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Tetrahedron Letters
Tetrahedron Letters 48 (2007) 8217–8219

Carboranylphosphites—new effective ligands for rhodium-catalyzed asymmetric hydrogenation of dimethyl itaconate

Sergey E. Lyubimov,* Andrey A. Tyutyunov, Valery N. Kalinin, Ernest E. Said-Galiev, Alexey R. Khokhlov, Pavel V. Petrovskii and Vadim A. Davankov

Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov street, 119991 Moscow, Russia

Received 31 July 2007; revised 5 September 2007; accepted 12 September 2007
Available online 18 September 2007

Abstract—Novel monodentate phosphites containing *ortho*- and *meta-closo*-dodecarboranyl groups have been synthesized and applied in the asymmetric Rh-catalyzed hydrogenation of dimethyl itaconate, providing excellent enantioselectivities (up to 99.8% ee in CH_2Cl_2 and up to 93% ee in supercritical CO_2).

1. Introduction

Carborane-containing organophosphorus derivatives are attractive candidates for asymmetric transition metal catalysis due to their high sterically congested structures and stability to oxidative destruction.[1] Surprisingly, none of these derivatives has been examined in asymmetric transformations, such as transitional metal-catalyzed asymmetric hydrogenation, a practical method of producing optically pure organic compounds as it involves inexpensive molecular hydrogen. Rhodium-catalyzed asymmetric hydrogenation of prochiral olefins has generally been conducted using bidentate phosphines.[2] In recent years, increasing attention has been directed to chiral monodentate phosphites and phosphoramidites, due to their ready accessibility and efficiency in the hydrogenation of dehydroamino acids and itaconic acid derivatives.[3] Nevertheless, results obtained with chiral monodentate phosphite-type ligands in supercritical carbon dioxide ($scCO_2$), as an inexpensive, environmentally friendly reaction medium, are much less impressive with the highest ee being 65% at 28% conversion, compared to bidentate phosphines (up to 99% ee, 100% conversion).[4] Herein, we report the first synthesis of BINOL-derived *ortho*- and *meta-closo*-dodecarboranyl monodentate phosphites and their successful application as chiral ligands in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate in CH_2Cl_2 and $scCO_2$.

The new monodentate phosphites were synthesized by a convenient one-step phosphorylation of the corresponding *ortho*- and *meta*-9-hydroxy-dicarba-*closo*-dodecaboranes **1** and **2** (Scheme 1). Products **3** and **4** were characterized by ^{31}P, ^{1}H and ^{11}B NMR spectroscopy and by elemental analysis.[5] They occur as white solids and are very stable under ambient atmosphere.

To examine the behaviour of ligands **3** and **4**, they were used in the Rh-catalyzed hydrogenation of the benchmark substrate, dimethyl itaconate **5** (Scheme 2). The catalyst was formed in situ by mixing a cationic Rh complex, $[Rh(COD)_2]BF_4$, with 2 equiv of the chiral ligands in CH_2Cl_2 under argon. Both ligands demonstrated similar high enantioselectivities and complete conversion occurred at ambient temperature under 5 atm of H_2 (Table 1).

Reaction of P-monodentate phosphite **4** with $[Rh(COD)_2]BF_4$ afforded the corresponding cationic rhodium complex **7**,[6] which provided the same level of enantioselectivity and conversion as the catalysts formed in situ (Scheme 3).

Cationic complex **7** was also tested as the catalyst for the hydrogenation (100 atm H_2) of **5** in supercritical carbon dioxide ($scCO_2$, 100 atm, 35 °C, 200 atm total pressure). Despite some loss in enantioselectivity (Table 1), in this

Keywords: Asymmetric synthesis; Carboranes; Hydrogenation; Rhodium; Supercritical fluids.
* Corresponding author. Tel./fax: +7 495 135 6471; e-mail: lssp452@mail.ru

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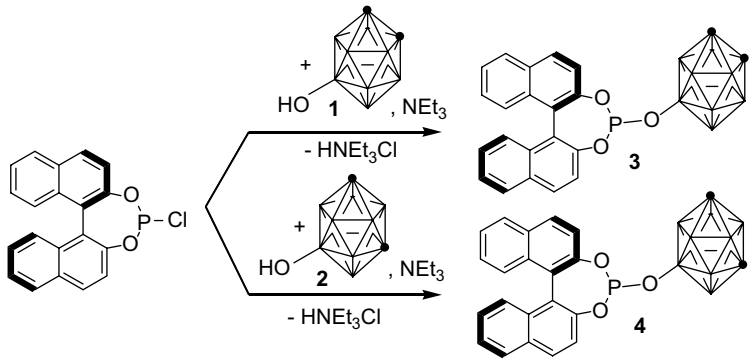
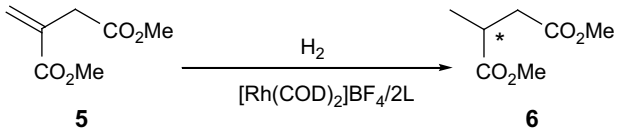
doi:10.1016/j.tetlet.2007.09.079



Scheme 1. Synthesis of chiral carborane-containing ligands.

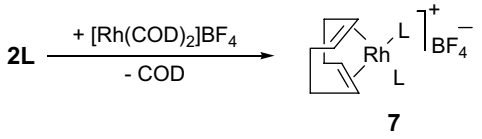


Scheme 2. Asymmetric hydrogenation of dimethyl itaconate.

Table 1. Rh-catalyzed hydrogenation of **5**

Catalyst[a]	Solvent	Cat. (mol %)	Time (h)	ee (%)
3	CH_2Cl_2	1	17	99.8 (*R*)
4	CH_2Cl_2	1	18	99.7 (*R*)
7	CH_2Cl_2	1	17	99.8 (*R*)
7	$scCO_2$	0.5	2	93.0 (*R*)

[a] Quantitative yields were observed in all cases according to ^1H NMR.



Scheme 3. Synthesis of Rh-complex **7**.

case, complete conversion of **5** occurred in 2 h with 0.5 mol % of catalyst, compared to 17–18 h and 1 mol % of catalyst in CH_2Cl_2.

In conclusion, we have prepared the first examples of chiral organophosphorus derivatives of carboranes. Initial studies of the monodentate carboranylphosphite ligands resulted in excellent enantioselectivities in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate (up to 99.8% ee in CH_2Cl_2 and up to 93% ee in supercritical CO_2). These ligands can also be regarded as attractive candidates for other asymmetric transition metal-catalyzed reactions in traditional and alternative 'green' solvents, such as $scCO_2$.

2. Experimental

2.1. General remarks

ortho- and *meta*-9-Hydroxy-dicarba-*closo*-dodecarboranes **1** and **2** were prepared as published.[1a,7] Hydrogenation of **5** in CH_2Cl_2 was performed according to the appropriate procedure.[3c] The ee's of **6** were determined by HPLC according to the literature.[8]

3. General procedure for the preparation of 3 and 4

ortho- or *meta*-9-Hydroxy-dicarba-*closo*-dodecarboranes (**1** or **2**) 0.205 g (1.27 mmol) was added to a vigorously stirred solution of (*R*)-2-chloro-dinaphtho[2,1-*d*:1′,2′-*f*][1,2,3] dioxaphosphine 0.45 g (1.27 mmol) and NEt_3 (0.212, 1.27 mmol) in benzene (25 ml). The mixture was stirred for 10 min. The reaction mixture was then heated at reflux for 20 min, cooled and filtered. Benzene was removed under reduced pressure (40 Torr) and the product was dried in vacuo (1 Torr, 2 h). Yields—(78% for **3** and 95% for **4**).

4. Hydrogenation procedure in $scCO_2$

A 5 ml stainless steel autoclave was charged with Rh-complex **7** (3.4 mg, 0.003 mmol) and dimethyl itaconate 100 mg (0.63 mmol). After repetitive purging with Ar, the autoclave was pressurized with hydrogen (100 bar) and then filled with $scCO_2$ (100 atm) by means of a syringe-press. The mixture was allowed to equilibrate to the reaction temperature of 35–36 °C and stirred for 2 h. After the hydrogen and CO_2 had been released, the mixture was diluted with hexane (3 ml) and filtered through a short silica gel column to remove the catalyst. The filtrate was concentrated in vacuo to afford the product.

Acknowledgement

This work was supported by the INTAS Open Call 05-1000008-8064 Grant.

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5. Compound **3**: ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 145.85$ (q, $^2J_{P,B} = 12.3$ Hz); ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.25$–3.46 (m, 12H, carboranyl), 7.19–7.94 (m, 12H, Ar). ^{11}B NMR (128.38 MHz, $CDCl_3$): $\delta = -19.42$–15.4 (m, 6B), 11.56 (d, $J = 151.4$ Hz, 2B), −4.90 (d, $J = 150.2$ Hz, 1B), 10.67 (s, 1B). Anal. Calcd for $C_{22}H_{24}B_{10}O_3P$: C, 55.57; H, 5.09; B, 22.74. Found: C, 55.78; H, 5.23; B, 22.91. Compound **4**: ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 145.86$ (q, $J_{P,B} = 12.3$ Hz); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$–3.49 (m, 12H, carboranyl), 7.21–7.97 (m, 12H, Ar). ^{11}B NMR (128.38 MHz, $CDCl_3$): $\delta = -25.01$ (d, $J = 176.2$ Hz, 1B), −19.94 (d, $J = 182.1$ Hz, 1B), −16.80–13.93 (m, 4B), −11.54 (d, $J = 150.2$ Hz, 1B), −7.71 (d, $J = 160.8$ Hz, 2B), 6.14 (s, 1B). ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 50.53$ (s, 2 CH carboranyl), 122.30–148.57 (Ar). Anal. Calcd for $C_{22}H_{24}B_{10}O_3P$: C, 55.57; H, 5.09; B, 22.74. Found: C, 55.70; H, 5.19; B, 22.67.
6. *[Rh(COD)(4)$_2$]BF$_4$* (**7**). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 125.13$ (br d, $J_{P,Rh} = 266.7$ Hz); ^{11}B{1H}NMR (128.38 MHz, $CDCl_3$): $\delta = -20.62$–13.63 (m, 6B), −17.63 (s, 2B), −4.81 (s, 1B), 11.03 (s, 1B). Anal. Calcd for $C_{52}H_{60}B_{21}F_4O_6P_2Rh$: C, 50.01; H, 4.84; B, 18.18. Found: C, 50.20; H, 4.96; B, 18.32.
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