Three Coordinate Phosphorus and Boron as π-Donor and π-Acceptor Moieties Respectively, in Conjugated Organic Molecules for Nonlinear Optics: Crystal and Molecular Structures of *E*-Ph–CH=CH–B(mes)$_2$, *E*-4-MeO–C_6H_4–CH=CH-B(mes)$_2$, and *E*-Ph_2P–CH=CH–B(mes)$_2$ [mes = 2,4,6-$Me_3C_6H_2$]

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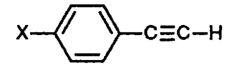
Hydroboration of π-donor substituted alkynes D–C≡C–H [D = Ph_2P, 4-X–C_6H_4- (X = H, MeS, MeO, H_2N), and (η^5-C_5H_5)Fe(η^5-C_5H_4-)] with dimesitylborane {[(mes)$_2$BH]$_2$, mes = 2,4,6-$Me_3C_6H_2$} yields air-stable 'push–pull' *E*-alkenes of the form *E*-D–CH=CH–B(mes)$_2$, which possess large molecular hyperpolarizabilities, β, as shown by electric-field induced second-harmonic generation (EFISH) experiments at 1.91 μm; single crystal X-ray diffraction studies indicate that *E*-Ph–CH=CH–B(mes)$_2$ and *E*-4-MeO–C_6H_4–CH=CH–B(mes)$_2$ crystallise in centrosymmetric space groups, whereas *E*-Ph_2P–CH=CH–B(mes)$_2$ crystallises in the acentric space group $P2_12_12_1$ and exhibits powder SHG of 1.064 μm laser light.

Conjugated π-donor–acceptor substituted organic molecules exhibit low lying charge-transfer states that can give rise to useful second-order optical nonlinearities.[1,2] A variety of donor and acceptor substituents have been examined to date, including transition-metal centres.[3,4] However, most studies have concentrated on a relatively small class of π-donors such as MeS, MeO, H_2N and Me_2N, and π-acceptors such as NO_2, CN, $C_2(CN)_3$, $[C_5H_4NMe]^+$, *etc.* Recent work[2d] has shown that weaker π-donors such as Br or I can provide large second-order optical nonlinearities in push–pull stilbene and



X = **a**; H **b**; MeS **c**; MeO **d**; H_2N

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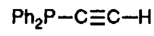

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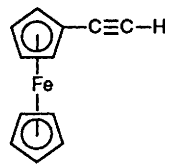

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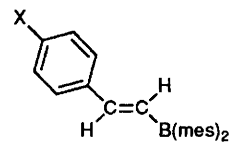

X = **a**; H **b**; MeS **c**; MeO **d**; H_2N

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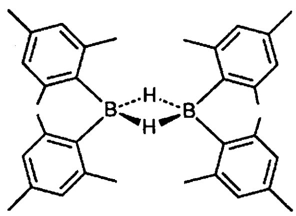

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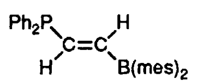

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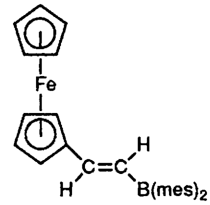

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tolan systems. Clearly, other donors and acceptors warrant examination. The potential acceptor properties of the $B(mes)_2$ (mes = 2,4,6-$Me_3C_6H_2$) unit in 4-X–C_6H_4–$B(mes)_2$ (X = π-donor)[5] and the [$CH_2C_6H_2$(3,5-Me_2){4-$B(mes)_2$}] anion[6] were indicated from UV–VIS[5] and X-ray structural[6] studies.

We have studied the use of π-donor and π-acceptor substituted acetylide ligands in organotransition-metal systems, and have observed significant second-order optical nonlinearities in a series of such complexes.[7] With the terminal acetylenes in hand, and the above observations in mind, we decided to examine the structural, spectroscopic and nonlinear optical properties of a series of push–pull alkenes bearing *para*-substituted aromatics, ferrocenyl and the Ph_2P group, as π-donors, and the $B(mes)_2$ moiety as a π-acceptor. Three coordinate boron possesses an empty p-orbital that should be a powerful π-acceptor. Hydroboration of suitably substituted terminal alkynes using dimesitylborane gave the desired *E*-alkenyl borane products in high yields. We report here the synthesis of a series of such compounds, the crystal and molecular structures of three alkenyl boranes, including the unusual monomeric III–V complex *E*-Ph_2P–CH=CH–$B(mes)_2$, and preliminary powder and solution measurements of their second-order optical nonlinearities. To our knowledge, only one simple alkenyl borane, $(MeCH{=}CSiMe_3)_3B$, has been characterized previously[8] by X-ray diffraction techniques.

The donor alkynes **1b–d** were prepared by $Pd(PPh_3)_2Cl_2$/CuI catalysed coupling of the appropriate *para*-substituted haloarene with $Me_3SiC{\equiv}CH$ in Et_2NH followed by deprotection with K_2CO_3 in MeOH. The basic procedure has been reported[9] by Hagihara *et al.*; details of the syntheses and spectroscopic properties of **1b–d** and related compounds will be reported elsewhere.[10] Hydroboration[11] of **1a–d**, **2**,[12] and **3**,[13] with **4**, yielded exclusively the air-stable *E*-substituted vinyl boranes **5–7**, which were characterized† by ^1H, ^{13}C NMR and UV–VIS spectroscopy, and, for **6**, by ^{31}P NMR; ^{11}B NMR spectra were generally broad and uninformative. In addition, single crystal X-ray diffraction studies‡ were conducted on **5a** (Fig. 1), **5c** (Fig. 2), and **6** (Fig. 3).

The molecular structures of **5a**, **c** and **6** provide information on the degree of ground-state electronic communication between the donor moiety and the vacant p-orbital on boron.

† *Selected spectroscopic data for* **5b**: ^1H NMR ($CDCl_3$) δ 7.46 (d, *J* 8.3 Hz, 2H, C_6H_4), 7.22 (d, *J* 8.3 Hz, 2H, C_6H_4), 7.35 (d, *J* 17.6 Hz, 1H, =CH-), 7.10 (d, *J* 17.6 Hz, 1H, =CH-), 6.84 (s, 4H, $C_6H_2Me_3$), 2.49 (s, 3H, MeS), 2.31 (s, 6H, 2Me), 2.20 (s, 12H, 4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 152.0, 136.7 (-CH=CH-), 140.9, 134.5, 128.6, 126.1 (-C_6H_4-), 142.2, 140.6, 138.4, 128.2 ($C_6H_2Me_3$), 23.3, 21.2 ($C_6H_2Me_3$), 15.4 (MeS); λ_{max} 366 nm (ε 21 000).

5c: ^1H NMR ($CDCl_3$) δ 7.48 (d, *J* 8.7 Hz, 2H, C_6H_4), 6.87 (d, *J* 8.7 Hz, 2H, C_6H_4), 7.23 (d, *J* 17.7 Hz, 1H, =CH-), 7.10 (d, *J* 17.7 Hz, 1H, =CH-), 6.87 (s, 4H, $C_6H_2Me_3$), 3.81 (s, 3H, MeO), 2.29 (s, 6H, 2Me), 2.19 (s, 12H, 4Me), at $-40\,°C$, splitting of the resonances for the 4-*ortho*-CH_3 groups indicates restricted rotation, presumably about B(1)–C(1); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 152.6, 135.2 (-CH=CH-), 160.9, 130.6, 129.7, 114.1 (-C_6H_4-), 142.3, 140.6, 138.2, 128.1 ($C_6H_2Me_3$), 55.4 (MeO), 23.2, 21.2 ($C_6H_2Me_3$); λ_{max} 348 nm (ε 33 000).

5d: ^1H NMR ($CDCl_3$) δ 7.15 (d, *J* 17.6 Hz, 1H, =CH-), 7.06 (d, *J* 17.6 Hz, 1H, =CH-), 3.87 (s, 2H, NH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 153.6, 133.4 (-CH=CH-); λ_{max} 372 nm (ε 28 000).

6: ^1H NMR ($CDCl_3$) δ 7.42–7.27 (m, 10H, C_6H_5), 6.74 (s, 4H, $C_6H_2Me_3$), 2.23 (s, 6H, 2Me), 2.10 (s, 12H, 4Me), vinyl Hs partially obscured by phenyl protons; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.4 (d, $J_{C\text{-}P}$ 21.8 Hz, =CH-), 132.6 (d, $J_{C\text{-}P}$ 21.2 Hz, =CH-); $^{31}P\{^1H\}$ NMR ($CDCl_3$) -1.8 ppm; λ_{max} 340 nm (ε 19 000).

7: ^1H NMR ($CDCl_3$) 7.09 (d, *J* 17.5 Hz, 1H, =CH-), 6.94 (d, *J* 17.5 Hz, 1H, =CH-), 4.50 (t, *J* 1.9 Hz, 2H, η-C_5H_4), 4.39 (t, *J* 1.9 Hz, 2H, η-C_5H_4), 4.13 (s, 5H, η-C_5H_5); λ_{max} 336 nm (ε 24 000), tails observed at 486, 378 nm.

‡ *Crystal data for* **5a**: $C_{26}H_{29}B$, M = 352.36, monoclinic, space group $P2_1/n$, a = 9.851(2), b = 11.679(4), c = 19.009(4) Å, β = 104.18(2)°, U = 2120.3(9) Å^3, Z = 4, D_c = 1.12 g cm^{-3}, $F(000)$ = 760, λ = 0.71073 Å, T = 200 ± 1 K, μ(Mo-Kα) = 0.57 cm^{-1}. Data were collected on a Nicolet R3m diffractometer using a crystal of dimensions 0.30 × 0.50 × 0.62 mm by the $2\theta - \theta$ scan method (3.5° ≤ 2θ ≤ 54°). From 4658 unique measured data, 3003 reflections with $I \geqslant 3\sigma(I)$ were used in the structure solution (direct methods) and subsequent full-matrix least-squares refinement. An analytical absorption correction was applied. Final R = 0.0486, R_w = 0.0594.

5c: $C_{27}H_{31}BO$, M = 382.39, monoclinic, space group $P2_1/c$, a = 14.416(3), b = 12.033(3), c = 13.264(2) Å, β = 90.38(2)°, U = 2301.2(8) Å^3, Z = 4, D_c = 1.10 g cm^{-3}, $F(000)$ = 824, λ = 0.71073 Å, T = 200 ± 1 K, μ(Mo-Kα) = 0.60 cm^{-1}. Data collection as above on a crystal of dimensions 0.42 × 0.56 × 0.50 mm by the ω scan method (3.5° ≤ 2θ ≤ 50°). From 4051 unique measured data, 2159 reflections with $I \geqslant 3\sigma(I)$ were used in the structure solution and refinement as above. A ψ scan absorption correction was applied. Final R = 0.0795, R_w = 0.0804.

6: $C_{32}H_{34}BP$, M = 460.44, orthorhombic, space group $P2_12_12_1$, a = 9.733(2), b = 9.818(4), c = 27.821(7) Å, U = 2659(1) Å^3, Z = 4, D_c = 1.15 g cm^{-3}, $F(000)$ = 984, λ = 0.71073 Å, T = 180 ± 1 K, μ(Mo-Kα) = 1.16 cm^{-1}. Data collection as above on a crystal of dimensions 0.32 × 0.46 × 0.48 mm by the ω scan method (3.5° ≤ 2θ ≤ 55°). From 3461 unique measured data, 2540 reflections with $I \geqslant 3\sigma(I)$ were used in the structure solution and refinement as above. A ψ scan absorption correction was applied. Final R = 0.0439, R_w = 0.0440. The enantiomorph was indeterminate.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

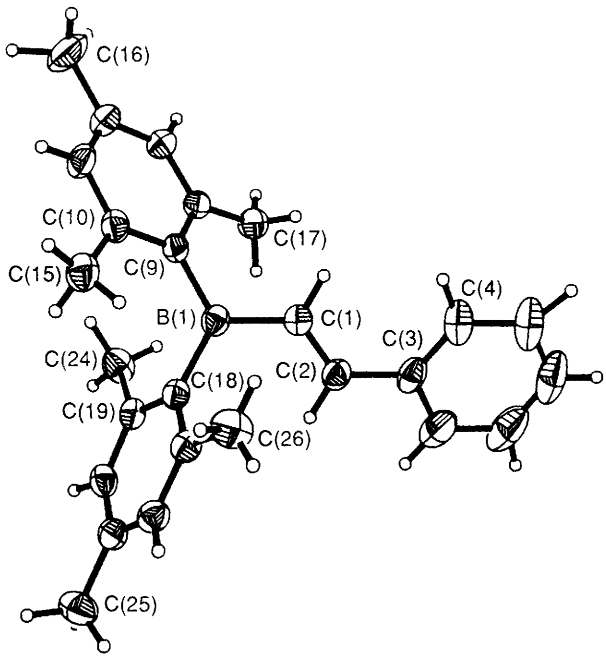

Fig. 1 ORTEP diagram of **5a**. Selected bond distances (Å) and angles (°) are: B(1)–C(1) 1.554(3), B(1)–C(9) 1.584(3), B(1)–C(18) 1.576(3), C(1)–C(2) 1.338(3), C(2)–C(3) 1.475(3), C(1)–B(1)–C(9) 118.4(2), C(1)–B(1)–C(18) 118.1(2), C(9)–B(1)–C(18) 123.4(2), B(1)–C(1)–C(2) 123.2(2), C(1)–C(2)–C(3) 127.0(2). Dihedral angles with respect to the plane [B(1), C(1), C(9), C(18)] are: [B(1), C(1), C(2)] 27.6, [C(9), C(10), C(11), C(12), C(13), C(14)] 49.9, [C(18), C(19), C(20), C(21), C(22), C(23)] 56.6, [C(3), C(4), C(5), C(6), C(7), C(8)] 37.8

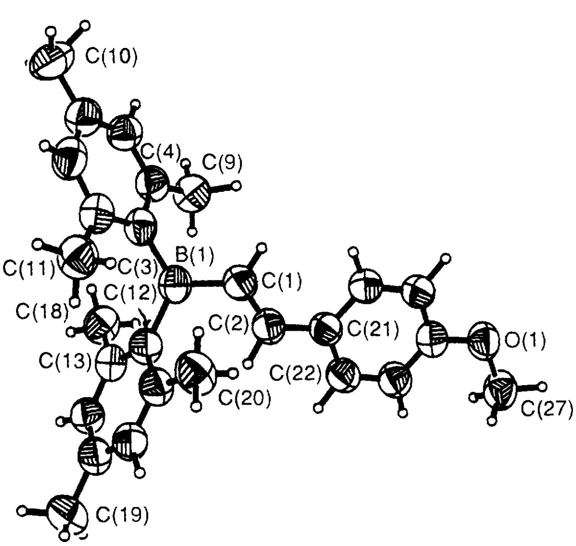

Fig. 2 ORTEP diagram of **5c**. Selected bond distances (Å) and angles (°) are: B(1)–C(1) 1.546(6), B(1)–C(3) 1.571(6), B(1)–C(12) 1.600(6), C(1)–C(2) 1.349(6), C(2)–C(21) 1.455(5), C(24)–O(1) 1.379(5), C(1)–B(1)–C(3) 119.4(3), C(1)–B(1)–C(12) 116.9(3), C(3)–B(1)–C(12) 123.6(3), B(1)–C(1)–C(2) 122.6(4), C(1)–C(2)–C(21) 129.3(4). Dihedral angles with respect to the plane [B(1), C(1), C(3), C(12)] are: [B(1), C(1), C(2)] 21.4, [C(3), C(4), C(5), C(6), C(7), C(8)] 48.1, [C(12), C(13), C(14), C(15), C(16), C(17)] 66.4, [C(21), C(22), C(23), C(24), C(25), C(26)] 23.7

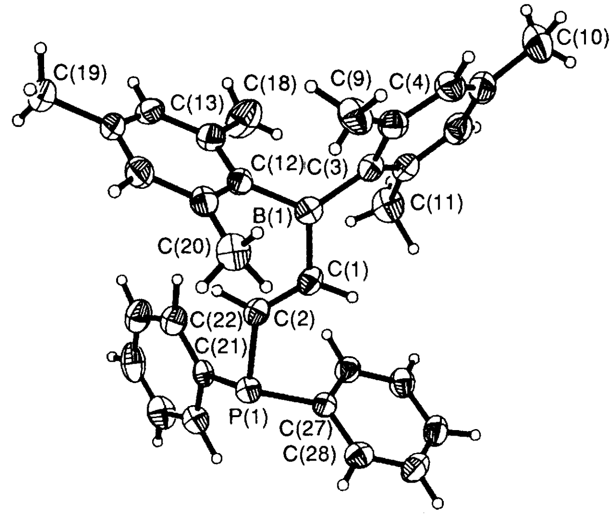

Fig. 3 ORTEP diagram of **6**. Selected bond distances (Å) and angles (°) are: B(1)–C(1) 1.561(5), B(1)–C(3) 1.571(5), B(1)–C(12) 1.591(5), C(1)–C(2) 1.345(5), P(1)–C(2) 1.810(3), P(1)–C(21) 1.842(3), P(1)–C(27) 1.839(3), C(1)–B(1)–C(3) 120.7(3), C(1)–B(1)–C(12) 117.3(3) C(3)–B(1)–C(12) 121.9(3), B(1)–C(1)–C(2) 121.8(3), C(1)–C(2)–P(1) 128.9(3), C(2)–P(1)–C(21) 101.6(2), C(2)–P(1)–C(27) 103.4(1), C(21)–P(1)–C(27) 102.8(1). Dihedral angles with respect to the plane [B(1), C(1), C(3), C(12)] are: [B(1), C(1), C(2)] 16.8, [C(3), C(4), C(5), C(6), C(7), C(8)] 59.4, [C(11), C(12), C(13), C(14), C(15), C(16)] 68.5

Thus, in **5a**, the [B(1), C(1), C(2)] plane is rotated by 27.6° with respect to the [B(1), C(1), C(9), C(18)] plane of the three-coordinate boron. A similar value of 25.8° was observed[6] for the rotation of the more hindered $CH_2C_6H_2$(3,5-Me_2) unit in [$CH_2C_6H_2$(3,5-Me_2){4-B(mes)$_2$}]$^-$. In the latter compound, substantial delocalization and 'boron ylide' character were observed. In **5c**, the [B(1), C(1), C(2)]–[B(1), C(1), C(3), C(12)] dihedral angle is reduced considerably to 21.4°, and, in **6**, the corresponding angle is only 16.8°. In **5a**, the angle between the C_6H_5 and BC_3 planes is 37.8°, whereas, in **5c**, the C_6H_4–BC_3 dihedral is 23.7°. In addition, in **6**, a peak attributable to the lone pair on P was observed in the final difference electron-density map, the position of which is perpendicular to the P–CH=CH–B plane. Substitution with π-donor groups decreases significantly the dihedral angles, improving conjugation with boron.§

For $\chi^{(2)}$, the second-order optical nonlinearity of a bulk material, to be non-zero, the material must not possess a centre of symmetry.[1] For crystalline materials a non centrosymmetric space group is required. We have tested several of the vinyl borane samples for second harmonic generation (SHG) using the Kurtz Powder Technique.[14] No SHG signal was observed for **5a** or **5c** which crystallise in the centric space groups $P2_1/n$ and $P2_1/c$ respectively. Similarly, samples of **5b**, **d** and **7** also failed to frequency double the 1.064 μm laser, presumably indicating that these materials also crystallise in centric space groups. In contrast, unsized powder samples of **6**, which crystallises in $P2_12_12_1$, did exhibit SHG with an

§ *Single-crystal X-ray diffraction studies on 4-Me_2N–C_6H_4–B(mes)$_2$*: [monoclinic, $P2_1/c$, a = 14.505(3), b = 11.605(3), c = 13.365(2) Å, β = 98.02(2)°, R = 0.0452, R_w = 0.0472] and *E-4-MeS–C_6H_4–CH=CH–B(1,2-$O_2C_6H_4$)* [monoclinic, $P2_1/n$, a = 7.072(1), b = 24.077(5), c = 7.712(2) Å, β = 95.54(2)°, R = 0.0345, R_w = 0.0450] have been carried out. In the former molecule, the [4-Me_2N–C_6H_4]–[BC_3] torsion angle is 19.6°, whereas the latter molecule is planar within 1.3° (Z. Yuan, N. J. Taylor and T. B. Marder, unpublished results).

intensity of *ca.* 1.0× an optimised, index-matched quartz sample (62 μm particle size). For comparison, an unoptimized urea sample gave a signal of 1.5 quartz under these conditions.

Although only one of these materials exhibited SHG as a powder, the molecular hyperpolarizabilities, β, are large. Measurements of β at 1.91 μm by the electric-field induced second-harmonic generation (EFISH) technique[15] gave values of 5.1, 9.3, 8.6 and 18 ($\times 10^{-30}$ esu ±10%) for **5a–d** respectively, 2.6 ± 1 × 10^{-30} esu for **6**, and 11 × 10^{-30} esu ±10% for 4-Me_2N–C_6H_4–B(mes)$_2$.§ In comparison,[15] β = 9.2 × 10^{-30} esu ±10% for 4-H_2N–C_6H_4–NO_2. It should be possible to provide the necessary bulk dipole alignment for large $\chi^{(2)}$ values by minor chemical modification of the materials or by incorporation into polymer films followed by poling. The stability of the vinyl boranes to the atmosphere is achieved by the bulky mesityl groups. This stability, the large values of β, and the transparency of the materials at wavelength >400 nm,† make them attractive candidates for further study.

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