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, $\omega$ and $\varphi$ 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, $\omega$ and $\varphi$ 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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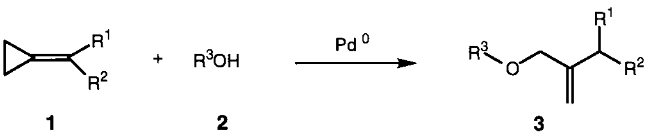
The activation of heteroatom–hydrogen bond or carbon–hydrogen bonds by transition metal catalysts is becoming an increasingly important method in organic synthesis.[1–4] The palladium-catalyzed addition of carbon pronucleophiles to an olefinic bond—that is, hydrocarbonation[1]—enabled the formation of 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).



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)$_3$]·CHCl$_3$ (dba = dibenzylideneacetone), Pd(OAc)$_2$, and [{($\eta^3$-C$_3$H$_5$)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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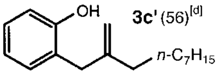
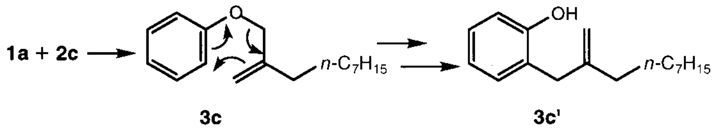
Table 1. Palladium-catalyzed addition of alcohols **2** to methylenecyclopropanes **1**.[a]

| Entry | 1 | 2 | 3 (yield [%])[b] |
|---|---|---|---|
| 1 | **1a** ($R^1 = n$-$C_7H_{15}$; $R^2 = H$) | $PhCH_2OH$ (**2a**)[c] | **3a** (69) |
| 2 | **1a** | $CF_3CH_2OH$ (**2b**) | **3b** (68) |
| 3 | **1a** | PhOH **2c**[c] |  **3c'** (56)[d] |
| 4 | **1a** | 2,4,6-trimethylphenol (**2d**) | **3d** (67)[e] |
| 5 | **1a** | *n*-butanol (**2e**)[f] | **3e** (63) |
| 6 | **1a** | *sec*-butanol (**2f**)[f] | **3f** (24) |
| 7 | **1a** | *tert*-pentanol (**2g**)[f] | **3g** (25) |
| 8 | **1a** | $H_2C{=}CHCH_2OH$ (**2h**)[f] | **3h** (35) |
| 9 | **1a** | $Et_3SiOH$ (**2i**) | **3i** (49) |
| 10 | **1b** ($R^1 = PhCH_2CH_2$; $R^2 = H$) | **2a**[c] | **3j** (67) |
| 11 | **1c** ($R^1 = R^2 = PhCH_2CH_2$) | **2a**[c] | **3k** (80) |

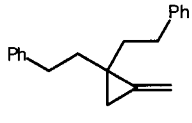
[a] Unless otherwise specified, all reactions were carried out in a microreactor in 1:1 molar ratio of the substrates (0.5 mmol) with 5 mol% $[Pd(PPh_3)_4]$ and 10 mol% $P(o\text{-tolyl})_3$ in THF at 100 °C for 3 d. [b] Yield of isolated product. [c] The solvent used was toluene. [d] See text. [e] The reaction was carried out at 70 °C. [f] The alcohol was used as the solvent.

cene (dppf), or $PPh_3$ yielded trace amounts of **3a**. The reaction of 2,2,2-trifluoroethanol (**2b**) with **1a** gave **3b** in 68% yield (entry 2). The reaction of phenol (**2c**) and **1a** also proceeded smoothly (entry 3), but the product **3c'** was formed. We assumed that **3c'** was formed by the Claisen rearrangement of the initial product **3c** (Scheme 2). The reaction of 2,4,6-trimethylphenol (**2d**) with **1a** proceeded

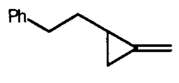


Scheme 2. The Claisen rearrangement of **3c** to **3c'**.

smoothly to give the allyl ether product **3d** in 67% yield (entry 4). An excess amount of *n*-butanol (**2e**) reacted with **1a** to afford **3e** in 63% yield (entry 5). The use of one equivalent of **2e** gave **3e** in poor yield, indicating that a normal aliphatic alcohol is less reactive than **2a**–**d**. Similarly the use of the bulky alcohols **2f** and **2g** as solvents afforded **3f** and **3g**, respectively (entries 6 and 7). The use of allyl alcohol as an oxygen pronucleophile also gave the desired product (entry 8). The low yield of **3h** could be attributed to the possible elimination of the allyl moiety in **3h** by palladium. Triethylsilanol (**2i**) also reacted with **1a** to afford **3i** in moderate yield (entry 9). The methylenecyclopropanes **1b** and **1c** with a 2-phenethyl substituent at the exocyclic methylene carbon atom also underwent hydroalkoxylation reactions with **2a** to give **3j** and **3k**, respectively (entries 10 and 11). However, the reactions of **1d** or **1e** with either **2a** or **2b** did not give the desired hydroalkoxylation products at all.



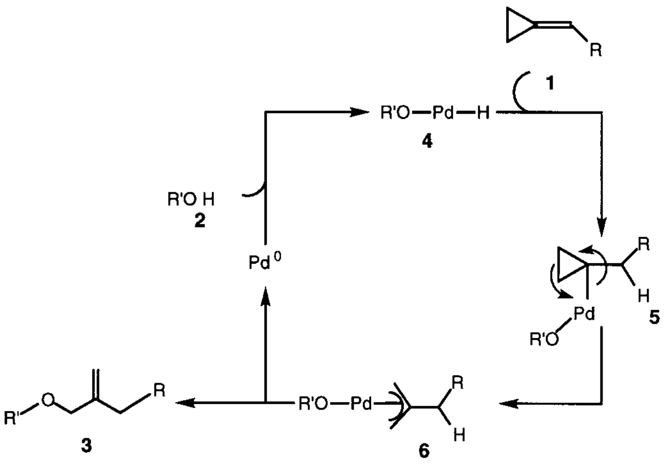
**1d**



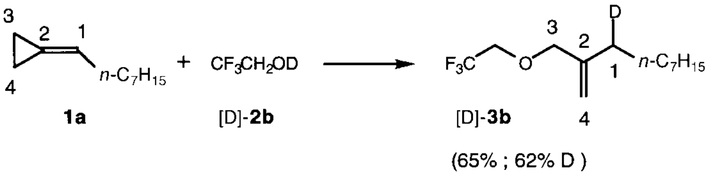
**1e**

We propose the mechanism shown in Scheme 3 to explain the observed reaction. Oxidative addition of $Pd^0$ into the O–H bond of alcohol **2** would produce the alkoxohydridopalladium species **4**.[7] The hydropalladation of methylenecyclopropane **1** with **4** would afford the alkylpalladium complex **5** by a Markovnikov-type addition. The distal bond cleavage of **5** would afford the π-allylpalladium species **6** by rearrangement. Reductive elimination of $Pd^0$ from **6** would produce **3** and regenerate $Pd^0$.

The proposed mechanism is in accordance with the palladium-catalyzed hydrocarbonation[1c] and hydroamination[2f] of methylenecylopropanes. The reaction of deuterated trifluoroethanol ([D]-**2b**) with **1a** (Scheme 4) substantiated the proposed hydroalkoxylation mechanism. Under the same conditions as above, the reaction gave [D]-**3b** in 65% yield; the deuterium content at C1 was 62%. Deuterium incorporation did not occur at the other carbon atoms of **1a**. The result supports the mechanism of Markovnikov hydropalladation and distal bond cleavage.



Scheme 3. Proposed mechanism for the addition of alcohols **2** to methylenecyclopropanes **1**.



Scheme 4. Reaction of methylenecyclopropane **1a** with deuterated trifluoroethanol ([D]-**2b**). See Scheme 1 for reaction conditions.

In summary, palladium-catalyzed addition of alcohols to methylenecyclopropanes has been achieved. Distal bond cleavage is characteristic of this reaction, making it highly regioselective. This reaction differs considerably from palladium-catalyzed hydrostannation[8] and rhodium-catalyzed hydrosilylation,[9] where proximal bond cleavage is observed. The high regioselectivity as well as the wide scope of alcohols that can undergo hydroalkoxylation with methylenecyclopropanes make this reaction a versatile process in organic synthesis.

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# The First Molecular Main Group Metal Species Containing Interstitial Hydride[**]

David R. Armstrong, William Clegg, Robert P. Davies, Stephen T. Liddle, David J. Linton, Paul R. Raithby, Ronald Snaith, and Andrew E. H. Wheatley[*]

As part of an ongoing study[1] into the mechanism by which "mixed" organolithium/organoaluminum reagents promote conjugate addition to $\alpha,\beta$-unsaturated ketones, we attempted to synthesize $Me_2(tBu)Al[N(2\text{-}Pyr)Ph]Li$ (2-Pyr = 2-pyridyl) by treating dimethyl(2-pyridylanilido)aluminum (**1**) with one equivalent of *t*BuLi. Remarkably, however, this reaction in toluene afforded in reasonable yield (over 40%) the ion-separated compound **2**, neither component of which contains any Al–N bonds. Rather, the anion is an unprecedented lithium bis(aluminate) while the cation, equally unprecedented, contains a hydride anion within a distorted $(Li^+)_8$ cubic cage. Treatment of the reaction mixture with THF results in removal of one $Li^+$ ion from this cage to give **3**.

$Me_2AlN(2\text{-}Pyr)Ph$ **1**

$[Li_8(H)\{N(2\text{-}Pyr)Ph\}_6]^+[Li(Me_2Al\mathit{t}Bu_2)_2]^-$ **2**

$Li_7(H)[N(2\text{-}Pyr)Ph]_6$ **3**

Treatment of **1** in toluene at −78 °C with one equivalent of *t*BuLi gave a suspension which can be dissolved in further toluene, the resultant solution affording colorless crystals of **2** as the only isolable product. Superior yields were obtained by using 1.5 equivalents of *t*BuLi (see Experimental Section). X-ray crystallography[2] showed that in the solid state **2** is a remarkable mixed aggregate which incorporates both an unprecedented lithium bis(aluminate) anion and a hydride-containing lithium amide cation. The $[Li(Me_2Al\mathit{t}Bu_2)_2]^-$ ion (Figure 1) contains two Al centers arranged such that two methyl substituents on each are tetrahedrally disposed about Li(5) to afford an $Al(\mu\text{-}C)_2Li(\mu\text{-}C)_2Al$ motif. This is one of the few examples of an alkali metal containing anion.[3] This molecular motif is related to the repeat unit of polymeric lithium tetra(alkyl)aluminates, and the mean $Li-(\mu\text{-}C)$ and $Al-(\mu\text{-}C)$ distances of 2.25 and 2.07 Å, respectively, are comparable to those of 2.30 and 2.02 Å in $LiAlEt_4$.[4]

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