaction of C_{60} with appropriate addenda, such as carbenes, nitrenes, conjugated dienes, 1,3-dipoles, *etc*.[8b] No example of *a catalytic multi-component coupling strategy* involving C_{60}, however, has been reported so far, although domino-type multi-component couplings catalyzed by a wide variety of transition metal complexes are now becoming a major focus in organic synthesis.[9] We herein report the first example of three-component coupling involving C_{60} catalyzed by a rhodium complex. Transition-metal promoted coupling reactions on fullerene are quite rare. This is ascribed to the finding that fullerenes preferentially form stable complexes with a wide range of transition metals. They are frequently too stable to show catalytic activity toward carbon–carbon bond formation with fullerene itself.[10] Only recently, the stoichiometric Ni-promoted cycloaddition of hepta-1,6-diynes and C_{60} was reported by Cheng *et al.*[11] Catalytic methods, however, are desirable as they are metal-economical and environmentally friendly processes. With these ideas in mind, we developed the Rh^I-catalyzed three-component domino coupling of C_{60}, hepta-1,6-diyne and hydrosilane *via* the silylative cyclization of the diyne followed by the Diels–Alder cycloaddition of the resultant diene and C_{60}.

We recently reported the rhodium-catalyzed silylative cyclization of hepta-1,6-diynes **1** with trialkylsilanes **2** leading to *cisoid* dienylsilane derivatives **3** (Scheme 1).[12] The obtained **3** has an exocyclic 1,3-diene moiety and can be utilized as a diene counterpart in the Diels–Alder cycloaddition toward fullerene. In fact, the thermal reaction between C_{60} and 1.5 equiv. of **3** [X = $C(CO_2Me)_2$, R_3Si = $PhMe_2Si$] in refluxing toluene for 1 h gave the desired cycloadduct **4a** in 58% isolated yield (88% yield based on consumed C_{60}). The structure of **4a** was determined on the basis of its ^1H and ^{13}C NMR, IR, and MS analyses.[13] First, its IR spectrum revealed that **4a** is the adduct of C_{60} and **3**, *i.e.* the typical absorption of the C_{60} core was observed at 527 cm^{-1} as well as the absorptions corresponding to the ester carbonyl groups and the silyl group at 1735 and 1249 cm^{-1}, respectively. In the ^1H NMR spectrum, cyclohexene ring protons [δ 3.13 (d, 1H, J 16.8 Hz), 3.38 (s, 1H), and 3.48 (m, 1H)] and cyclopentene ring protons [δ 3.64-3.77 (m, 2H) and 3.97–4.07 (m, 2H)] were observed along with the peaks assigned to the methyl and phenyl proton signals of the organic silyl group, and the methyl ester protons.[13] The molecular ion peak at *m/z* 1064 in the FAB-MS spectrum clearly indicated that **4a** is the expected 1:1 adduct. Furthermore, the ^{13}C NMR spectrum shows that the cycloaddition took place on the junction of two six-membered rings; among the ten peaks in the aliphatic region, the lowest-field signal at δ 66.62 is reasonably attributed to the fullerene sp^3 carbons of the 6,6-ring junction. The four sp^2 signal observed at δ 155.76, 156.39, 159.61 and 161.21 are also assigned to the C_{60} carbons next to the sp^3 carbon of the 6,6-junction.

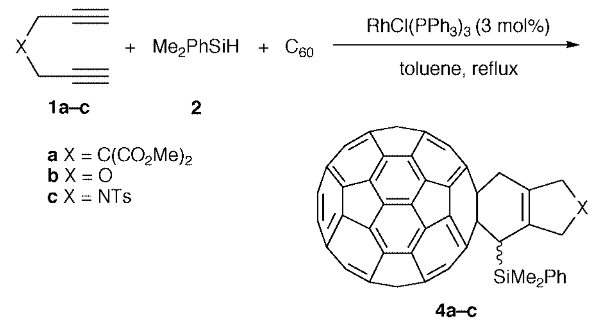
The dienylsilane **3** is definitely an effective diene component in the Diels–Alder cycloaddition with C_{60}. Next, we investigated the three-component coupling from **1a**, **2** and C_{60}. Such three-component coupling is an attractive and more straightforward protocol for transition-metal-catalyzed carbocyclization on the fullerene framework in a single operation. The reaction of C_{60} (0.05 mmol) with **1a** (0.5 mmol) and **2** (0.5 mmol) under N_2 in refluxing toluene for 35 min in the presence of 3 mol% $RhCl(PPh_3)_3$ gave the expected **4a** in 36% isolated yield (55% yield based on consumed C_{60}; entry 1, Table 1). The spectral features of the product are identical to those from the Diels–Alder adduct of **3** with C_{60}. A decrease in the amounts of the diyne and the silane gave better results although longer reaction times are required (entries 2 and 3). The best yield (71%) was realized when 7 equiv. of **1a** and **2** were employed in refluxing toluene for 1 h (entry 2).

The significant feature of the present three-component domino coupling is that C_{60}, in spite of its strong tendency to form complexes with various transition metals,[10] never suppressed the catalytic silylative cyclization step. In sharp contrast, the three-component couplings of **1a**, **2** and *N*-phenylmaleimide (**5**) or maleic anhydride (**6**) failed although the Diels–Alder reaction of the isolated **3** gave the corresponding adducts with **5** or **6** in high yield.[14] These results suggest that



Scheme 1

Table 1 Rhodium-catalyzed three-component coupling of C_{60} with diynes **1a–c** and silane **2**



Entry	1	Amount of **1** and **2**/ equiv.	Product	*t*/min	Yield (%)[a]
1	**1a**	10	**4a**	40	53 (36)
2	**1a**	7	**4a**	60	71 (58)
3	**1a**	5	**4a**	110	63 (34)
4	**1b**	15	**4b**	200	41 (34)
5	**1c**	10	**4c**	45	32 (28)

[a] The yield was based on comsumed C_{60} and isolated yield was shown in parenthesis.

these strong dienophiles inhibited the catalytic cycle *via* complex formation with a Rh^I species.

The other important feature is that dipropargyl ether **1b** and *N*,*N*-dipropargyl tosylamide **1c** were successfully adapted to the domino coupling, whereas they hardly gave silylative cyclization products in the absence of C_{60}.[14]As a result, interesting C_{60}-bound heterocycles **4a** and **4b** were successfully isolated in 41 and 32% conversion yields, respectively (entries 4 and 5). It seems reasonable to assume that unstable exocyclic diene intermediates **3b** and **3c** were immediately coupled with C_{60} before decomposition under the reaction conditions.

In conclusion, we have developed the Rh^I-catalyzed three-component domino coupling of C_{60}, hepta-1,6-diynes and a hydrosilane. Dienophile C_{60} did not interfere with the catalytic silylative cyclization and efficiently trapped the exocyclic 1,3-diene intermediates to furnish the corresponding C_{60}-linked carbo- and heterocycles in fair to good yields. The present method is the first example of transition-metal catalyzed domino coupling on the fullerene conducted in a single operation.

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13 *Selected data* for **4a**: ν_{max}(KBr)/cm^{-1} 1735 (s), 1428 (m), 1249 (m), 1159 (w), 1112 (m), 820 (w), 699 (w), 527 (m); δ_H(300 MHz, $CDCl_3$) 0.79 (s, 3H), 0.88 (s, 3H), 3.13 (d, 1H, *J* 16.8), 3.38 (s, 1H), 3.48 (m, 1H), 3.64–3.77 (m, 2H), 3.80 (s, 3H), 3.87 (S, 3H), 3.97–4.07 (m, 2H), 7.34–7.39 (m, 3H), 7.70–7.74 (m, 2H); δ_C(75 MHz, $CDCl_3$) −0.71, −0.53, 40.58, 44.37, 45.47, 45.83, 52.95, 52.98, 58.92, 66.62, 128.08, 129.50, 133.09, 133.57, 134.32, 135.26, 135.32, 135.60, 137.75, 138.85, 139.70, 139.97, 140.07, 140.36, 141.35, 141.51, 141.61, 141.73, 141.80, 141.92, 142.05, 142.09, 142.18, 142.56, 142.59, 142.63, 142.64, 142.68, 143.12, 143.18, 144.07, 144.58, 144.63, 144.73, 144.80, 144.86, 144.92, 145.28, 145.34, 145.37, 145.44, 145.46, 145.61, 145.73, 145.84, 145.85, 146.10, 146.16, 146.23, 146.28, 146.43, 146.52, 147.62, 147.68, 155.76, 156.39, 159.61, 161.21, 172.30, 172.52 (*cf.* because of signal coincidence, only 52 peaks of the expected 58 peaks of the C_{60} core were observed); *m/z* (FAB-MS) 1064 (M^+, 11%), 720 (100).

14 T. Muraoka, I. Matsuda and K. Itoh, unpublished results.

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