Photocycloaddition of Some Difluoro(aminoenonato)boron Complexes with Arylalkenes

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The photocycloaddition of some difluoro[(methylamino-κN)alkenonato-κO]boron complexes **1** with arylalkenes **2** is discussed. The resulting [2+2] photoaddition gave the cyclobutane and azetidine derivatives (*Schemes 1*, *3*, and *5*). Rearrangements of the cyclobutane gave 1,5-diketones derivatives (*Schemes 2*, *4*, and *5*). The yields of the photoadducts were governed by the reduction and oxidation potentials. Furthermore, the configurations of the products established high regio- and stereoselectivity, suggesting the presence of a singlet exciplex. The reactivity and the stereochemistry were rationalized by means of FMO (frontier molecular orbital) calculations.

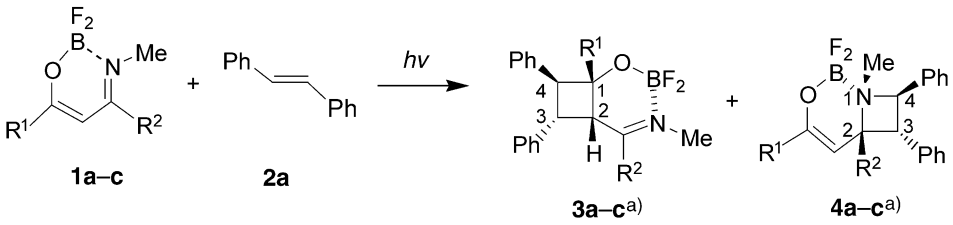
Introduction. – The photochemical cycloaddition of 1,3-diketones (*via* their enols) with various olefins has been generally known as the *de Mayo* reaction [1], which, because of its versatile intermediates, can be useful in natural-product synthesis [2]. Many reports concerning the mechanism of the photoaddition have appeared [3]. However, except for cyclic imino ketone compounds [4], the photoreaction of a corresponding carbonyl compound containing an α-enamine group moiety (aminoenone) has not been investigated, although it is known that the expected photoadducts may serve in various ways as potential intermediates leading to N-atom-containing compounds. Notably, irradiation of such aminoenones with a considerable number of olefins yields no photoadducts [5]. Thus, because of the greatly increased reactivity of 1,3-diketones after complex formation with boron trifluoride [6], we prepared some (aminoenonato)difluoroboron complexes. In a previous paper [7], we reported that, in the reaction of cyclic and acyclic olefins, only a (3-amino-1,3-diphenylprop-3-en-1-onato)difluoroboron complex (=difluoro[(1*Z*)-2-(methylimino-κN)-1,3-diphenylprop-1-en-1-ol-κO]boron) generated a reasonable amount of certain products and furnished interesting derivatives from the [2+2] photoadduct. Here, we examine the photoreactions of some difluoroboron complexes, *i.e.*, of **1a**–**c**, with arylalkenes **2a**–**d** and report the photoproducts, the reactivity, and the reaction scheme.

Results. – Irradiation of the B-complexes **1a**–**c** and *trans*-stilbene (**2a**) with a high-pressure Hg lamp for 24 h in a *Pyrex* test tube gave the cyclobutane derivatives **3a**–**c** and the azetidine derivatives **4a**–**c** (*Scheme 1*) *Table 1*. Each of the photoadducts was obtained in pure form after column chromatography followed by recrystallization. In the reaction of **1a** and **1b**, the yields of the cyclobutane derivatives **3a, b** and of the azetidine derivatives **4a**, **b** were about equal, but, in the reaction of **1c**, the cyclobutane derivative **3c** was obtained as the major product besides a small amount of **4c**. The

overall yield of the products increased with the number of Ph groups in the complex. The structures of the products were determined on the basis of the spectral data.

Typically, the MS of **3b** showed a molecular-ion peak (M^+ at m/z 403) indicating the addition of stilbene (**2a**) to the B-complex **1b**. Its ^{1}H-NMR spectra displayed the signals due to the three CH groups (δ 4.07, 4.33, and 5.11) characteristic of cyclobutane formation. A ^{13}C-NMR signal for the imino C-atom was observed at δ 183.8. The configuration of **3b** was mainly determined by NOESY (nuclear-*Overhauser*-effect spectroscopy) experiments. A cross-peak appeared for H–C(2)/H–C(3), but no NOE was observed for H–C(3)/H–C(4), indicating *cis*-orientation for the former and *trans*-orientation for the latter.

Scheme 1[a])



[a]) For R^1 and R^2, see *Table 1*.

Table 1. *Photocycloaddition of B-Complexes* **1a–c** *with* trans-*Stilbene* (**2a**)

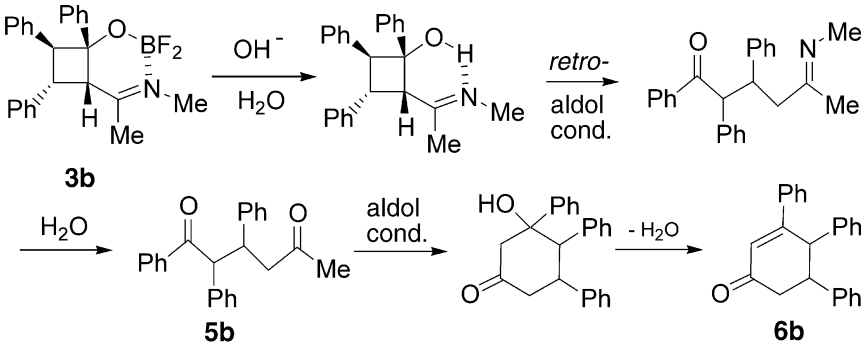
	R^1	R^2	Products		Recovered **1**
			3	**4**	
1a	Me	Me	12%	14%	55%
1b	Ph	Me	39%	32%	–
1c	Ph	Ph	74%	8%	–

The determination of the structure of the azetidine derivatives **4a–c** was considered in more detail. In a COLOC (correlation by long-rang coupling) spectrum of **4b**, *e.g.*, a cross-peak appeared for the MeN protons (δ 2.52) and C(4) of the ring (δ 66.5), but no cross-peak existed for the MeN protons and the olefinic C-atom (δ 151.2). These observations indicated that **4b** should have an azetidine rather than an oxetane structure. The NOESY plots of **4b** showed that both H–C(3)/H–C(4) and H–C(4)/MeN are *trans*-orientated.

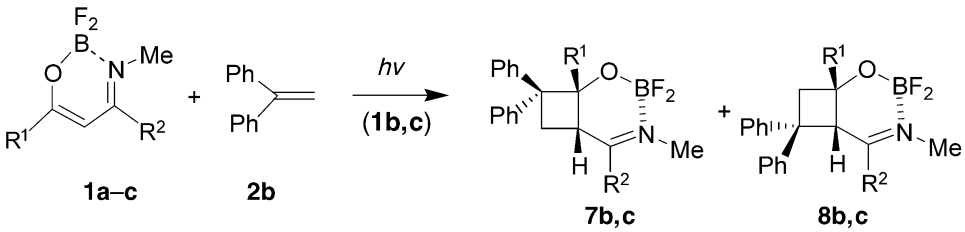
In addition, the structure of **3b** was confirmed by alkaline hydrolysis to give 1,2,3-triphenylhexane-1,5-dione (**5b**) in 46% yield by a *retro*-aldol ring cleavage, and 3,4,5-triphenylcyclohex-2-en-1-one **6b** in 42% yield) by subsequent aldol-cyclization/dehydration (*Scheme 2*).

Irradiation of 1,1-diphenylethene (**2b**) and the B-complexes **1a–c** under conditions similar to those used for *trans*-stilbene (**2a**) gave two isomers of the cyclobutane derivatives, *i.e.* **7b**,**c** and **8b**,**c** by [2 + 2] photoaddition (*Scheme 3* and *Table 2*). Product yields were remarkably lower than in the case of *trans*-stilbene, in particular, substrate **1a** did not react. The ratios of the amounts of **7** and **8** were approximately equal. These cyclobutane photoadducts **7** and **8** are regioisomers at the position of addition to 1,1-diphenylethene (**7**: head-to-head; **8**: head-to-tail). This position was determined from the coupling of the protons of the cyclobutane ring in the ^{1}H-NMR spectra (**7b**: J = 8.8 Hz (δ 3.64); **7c**: J = 9.5 Hz (δ 4.01); **8b**: *s* at δ 4.55; **8c**: *s* at δ 4.83).

Scheme 2



Scheme 3[a])



[a]) For R^1 and R^2, see *Table 2*.

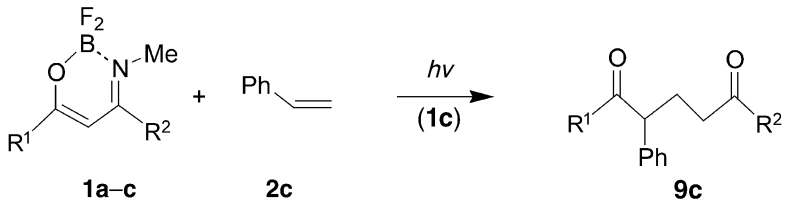
Table 2. *Photocycloaddition of B-Complexes* **1a**–**c** *with 1,1-Diphenylethene* (**2b**)

	R^1	R^2	Products		Recovered **1**
			7	**8**	
1a	Me	Me	–	–	97%
1b	Ph	Me	10%	7%	74%
1c	Ph	Ph	19%	18%	58%

Irradiation of styrene (**2c**) with the B-complexes **1a**–**c** under conditions similar to those used for *trans*-stilbene (**2a**) gave only the 1,5-diketone derivative **9c** (*Scheme 4*, *Table 3*), no products being isolated from **1a** and **1b**, *i.e.*, the product yield decreased even more than in case of **2b** with respect to **2a**. Diketone **9c** is derived by a *retro*-aldol ring cleavage from the head-to-head (not the head-to-tail) cyclobutane adduct, as it is the case for 1,3-diketones in the well-known *de Mayo* reaction.

Irradiation of the α-methylstyrene (=2-methylprop-1-ene; **2d**) and the B-complexes **1a**–**c** under conditions comparable to those used for *trans*-stilbene (**2a**) gave the cyclobutane derivatives (**10b**,**c**, **11b**,**c**, and **12b**, the azetidine derivative **13b**, and the 1,5-diketone **14c** (*Scheme 5*, *Table 4*)). The product yields are much higher than in the case of 1,1-diphenylethene (**2b**). The head-to-head adducts **10** and **11** are present in greater amounts than the head-to-tail adduct **12**, and compounds **10** with *cis*-positioned Ph groups are much more abundant than the corresponding *trans*-isomers **11**. The

Scheme 4[a])

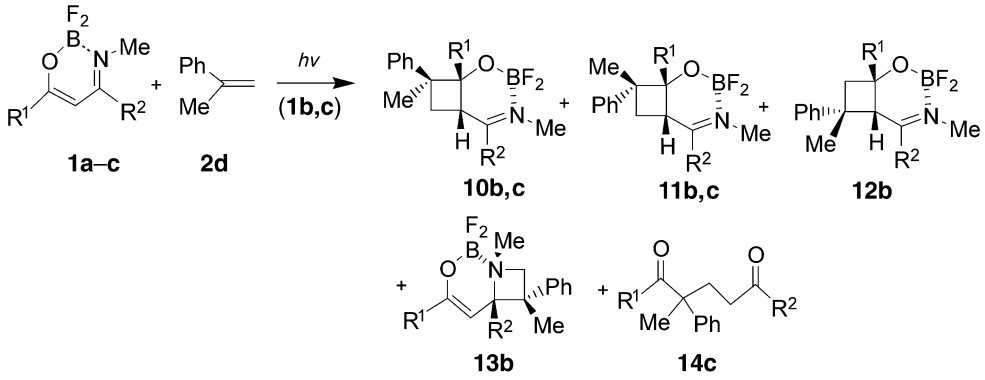


[a]) For R^1 and R^2, see *Table 3*.

Table 3. *Photocycloaddition of B-Complexes* **1a**–**c** *with Styrene* (**2c**)

	R^1	R^2	Product **9**	Recovered **1**
1a	Me	Me	–	*ca.* 100%
1b	Ph	Me	–	65%
1c	Ph	Ph	27%	53%

Scheme 5[a])



[a]) For R^1 and R^2, see *Table 4*.

Table 4. *Photocycloaddition of B-Complexes* **1a**–**c** *with 1-Methylstyrene* (**2d**)

	R^1	R^2	Products					Recovered **1**
			10	**11**	**12**	**13**	**14**	
1a	Me	Me	–	–	–	–	–	*ca.* 100%
1b	Ph	Me	14%	8%	17%	2%	–	52%
1c	Ph	Ph	28%	5%	–	–	26%	27%

configuration of these products was determined from the coupling of the methine proton of the cyclobutane ring in the ^{1}H-NMR spectra. (**10b**: $J = 6.3$, 11.0 Hz (δ 3.43); **11b**: $J = 9.7$ Hz (δ 3.83); **10c**: $J = 6.6$, 11.6 Hz (δ 3.86); **11c**: $J = 9.3$ Hz ($\delta = 3.10$)). The *cis*/*trans* forms were distinguished by the presence or absence of a cross-peak between

the Me protons and the methine proton in the NOESY plots (**11b**: δ 1.11–3.83; **11c**: δ 1.10–3.10; **12b**: δ 1.92–3.72). In the case of **1c**, a considerable amount of 1,5-diketone **14c** derived from the head-to-head cyclobutane adduct was obtained. As in the case of *trans*-stilbene (**2a**), a small amount of the azetidine derivative **13b** was obtained.

Discussion. – The presented photocycloadditions revealed some interesting features: *i*) The yields of the photoproducts are governed by both the reduction and the oxidation potentials of the substrates. *ii*) The stereochemistry of the reactions shows high regio- and stereoselectivity. The structures of the products have sterically unfavorable *cis*- or *endo*-configuration. *iii*) The formation of the azetidine derivatives is encountered less frequently than that of the cyclobutane derivatives. *iv*) In some [2 + 2] photoadducts, a *retro*-aldol reaction occurs, producing the 1,5-diketones. Some of these phenomena (*i*)–*iii*)) may be readily interpreted by assuming the presence of an adduct (intermediate) such as the B-complex **1**/arylalkene **2** complex, *i.e.*, as an exciplex [7][8] produced *via* a photoinitiated electron-transfer reaction. The difluoroboron complex is known to possess a lower reduction potential than that of the parent didentate ligand [9], and those of **1a**–**c** are lower by 0.4–0.5 V. The oxidation and reduction potentials of the B-complexes **1a**–**c**, the parent didentate ligands **1a′**–**c′**, and the arylalkenes **2a**–**d** are summarized in *Tables 5* and *6*. With an increasing number of phenyl groups, the potentials of **1** decrease. Although the parent didentate ligands **1a′**–**c′** are not photoreactive, their complexes **1a**–**c** are reactive. Thus, the difluoroboron complexes are used as they are the stronger electron acceptors. The ease of adduct formation suggests a high reactivity, in the order **1a** < **1b** < **1c**. On other hand, the oxidation potential of *trans*-stilbene (**2a**) is lower than that of the other arylalkenes **2b**–**d** by *ca.* 0.3 V, and its high reactivity is consistent with the adduct yields. The interaction occurs between the excited difluoroboron complex as the electron acceptor and the arylalkenes as the electron donor. That is, as described in *Weller*'s equation [10]

Table 5. *Reduction Potentials of the B-Complexes* **1a**–**c** *and of Their Parent Didentate Ligands* **1a′**–**c′** *by Cyclic Voltammetry*[a])

B-Complex	1st Wave	2nd Wave	Parent ligand	1st Wave	2nd Wave
1a	– 2.42	–	**1a′**	– 2.80	–
1b	– 2.00	– 2.62	**1b′**	– 2.55	– 2.81
1c	– 1.81	– 2.36	**1c′**	– 2.25	– 2.44

[a]) Conditions: 1 mM **1**, MeCN, $(Et_4N)ClO_4$ (0.05M), glassy carbon cathode, reference electrode Ag/Ag^+, $25 \pm 0.1°$.

Table 6. *Oxidation Potentials of the Arylalkenes* **2a**–**d** *by Cyclic Voltammetry*[a])

	trans-Stilbene (**2a**)	1,1-Diphenylethene (**2b**)	Styrene (**2c**)	α-Methylstyrene (**2d**)
Peak potential [V]	1.21	1.48	1.57	1.45

[a]) Conditions: 1 mM **2**, MeCN, $(Et_4N)ClO_4$ (0.05M), glassy carbon cathode, reference electrode Ag/Ag^+, $25 \pm 0.1°$.

(*Eqn. 1*), a one-electron transfer from a donor to an excited acceptor quantitatively accounts for the stabilization. *Weller*'s classic empirical analysis of exciplex association in terms of the excitation energies and redox properties of the partners provides a good guide to the tendency of any photochemical system to undergo exciplex formation; for this process in hydrocarbon solvent, *Eqn. 1* holds.

$$\Delta H = \Delta E_{0,0} - [E^{ox}_{1/2}\,(D) - E^{red}_{1/2}\,(A) + 0.13\ V] \quad (1)$$

The cyclobutane derivatives **3b**,**c** and **10b**,**c**, which are the major products (*Tables 1* and *4*), have a sterically unfavorable configuration between Ph–C(1) and Ph–C(4). The product structures suggest that they arise from stable exciplexes possessing a sandwich-type structure with strong π-orbital overlap between the aromatic moieties of both compounds, as illustrated in the *Figure* [11][1]). In other words, the rule of conservation of orbital symmetry, commonly known as the *Woodward–Hoffmann* rule [12], plays an important role in determining the pathway of cycloaddition. Because of the strong π-orbital overlap, the reaction of the B-complexes **1b**,**c** with *trans*-stilbene (**2a**) gives the cyclobutane derivatives **3b**,**c** as the major products (*Scheme 1*). In contrast, each of the reactions of 1,1-diphenylethene (**2b**) and α-methylstyrene (**2d**) yields the regioisomeric cylcobutane derivatives **8b**,**c** and **12b** (*Schemes 3* and *5*, resp.). These reactions suggest that the existence of a maximum secondary orbital overlap influences the stereochemistry of the additions [13]. The *Figure* demonstrates the overlap between Ph–C(3) of the *trans*-stilbene (**2a**) and Ph–C(5) of the B-complex **1c**. The degree of stereoselectivity seems to depend on the extent of π-orbital overlap in the exciplex. For example, the photocycloaddition of 2-naphthonitrile with alkyl vinyl ethers gives both *endo*- and *exo*-cycloadducts [14]. The photoaddition of furan to 1-naphthonitrile also gives a [4 + 4] cycloadduct with an *anti*-configuration, but that of 2-naphthonitrile occurs in the *syn*-direction to produce a cage-like compound [15]. These data suggest that the flexibility of the structure of the exciplexes may be due to the role that dipole–dipole interactions, the polarity, and the crowding of the exciplex play in the orientation of cycloaddition [16].

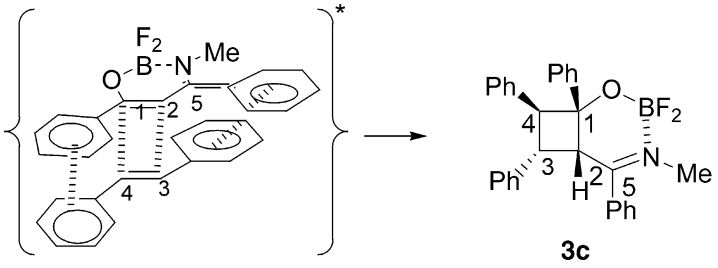


Figure. *Maximum-orbital-overlap 'sandwich' model for the* **1c**–**2a** *Exciplex*

[1]) Exciplexes with olefins are assumed to be formed and act as the discrete intermediates in the photocycloaddition although, unfortunately, the corresponding exciplex spectral bands have not been detected.

In the described reaction, a number of different stereoisomers were obtained. However, in most singlet-state reactions, the configuration of the olefins is retained in the cycloadduct [8]. In other words, the major products (*ca.* 90%) derived from the *cis*- and *trans*-olefins are cyclobutanes with the aryl substituents *endo* to the aromatic moieties. Furthermore, *Farid* and co-worker [17] reported that a reaction of singlet-excited phenanthrene with fumarate ester gave *trans*-cyclobutane derivatives together with oxetane derivatives, but triplet-exciplexes gave both *trans*- and *cis*-cyclobutane derivatives. Therefore, the present reaction may take place *via* a singlet-exciplex state as does a similar photoaddition of the difluoro(1,3-dionato)boron complex to olefins [9]:

B-Complex + *trans*-stilbene (**2a**) $\rightarrow$ ^{1}(B-Complex$^-$ – TS$^+$)* $\rightarrow$ azetidine **4** + cyclobutane **3**

It is well known that 3-amino-alk-2-en-1-ones exist in an aminoenone $\rightleftharpoons$ iminoenal tautomer equilibrium [18]. X-Ray analysis of the B-complex (**1a**–**c**) has established that the 6-membered chelate ring shows a shift to an enol form such as (O)–C=C– is 1.367(7) Å, (N)–C=C– is 1.404(8) Å, and (C)–C=N– is 1.301(6) Å for **1c** [19]. The structures of the photoaddition products suggest that the excited B-complexes **1a**–**c** react in the enolato form. Therefore, in the photoaddition, not only the cyclobutane derivative but also the azetidine derivative should be obtained. The formation of the azetidine derivatives **4a**–**c** and **13b** is interesting, because it is known that the photoaddition of the singlet state of rigid-framed cyclohex-2-en-1-one yields the oxetane [17]. Also, there are a few example of the formation of azetidine by a photoreaction [4].

We then examined and rationalized the reactivity and the stereochemistry by the FMO[2]). The energy gap between the frontier orbitals indicates that the most favorable interaction occurs between the LSOMO of the B-complexes **1a**–**c** in the singlet state and the HOMO of the arylalkenes **2a**–**d** (*Table 7*). Furthermore, the atomic

Table 7. *Energy Gap between LSOMO of* **1** *and HOMO of* **2**, *and HSOMO of* **1** *and LUMO of* **2** *in the Singlet State*

B-Complex	Arylalkene	Energy gap [eV]	
		LSOMO–HOMO	HSOMO–LUMO
1a	**2a**	2.156	3.206
	2b	2.659	3.743
	2c	2.769	3.811
	2d	2.578	3.843
1b	**2a**	1.991	3.336
	2b	2.494	3.873
	2c	2.604	3.941
	2d	2.413	3.973
1c	**2a**	1.671	4.158
	2b	2.174	4.693
	2c	2.284	4.763
	2d	2.093	4.795

[2]) Frontier MO (FMO) calculations were achieved by the PM3 method contained in the Win MOPAC program (Ver. 3.0).

Table 8. *Frontier Molecular Orbitals* (LSOMO) *of the B-Complexes*

B-Complex		Coefficients of pπ-orbital			
		C(1)	C(2)	C(3)	N
1a	singlet	– 0.189	– 0.495	– 0.080	0.604
	triplet	– 0.615	– 0.109	– 0.012	– 0.237
1b	singlet	– 0.164	– 0.572	– 0.112	– 0.551
	triplet	– 0.156	– 0.552	– 0.077	– 0.484
1c	singlet	– 0.002	– 0.106	0.006	– 0.185
	triplet	0.190	0.533	0.108	– 0.058

coefficients of the N=C bond and the C=C bond are similar for **1a** and **1b** (*Table 8*). Therefore, we concluded that the observed regioselectivity and reactivity could be nicely explained. Furthermore, as in the previous discussion, the process *via* the singlet exciplex is consistent with the atomic coefficients, especially in the case of the singlet state of **1c**.

The interesting characteristic of the present photocycloaddition is that it gives the cyclobutane derivative *via* the [2 + 2] photoadduct. This is in sharp contrast to the case of 1,3-diketones (known as *de Mayo* reaction) [1]; moreover, the difluoroboron complex yields no cyclobutane but, instead, produces 1,5-diketones **6** [6][9] from the cyclobutane by a *retro*-aldol cleavage. This result seems to stem from a difference in the coordination strength of the B-atom. The B-atom possesses a vacant p-orbital, which is stabilized by pπ–pπ conjugation to the neighboring lone pair of the hetero atoms. The basicity of the N-atom is stronger than that of the O-atom; furthermore, the N-atom receives a contribution from the Me group. Therefore, the coordination bond between the N-atom and the B-atom is stronger than that between the N-atom and the O-atom, and may overcome the strain energy possessed by the cyclobutane ring.

Experimental Part

1. *General*. The aminoenones and their B-complexes **1** were prepared and described previously [7][19][20]. IR Spectra: KBr tablets; *Hitachi I-2000*; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Jeol FX-90Q* and *Bruker AC-250* spectrometers, $CDCl_3$ solns.; δ in ppm rel. to $SiMe_4$ as the internal reference, *J* in Hz. MS: *ESCO EMD-05A*; in *m*/*z*. M.p.: *Yanaco* micro-hot-plate apparatus; uncorrected.

2. *Photocycloaddition: General Procedure.* A soln. of B-complex **1** (0.5 mmol) in MeCN (25 ml) and the aryl alkene **2** (5 mmol) in a *Pyrex* tube were degassed with N_2 and irradiated at 0° for 10 h. Then the mixture was evaporated and the residue chromatographed (silica gel, benzene Et_2O 1:0 → 4:1).

3. *Photoaddition of* **1a** *with* trans-*Stilbene* (**2a**). *Difluoro[1-methyl*-c-*2-[1-(methylimino-*κN*)ethyl]*-c-*3*,t-*4-diphenylcyclobutan*-r-*1-olato-*κO*]boron* (**3a**): M.p. 166.0–167.0°. IR: 1668, 1168, 1068, 1492, 1440, 1376, 896, 702. ^{1}H-NMR ($CDCl_3$): 1.18 (*s*, 3 H); 1.44 (*s*, 3 H); 3.23 (*s*, 3 H); 3.41 (*d*, *J* = 11.0, 1 H); 4.02 (*t*, *J* = 10.2, 1 H); 4.81 (*d*, *J* = 11.7, 1 H); 7.26 (*s*, 5 H); 7.33 (*s*, 5 H). ^{13}C-NMR ($CDCl_3$): 22.4; 24.1; 35.3; 41.0; 51.5; 55.8; 71.7; 126.5; 127.1; 128.1; 128.3; 129.3; 137.1; 138.2; 184.3. MS: 341 (M^+), 322 ([M – F]$^+$), 275 ([M – BF_2OH]$^+$), 260, 205. Anal. calc. for $C_{20}H_{22}BF_2NO$: C 70.40, H 6.50, N 4.11; found: C 70.29, H 6.36, N 4.11.

*Difluoro[(1*Z*)-1-(*t-*1,2-dimethyl-c-3*,t-*4-diphenylazetidine*-r-*2-yl-*κN^1*)prop-1-en-2-olato-*κO*]boron* (**4a**): M.p. 156.5–157.5°. IR: 1680, 1384, 1226, 1194, 1126, 918, 900, 758, 700. ^{1}H-NMR ($CDCl_3$): 1.55 (*s*, 3 H); 1.86 (*s*, 3 H); 2.46 (*s*, 3 H); 3.83 (*s*, 1 H); 4.49 (*d*, *J* = 12, 1 H); 5.82 (*d*, *J* = 12.0, 1 H); 7.11–7.57 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 21.7; 22.8; 32.4; 52.5; 66.3; 72.3; 98.7; 128.0; 128.7; 128.9; 129.6; 129.7; 129.9; 131.1; 134.5; 151.2. MS: 341 (M^+), 275 ([M – BF_2OH]$^+$), 260, 221, 206. Anal. calc. for $C_{20}H_{22}BF_2NO$: C 70.40, H 6.50, N 4.11; found: C 70.62, H 6.63, N 4.12.

4. *Photoaddition of* **1b** *with* trans-*Stilbene* (**2a**). *Difluoro{*c-*2-[1-(methylimino-*κN*)ethyl]-1,*c-*3,*t-*4-triphenylcyclobutan-*r-*1-olato-*κO*}boron* (**3b**): M.p. 198.5–200.5°. IR: 1670, 1498, 1450, 1374, 1166, 1062, 898, 758. ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, 3 H); 3.24 (*s*, 3 H); 4.07 (*d*, *J* = 10.5, 1 H); 4.33 (*t*, *J* = 10.3, 1 H); 5.11 (*d*, *J* = 11.2, 1 H); 6.95–7.49 (*m*, 15 H). ^{13}C-NMR ($CDCl_3$): 22.4; 35.1; 42.4; 54.1; 54.7; 75.8; 125.7; 126.1; 126.9; 127.3; 127.7; 128.1; 128.2; 129.2; 137.2; 137.9; 141.5; 183.8. MS: 403 (M^+), 383, 355, 260, 222. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.47; found: C 74.42, H 6.07, N 3.52.

*Difluoro[(1*Z*)-2-(*t*-1,2-dimethyl-*c*-3,t-4-diphenylazetidin-*r*-2-yl-*κN^1*)1-phenylethen-1-olato-*κO*]boron* (**4b**): M.p. 152.5–153.5°. IR: 1652, 1450, 1242, 1140, 1104, 922, 754, 696. ^{1}H-NMR ($CDCl_3$): 1.66 (*s*, 3 H); 2.52 (*s*, 3 H); 4.59 (*q*, *J* = 11.5, 1 H); 4.59 (*s*, 1 H); 5.94 (*d*, *J* = 11.5, 1 H); 7.23–7.57 (*m*, 15 H). ^{13}C-NMR ($CDCl_3$): 22.6; 32.3; 52.9; 66.5; 72.5; 98.3; 125.5; 128.1; 128.5; 128.7; 128.8; 129.6; 129.8; 130.9; 134.1; 136.2; 151.2. MS: 403 (M^+), 390, 337, 336, 261, 260. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.47; found: C 74.56, H 6.00, N 3.54.

5. *Photoaddition of* **1c** *with* trans-*Stilbene* **2a**. *Difluoro{*c-*2-[(methylimino-*κN*)(phenyl)methyl]-1,*c-*3,*t-*4-triphenylcyclobutan-*r-*1-olato-*κO*}boron* (**3c**): M.p. 165.0–166.0°. IR: 1656, 1498, 1448, 1152, 1068, 896, 770, 702. ^{1}H-NMR ($CDCl_3$): 3.25 (*s*, 3 H); 4.23 (*t*, *J* = 10.8, 1 H); 4.58 (*d*, *J* = 10.8, 1 H); 5.07 (*d*, *J* = 10.8, 1 H); 6.48–6.51 (*m*, 2 H); 6.91–7.55 (*m*, 18 H). ^{13}C-NMR ($CDCl_3$): 37.2; 43.7; 52.3; 56.5; 77.6; 125.9; 126.0; 126.3; 126.8; 127.5; 127.6; 127.8; 128.1; 128.6; 128.8; 129.1; 130.8; 131.8; 138.1; 138.4; 142.1; 181.7. MS: 399 ([$M - BF_2OH$]$^+$), 382, 322, 173, 105. Anal. calc. for $C_{30}H_{26}BF_2NO$: C 77.23, H 5.63, N 3.01; found: C 77.23, H 5.40, N 3.13.

*Difluoro[(1*Z*)-2-(*t*-1-methyl-2,*c*-3,t-4-triphenylazetidin-*r*-2-yl-*κN^1*)-1-phenylethen-1-olato-*κO*]boron* (**4c**): M.p. 130.0–132.0°. IR: 1650, 1498, 1450, 1358, 1154, 1102, 926, 754, 694. ^{1}H-NMR ($CDCl_3$): 2.02 (*s*, 3 H); 4.81 (*s*, 1 H); 5.52 (*d*, *J* = 11.3, 1 H); 5.98 (*d*, *J* = 11.3, 1 H); 7.23–7.97 (*m*, 20 H). ^{13}C-NMR ($CDCl_3$): 34.3; 47.1; 66.3; 77.4; 99.1; 125.6; 128.1; 128.2; 128.6; 128.8; 128.9; 129.2; 129.6; 129.9; 130.1; 130.2; 131.0; 134.6; 136.2; 150.9; 151.2. MS: 399 ([$M - BF_2OH$]$^+$), 382, 370, 322, 307. Anal. calc. for $C_{30}H_{26}BF_2NO$: C 77.43, H 5.63, N 3.01; found: C 77.56, H 6.00, N 3.47.

6. *Hydrolysis of the Cyclobutane Derivative* **3b**. To **3b** (1 mg, 0.13 mmol) in MeOH (30 ml), 10% aq. NaOH soln. (0.05 ml) was added. The mixture was refluxed for 2 h and then quenched with 5% aq. HCl soln. The mixture was evaporated and the residue chromatographed (silica gel, hexane/acetone 6:1): **5b** (46%) and **6b** (42%).

Data of 1,2,3-Triphenylhexane-1,5-dione (**5b**): M.p. 83.5–84.0°. IR: 1710, 1680, 1450, 1358, 1266, 864, 698. ^{1}H-NMR ($CDCl_3$): 2.00 (*s*, 3 H); 2.49 (*dd*, *J* = 4.3, 16.0, 1 H); 2.66 (*dd*, *J* = 9.8, 16.0, 1 H); 4.20 (*ddd*, *J* = 4.3, 9.8, 10.8, 1 H); 5.11 (*d*, *J* = 10.8, 1 H); 7.02–7.48 (*m*, 13 H); 7.92–8.06 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 30.1; 45.2; 48.2; 59.0; 126.4; 126.9; 128.0; 128.3; 128.5; 128.8; 133.0; 136.8; 137.0; 141.1; 199.2; 206.8. MS: 342 (M^+), 341, 284, 283, 236. Anal. calc. for $C_{24}H_{22}O$: C 84.18, H 6.72%; found: C 84.16, H 6.74.

Data of 3,4,5-Triphenylcyclohex-2-en-1-one (**6b**): M.p. 107.4–108.2°. IR: 1674, 1448, 1268, 768, 698. ^{1}H-NMR ($CDCl_3$): 3.45 (*d*, *J* = 8.0, 1 H); 3.47 (*d*, *J* = 5.9, 1 H); 4.10–4.40 (*m*, 1 H); 5.00 (*d*, *J* = 10.5, 1 H); 7.02 (*s*, 5 H); 7.06 (*s*, 5 H); 7.23–7.50 (*m*, 6 H); 7.83–8.07 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 43.5; 45.8; 50.4; 126.4; 127.0; 128.0; 128.1; 128.2; 128.3; 128.5; 128.6; 128.7; 129.0; 129.2; 129.3; 132.8; 133.1; 137.0; 137.2; 137.3; 141.1; 198.5; 199.5. MS: 404, 299, 298, 284, 283. Anal. calc. for $C_{29}H_{24}O_2$: C 86.11, H 5.98; found: C 86.19, H 5.93.

7. *Photoaddition of* **1b** *with 1,1-Diphenylethene* (**2b**). *Difluoro{*c-*4-[1-(methylimino-*κN*)ethyl]-1,2,2-triphenylcyclobutan-*r-*1-olato-*κO*}boron* (**7b**): M.p. 155.3–156.0°. IR: 1682, 1494, 1440, 1142, 888, 760, 700. ^{1}H-NMR ($CDCl_3$): 2.06 (*s*, 3 H); 2.92 (*s*, 3 H); 2.97 (*t*, *J* = 8.8, 1 H); 3.55 (*t*, *J* = 8.8, 1 H); 3.64 (*t*, *J* = 8.8, 1 H); 6.85–7.31 (*m*, 15 H). ^{13}C-NMR ($CDCl_3$): 20.2; 34.6; 34.8; 41.0; 59.7; 82.1; 125.6; 126.0; 126.9; 127.7; 127.8; 127.9; 128.0; 128.1; 141.6; 141.7; 146.1; 182.3. MS: 363 (M^+), 347, 223. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.41; found: C 74.16, H 6.24, N 3.45.

*Difluoro{*c-*2-[1-(methylimino-*κN*)ethyl]-1,3,3-triphenylcyclobutan-*r-*1-olato-*κO*}boron* (**8b**): M.p. 166.0–167.0°. IR: 1682, 1498, 1446, 1160, 1132, 1078, 1056, 948, 892, 758, 704. ^{1}H-NMR ($CDCl_3$): 1.66 (*s*, 3 H); 2.98 (*s*, 3 H); 3.03 (*d*, *J* = 13.2, 1 H); 3.74 (*d*, *J* = 13.2, 1 H); 4.55 (*s*, 1 H); 7.13–7.46 (*m*, 15 H). ^{13}C-NMR ($CDCl_3$): 20.9; 34.7; 51.2; 55.6; 57.0; 71.9; 125.1; 126.9; 127.0; 127.1; 127.3; 128.0; 128.2; 129.0; 129.2; 144.0; 146.8; 147.1; 180.9. MS: 403 (M^+), 402, 347, 322, 283, 282, 260. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.47; found: C 74.50, H 6.12, N 3.52.

8. *Photoaddition of* **1c** *with 1,1-Diphenylethene* (**2b**). *Difluoro{*c-*4-[(methylimino-*κN*)(phenyl)methyl]-1,2,2-triphenylcyclobutan-*r-*1-olato-*κO*}boron* (**7c**): M.p. 166.0–168.0°. IR: 1672, 1496, 1446, 1144, 1108, 892, 728, 698. ^{1}H-NMR ($CDCl_3$): 3.08 (*s*, 3 H); 3.19 (*t*, *J* = 10.5, 1 H); 3.46 (*dd*, *J* = 9.5, 10.5, 1 H); 4.01 (*t*, *J* = 9.5, 1 H); 6.85–7.62 (*m*, 20 H). ^{13}C-NMR ($CDCl_3$): 35.4; 37.2; 41.3; 59.9; 83.0; 125.6; 125.9; 126.2; 126.9; 127.1; 127.2; 127.8; 128.0; 129.7; 131.6; 132.8; 141.6; 146.0; 181.6. MS: 446, 398, 322. Anal. calc. for $C_{30}H_{26}BF_2NO$: C 77.43, H 5.63, N 3.01; found: C 77.50, H 5.56, N 3.03.

*Difluoro{*c*-2-[(methylimino-*κ*N)(phenyl)methyl]-1,3,3-triphenylcyclobutan-*r*-1-olato-*κ*N}boron* (**8c**): M.p. 144.5–146.0°. IR: 1662, 1496, 1446, 1354, 1084, 942, 882, 758, 702. ^{1}H-NMR ($CDCl_3$): 3.02 (*s*, 3 H); 3.18 (*d*, *J* = 13.4, 1 H); 3.72 (*d*, *J* = 13.4, 1 H); 4.83 (*s*, 1 H); 6.32–6.41 (*m*, 2 H); 6.87–6.90 (*m*, 2 H); 7.21–7.36 (*m*, 13 H); 7.42–7.53 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$): 37.3; 52.1; 56.5; 57.8; 72.8; 125.2; 126.5; 126.7; 127.1; 127.2; 127.5; 128.0; 128.2; 128.6; 128.9; 130.0; 131.5; 132.1; 144.4; 146.9; 147.4; 180.7. MS: 400, 399, 322, 321, 307. Anal. calc. for $C_{30}H_{26}BF_2NO$: C 77.43, H 5.63, N 3.01; found: C 77.29, H 5.70, N 3.17.

9. *Photoaddition of* **1c** *with Styrene* (**2c**). *1,2,5-Triphenylpentane-1,5-dione* (**9c**): M.p. 93.5–94.0°. IR: 1686, 1676, 1450, 1246, 1224, 1180, 754, 698. ^{1}H-NMR ($CDCl_3$): 2.35–2.21 (*m*, 1 H); 2.52–2.66 (*m*, 1 H); 2.85–3.05 (*m*, 2 H); 4.78 (*t*, *J* = 7.3, 1 H); 7.17–7.55 (*m*, 11 H); 7.89 (*d*, *J* = 7.2, 2 H); 7.97 (*d*, *J* = 7.2, 2 H). ^{13}C-NMR ($CDCl_3$): 28.3; 36.0; 52.5; 127.2; 128.0; 128.3; 128.5; 128.7; 129.0; 132.9; 133.0; 136.7; 136.9; 139.2; 199.6; 199.8. MS: 328 (M^+), 327, 223, 222, 209, 195. Anal. calc. for $C_{23}H_{20}O_2$: C 84.12, H 6.14; found: C 84.16, H 6.33.

10. *Photoaddition of* **1b** *with 2-Phenylprop-1-ene* (**2d**). *Difluoro{*c*-2-methyl-*c*-4-[1-(methylimino-*κ*N)ethyl]-1,*t*-2-diphenylcyclobutan-*r*-1-olato-*κ*N}boron* (**10b**): M.p. 165.0–166.5°. IR: 1676, 1452, 1174, 1134, 1068, 906, 734, 700. ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, 3 H); 2.21 (*s*, 3 H); 2.28 (*dd*, *J* = 6.3, 11.0, 1 H); 3.17 (*t*, *J* = 11.0, 1 H); 3.43 (*dd*, *J* = 6.3, 11.0, 1 H); 6.88–7.26 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 19.3; 27.2; 34.2; 34.8; 44.2; 53.0; 79.5; 125.4; 126.3; 126.5; 127.1; 127.5; 144.0; 144.8; 183.7. MS: 340 (M^+), 322, 276, 260, 221. Anal. calc. for $C_{20}H_{22}BF_2NO$: C 70.40, H 6.50, N 4.10; found: C 70.35, H 6.74, N 4.15.

*Difluoro{*t*-2-methyl-*c*-4-[1-(methylimino-*κ*N)ethyl]-1*c*-2-diphenylcyclobutan-*r*-1-olato-*κ*O}boron* (**11b**): M.p. 172.0–173.0°. IR: 1674, 1498, 1446, 1368, 1142, 1082, 948, 890, 768, 702. ^{1}H-NMR ($CDCl_3$): 1.11 (*s*, 3 H); 2.16 (*s*, 3 H); 2.37 (*t*, *J* = 9.7, 1 H); 2.94 (*t*, *J* = 9.7, 1 H); 3.09 (*s*, 3 H); 3.83 (*t*, *J* = 9.4, 1 H); 7.19–7.49 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 19.9; 26.8; 34.5; 35.7; 49.4; 80.6; 125.9; 126.7; 127.0; 127.2; 127.6; 127.8; 141.9; 144.3; 182.6. MS: 340 (M^+), 322, 260, 258, 221, 203. Anal. calc. for $C_{20}H_{22}BF_2NO$: C 70.40, H 6.50, N 4.10; found: C 70.18, H 6.46, N 4.14.

*Difluoro{*t*-3-methyl-*c*-2-[1-(methylimino-*κ*N)ethyl]-1,*c*-3-diphenylcyclobutan-*r*-1-olato-*κ*O}boron* (**12b**): M.p. 155.0–156.0°. IR: 1684, 1448, 1110, 1076, 904, 758, 702. ^{1}H-NMR ($CDCl_3$): 1.47 (*s*, 3 H); 1.92 (*s*, 3 H); 2.37 (*d*, *J* = 13.4, 1 H); 2.90 (*s*, 3 H); 3.25 (*d*, *J* = 13,4, 1 H); 3.72 (*s*, 1 H); 7.25–7.82 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 20.7; 29.2; 34.1; 42.2; 52.2; 71.4; 125.3; 127.1; 127.5; 128.2; 128.4; 142.9; 146.8; 181.0. MS: 341 (M^+), 275, 260, 223, 203, 145. Anal. calc. for $C_{20}H_{22}BF_2NO$: C 70.40, H 6.50, N 4.10; found: C 70.29, H 6.46, N 4.09.

*Difluoro[(1Z)-1-(*t*-1,2,*t*-3-trimethyl-*c*-3-phenylazetidin-*r*-2-yl-*κ*N^1)-1-phenylethen-1-olato-*κ*O]boron* (**13b**): M.p. 152.5–153.5°. IR: 1658, 1446, 1358, 1226, 1178, 1110, 1060, 954, 920, 768, 702. ^{1}H-NMR ($CDCl_3$): 1.70 (*s*, 3 H); 1.83 (*s*, 3 H); 3.07 (*s*, 3 H); 3.28 (*d*, *J* = 10.95, 1 H); 4.63 (*s*, 1 H); 4.91 (*d*, *J* = 10.9, 1 H); 6.98–7.31 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 19.2; 27.9; 39.8; 50.0; 61.3; 75.3; 102.9; 125.5; 125.6; 126.7; 127.8; 128.4; 128.7; 136.5; 144.3; 149.7; 149.8; 181.2. MS: 341, 298, 275, 260, 223, 222, 118. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.47; found: C 74.56, H 6.00, N 3.54.

11. *Photoaddition of* **1c** *with 2-Phenylprop-1-ene* (**2d**). *Difluoro{*c*-2-methyl-*c*-4-[(methylimino-*κ*N)(phenyl)methyl]-1,*t*-2-diphenylcyclobutan-*r*-1-olato-*κ*O}boron* (**10c**): M.p. 164.5–165.2°. IR: 1668, 1448, 1346, 1144, 1022, 922, 768, 700. ^{1}H-NMR ($CDCl_3$): 1.58 (*s*, 3 H); 2.15 (*dd*, *J* = 6.6, 11.6, 1 H); 2.99 (*d*, *J* = 11.6, 1 H); 3.31 (*s*, 3 H); 3.86 (*dd*, *J* = 6.6, 11.6, 1 H); 6.78–7.63 (*m*, 15 H). ^{13}C-NMR ($CDCl_3$): 27.4; 34.5; 37.7; 44.1; 53.2; 80.1; 125.5; 125.6; 126.6; 127.4; 127.6; 129.7; 131.7; 132.1; 143.9; 144.8; 183.4. MS: 337, 322, 285, 258. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.47; found: C 74.41, H 6.14, N 3.55.

*Difluoro{*t*-2-methyl-*c*-4-[(methylimino-*κ*N)(phenyl)methyl]-1,*c*-2-diphenylcyclobutan-*r*-1-olato-*κ*O}boron* (**11c**): M.p. 164.5–165.2°. IR: 1668, 1448, 1346, 1144, 1022, 922, 768, 700. ^{1}H-NMR ($CDCl_3$): 1.10 (*s*, 3 H); 2.23 (*dd*, *J* = 9.3, 9.7, 1 H); 3.11 (*dd*, *J* = 9.2, 9.7, 1 H); 3.15 (*s*, 3 H); 4.13 (*dd*, *J* = 9.2, 9.7, 1 H); 7.20–7.40 (*m*, 4 H); 7.55–7.62 (*m*, 11 H). ^{13}C-NMR ($CDCl_3$): 22.3; 26.7; 36.2; 37.0; 39.6; 49.3; 80.9; 126.1; 126.6; 126.9; 127.4; 127.9; 129.6; 131.6; 132.9; 141.7; 144.0; 183.1. MS: 337, 322, 285, 258. Anal. calc. for $C_{25}H_{24}BF_2NO$: C 74.46, H 6.00, N 3.47; found: C 74.41; H 6.14; N 3.55.

2-Methyl-1,2,5-triphenylpentane-1,5-dione (**14c**): M.p. 99.5–100.0°. IR: 1682, 1448, 1240, 980, 744, 712. ^{1}H-NMR ($CDCl_3$): 1.66 (*s*, 1 H); 2.44–2.55 (*m*, 3 H); 2.79–2.88 (*m*, 2 H); 7.19–7.42 (*m*, 11 H); 7.48–7.52 (*m*, 2 H); 7.79–7.83 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 24.4; 34.3; 35.0; 54.4; 126.4; 128.2; 128.6; 129.2; 129.6; 127.2; 131.9; 132.9; 136.7; 137.0; 143.8; 199.9; 203.2. MS: 237 ([M – PhCO]$^+$), 223, 219, 204. Anal. calc. for $C_{24}H_{22}O_2$: C 84.18, H 6.48%; found. C 83.99, H 6.30.

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