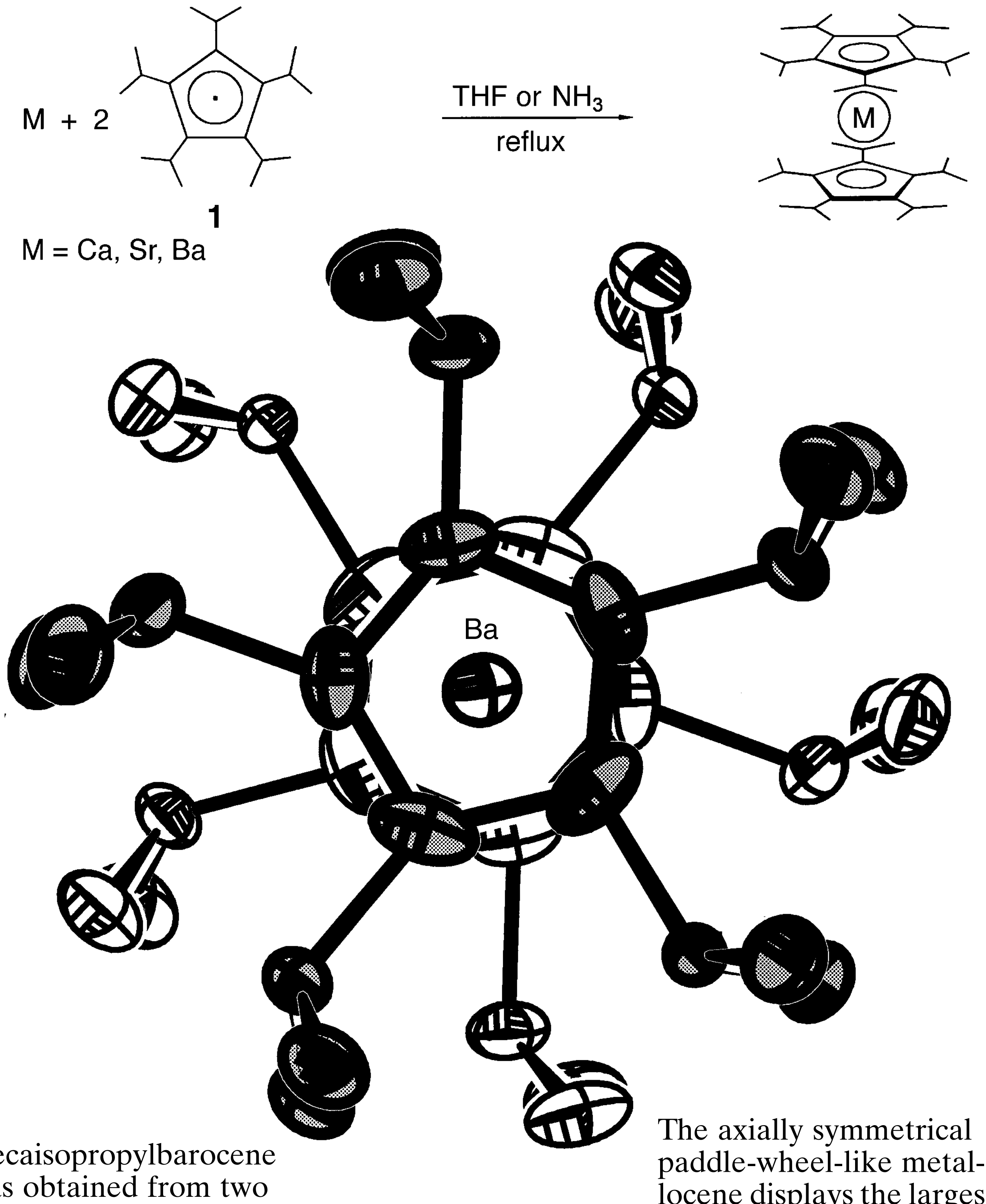


Decaisopropylbarocene was obtained from two equivalents of the cyclopentadienyl radical $[C_5R_5]^{\bullet}$ ($R = CHMe_2$) and elemental barium.

The axially symmetrical paddle-wheel-like metallocene displays the largest distance between two neighboring parallel rings of a sandwich compound

More details on the following pages.

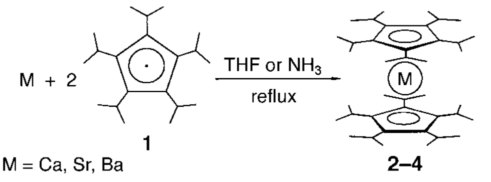
# Synthesis of Symmetric Metallocenes from Metallic Calcium, Strontium, or Barium and Pentaisopropylcyclopentadienyl Radicals**

Helmut Sitzmann,* Thomas Dezember, and
Michael Ruck

*Dedicated to Professor Otto J. Scherer on the occasion of his 65th birthday*

The bent sandwich geometry of the heavy alkaline earth metallocenes has been intensively investigated and is the subject of many review articles[1] and theoretical studies.[2] In order to achieve a symmetrical metallocene structure, the cyclopentadienyl ligand must possess axial symmetry and sufficient steric bulk. Since the pentaphenylcyclopentadienyl ring did not yield the desired decaphenylbarocene,[3] the pentaisopropylcyclopentadienyl ring appeared to be the only remaining candidate for the synthesis of symmetric calcium, strontium, or barium metallocenes. Furthermore, the availability of the stable pentaisopropylcyclopentadienyl radical (**1**)[4] as a starting material offered an unprecedented synthetic pathway to metallocene synthesis.

The reaction of metallic calcium, strontium, or barium with two equivalents of **1** proceeds smoothly in THF to form decaisopropylcalcocene (**2**), decaisopropylstrontocene (**3**), and decaisopropylbarocene (**4**) in good yields [Eq. (1)]. Sonication speeds up the reaction but is not essential.



(1)

Solutions of the heavy alkaline earth metals in liquid ammonia also react with **1** to form **2**–**4**. The solubility of all three metallocenes is, like decaisopropylstannocene[5] and -plumbocene,[6] low to moderate in pentane and toluene at room temperature, but can be increased by warming. When the solutions are cooled, the compounds crystallize readily in the form of colorless crystals. The crystalline calcocene and strontocene derivatives remain unchanged in air for several weeks. The barocene derivative develops a faint yellow tinge with time, which indicates very slow decomposition in air.

NMR spectra in the temperature range between 298 and 373 K indicate a gear-meshed conformation of the two pentaisopropylcyclopentadienyl rings, where the isopropyl groups have an equal or opposing orientation, thus giving rise to *rac* and *meso* isomers.[7] The isomers interconvert by isopropyl group rotation with Gibbs free activation enthalpy values of 71.8(1.5)/72.0(1.5) (**2**), 72.5(1.5)/72.8(1.5) (**3**), and 74.0(1.5)/74.6(1.5) kJ mol$^{-1}$ (**4**). These values compare well with those found for the decaisopropylstannocene (74.8/75.5 kJ mol$^{-1}$) and -plumbocene isomers (73.0/73.7 kJ mol$^{-1}$), and with 71.3 kJ mol$^{-1}$ found for the 1,2,3,4,5-pentaisopropylcobaltocenium cation.[8] The substantially larger rotational barrier found for the decaisopropylrhodocenium cation (85.5 kJ mol$^{-1}$)[9] is presumably due to a relatively small interplanar distance with significant repulsive forces between adjacent rings.

The structure of **4** was determined by X-ray crystal structure analysis and is shown in Figure 1. Although the *meso* and *rac* isomers were distributed randomly throughout the crystal in a 1:1 ratio, the structure model could be refined very well.[10] The molecule was located on a center of symmetry with parallel and staggered arrangements of the pentaisopropylcyclopentadienyl rings. The inter-ring distance of 5.497(3) Å in barocene **4** is only 5.6 % smaller than the value of 5.82 Å found for the free pentaisopropylcyclopentadienyl radical (**1**).[4] This is the largest interplanar distance yet reported for any sandwich compound to our knowledge.[11] The isopropyl methine carbon atoms connected to the five-membered ring are bent away from the central atom and are displaced out of the ring plane by an average of 0.139 Å. The distance between two adjacent pentaisopropylcyclopentadienyl rings of different molecules is 6.39 Å. This cannot be compared directly to the distance between rings in the free pentaisopropylcyclopentadienyl radical since the isopropyl groups are bent out of plane. The barocene molecules are stacked along the crystallographic *c* axis and are tilted towards this axis by approximately 11° (Figure 2). The Ba$\cdots$Ba distance within a stack is 12.123(2) Å. Barocene **4** forms

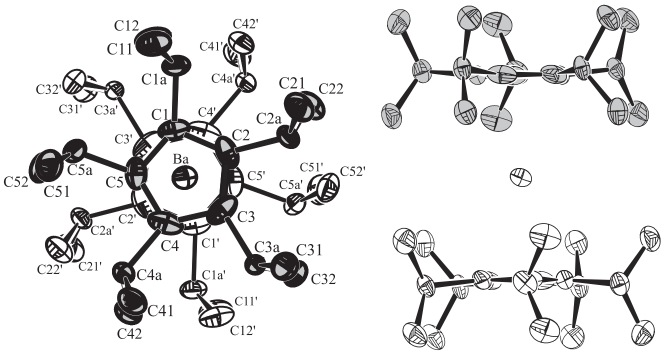


Figure 1. Molecular structure of **4** in the crystal (ellipsoids are drawn at the 50 % probability level). Selected bond lengths [Å] and angles [°]: Ba–C1 2.981(2), Ba–C2 2.995(2), Ba–C3 3.014(2), Ba–C4 3.008(2), Ba–C5 2.989(2), C1–C2 1.402(3), C2–C3 1.407(3), C3–C4 1.413(3), C4–C5 1.401(3), C5–C1 1.405(3); Cp$_{center}$–Ba 2.748(2), Cp$_{center}$-Ba-Cp$'_{center}$ 180. For clarity, only the *meso* isomer is shown.

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[*] Prof. Dr. H. Sitzmann, Dr. T. Dezember
FB Chemie der Universität
Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern (Germany)
Fax: (+49) 631-205-2187
E-mail: sitzmann@rhrk.uni-kl.de
http://www.uni-kl.de/FB-Chemie/Sitzmann/index.html
Priv.-Doz. Dr. M. Ruck
Institut für Anorganische Chemie der Universität
(TH) Karlsruhe (Germany)

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1433-7851/98/3722-3114 $ 17.50+.50/0

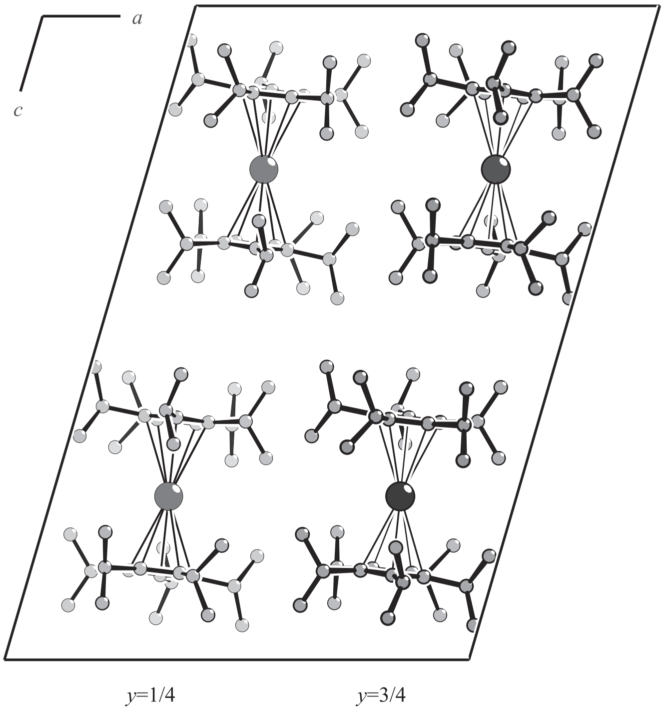

Figure 2. Stacking of **4** in the monoclinic unit cell.

near-hexagonal layers parallel to the *a*,*b* plane with Ba⋯Ba distances of 9.652(2) and 9.963(2) Å.

The only previous attempt known to us to use a cyclopentadienyl radical for metallocene synthesis was by Wilke et al.[12] who treated bis(1,5-cyclooctadiene)nickel(0) with Ziegler's pentaphenylcyclopentadienyl radical. From a formal point of view, the combination of a metal atom with two cyclopentadienyl radicals represents the simplest concept for metallocene synthesis. With the formation of **2**–**4**, this concept could be verified for the first time with the heavy alkaline earth metals calcium, strontium, and barium, and the pentaisopropylcyclopentadienyl radical $[C_5R_5]^{\bullet}$ ($R = CHMe_2$).

## *Experimental Section*

**1**: Silver chloride (0.99 g, 6.96 mmol) was added to a solution of lithium pentaisopropylcyclopentadienide-diethyl ether adduct (2.48 g, 6.96 mmol) (prepared according to the published procedure[13]) in diethyl ether (50 mL) and the mixture was stirred for 48 h at room temperature. The silver precipitate was removed by centrifugation and the residue of the evaporated solution was recrystallized from petroleum ether at −30 °C to yield light green-yellow crystals of **1** (1.45 g, 5.27 mmol; 76 %). (For the characterization of **1** see ref. [4a].)

Synthesis of **4** (**2** and **3** were synthesized by the same procedure): Barium metal (380 mg, 2.76 mmol) was dissolved in liquid ammonia (150 mL) and a solution of **1** (1.52 g, 5.52 mmol) in diethyl ether (15 mL) was added dropwise within a few minutes. The mixture was stirred under reflux for 2 h. After removal of solvent, the residue was extracted with pentane (50 mL) at 0 °C and with toluene (50 mL) at 60–70 °C. The volatile products were sublimed off at 80 °C (0.1 mbar) from the residue of the pentane extract (340 mg). After sublimation, 170 mg of **4** was obtained and combined with the main fraction from the toluene extract. Yield: 1.51 g (2.23 mmol; 81 %). Recrystallization from hot toluene gave analytically pure crystalline **4**.

Alternative synthesis of **3** (**2** and **4** were synthesized by the same procedure): Strontium metal (131 mg, 1.50 mmol), **1** (827 mg, 3.00 mmol), and THF (15 mL) were sealed in a glass tube and sonicated in an ultrasonic bath for 12 h at 60 °C. The tube was opened in a glove box and the white suspension was collected, evaporated to dryness, extracted with toluene (40 mL) at 60–70 °C, filtered over celite and finally evaporated to ca. 5 mL residual volume. At −30 °C, the product precipitated as a microcrystalline, white solid which was washed with two 5 mL portions of pentane at 0 °C and dried in vacuo. Yield: 0.81 g (1.27 mmol; 84 %).

**2**: $^1H$ NMR (400 MHz, 313 K, $C_6D_6$): $\delta = 3.28$ (sept, 10 H; C*H*Me$_2$), 1.56 (d, $^3J(H,H) = 7.0$ Hz, 15 H; inner CH$_3$ of one isomer), 1.54 (d, $^3J(H,H) = 7.0$ Hz, 15 H; inner CH$_3$ of other isomer), 1.24 (d, $^3J(H,H) = 6.6$ Hz, 15 H; outer CH$_3$ of both isomers); m.p. = 389 °C (decomp).

**3**: $^1H$ NMR (400 MHz, 313 K, $C_6D_6$): $\delta = 3.25$ (sept, 10 H; C*H*Me$_2$), 1.46 (d, $^3J(H,H) = 7.2$ Hz, 15 H; inner CH$_3$ of one isomer), 1.44 (d, $^3J(H,H) = 7.2$ Hz, 15 H; inner CH$_3$ of other isomer), 1.29 (d, $^3J(H,H) = 6.8$ Hz, 15 H; outer CH$_3$ of both isomers); $^{13}C\{^1H\}$ NMR (100 MHz, 363 K, $C_6D_6$): $\delta = 125.6$ (s, 10 C; ring C), 27.2 (s, 10 C; *C*HMe$_2$), 24–26 (very broad, 20 C; CH$_3$); CI-MS (isobutane, 120 eV): *m*/*z* (%): 638.1 (16) [$M^+$], 363.2 (6) [$M^+ - C_5(CHMe_2)_5$], 107.1 (100) [$C_5H_4(CHMe_2)^+$]. Compound **3** decomposed slowly above 400 °C without melting.

**4**: $^1H$ NMR (400 MHz, 313 K, $C_7D_8$): $\delta = 3.57$ (sept, 10 H; C*H*Me$_2$), 1.58 (d, $^3J(H,H) = 7.1$ Hz, 15 H; inner CH$_3$ of one isomer), 1.56 (d, $^3J(H,H) = 6.7$ Hz, 15 H; inner CH$_3$ of other isomer), 1.47 (d, $^3J(H,H) = 7.1$ Hz, 15 H; outer CH$_3$ of both isomers); CI-MS (isobutane, 120 eV): *m*/*z* (%): 688.6 (2.4) [$M^+$], 413.3 (100) [$M^+ - C_5(CHMe_2)_5$], 275.4 (8.6) [$C_5(CHMe_2)_5^+$], 233.3 (2.9) [$C_5H(CHMe_2)_4^+$], 191.3 (11) [$C_5H_2(CHMe_2)_3^+$], 149.2 (45) [$C_5H_3(CHMe_2)_2^+$], 107.1 (95) [$C_5H_4(CHMe_2)^+$]. Compound **4** decomposed slowly above 400 °C without melting.

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D-76344 Eggenstein-Leopoldshafen (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-408943.

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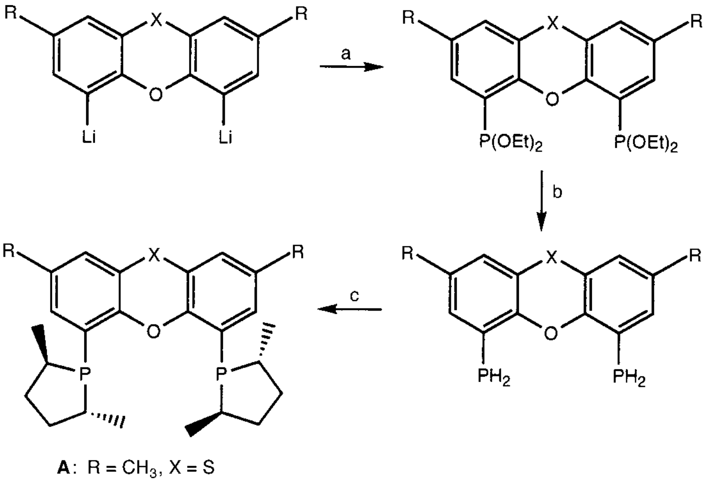
## Versatile Ligands for Palladium-Catalyzed Asymmetric Allylic Alkylation[**]

Peter Dierkes, Shailesh Ramdeehul, Laurent Barloy, Andre De Cian, Jean Fischer, Paul C. J. Kamer, Piet W. N. M van Leeuwen, and John A. Osborn[*]

The search for chiral ligands for asymmetric allylic substitution reactions with Pd complexes as catalysts continues apace.[1] High enantiomeric excesses (*ee*) were found for carbon-centered and other nucleophiles with *O*-acetyl-1,3-diphenyl-2-propen-3-ol as the model substrate. Much lower product *ee* values are generally observed for substrates with small substituents[1a] and with less sterically demanding cyclic substrates,[2] although for one family of diphosphane ligands the opposite appears to be true.[2b] The origin of enantioselectivity in these catalytic processes is still under debate, and several parameters are involved. It is generally accepted that in the attack of the nucleophile on the intermediate cationic ($\eta^3$-allyl)Pd$^{II}$ complex, the repulsive interactions in the transition state[3] between the chiral ligand and the organic entity bound to the Pd center are an important factor which can largely determine the selectivity. To intensify these repulsive interactions at the Pd center, we synthesized rigid chelating chiral ligands with a large bite angle. Xanthene (dibenzo[*b*,*d*]pyran) and phenoxathiin (dibenzo-1,4-thioxin) were selected as rigid backbones, since 4,5 substitution of the former (older, nonsystematic numbering) and 4,6 substitution of the latter by phosphorus-containing groups leads to a large bite angle (>100°), as in Xantphos complexes.[4]

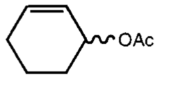
By attaching the chiral (2*R*,5*R*)-2,5-dimethylphospholano groups that were originally used in DUPHOS,[5] a family of several duxantphospholane-type chiral ligands are accessible. The new ligands were obtained in four steps by dilithiation of the backbone, reaction with diethyl chlorophosphonite, reduction with $LiAlH_4$, and treatment of the resulting phosphane with the cyclic sulfate of (2*S*,5*S*)-2,5-hexanediol. This is illustrated by the synthesis of the (*R*,*R*)-duthixantphospholane **A** (Scheme 1). The related chiral ligand, (*R*,*R*)-duxantphospholane **B**, in which the bridging S atom of **A** is formally replaced by a $C(CH_3)_2$ group, was prepared by the same method.[6]



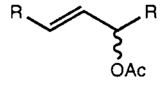
**A**: R = $CH_3$, X = S
**B**: R = H, X = $C(CH_3)_2$

Scheme 1. Synthesis of the chiral P ligand **A**. a) $ClP(OEt)_2$; b) 1) 6 equiv $LiAlH_4$/TMSCl; 2) 30 equiv MeOH; c) 1) 2.0 equiv *n*BuLi; 2) cyclic sulfate of (2*S*,5*S*)-hexane-2,5-diol; 3) 2.2 equiv *n*BuLi. TMS = trimethylsilyl.

The effectiveness of such ligands in Pd-catalyzed allylation reactions was tested by employing dimethyl malonate as the nucleophile and three racemic allyl acetates possessing different steric properties: *O*-acetylcyclohex-2-enol (**1**), *O*-acetylpent-2-en-3-ol (**2**), and *O*-acetyl-1,3-diphenylprop-1-en-2-ol (**3**). Typically a 1 mol% solution of the catalyst was prepared



*rac*-**1**



*rac*-**2** R = $CH_3$
*rac*-**3** R = $C_6H_5$

by the addition of one equivalent of **A** (or **B**) to 0.5 mol of [{Pd($\eta^3$-$C_3H_5$)Cl}$_2$] and stirring under nitrogen for 15 min before adding the reactants (Table 1). The catalytic reactions are rapid with the less sterically hindered substrates **1** and **2**

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[*] Prof. J. A. Osborn, S. Ramdeehul, Dr. L. Barloy
Laboratoire de Chimie des Métaux de Transition et de Catalyse
Université Louis Pasteur
Institut Le Bel, UMR 7513 CNRS
4 rue Blaise Pascal, F-67070 Strasbourg Cedex (France)
Fax: (+33) 388-416-171
E-mail: osborn@chimie.u-strasbg.fr

Prof. P. W. N. M van Leeuwen, Dr. P. Dierkes, Dr. P. C. J. Kamer
Universiteit van Amsterdam
Institute for Molecular Chemistry
van't Hoff Research Institute
Nieuwe Achtergracht 166
NL-1018 WV Amsterdam (The Netherlands)

Prof. J. Fischer, Dr. A. De Cian
Laboratoire de Cristallochimie et Chimie Structurale
Université Louis Pasteur
Institut Le Bel, UMR 7513 CNRS
4 rue Blaise Pascal, F-67070 Strasbourg Cedex (France)

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