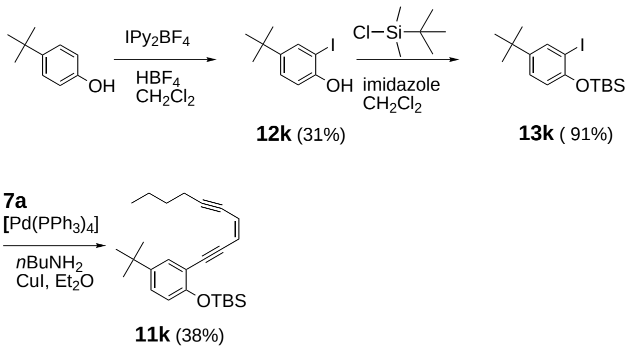
3.98–3.91 (m, 2H), 3.60–3.53 (m, 2H), 3.40–3.35 (m, 2H), 2.21–2.14 (m, 2H), 1.93–1.57 ppm (m, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 155.9$, 152.2, 135.3, 133.0, 127.6, 126.1, 125.7, 125.5, 124.8, 122.9, 122.2, 121.9, 120.8, 120.0, 118.4, 111.7, 98.8, 66.8, 62.1, 30.9, 30.6, 29.6, 25.4, 19.5 ppm; HRMS (EI) calcd for $C_{24}H_{24}O_3$ 224.1201, found 224.1207. **2i**: ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 8.49$ (s, 1H), 8.06 (s, 1H), 7.93–7.87 (m, 1H), 7.82 (s, 1H), 7.79–7.46 (m, 5H), 7.36–7.24 (m, 2H), 2.60 (t, $J = 6.8$ Hz, 2H), 1.77–1.37 (m, 4H), 1.00 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 154.5$, 154.2, 134.0, 132.4, 132.3, 132.0, 131.3, 128.3, 127.9, 127.2, 127.1, 126.8, 126.8, 125.9, 124.6, 122.8, 121.2, 118.3, 110.9, 105.8, 30.6, 29.7, 19.5, 13.6 ppm; HRMS (EI) calcd for $C_{24}H_{20}O$ 324.1515, found 324.1512. **2j**: ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 8.50$ (s, 1H), 8.07 (s, 1H), 7.84 (s, 1H), 7.80–7.29 (m, 8H), 2.60 (t, $J = 6.8$ Hz, 2H), 1.83–1.22 (m, 6H), 0.95 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta =$ 154.3, 154.1, 134.1, 132.4, 132.3, 132.0, 131.4, 128.3, 127.3, 127.1, 126.9, 126.8, 126.5, 125.8, 124.6, 122.8, 121.2, 119.0, 111.0, 105.8, 31.3, 29.6, 22.3, 19.8, 14.0 ppm; HRMS (EI) calcd for $C_{25}H_{22}O$ 338.1671, found 338.1667. **2k**: ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 7.99$ (t, $J = 1.2$ Hz, 1H), 7.52 (d, $J = 1.4$ Hz, 2H), 7.44–7.31 (m, 2H), 7.11 (dd, $J = 6.8$, 1.4 Hz, 1H), 3.15 (t, $J = 7.6$ Hz, 2H), 1.89–1.74 (m, 2H), 1.65–1.50 (m, 2H), 1.45 (s, 9H), 1.03 ppm (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta =$ 156.7, 154.2, 145.6, 138.4, 126.6, 124.1, 123.9, 122.9, 122.5, 118.7, 110.7, 109.0, 34.7, 33.8, 32.0, 31.8, 22.9, 14.0 ppm; HRMS (EI) calcd for $C_{20}H_{24}O$ 280.1828, found 280.1816.

[8] Treatment of *p-tert*-butylphenol with bis(pyridium)iodonium(I)tetrafluoroborate (Ipy$_2$BF$_4$) gave 2-iodo-4-*tert*-butylphenol in 31% yield. Compound **12k** was treated with *tert*-butyldimethylsilyl chloride using imidazole as a base to give **13k** in 91% yield. Finally, compound **13k** was coupled with **7a** using palladium as a catalyst to give **11k** (TBS = *tert*-butyldimethylsilyl) in 38% yield.



The HfCl$_4$-Mediated Diels–Alder Reaction of Furan**

Yujiro Hayashi,* Masahiko Nakamura,
Shigehiro Nakao, Tae Inoue, and Mitsuru Shoji

7-Oxabicyclo[2.2.1]hept-2-ene derivatives are useful intermediates for the synthesis of natural products such as carbohydrates and prostaglandins.[1] One of the most straightforward methods for the construction of the 7-oxabicyclo[2.2.1]hept-2-ene skeleton is the Diels–Alder reaction between furan and appropriate dienophiles. However, the facile retro-Diels–Alder reaction and the low reactivity of furan as a diene, as a result of its aromatic character, make the Diels–Alder reaction of furan one of the most difficult cycloadditions.[2] In addition to the use of highly reactive dienophiles in the Diels–Alder reaction,[3] several methods have been developed to overcome these difficulties, such as the use of high pressure[4] or Lewis acid mediated reactions.[5] Although several Lewis acids have been reported to promote the reaction efficiently, there are problems in terms of generality. For example, $BF_3 \cdot OEt_2$ is a good catalyst for methyl acrylate but a poor promoter for other dienopliles,[5c] ZnI_2 is suitable for acrylonitrile but not for α,β-unsaturated esters,[5a] while methyl vinyl ketone and acrylonitrile are activated by $BiCl_3$.[5l] Some Lewis acids supported on silica gel have also been utilized for the promotion of a particular dienophile with furan.[5e,g,i,j] However, low *endo*/*exo* selectivity is generally obtained because of the facile retro-Diels–Alder reaction. Herein we report the *endo*-selective Diels–Alder reaction of furan with α,β-unsaturated esters catalyzed by $HfCl_4$.

First, we looked for an appropriate Lewis acid using the reaction of furan and dimethyl maleate as a model and employing furan as the solvent (40 equiv). The reaction was performed in the presence of an equimolar amount of Lewis acid at room temperature for 15 h. Of the several Lewis acids screened,[6] $HfCl_4$ was found to have suitable Lewis acidity to promote the Diels–Alder reaction in moderate yield (60%).[7] Although most of the reported Lewis acids lose their Lewis acidity by coordination with furan, which acts as a Lewis base, $HfCl_4$ still activates α,β-unsaturated esters efficiently even in the presence of an excess amount of furan. Next, the use of a solvent was examined, and CH_2Cl_2 was found to be the best with respect to both yield and *endo*/*exo* selectivity.[8] For example, the Diels–Alder reaction of dimethyl maleate and furan proceeds in CH_2Cl_2 at −20°C within 5 h to afford the cycloadduct in good yield (91%) and high diastereoselectivity

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[**] This research was supported by the Asahi Glass Foundation and a Grant-in-Aid for Scientific Research on Priority Areas (A) “Exploitation of Multi-Element Cyclic Molecules” from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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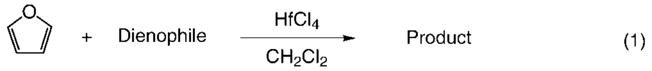
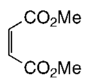
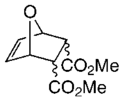
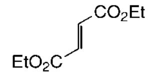
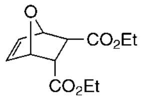
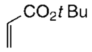
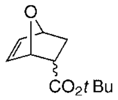
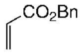
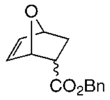
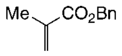
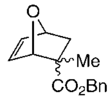
Table 1. The Diels–Alder reaction of furan.[a]



(1)

Entry	Dienophile	Product	Equiv of $HfCl_4$	T [°C]	t [h]	Yield [%][b]	*endo*/*exo*[c]
1			1.1	0	4	88	72/28
2			1.1	−20	5	91	93/7
3			1.1	−50	66	91	98/2
4			0.2	0	20	88	89/11
5			1.1	−20	7	84	–
6			1.1	−50	17	82	–
7			0.2	0	26	39	–
8			1.1	−50	25	84	69/31
9			1.1	−50	8	98	78/22
10			0.2	0	20	56	76/24
11			0.2	0	40	73	60/40
12			0.2	0	51	88	50/50
13			1.1	−10	48	34	18/82

[a] Furan/dienophile = 20/1. [b] Yield of isolated product. [c] The ratio (*endo*/*exo*) is determined by ^1H NMR analysis (400 MHz).

(*endo*/*exo* = 93/7; Table 1, entry 2). The effect of temperature on the yield and diastereoselectivity of the reaction is shown in entries 1–3. As the temperature is lowered, the diastereoselectivity increases, and very high *endo* selectivity (98/2) was attained when the reaction was conducted at −50 °C. This is only the second highly *endo*-selective Diels–Alder reaction of furan with a maleic acid derivative, the first being a reaction performed under high-pressure conditions,[4a] and the present reaction is complimentary to the thermal Diels–Alder reaction of maleic anhydride and furan, which affords predominantly the thermodynamically stable *exo* isomer.[3c]

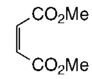
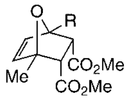
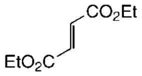
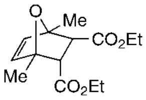
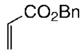
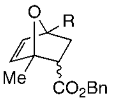
The generality of this $HfCl_4$-mediated Diels–Alder reaction of furan with respect to dienophiles was investigated (Table 1). The reaction of diethyl fumarate proceeds smoothly at −20 °C to afford the Diels–Alder product in good yield (entry 5). The ester group has a large effect both on the yield and selectivity in the reaction of acrylate derivatives; the reaction of the benzyl ester is faster (8 h) and more selective (*endo*/*exo* = 78/22, entry 9) than that of the *tert*-butyl ester (25 h, *endo*/*exo* = 69/31, entry 8). Methyl methacrylate is not a reactive dienophile, and its Diels–Alder cycloadduct is formed in very low yield (8 %), even under high-pressure conditions (15 kbar).[4a] $HfCl_4$, however, accelerates the Diels–Alder reaction of benzyl methacrylate and furan to afford the cycloadduct in 34 % yield, with the *exo* isomer predominating (entry 13). Though there is room for improvement of the yield, this is the first example of a Diels–Alder reaction of furan with a methacrylate derivative.

We found that $HfCl_4$ behaves as a true catalyst of this reaction. That is, when the reaction of furan and diethyl maleate was performed in the presence of only a catalytic amount (20 mol %) of $HfCl_4$, the reaction proceeded at 0 °C to afford the Diels–Alder adducts in good yield (88 %), and with high *endo*/*exo* selectivity (entry 4). On the other hand, fumarate ester is not a suitable substrate for the present reaction, with the Diels–Alder adducts being formed in low yield when the amount of $HfCl_4$ was reduced to 20 mol % (entry 7). The yield for the catalytic reaction using benzyl acrylate as the dienophile increased with increasing reaction time, while the diastereoselectivity decreased (entries 10–12). This observation can be attributed to thermodynamic equilibration in the presence of $HfCl_4$ at 0 °C in favor of the *exo* isomer. High *endo* selectivity in the reaction using an equimolar amount of $HfCl_4$ at low temperature can be achieved under kinetic control (Table 1, entry 9).

Next, substituted furans were employed in the Diels–Alder reaction (Table 2). Not only furan, but substituted furans also react efficiently with several dienophiles in the presence of both equimolar and catalytic amounts of $HfCl_4$. The higher HOMO levels of 2-methylfuran and 2,5-dimethylfuran relative to those of the parent furan means the reactions proceed much faster. Although a long reaction time (66 h) is necessary for the reaction of dimethyl maleate and furan at −50 °C in the presence of an equimolar amount of $HfCl_4$ (Table 1, entry 3), the reaction of the same dienophile with 2-methylfuran and with 2,5-dimethylfuran proceeds within 5 h at the same temperature with the same loading of the catalyst (Table 2, entries 1,3). High *endo* selectivity was attained in these reactions of dimethyl maleate (Table 2, entries 1–4). Diethyl fumarate also reacts with 2,5-dimethylfuran to give the cycloadduct in 81 % yield (Table 2, entry 5). Benzyl acrylate also reacts with substituted furans to give the Diels–Alder products in good yield with moderate *endo* selectivity. Higher *endo*/*exo* selectivity was obtained in this reaction when a catalytic amount of $HfCl_4$ was employed, compared with that of the reaction using an equimolar amount of Lewis acid (Table 2, entries 6–9).

Table 2. The Diels–Alder reaction of substituted furan.[a]

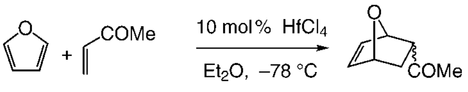
(2)

Entry	R	Dienophile	Product	Equiv of HfCl$_4$	T [°C]	t [h]	Yield [%][b]	*endo*/*exo*[c]
1	H			1.1	−50	5	82	> 98/2
2	H			0.2	−30	10	94	84/16
3	Me			1.1	−50	5	81	> 98/2
4	Me			0.2	−30	11	97	> 98/2
5	Me			1.1	−20	11	81	–
6	H			1.1	−50	4	85	69/31
7	H			0.2	−30	12	84	72/28
8	Me			1.1	−50	4	84	70/30
9	Me			0.2	−20	16	98	80/20

[a] Furan/dienophile = 20/1. [b] Yield of isolated product. [c] The ratio (*endo*/*exo*) is determined by ^{1}H NMR analysis (400 MHz).

The regio- and stereochemistries of the Diels–Alder adducts of 2-methylfuran and benzyl acrylate (Table 2, entries 6,7) were determined from NOESY spectra, and by conversion of the major isomer into the corresponding iodolactone.

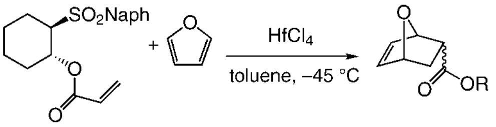
Methyl vinyl ketone, however, did not afford the Diels–Alder product under the same reaction conditions, but instead gave 4-furyl-2-butanone as a major product. As this was reasoned to be generated by over-reaction of the initially formed Diels–Alder product, the reaction conditions were screened to reduce the Lewis acidity of HfCl$_4$. It was found that the Diels–Alder product was obtained in 65 % yield with moderate *endo*/*exo* selectivity (67/33) when a catalytic amount of HfCl$_4$ was employed at low temperature (−78 °C) for 17 h in Et$_2$O [Eq. (3)].



(3)

65%, *endo*/*exo* = 67/33

This HfCl$_4$-mediated Diels–Alder reaction was further applied to the diastereoselective reaction of a chiral dienophile, since the chiral 7-oxabicyclo[2.2.1]hept-5-ene derivatives obtained are important chiral building blocks for natural product synthesis.[9] There are few successful examples of this kind of reaction, however, because of the easy reversibility of the reaction. For example, (1*R*,2*S*,5*R*)-8-phenylmenthyl acrylate,[10] which is a widely used chiral dienophile in the carbo-Diels–Alder reaction, reacts at 25 °C over 24 h with furan in the presence of a catalyst of TiCl$_4$ supported on silica gel to afford the cycloadduct in 79 % yield with low to moderate selectivity (*endo*/*exo* = 33/67, *endo* = 33 % *de*, *exo* = 70 % *de*).[9h] We applied our HfCl$_4$-mediated Diels–Alder reaction to the (−)-(1*R*,2*R*)-2-(naphthalene-2-sulfonyl)cyclohexyl acrylate developed by Sarakinos and Corey[11] expecting to achieve a high diastereomeric excess because the high activity of HfCl$_4$ enables the reaction to proceed at low temperature under kinetic control. As expected, the Diels–Alder reaction [Eq. (4)] proceeds at low temperature (−45 °C) to afford the cycloadduct in good yield (83 %) with high diastereomeric excess (*endo*/*exo* = 68/32, *endo* = 87 % *de*, *exo* = 91 % *de*). The absolute stereochemistry of the *endo* isomer was determined by comparison of its optical rotation with the literature value after conversion into the corresponding iodolactone.[12] This highly diastereoselective Diels–Alder reaction is synthetically useful and practical, as demonstrated by our recent total synthesis of epoxyquinols A and B from the *endo* isomer in high optical purity.[13]



(4)

83%, *endo*/*exo* = 68/32, *endo* 87% *de*, *exo* 91% *de*

In summary the Diels–Alder reaction of furan is efficiently promoted by a catalytic amount of HfCl$_4$ to give cycloadducts in good yield with high *endo* selectivity. As HfCl$_4$ is an active Lewis acid catalyst, even in the presence of an excess amount of furan, the reaction proceeds at low temperature and prevents the usual *endo*/*exo* isomerization and gives high *endo* selectivity. This is a unique feature of HfCl$_4$ compared with the other Lewis acids,[5] the Lewis acidity of which are reduced by the coordination with furan to give low yields and low *endo* selectivity. A wide range of reactive α,β-unsaturated esters and methyl vinyl ketone can be successfully employed as dienophiles in the HfCl$_4$-mediated reactions, and not only furan but substituted furans can also be employed as dienes, again with high *endo* selectivity, this not having been achieved by previous methods mediated by Lewis acids. The highly diastereoselective Diels–Alder reaction of a chiral acrylate has also been achieved.

Experimental Section

Typical procedure (Table 1, entry 4): Dimethyl maleate (80 μL, 0.64 mmol) and freshly distilled furan (0.93 mL, 12.8 mmol) were added successively at 0 °C to a suspension of HfCl$_4$ (40.8 mg, 0.13 mmol) in CH$_2$Cl$_2$ (0.5 mL). After stirring the reaction mixture for 20 h at the same temperature, aqueous NaHCO$_3$ was added. After filtration of the inorganic materials, the organic materials were extracted with CHCl$_3$ (× 3) and the combined organic phase was dried over anhydrous MgSO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica gel (ethyl acetate/hexane = 1/10–1/1) gave 105.6 mg (78 %) of the *endo* isomer and 13.1 mg (10 %) of the *exo* isomer.

Received: February 25, 2002
Revised: August 20, 2002 [Z18768]

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Planar Hypercoordinate Carbons Joined: Wheel-Shaped Molecules with C–C Axles[**]

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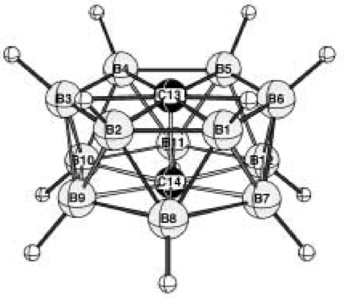
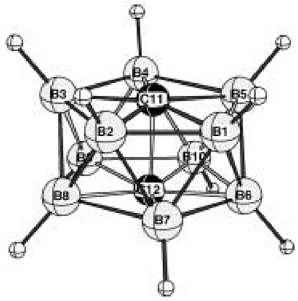
After two centuries of organic chemistry and the characterization of over 14 million carbon compounds with conventional bonding, our recent computational predictions of molecules with planar hexacoordinate [1] and pentacoordinate carbon atoms[2] has demonstrated that the bonding capabilities of this central element have not been exhausted. We now show computationally [3] that the coordination of carbon can be raised to seven (or six) by the perpendicular extension of two planar hexacoordinate (or pentacoordinate) carbon atoms to form wheel-shaped (**W**) molecules (e.g. **1W** and **2W,** respectively).



1W ($C_2B_{12}H_{12}$)



2W ($C_2B_{10}H_{10}$)

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[**] This work was supported by the University of Georgia.

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