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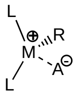
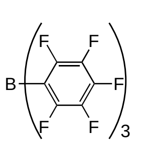
Organo-Lewis Acid Cocatalysts in Single-Site Olefin Polymerization—A Highly Acidic Perfluorodiboraanthracene**

Matthew V. Metz, David J. Schwartz,
Charlotte L. Stern, Peter N. Nickias, and
Tobin J. Marks*

For early transition metal single-site homogeneous olefin polymerization catalysts **I**[1], organo-Lewis acids such as alumoxanes and tris(perfluoroaryl)boranes (e.g., **II**–**IV**)[2] play a key role both in catalyst activation and in mechanistic understanding. For example, growing evidence indicates that the cation–anion pairing, as modulated by the steric and electronic characteristics of the cocatalyst/counter anion (A^- in **I**),[2, 3] can have a profound influence on polymerization and chain-transfer rates, enchainment stereochemistry, and catalyst stability.[2–4] With the goal of further modifying fluoroarylborane architecture to enhance Lewis acidity (multiple electron-deficient centers, conjugative negative-charge delocalization, open structure), we focused on the perfluorodiboraanthracene skeleton **V**,[5] for which calculations at the B3LYP/6-31++G** level indicate **Vb** to have about 10 kcal mol^{-1} greater affinity for CH_3^- than does $B(C_6F_5)_3$.[6] We communicate here the synthesis, characterization, and unusual properties of **Vb**, including significantly enhanced Lewis acidity and cocatalytic olefin polymerization activity.[7]


I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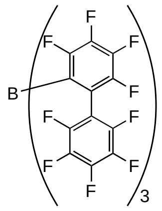
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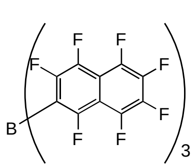
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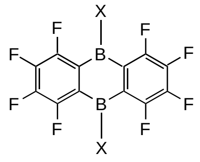
Va X = Cl
Vb X = C_6F_5

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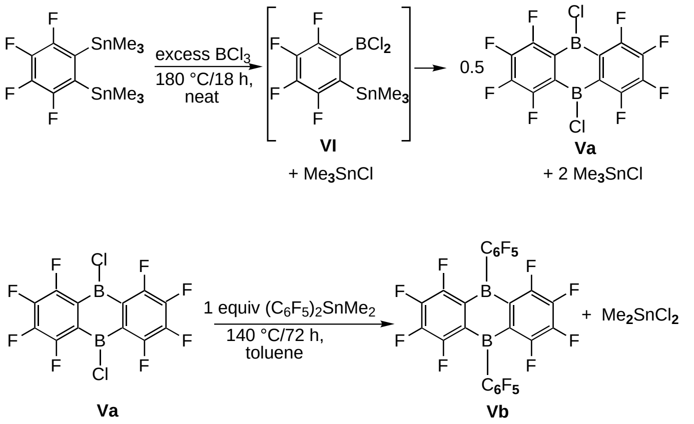
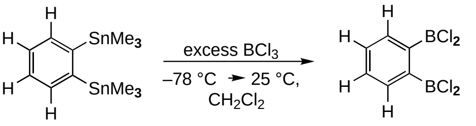
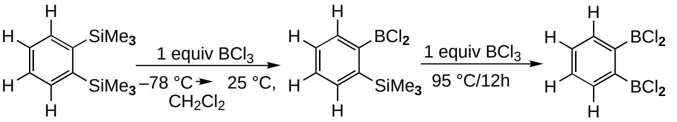
Parent dichlorodiboraanthracene **Va** was prepared by reaction of 1,2-$C_6F_4(SnMe_3)_2$[8] with BCl_3 (Scheme 1). Monosubstituted 1,2-$C_6F_4(SnMe_3)BCl_2$ (**VI**) is formed initially, and subsequent heating affords **Va** in high yield. No ^{19}F NMR signals for 1,2-$C_6F_4(BCl_2)_2$ were detected at any time during the reaction. In marked contrast, nonfluorinated 1,2-$C_6H_4(SnMe_3)_2$ is reported to undergo rapid metalloid metathesis with BCl_3 at 25 °C to yield 1,2-$C_6H_4(BCl_2)_2$[9] [Eq. (1)], and both $C_6H_4(SiMe_3)BCl_2$ and 1,2-$C_6H_4(BCl_2)_2$ are readily accessible from 1,2-$C_6H_4(SiMe_3)_2$ [Eq. (2)].[10] In the present case, the decreased nucleophilicity of the perfluoroaryl compound **VI** relative to the C_6H_4 analogue apparently disfavors the second electrophilic aromatic substitution/metalloid metathesis step relative to coupling to yield **Va**.



Scheme 1. Synthesis of diboraanthracenes **Va** and **Vb**.



(1)



(2)

Reaction of **Va** with one equivalent of $(C_6F_5)_2SnMe_2$ yields the diboraanthracene **Vb** as a pale yellow, air-sensitive crystalline solid (Scheme 1). The reaction requires prolonged heating but is very clean; the crude reaction mixture contains **Vb** in 95 % or greater purity. For selective B–Cl/B–C_6F_5 metathesis, $(C_6F_5)_2SnMe_2$ appears to be a general, mild reagent that effects little or no competing alkyl exchange.[11] In contrast, reaction of **Va** with two equivalents of LiC_6F_5 in pentane or diethyl ether affords a complex mixture of products, while reaction with two equivalents of $C_6F_5SnR_3$ (R = Me, *n*Bu) results in clean alkyl/chloride exchange, in preference to the desired Cl/C_6F_5 exchange.

Compound **Vb** was characterized by standard spectroscopic and analytical techniques (see Experimental Section) and by X-ray diffraction. The ^{19}F NMR spectrum reveals significant upfield displacements of the *o*-, *m*-, and *p*-C_6F_5 signals versus $B(C_6F_5)_3$ ($\Delta\delta = -5, -2, -10$, respectively), while the C_6F_4 signals are shifted considerably downfield of those of **Va** ($\Delta\delta = +5, +5$) and $B(C_6F_5)_3$. These data therefore suggest minimal π conjugative interaction of the C_6F_5 rings in **Vb** with the $(C_6F_4B)_2$ π system, which is rather electron-deficient.

In the solid-state structure of **Vb** (Figure 1),[12] the $(C_6F_4B)_2$ skeleton is planar, with an average atomic deviation from the mean plane of 0.013 Å. The C_6F_4 rings are bent slightly out of the central B_2C_4 plane, with an average inter-ring dihedral angle of 0.6°. As expected from steric considerations, the C_6F_5 rings are twisted out of the diboraanthracene plane; the crystallographically independent $(C_6F_4B)_2$/C_6F_5 twist angles are both 75°. All bond lengths and angles (Figure 1, caption) are within normal ranges for fluoroarylboranes[2], with the exception of a significant lengthening of the C1–C2 bond to 1.435(2) Å. While this may in part reflect withdrawal of π-bonding electron density from the C_6F_4 units by the electron-deficient boron centers, note that some elongation at this position is typically observed in anthracenes.[13]

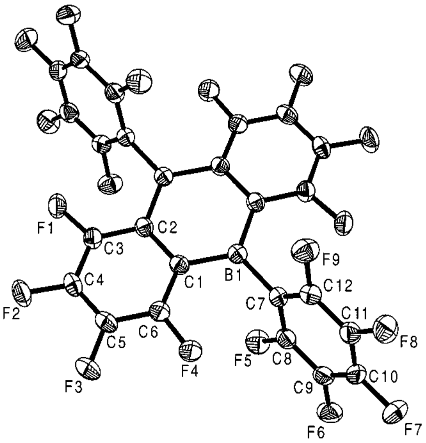


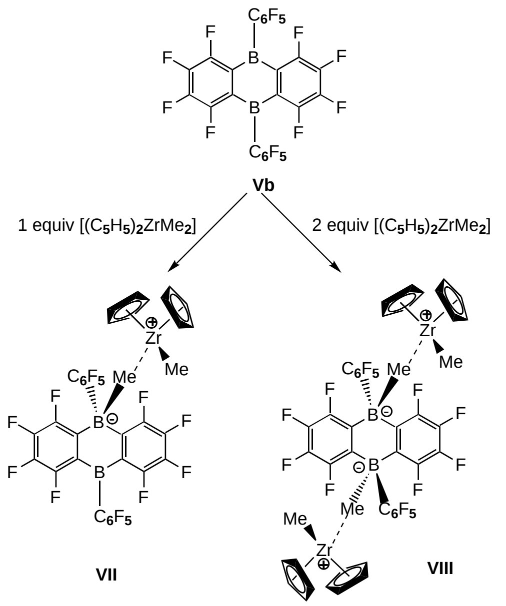
Figure 1. ORTEP diagram of **Vb** (50 % probability thermal ellipsoids). Selected bond lengths [Å] and angles [°] for one of the crystallographically independent molecules of **Vb** (corresponding distances/angles for the other molecule are very similar): B1-C1 1.554(2), C1-C2 1.435(2), B1-C2A 1.560(2) B1-C7 1.583(2), C2-C3 1.388(2), C3-C4 1.392(2), C4-C5 1.365(2), C5-C6 1.392(2), C1-C6 1.389(2); B1-C1-C2 120.2(1), C1-B1-C2A 119.6(2), C1-C2-B1A 120.1(1), C1-B1-C7 120.5(1), C2A-B1-C7 119.8(1).

In regard to the Lewis acidity of **Vb**, equilibration studies with $CH_3CN \cdot B(C_6F_5)_3$[2c] over a temperature range of 67 K in [D$_8$]toluene followed by van't Hoff analysis of the ^{19}F NMR data yield $\Delta H = +1.4(2)\ \mathrm{kcal\,mol^{-1}}$ and $\Delta S = -5.3(1)\ \mathrm{J\,K^{-}mol^{-}}$ for reaction (3). These data indicate that

$$CH_3CN \rightarrow \mathbf{Vb} + B(C_6F_5)_3 \underset{\text{toluene}}{\rightleftharpoons} \mathbf{Vb} + CH_3CN \rightarrow B(C_6F_5)_3 \quad (3)$$

Vb is a stronger Lewis acid than $B(C_6F_5)_3$ with respect to acetonitrile, while the negative ΔS suggests loss of degrees of freedom, consistent with greater steric congestion in $CH_3CN \cdot B(C_6F_5)_3$. The perfluorodiboraanthracene **Vb** is the strongest organo-Lewis acid synthesized to date, and the magnitude of the enthalpy of reaction with acetonitrile decreases in the order **Vb** [−18.5(2)] > **IV** [−17.8(2)][2c] > $B(C_6F_5)_3$ [−17.1(9)][2a] > **III** [−11.5(3) kcal mol^{-1}].[2a]

Reaction of **Vb** with metallocene dimethyl complexes such as $[(C_5H_5)_2ZrMe_2]$ proceeds with clean, instantaneous methyl anion abstraction to generate catalytically active (vide infra) cation–anion pairs (Scheme 2). Reaction with one equivalent of $[(C_5H_5)_2ZrMe_2]$ on an NMR-tube scale resulted in **VII**—the first mixed borane/borate metallocene catalyst. The ^1H and ^{19}F NMR data (see Experimental Section) indicate a static, unsymmetrical structure with an anionic BMe group. At 25 °C the spectrum[14] indicates that both BMe/B and ZrMe/BMe interchanges[2d,g] are slow on the NMR time scale, and distinct pairs of magnetically inequivalent C_6F_5 *ortho-* and *meta*-^{19}F nuclei indicate restricted rotation about the B−C_6F_5 bond. Reaction of **Vb** with two equivalents of $[(C_5H_5)_2ZrMe_2]$ results in instantaneous formation of symmetrical bis-borate **VIII** (see Scheme 2; both C_{2v} and C_{2h} idealized structures are possible). This is the first example of a bis-anion in cationic metallocene catalysis and demonstrates that borane/borate **VII** is sufficiently Lewis acidic to abstract a zirconocene methanide group. Again, room-temperature ^1H and ^{19}F NMR data (see Experimental Section) indicate a static structure, with slow ZrMe/BMe interchange and hindered rotation of the (now magnetically equivalent) C_6F_5 rings. The above transformations are accompanied by ^{19}F NMR chemical shift displacements consistent with the aforementioned ability of the $(C_6F_4B)_2$ framework to effectively disperse negative charge (Figure 2), with major upfield shifts in these signals and smaller shifts in the C_6F_5 signals relative to $B(C_6F_5)_3 \rightarrow CH_3B(C_6F_5)_3^-$.



Scheme 2. Reaction of **Vb** with 1.0 and 2.0 equiv $[(C_5H_5)_2ZrMe_2]$ in CD_2Cl_2 at 25 °C. The "*trans*" isomer of **VIII** is shown. The NMR data do not allow an unambiguous differentiation between *cis* and *trans* (C_{2v} vs C_{2h}) isomers, however steric considerations would appear to favor the "*trans*" isomer.

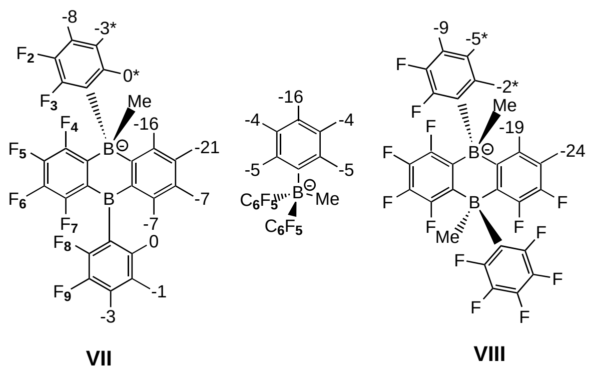


Figure 2. ^{19}F NMR chemical shift displacements for $B(C_6F_5)_3$ and **Vb** upon methyl anion abstraction from $[(C_5H_5)_2ZrMe_2]$. All values at 25 °C in CD_2Cl_2. Data for **VII** are assigned under the assumption that fluoroarylborate ^{19}F signals are shifted further upfield than fluoroarylborane signals. The asterisks denote chemical shifts that are the averaged values for the two magnetically non-equivalent sites.

The cocatalytic characteristics of **Vb** for ethylene and propylene polymerization were examined by using previously described batch-reactor methods.[2b,c] Activating $[(C_5H_5)_2ZrMe_2]$, $[(Me_5C_5)_2ZrMe_2]$, or $[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe_2]$ with **Vb** leads to extremely active catalysts (Table 1). In general, catalysts derived from **Vb** exhibit significantly higher polymerization activities than the

Table 1. Comparative olefin polymerization data for catalysts activated by $B(C_6F_5)_3$ and **Vb**.

Entry	Catalyst	Monomer[a]	μmol Cat.[b]	Conditions [°C, s][c]	Polymer yield [g]	Activity[d, e]	$10^{-3} M_w$[f]	M_w/M_n
1[g]	$[(C_5H_5)_2ZrMe]^+MeB(C_6F_5)_3^-$	E	15	25, 60	1.0	4.0×10^6	124	2.03
2	$[(C_5H_5)_2ZrMe]^+Me[C_6F_4B(C_6F_5)]_2^-$	E	7.5	20, 30	0.28	4.5×10^6	218	2.12
3[g]	$[(C_5Me_5)_2ZrMe]^+MeB(C_6F_5)_3^-$	E	15	25, 60	0.80	3.2×10^6	136	2.54
4	$[(C_5Me_5)_2ZrMe]^+Me[C_6F_4B(C_6F_5)]_2^-$	E	7.7	20, 16	0.56	1.6×10^7	135	2.34
5	$[(C_5Me_5)_2ZrMe]^+{}_2Me_2[C_6F_4B(C_6F_5)]_2^{2-}$	E	16	20, 17	0.92	1.3×10^7	118	2.00
6[g]	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+MeB(C_6F_5)_3^-$	E	15	25, 600	0.20	8.0×10^4	1058	9.54
7	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+Me[C_6F_4B(C_6F_5)]_2^-$	E	10	25, 40	0.04	3.6×10^5		
8	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+Me[C_6F_4B(C_6F_5)]_2^-$	E	7.9	65, 22	0.50	1.0×10^7	169	2.14
9[h]	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+MeB(C_6F_5)_3^-$	E/O	2.0	140, 900	131	7.7×10^7		
10[h]	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+Me[C_6F_4B(C_6F_5)]_2^-$	E/O	2.0	140, 900	262	1.5×10^8		
11	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+MeB(C_6F_5)_3^-$	P	6.0	70, 600	11	1.0×10^5	175	2.10
12	$[\{(Me_2Si)Me_4C_5\}(tBuN)TiMe]^+Me[C_6F_4B(C_6F_5)]_2^-$	P	0.75	70, 600	216	2.0×10^6	182	2.14

[a] E = ethylene, E/O = ethylene + 1-octene, P = propylene. [b] Based on moles of metallocene added. [c] Polymerization temperature, reaction time. [d] Entries 1–10: (g polymer)(mol cationic metallocene)$^{-1}$(atm)$^{-1}$(h)$^{-1}$. [e] Entries 11 and 12: (g polymer)(g Ti)$^{-1}$(h)$^{-1}$. [f] By gel-permeation chromatography relative to polystyrene standards. [g] Data from ref. [2g]. [h] Large-scale reactor procedure of ref. [2c].

$B(C_6F_5)_3$-based analogues (cf. entries 3 and 4, 6 and 7, and 11 and 12). Note also that using a zirconocene:**Vb** ratio of 2:1, which presumably generates a dianionic cocatalyst, has only minor effects on polymerization activity, polymer molecular weight, and product polydispersity (entries 4 and 5).

These results demonstrate the substantial and efficacious differences in organo-Lewis acid characteristics and in those of derived metallocenium ion pairs that can be effected by manipulation of fluoroarylborane cocatalyst architecture. These include enhanced Lewis acidity, significant olefin polymerization activity enhancements over $B(C_6F_5)_3$, and the first examples of effective dianionic metallocene cocatalysts.

Experimental Section

All manipulations of air-sensitive materials were performed as described elsewhere[2b–d] with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum line (10^{-6} Torr), or in a N_2-filled Vacuum Atmospheres glove box with a high-capacity recirculator (<1 ppm O_2). All solvents for high-vacuum line manipulations were stored in vacuo over Na/K alloy in Teflon-valved bulbs.

Va: An excess of BCl_3 (5.0 g, 44 mmol) was condensed into a thick-walled tube fitted with a J. Young valve and containing 1,2-$C_6F_4(SnMe_3)_2$[8] (5.3 g, 11.1 mmol) at −196 °C. The flask was next evacuated to 0.05 Torr, and the valve closed. The reaction mixture was then heated at 180 °C for 18 h. [**Caution**: Heating this closed system results in a pressure build-up. In addition to evacuating the system prior to heating, the reaction tube was enclosed in a steel pipe behind a blast shield.] After cooling the reaction mixture to room temperature, excess BCl_3 was removed under dynamic vacuum, and a slightly moist, beige solid was obtained. The product was extracted with pentane (3 × 20 mL), leaving behind about 65 % of the Me_3SnCl by-product. The remaining Me_3SnCl was removed by sublimation at 40 °C/10^{-5} Torr. The product was then sublimed at 90 °C/10^{-5} Torr, affording **Va** as a yellow solid (1.15 g, 53 % yield). ^{19}F NMR (282 MHz, C_6D_6): $\delta = -122.7$ (m, 4F), −143.9 (m, 4F); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.6$ (d, $^1J_{C,F} = 262$ Hz), 144.6 (d, $^1J_{C,F} = 260$ Hz), 122.8 (br, BC); MS (EI, 8.7 eV): m/z (%): 392 (16), 391 (18), 390 (67), 389 (M^+, 47), 388 (100), 387 (51), 342 (21), 318 (22), 304 (28), 250 (25), 201 (30); analysis calcd for $C_{12}F_8B_2Cl_2$: C 37.1, H 0.0; found: C 38.2, H 0.3.

Vb: A thick-walled tube fitted with a J. Young valve was charged with **Va** (0.265 g, 0.68 mmol) and $(C_6F_5)_2SnMe_2$ (0.33 g, 0.68 mmol). The flask was cooled to −78 °C, toluene (20 mL) was condensed in, and the valve was closed. The reaction mixture was heated to 140 °C for 72 h to give a bright yellow solution. After the mixture was cooled to room temperature, the solvent was removed under dynamic vacuum. The Me_2SnCl_2 by-product was also removed under dynamic vacuum (10^{-5} Torr/12 h). The crude product was then crystallized twice from toluene (10 mL, slow cooling to −78 °C) to give **Vb** as a light yellow crystalline solid (0.35 g, 80 % yield). ^{19}F NMR ([D_8]toluene): $\delta = -118.2$ (br, 4F, *o*-C_6F_4), −133.9 (dd, $^3J_{F,F} = 25.1$, $^4J_{F,F} = 7.9$ Hz, 4F, *o*-C_6F_5), −138.9 (m, 4F, *m*-C_6F_4), −152.1 (t, $^3J_{F,F} = 21$ Hz, 2F, *p*-C_6F_5), −161.4 (ddd, $^3J_{F,F} = 22$, $^3J_{F,F} = 22$, $^5J_{F,F} = 7$ Hz, 4F, *m*-C_6F_5); ^{13}C NMR ($CDCl_3$): $\delta = 156.1$ (d, $^1J_{C,F} = 267$ Hz), 145.9 (d, $^1J_{C,F} = 265$ Hz), 144.3 (d, $^1J_{C,F} = 241$ Hz), 141.6 (d, $^1J_{C,F} = 265$ Hz), 137.6 (d, $^1J_{C,F} = 253$ Hz), 128.3 (br), 123.7 (br); analysis calcd for $C_{24}F_{18}B_2$: C 44.22, H 0.00; found: C 42.61, H 0.52. This compound consistently proved difficult to combust, despite attempts with X-ray quality crystals.

In situ generation of **VII**: ^{19}F NMR: (CD_2Cl_2, 25 °C): $\delta = -123.1$ (br, 2F, F7; see Figure 2 for assignments), −132.4 (m, 3F, F3 + F4 or F8), −134.0 (br, 2F, F4 or F8), −134.8 (br, 1F, F3), −145.0 (br, 2F, F6), −155.4 (t, $^3J_{F,F} = 21$ Hz, 1F, F10), −158.9 (m, 2F, F5), −160.0 (m, 1F, F1), −161.8 (br, 1F, F2), −162.5 (br, 1F, F2), −164.1 (br, t, $^3J_{F,F} = 21$ Hz, 2F, F9); ^1H NMR: (CD_2Cl_2, 25 °C): $\delta = 6.34$ (s, 10H), 0.66 (s, 3H), 0.17 (br, 3H).

In situ generation of **VIII**: ^{19}F NMR: (CD_2Cl_2, 25 °C): $\delta = -132.7$ (br, 2F, *o*-C_6F_5), −134.7 (br, 4F, *o*-C_6F_4), −136.4 (br, 2F, *o*-C_6F_5), −161.6 (t, $^3J_{F,F} = 20$ Hz, 2F, *p*-C_6F_5), −162.6 (d, $^3J_{F,F} = 19$ Hz, 4F, *m*-C_6F_4), −164.4 (br, 2F, *m*-C_6F_5), −165.4 (br, 2F, *m*-C_6F_5); ^1H NMR: (CD_2Cl_2, 25 °C): $\delta = 6.22$ (s, 10H), 0.69 (s, 3H), 0.19 (br, 3H); a slight excess of $[(C_5H_5)_2ZrMe_2]$ was present in this sample, and signals attributable to this compound were also detected.

Polymerization experiments: Table 1, entries 1–8: Experiments were carried out[2b] on a high-vacuum line (10^{-6} Torr) in 100 mL toluene at 1.0 atm ethylene pressure. Activities given in Table 1 are the average of two trials; reproducibility was within ±5 %. The experiments of entries 9 and 10 in Table 1 were carried out in a stirred 2.0-L Parr reactor charged with 740 g Isopar-E mixed alkanes solvent and 118 g of 1-octene comonomer.[2c] Hydrogen (25 psi) was added to control polymer molecular weight. The reactor was heated to 140 °C and saturated with ethylene at 500 psi. Next, with rapid stirring, 2.0 μmol catalyst/cocatalyst mixture was injected into the reactor as a 0.0050 M solution, and the conditions maintained for 15 min with ethylene on demand. The experiments of entries 11 and 12 in Table 1 were carried out[2c] in a stirred 2.0-L autoclave reactor charged with 640 g Isopar-E mixed alkanes solvent and 216 g propylene. Hydrogen (26 psi) was added to control polymer molecular weight. The reactor was heated to 70 °C, and a 0.0050 M catalyst/cocatalyst solution in toluene was injected into the reactor with rapid stirring. Polymerization conditions were maintained for 10 min. In these polymerization experiments, 1,2-$C_6H_4F_2$ was used as the solvent for the catalyst solutions, by mixing the metallocene complex and borane, then allowing the resulting solution to stand for 5 min.

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[12] Crystallographic data for **Vb**: $C_{24}F_{18}B_2 \cdot 2C_7H_8$; monoclinic, space group $P2_1/c$; $a = 22.855(2)$, $b = 10.865(1)$, $c = 13.750(1)$ Å, $\beta = 99.689(1)^\circ$, $V = 3366(1)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.650$ g cm^{-3}; $\mu = 1.65$ cm^{-1}; $T = -120$ °C. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions and not refined. The final cycle of full-matrix least-squares refinement was based on 8069 observed reflections ($I > 2.00\sigma(I)$) and 523 variable parameters and converged (largest parameter shift was 0.087 times its esd) with unweighted and weighted agreement factors of $R = 0.042$ and $Rw = 0.118$. For clarity of the crystallographic discussion, note that there are two half molecules in the asymmetric unit, and consequently there are two independent bond lengths and angles for each bond length/angle of **Vb**. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135514. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] Because of limited solubility of **VII** in [D$_6$]benzene and [D$_8$]toluene, NMR spectra were recorded in CD_2Cl_2, in which at room temperature and below, the complexes are sufficiently stable for adequate spectroscopy.

Photocontrol of Triple-Helix Formation by Using Azobenzene-Bearing Oligo(thymidine)**

Hiroyuki Asanuma, Xingguo Liang, Takayuki Yoshida, Akira Yamazawa, and Makoto Komiyama*

Triple-helix formation by oligonucleotides is one of the most promising methods for sequence-specific recognition of DNA double helices.[1] Various applications (for example, regulation of gene expression and cell growth) have already been demonstrated.[2] However, little is known on the regulation of triple-helix formation by external signals. If triple helixes can be formed at will (as triggered by a signal), the scope of their applications would be extended.

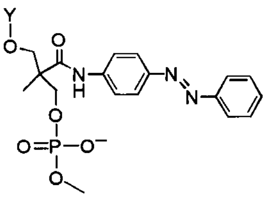
Previously, it was shown that intercalating agents stabilize triple helixes when tethered to oligonucleotides.[1b, d, h, 2a] Furthermore, formation of DNA double helices was regulated by photoisomerization of the azobenzene-tethered oligonucleotides.[3, 4] These findings have prompted us to study on photoregulation of triple-helix formation. Here, we show modified oligo(thymidine) (oligo(T)) species, which carry an azobenzene at the appropriate position, form stable triple helices with oligo(T)/oligo(dA) double helices (oligo(dA) = oligo(deoxyadenosine)). More importantly, these triple helices can be formed and dissociated repeatedly by photo-induced *cis-trans* isomerization of the azobenzene.

The double helix [**t/a**] is formed from two complementary 32-mer oligonucleotides, and involves a T_{14} and dA_{14} block (from the **t** and **a**, respectively) (Scheme 1).[5] Its melting temperature (T_m) is 73.0 °C at pH 7.0 ([$MgCl_2$] = 0.1 M; other conditions are presented in the Experimental Section). With addition of oligonucleotide $\mathbf{T_{13}}$ to the [**t/a**] double helix, the melting curve for the system is double-sigmoidal, corresponding to the formation of the [$\mathbf{T_{13}}$/**t/a**] triple helix (T_m = 18.0 °C). When the modified oligonucleotide $\mathbf{XT_{13}}$ is used in place of $\mathbf{T_{13}}$, a double-sigmoidal curve is also obtained (Figure 1). Here, the azobenzene mostly (90 %) takes its *trans*-form with respect to the stereochemistry of the N=N bond, as indicated by the reversed-phase HPLC analysis. The T_m for the [*trans*-$\mathbf{XT_{13}}$/**t/a**] triple helix is 26.0 °C. This T_m value is higher than that of either [$\mathbf{T_{13}}$/**t/a**] or [$\mathbf{T_{14}}$/**t/a**] triple helices (Table 1). The *trans*-azobenzene moiety stabilizes the triple helix, at least in this case, to a greater extent than thymine.

t: 5'-GCCACGAAATTTTTTTTTTTTTTAAACCGACG-3'
a: 3'-CGGTGCTTTAAAAAAAAAAAAAATTTGGCTGC-5'

$\mathbf{T_{11}}$: 5'-TTTTTTTTTTT-3'
$\mathbf{T_{12}}$: 5'-TTTTTTTTTTTT-3'
$\mathbf{XT_{11}}$: 5'-XTTTTTTTTTTT-3'
$\mathbf{TXT_{10}}$: 5'-TXTTTTTTTTTT-3'
$\mathbf{T_{13}}$: 5'-TTTTTTTTTTTTT-3'
$\mathbf{T_{14}}$: 5'-TTTTTTTTTTTTTT-3'
$\mathbf{XT_{13}}$: 5'-XTTTTTTTTTTTTT-3'

X =



(Y = H or phosphodiester linkage)

Scheme 1. The oligonucleotides used in this study; **X** denotes the residue carrying an azobenzene moiety in the side chain. The configuration of the N=N bond in **X** is noted.

Upon irradiating the [*trans*-$\mathbf{XT_{13}}$/**t/a**] solution with light (300 < λ < 400 nm), the azobenzene in $\mathbf{XT_{13}}$ isomerized to the *cis*-form. Concurrently, the melting curve for the [*cis*-$\mathbf{XT_{13}}$/**t/a**] triple helix (see Figure 1) notably shifts towards lower temperatures with respect to the [*trans*-$\mathbf{XT_{13}}$/**t/a**]

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