Treatment of Naphthols with $B(C_6F_5)_3$: Formation and Characterization of the Lewis Acid Adducts of Their Keto Isomers[**]

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Dedicated to Dr. Pol Bamelis
on the occasion of his 60th birthday

The formation of kinetically persistent nonstabilized enols from simple aldehydes and ketones is difficult, but has been achieved in several cases.[1] It is equally problematic to generate the keto tautomers of the phenols and related "aromatic enols" (except in specific instances[2b]) and stabilize them under ambient conditions. This has been achieved in a number of cases by π complexation of, for example, the cyclohexadienone isomers of phenol and phenol derivatives with a variety of late transition metal complex fragments.[2, 3] We have now found that the keto tautomers of a number of naphthol derivatives can be obtained and isolated as stable κ-O-adducts by treatment with the strong Lewis acid tris(pentafluorophenyl)borane (**1**).[4]

A suspension of $B(C_6F_5)_3$ (**1**) and α-naphthol (**2**; 1:1) in pentane was stirred for 12 h at room temperature. The resulting solid was collected by filtration, and a sample was crystallized from toluene at 4 °C. The single crystals obtained were suitable for an X-ray crystal structure analysis, which revealed that the $B(C_6F_5)_3$ adduct **3** of the 1-naphthol tautomer benzocyclohexadiene was obtained [Eq. (1)].

(1)

2 **1** **3**

In **3** the borane Lewis acid is attached to the carbonyl oxygen atom (B–O: 1.547(3) Å, C1–O: 1.273(3) Å, angle C1-O-B: 130.9(2)°). The cyclohexadienone part of the adduct molecule features the expected long-long-short-long-long-short array of carbon–carbon bonds along the six-membered ring (Figure 1). The annelated aromatic C_6H_4 ring is devoid of this alternation. Its C$\overset{...}{-}$C bond lengths are between 1.40 and 1.37 Å, with the typical tendency of a slight bond lengthening of the "inner" more highly substituted carbon–carbon bonds. The hydrogen atoms at the $C_{10}H_8O$ nucleus were located in the early stages of the structure solution.[5a] Two hydrogen atoms are attached to C4, and the angle C3-C4-C4a (116.2(3)°) is the smallest observed inside the framework.

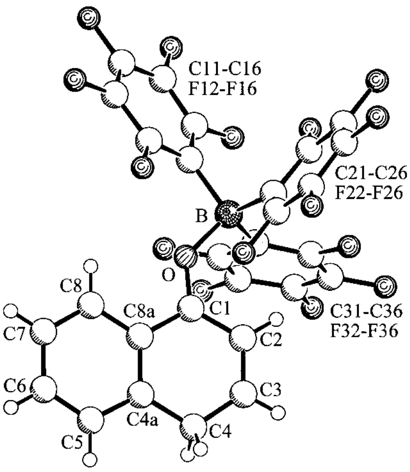
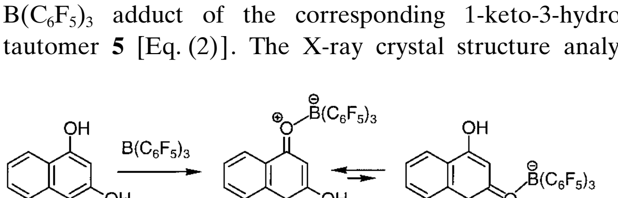


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: C1–O 1.273(3), C1–C2 1.432(4), C1–C8a 1.452(4), C2–C3 1.338(4), C3–C4 1.456(5), C4–C4a 1.488(5), C4a–C8a 1.396(4), C4a–C5 1.402(5), C5–C6 1.367(6), C6–C7 1.376(6), C7–C8 1.375(4), C8-C8a 1.397(4), O–B 1.547(3), B–C11 1.634(4), B–C31 1.636(3), B–C21 1.638(4); O-C1-C2 123.7(2), O-C1-C8a 115.9(2), C2-C1-C8a 120.4(2), C3-C2-C1 119.6(3), C2-C3-C4 123.8(3), C3-C4-C4a 116.2(3), C8a-C4a-C5 118.0(3), C8a-C4a-C4 120.0(3), C5-C4a-C4 122.0(3), C6-C5-C4a 120.9(3), C5-C6-C7 120.8(3), C8-C7-C6 119.8(4), C7-C8-C8a 120.2(3), C4a-C8a-C8 120.3(3), C4a-C8a-C1 119.5(3), C8-C8a-C1 120.2(2), C1-O-B 130.9(2).

The solid product was dissolved in [D$_6$]benzene. The NMR analysis revealed that compound **3** is persistent in solution, but that there is an equilibrium (ca. 75:25) between the benzocyclohexadienone–$B(C_6F_5)_3$ adduct and the free naphthol/$B(C_6F_5)_3$ mixture [Eq. (1)]. The rate of the equilibration is sufficiently low on the NMR time scale, so that sharp signals for the components are observed. Typically, the ^{13}C NMR resonances for C1 and C4 of 1-naphthol are found at $\delta = 145.4$ and $\delta = 120.8$, respectively, and the ^{1}H NMR signal for OH is at $\delta = 4.26$. The tautomer adduct **3**, in contrast, exhibits clearly distinguished resonances for C1 ($\delta = 189.9$) and C4 ($\delta = 33.7$). The adduct shows a ^{11}B NMR resonance at $\delta \approx 0$ ($w_{1/2} \approx$ 380 Hz; $B(C_6F_5)_3$: $\delta \approx 60$) and a set of ^{19}F NMR signals ($\delta = -128.7$ (*o*), -151.8 (*p*), -158.6 (*m*)) that are distinguishable from the corresponding $B(C_6F_5)_3$ signals ($\delta = -124.4$ (*o*), -138.5 (*p*), -155.5 (*m*)) in the mixture.

1,3-Dihydroxynaphthalene was treated with $B(C_6F_5)_3$ in an analogous manner. Again, a solid adduct was isolated. Recrystallization from toluene gave single crystals of the $B(C_6F_5)_3$ adduct of the corresponding 1-keto-3-hydroxy tautomer **5** [Eq. (2)]. The X-ray crystal structure analysis



(2)

4 **5** **6**

(Figure 2) shows the presence of only a single intact C_6H_4 ring, which is annelated to the keto tautomer of the *m*-dihydroxyarene. $B(C_6F_5)_3$ is attached at the resulting C=O group[6, 7] (B–O: 1.553(5) Å, C1–O: 1.276(5) Å, angle C1-O-B: 129.6(3)°). The adjacent C1–C8a bond in **5** is rather long (1.463(6) Å), as in **3**. The C1–C2 bond is much shorter

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[+] X-ray crystal structure analyses.

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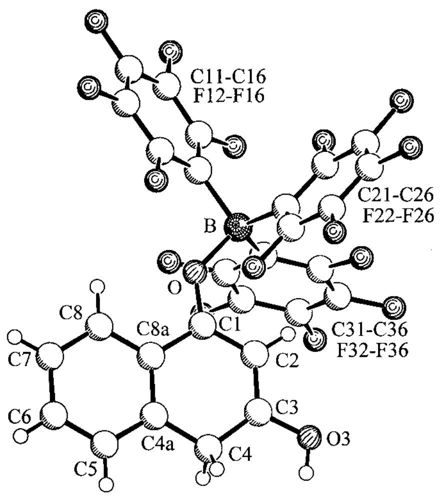
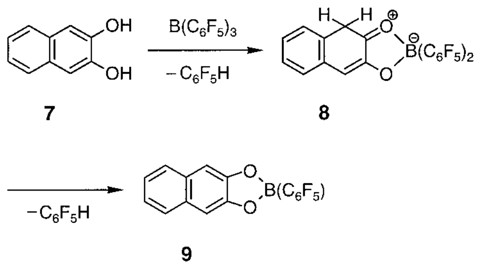


Figure 2. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: C1–O 1.276(5), C1–C2 1.392(6), C1–C8a 1.463(6), C2–C3 1.357(6), C3–O3 1.321(5), C3–C4 1.468(7), C4–C4a 1.477(7), C4a–C5 1.387(6), C4a–C8a 1.398(6), C5–C6 1.362(7), C6–C7 1.382(7), C7–C8 1.396(6), C8–C8a 1.382(6), O–B 1.553(5), B–C31 1.634(6), B–C21 1.634(6), B–C11 1.639(6); O-C1-C2 124.6(4), O-C1-C8a 115.3(4), C2-C1-C8a 120.2(4), C3-C2-C1 120.5(4), O3-C3-C2 118.1(4), O3-C3-C4 118.2(4), C2-C3-C4 123.7(4), C3-C4-C4a 114.8(4), C5-C4a-C8a 118.9(4), C5-C4a-C4 120.0(4), C8a-C4a-C4 121.1(4), C6-C5-C4a 120.4(5), C5-C6-C7 121.5(5), C6-C7-C8 118.8(5), C8a-C8-C7 120.0(5), C8-C8a-C4a 120.3(4), C8-C8a-C1 120.2(4), C4a-C8a-C1 119.5(4), C1-O-B 129.6(3).

(1.392(6) Å), now being part of a W-shaped 1,3-diketone mono-enol tautomer.[8] Both the C4a–C8a (1.398(6) Å) and the C2–C3 enol double bonds (1.357(6) Å) are short (C3–O3(H): 1.321(5) Å), and C4, which bears two hydrogen atoms, is approaching sp^3 hybridization (C4–C4a: 1.477(7) Å, C3–C4: 1.468(7) Å, angle C3-C4-C4a: 114.8(4)°).

The solid was dissolved in [D$_6$]benzene and shown by NMR spectroscopy to consist of a 70:30 mixture of the two regioisomeric keto tautomer adducts **5** and **6** [Eq. (2)]. In this case we did not detect free 1,3-dihydroxynaphthalene in the equilibrium mixture. The major regioisomer corresponds to the structure found in the solid state (see above and Figure 2). It shows the ^{1}H NMR signals of the free enol moiety at $\delta = 5.88$ (2-H) and 4.98 (OH). The newly formed CH$_2$ group shows ^{1}H ^{13}C NMR features at $\delta = 2.18$ (4-H, H′) and 33.6 (C4), respectively. The ^{13}C NMR resonance of the boron-activated C=O group of **5** occurs at $\delta = 189.4$ (C1), whereas the enolate carbon signals are observed at $\delta = 102.6$ (C2) and 185.9 (C3). The minor isomer (**6**) also shows the typical NMR signals of the C4 methylene group (^{1}H: $\delta = 3.31$; ^{13}C: $\delta = 39.6$) as part of a clearly distinguished set of ^{1}H/^{13}C NMR features (for details, see the Experimental Section). The ^{19}F and ^{11}B NMR signals of the isomers **5** and **6** could not be observed separately.

The reaction of B(C$_6$F$_5$)$_3$ with 2,3-dihydroxynaphthalene takes a slightly different course. When carried out in [D$_6$]benzene under direct NMR control, the immediate formation of pentafluorobenzene was observed.[9] A reactive intermediate was produced, to which we assign the structure of **8** [Eq. (3); ^{1}H NMR: $\delta = 2.90$ (1-H,H′); ^{13}C: $\delta = 203.4$ (C2), 155.0 (C3), 125.5 (C4), 29.9 (C1)]. The reaction rapidly proceeds further with formation of the stable product **9**. This compound was also prepared on a preparative scale (isolated in ca. 30% yield) and characterized by X-ray diffraction (Figure 3).



(3)

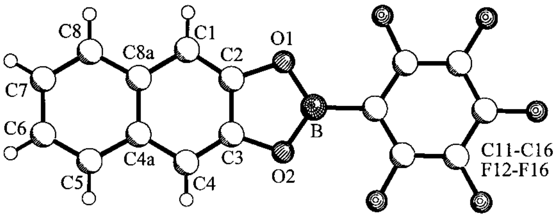
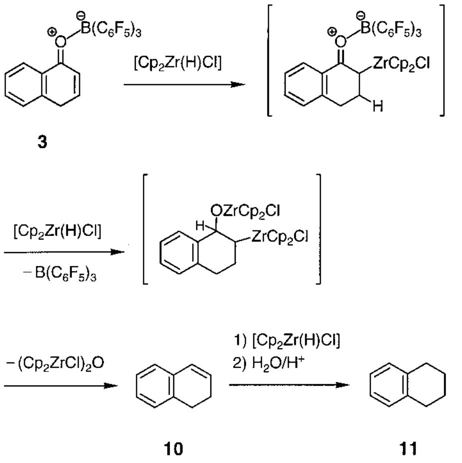


Figure 3. Molecular structure of **9**. Selected bond lengths [Å] and angles [°]: C1–C2 1.355(2), C1–C8a 1.418(2), C2–O1 1.383(2), C2–C3 1.403(2), C3–C4 1.353(2), C3–O2 1.390(2), C4–C4a 1.424(2), C4a–C5 1.417(2), C4a–C8a 1.430(2), C5–C6 1.368(2), C6–C7 1.406(2), C7–C8 1.361(2), C8–C8a 1.413(2), O1–B 1.378(2), O2–B 1.381(2), B–C11 1.550(2); C2-C1-C8a 116.99(13), C1-C2-01 128.59(14), C1-C2-C3 122.57(15), O1-C2-C3 108.84(13), C4-C3-O2 128.45(13), C4-C3-C2 122.93(14), O2-C3-C2 108.60(13), C3-C4-C4a 116.67(13), C4-C4a-C8a 120.45(14), C1-C8a-C4a 120.37(14), B-O1-C2 105.20(12), B-O2-C3 104.89(12), O1-B-O2 112.44(14), O1-B-C11 122.92(14), O2-B-C11 124.60(14).

Synthetic applications are still to be developed, but we have found a first reaction out of the **2** + **1** → **3** equilibrium mixture where the B(C$_6$F$_5$)$_3$ adduct **3** of the benzocyclohexadienone tautomer is involved. Treatment of the α-naphthol/B(C$_6$F$_5$)$_3$ reaction mixture with the hydrozirconation reagent [Cp$_2$Zr(H)Cl] in benzene resulted in complete consumption of the starting material with formation of μ-oxo-bis(zirconocene chloride) (identified by spectroscopy and X-ray diffraction[10]) and a mixture of the following organic products, which were identified spectroscopically: 1,2-dihydronaphthalene (**10**; ^{1}H NMR: $\delta = 6.39$ ($^3J = 9.6$ Hz, 4-H), 5.81 ($^3J = 9.6$, 4.5 Hz, 3-H), 2.59 (1-H), 1.98 (2-H)), 1,2,3,4-tetrahydronaphthalene (**11**; ^{1}H: $\delta = 2.57$ (1-H, 4-H), 1.52 (2-H, 3-H)), and α-naphthol in a 1.6:4.5:1.0 ratio. The hydrozirconation route[11] schematically depicted in Scheme 1, which starts from the B(C$_6$F$_5$)$_3$ adduct **3**, readily explains the straightforward formation of these observed organic and organometallic products.[12] This shows that B(C$_6$F$_5$)$_3$ adduct formation may open new routes to generate and eventually utilize the keto tautomers of the hydroxyarenes synthetically. Such studies are presently being pursued in our laboratory.

Experimental Section

3: A Schlenk tube was charged with **2** (288 mg, 2.00 mmol) and **1** (1.02 g, 2.00 mmol). At 0 °C pentane (20 mL) was added. The suspension was warmed to room temperature with stirring and then stirred for 12 h. The solid was collected by filtration, washed with pentane (5 mL), and dried in



Scheme 1. Hydrozirconation of **3** and subsequent reactions.

vacuo to yield **3** (1.17 g, 89%) as a slightly green solid, m.p. 134 °C. Elemental analysis (%) calcd for $C_{28}H_8OBF_{15}$ (656.15): C 51.25, H 1.23; found: C 51.16, H 1.59. Diffusion of pentane vapor into a solution of **3** in toluene at 40 °C over 3 d furnished single crystals that were suitable for X-ray crystal structure analysis.[5a] IR (KBr): $\tilde{\nu} = 3587, 1646, 1621\,cm^{-1}$. The NMR spectra showed the presence of an equilibrium mixture (**2** + **1** $\rightleftharpoons$ **3**; 25:75) in solution. **3**: ^1H NMR ([D$_6$]benzene, 599.8 MHz): $\delta = 8.43$ (d, $^3J = 8.1$ Hz, 1H, 8-H), 6.94 (m, 1H, 6-H), 6.87 (m, 1H, 7-H), 6.78 (d, $^3J = 10.0$ Hz, 1H, 2-H), 6.40 (d, $^3J = 7.8$ Hz, 1H, 5-H), 6.26 (m, 1H, 3-H), 2.31 (br., 2H, 4-H); ^{13}C NMR ([D$_6$]benzene, 150.8 MHz): $\delta = 189.9$ (C1), 162.4 (C3), 145.4 (C4a), 136.0 (C6), ≈129 (C7, C8a), 128.3 (C5), 123.3 (C2), 33.7 (C4), $B(C_6F_5)_3$ signals at 148.4 ($^1J_{CF} = 247$ Hz), 140.7 ($^1J_{CF} = 256$ Hz), 137.7 ($^1J_{CF} = 254$ Hz) (*o*-, *p*-, *m*-CF); ^{11}B NMR ([D$_6$]benzene, 64.2 MHz): $\delta = 0.1$ ($w_{1/2} = 380 \pm 20$ Hz); ^{19}F NMR ([D$_6$]benzene, 282.4 MHz): $\delta = -128.7, -151.8, -158.6$ (*o*-, *p*-, *m*-F).

5 and **6**: The reaction of **4** (100 mg, 625 μmol) with $B(C_6F_5)_3$ (320 mg, 625 μmol) in pentane (20 mL) was carried out analogously to that of **1** and **2** to yield **5** (400 mg, 95%) as an off-white solid, m.p. 78 °C. Elemental analysis (%) calcd for $C_{28}H_8O_2BF_{15}$ (672.16): C 50.03, H 1.20; found: C 49.61, H 1.98; IR (KBr): $\tilde{\nu} = 3563, 1646, 1609\,cm^{-1}$. Single crystals were obtained from toluene/pentane by the diffusion method.[5b] In solution the NMR signals of a 70:30 mixture of the regioisomers **5** (major product) and **6** (minor product) were observed. **5**: ^1H NMR ([D$_6$]benzene, 599.8 MHz): $\delta = 8.37$ (d, $^3J = 7.5$ Hz, 1H, 8-H), 6.90 (m, 1H, 6-H), 6.88 (m, 1H, 7-H), 6.19 (d, $^3J = 7.2$ Hz, 1H, 5-H), 5.88 (s, 1H, 2-H), 4.98 (s, 1H, OH), 2.18 (s, 2H, 4-H); ^{13}C NMR ([D$_6$]benzene, 150.8 MHz): $\delta = 189.4$ (C1), 185.9 (C3), 137.8 (C4a), 134.7 (C6), 128.7 (C7), 128.1 (C8), ≈128 (C5, C8a), 102.6 (C2), 33.6 (C4), $B(C_6F_5)_3$ signals at 148.5 ($^1J_{CF} = 241$ Hz), 140.5 ($^1J_{CF} = 246$ Hz), 137.7 ($^1J_{CF} = 248$ Hz), 118.8 (br) (*o*-, *p*-, *m*-, *ipso*-C of C_6F_5); ^{19}F NMR ([D$_6$]benzene, 282.4 MHz): $\delta = -133.6, -157.0, -163.8$ (*o*-, *p*-, *m*-F); ^{11}B NMR ([D$_6$]benzene, 64.2 MHz): $\delta = -0.6$ ($w_{1/2} = 400 \pm 20$ Hz). **6**: ^1H NMR ([D$_6$]benzene, 599.8 MHz); $\delta = 7.21$ (d, $^3J = 8.1$ Hz, 1H, 8-H), 6.81 (m, 1H, 6-H), 6.68 (m, 1H, 7-H), 6.31 (d, $^3J = 8.0$ Hz, 1H, 5-H), 5.52 (s, 1H, 2-H), 5.36 (s, 1H, OH), 3.31 (s, 2H, 4-H); ^{13}C NMR ([D$_6$]benzene, 150.8 MHz): $\delta = 199.6$ (C3), 179.5 (C1), 139.1 (C4a), 134.2 (C6), 128.1 (C5), 127.9 (C7), 125.8 (C8), 123.6 (C8a), 101.7 (C2), 39.6 (C4); $B(C_6F_5)_3$ signals are undistinguishable from those of **5**.

9: A mixture of **7** (160 mg, 1.00 mmol) and **1** (512 mg, 1.00 mmol) was dissolved in toluene (15 mL) at 0 °C. The solution was warmed to room temperature and then allowed to stand at that temperature for 2 d. The supernatant solution was decanted from the precipitated green product. The solid was washed with pentane (5 mL) and dried in vacuo to give **9** (104 mg, 31%), m.p. 261 °C. Elemental analysis (%) calcd for $C_{16}H_6O_2BF_5$ (336.02): C 57.19, H 1.80; found: C 56.93, H 2.04. Single crystals of **9** were obtained from a solution in benzene after 2 d at room temperature.[5c] ^1H NMR ([D$_8$]THF, 599.8 MHz): $\delta = 7.69$ (dd, $^3J = 6.2$ Hz, $^4J = 3.3$ Hz, 2H, 6-H, 7-H), 7.34 (s, 2H, 1-H, 4-H), 7.26 (dd, $^3J = 6.2$ Hz, $^4J = 3.3$ Hz, 2H, 5-H, 6-H); ^{13}C NMR ([D$_8$]THF, 150.8 MHz): $\delta = 150.8$ (C2, C3), 131.5 (C4a, C8a), 127.8 (C6, C7), 124.4 (C5, C8), 106.9 (C1, C4), $B(C_6F_5)_3$ signals at 150.0 ($^1J_{CF} = 252$ Hz), 142.8 ($^1J_{CF} = 255$ Hz), 138.3 ($^1J_{CF} = 252$ Hz) (*o*-, *p*-, *m*-C of C_6F_5; *ipso*-C not observed); ^{19}F NMR ([D$_8$]THF, 282.4 MHz): $\delta = -128.5, -151.2, -161.2$ (*o*-, *p*-, *m*-F); ^{11}B NMR ([D$_8$]THF, 64.2 MHz): $\delta = 19.0$ ($w_{1/2} = 260 \pm 20$ Hz); IR (KBr): $\tilde{\nu} = 3063, 1655, 1531\,cm^{-1}$. The reaction of **7** with **1** was also directly monitored by NMR spectroscopy. This led to the detection of the product C_6F_5H and the intermediate **8**. **8**: ^1H NMR ([D$_6$]benzene, 599.8 MHz): $\delta = 6.83$ (m, 2H, 6-H, 7-H), 6.64 (d, $^3J = 7.4$ Hz, 1H, 8-H), 6.49 (s, 1H, 4-H), 6.35 (d, $^3J = 7.3$ Hz, 1H, 5-H), 2.90 (s, 2H, 1-H); ^{13}C NMR ([D$_6$]benzene, 150.8 MHz): $\delta = 203.4$ (C2), 155.0 (C3), 131.0 (C8a), 129.6 (C4a), 128.2 (C6, C7), 128.1 (C8), 127.1 (C5), 125.5 (C4), 29.9 (C1), $B(C_6F_5)_3$ signals at 148.3 ($^1J_{CF} = 248$ Hz), 146.0 ($^1J_{CF} = 248$ Hz), 137.6 ($^1J_{CF} = 256$ Hz) (*o*-, *p*-, *m*-CF), 113.7 (br, *ipso*-C of C_6F_5); ^{11}B NMR ([D$_6$]benzene, 64.2 MHz): $\delta = 14.4$ (br, $w_{1/2} = 260 \pm 20$ Hz); ^{19}F NMR ([D$_6$]benzene, 282.4 MHz): $\delta = -135.1, -154.4, -162.9$ (*o*-, *p*-, *m*-F).

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[5] a) X-ray crystal structure analysis of **3**:[5d] $C_{28}H_8OBF_{15}$, $M_r = 656.15$, colorless crystal, $0.40 \times 0.30 \times 0.30$ mm, $a = 12.560(1)$, $b = 10.444(1)$, $c = 19.857(1)$ Å, $\beta = 102.88(1)°$, $V = 2539.2(3)$ Å^3, $\rho_{calcd} = 1.716\,g\,cm^{-3}$, $F(000) = 1296$ e, $\mu = 16.29\,cm^{-1}$, absorption correction with ψ scan data ($0.562 \leq T \leq 0.641$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans; of 4533 reflections collected ($-h, -k, \pm l$), $[(\sin\theta)/\lambda]_{max} = 0.55$ Å^{-1}, 4319 were independent and 3787 observed [$I \geq 2\sigma(I)$]; 407 refined parameters, $R = 0.065$, $wR^2 = 0.176$, max./min. residual electron density $0.49/-0.47\,e\,Å^{-3}$;

hydrogen atoms were calculated and refined as riding atoms. The data set was collected with a Enraf Nonius CAD4 diffractometer. Programs used: data reduction: MolEN (K. Fair, Enraf Nonius B. V., 1990), structure solution: SHELXS-86 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473), structure refinement: SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics: SCHAKAL (E. Keller, Universität Freiburg, 1997). b) X-ray crystal structure analysis of **5**:[5d] $C_{42}H_{24}O_2BF_{15}$, $M_r = 856.42$, crystal size 0.40 × 0.30 × 0.25 mm, $a = 10.436(1)$, $b = 14.121(1)$, $c = 14.438(1)$ Å, $\alpha = 66.74(1)$, $\beta = 71.45(1)$, $\gamma = 77.15(1)^\circ$, $V = 1841.7(3)$ Å^3, $\rho_{calcd} = 1.544$ g cm^{-3}, $F(000) = 864$ e, $\mu = 1.46$ cm^{-1}, absorption correction with SORTAV ($0.944 \leq T \leq 0.965$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans; of 18063 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]_{max} = 0.59$ Å^{-1}, 6348 were independent and 3592 observed $[I \geq 2\sigma(I)]$, 544 refined parameters, $R = 0.078$, $wR^2 = 0.183$, max./min. residual electron density 0.39/ – 0.34 e Å^{-3}; hydrogen atoms were calculated and refined as riding atoms. The structure contains two toluene molecules in the asymmetric unit. The data set was collected with a Nonius KappaCCD diffractometer on a rotating anode generator (FR 591). Programs used: data acquisition: COLLECT (Nonius B. V., 1998), data reduction: Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326), absorption correction: SORTAV (R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421–426), structure solution: SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473), structure refinement: SHELXL-97, graphics: SCHAKAL-92. c) X-ray crystal structure analysis of **9**:[5d] $C_{16}H_6O_2BF_5$, $M_r = 336.02$, crystal size 0.30 × 0.25 × 0.05 mm, $a = 11.110(1)$, $b = 8.344(1)$, $c = 13.876(1)$ Å, $\beta = 93.19(1)^\circ$, $V = 1284.3(2)$ Å^3, $\rho_{calcd} = 1.738$ g cm^{-3}, $F(000) = 672$ e, $\mu = 1.61$ cm^{-1}, absorption correction with SORTAV ($0.953 \leq T \leq 0.992$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans; 9733 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.71$ Å^{-1}, 3885 were independent and 2941 observed $[I \geq 2\sigma(I)]$, 217 refined parameters, $R = 0.051$, $wR^2 = 0.112$, max./min. residual electron density 0.33/ – 0.22 e Å^{-3}; hydrogen atoms were calculated and refined as riding atoms. The data set was collected with a Nonius KappaCCD diffractometer on a rotating anode generator (FR 591). d) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-120955 (**3**), -120956 (**5**), and -120957 (**9**). 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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Palladium-Catalyzed Hydroalkoxylation of Methylenecyclopropanes

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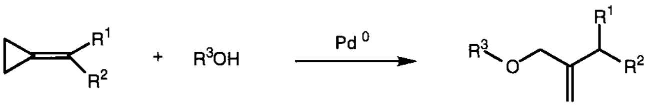
The activation of heteroatom–hydrogen bond or carbon–hydrogen bonds by transition metal catalysts is becoming an increasingly important method in organic synthesis.[1–4] The palladium-catalyzed addition of carbon pronucleophiles to an olefinic bond—that is, hydrocarbonation[1]—enabled the formation of C–C bonds to unsaturated hydrocarbons. Likewise, hydroamination,[2] hydrocarboxylation,[3] and hydrosulfination[4] of unsaturated carbon–carbon bonds have also been developed.

The transition metal catalyzed addition of alcohols to olefins to form a C–O bond—that is, hydroalkoxylation—is also an important synthetic method. The addition reactions of alcohols to dienes[5] or allenes[6] presumably proceed via cyclic palladium intermediates,[5c] where dimerization of the acceptors occurs. These processes are therefore different from pronucleophilic additions. In our continuing study of pronucleophiles, we concentrated on the addition of alcohols to nonconjugated olefins. We report herein that the palladium-catalyzed reaction of alcohols **2** with methylenecylopropanes **1** affords the hydroalkoxylation products **3** regioselectively and in good yields (Scheme 1).



1 **2** **3**

Scheme 1. Palladium-catalyzed synthesis of **3**. Reaction conditions: 1 equiv of **1** and **2** (0.5 mmol), 5 mol% $[Pd(PPh_3)_4]$, 10 mol% P(*o*-tolyl)$_3$, THF, 100°C, 3 d.

The results are summarized in Table 1. In the presence of catalytic amounts of tetrakis(triphenylphosphane)palladium (5 mol%) and tri-*o*-tolylphosphane (10 mol%) the reaction of octylidenecyclopropane (**1a**) with benzyl alcohol (**2a**) in THF at 100°C gave the hydroalkoxylated product **3a** in 69% yield (entry 1). No addition product or ring opening of **1a** was observed in the absence of palladium catalyst. Other catalysts such as $[Pd_2(dba)_3] \cdot CHCl_3$ (dba = dibenzylideneacetone), $Pd(OAc)_2$, and $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ in combination with P(*o*-tolyl)$_3$ and 1,3-bis(diphenylphosphanyl)propane (dppp) did not promote the reaction at all. The use of $[Pd(PPh_3)_4]$ without P(*o*-tolyl)$_3$ ligand gave **3a** in lower yield (46%). The combination of $[Pd(PPh_3)_4]$ with other ligands such as bis(diphenylphosphanyl)methane (dppm), 1,2-bis(diphenylphosphanyl)ethane (dppe), dppp, 1,4-bis(diphenylphosphanyl)butane (dppb), 1,1′-bis(diphenylphosphanyl)ferro-

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