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Communication

The use of a new carboranylamidophosphite ligand in the asymmetric Pd-catalysed allylic alkylation in organic solvents and supercritical carbon dioxide

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ABSTRACT

A novel *P*-monodentate ligand based on carboranyl alcohol and (*S*)-2-(anilinomethyl)pyrrolidine provides high enantioselectivities (ee's up to 95%) in the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate. The first example of the Pd-catalysed allylic alkylation in supercritical carbon dioxide is also described.

1. Introduction

The development of novel optically active ligands remains one of the most attractive areas in the field of transition metal-catalyzed asymmetric reactions. To achieve the highest levels of reactivity and selectivity in enantioselective catalytic reactions, different reaction parameters must be explored and adjusted. In this optimization process, not only a careful selection of the chiral ligand but also reaction conditions, such as temperature, solvents are always important. Recently, we designed a novel class of chiral mono- and bidentate phosphite-type ligands containing sterically congested carborane fragments and showed their high efficiency for the Rh-catalyzed asymmetric hydrogenation of functionalized olefins (up to 99.8% ee) [1]. Further examination of catalytic activity and selectivity of the ligands shows that monodentate ligands are more effective compared to bidentate carboranylphosphite-type ligands and electron-donating carboranyl substituents are essential to obtain high levels of enantiodiscrimination and conversion [2–4]. Along with the design of chiral ligands, another significant challenge in metal complex asymmetric catalysis is the use of alternative solvents often called as "green media" for catalytic transformations [5]. Recently we showed that phosphite-type ligands, including carborane-containing ones, are very effective catalysts for asymmetric hydrogenation (up to 99% ee) in supercritical carbon dioxide ($scCO_2$) [1,2,6,7]. Encouraged by the excellent enantioselectivities in the asymmetric hydrogenation processes and motivated by our continuing efforts in the design of novel chiral carboranylphosphite-type ligands, we have prepared a novel sterically congested carborane-containing monodentate diamidophosphite ligand for application in other important asymmetric catalytic transformations, namely Pd-catalyzed allylic substitution in organic solvents and $scCO_2$. The high synthetic utility of this type of catalytic processes is now well established through numerous efficient syntheses of enantiopure natural and unnatural products [8]. Our recent attempt to use bidentate carborane-containing ligands in the Pd-catalyzed allylic substitution gave promising results (up 83% ee) [9], but these results remained below the ee's of 99.8% which were achieved with monodentate carborane-containing phosphites in the asymmetric hydrogenation processes.

2. Results and discussion

The new monodentate diamidophosphite ligand **3** was synthesized by a convenient one-step phosphorylation of the corresponding *ortho*-9-hydroxy-1,2-dimethyldicarba-*closo*-dodecaborane (**2**, Scheme 1). The ligand **3** was characterized by ^{31}P, ^{13}C, and ^{11}B NMR spectroscopy and by elemental analysis (see Section 3). It is a white solid and is air stable under ambient conditions.

Complexation of the novel diamidophosphite **3** with $[Pd(allyl)Cl]_2$ (in the presence of $AgBF_4$) produced cationic Pd(II) complex **4** (Scheme 2).

To study the potential of the carboranylphosphite ligand **3** and its Pd complex **4**, we tested them in the Pd-catalyzed allylic

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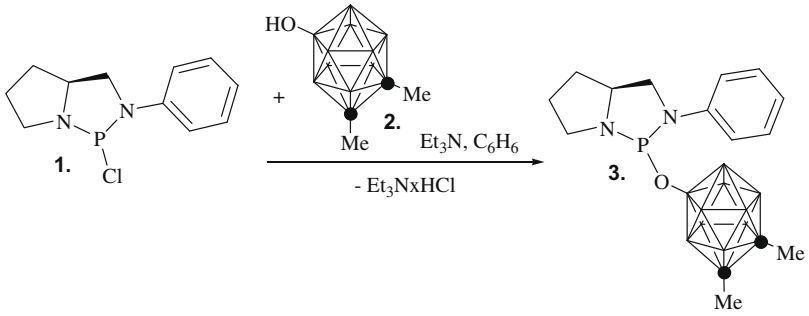
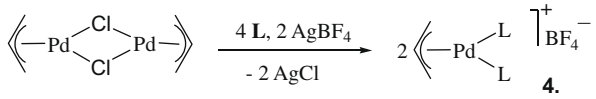
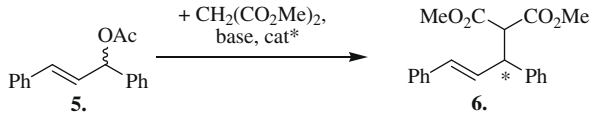


Scheme 1. Synthesis of chiral carborane-containing diamidophosphite ligand.



Scheme 2. Synthesis of Pd complex **4**.



Scheme 3. Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate.

substitution of (*E*)-1,3-diphenylallyl acetate **5** (which is widely used as a model substrate) with dimethyl malonate (Scheme 3 and Table 1).

The use of CH_2Cl_2 or THF as standard solvents for the reaction and BSA (*N*,*O*-bis(trimethylsilyl)acetamide) as base showed excellent enantioselectivities (90–95% ee) and complete conversion in all cases, independent of the L/Pd ratio (Table 1, entries 1–6). Testing the pre-formed complex **4** and a simple and inexpensive base, such as K_2CO_3 under phase-transfer conditions (Bu_4NBr) developed by us earlier for achiral allylic substrates [10], gave complete conversion of **5** in 16 h compared to 36 h with the liquid base – BSA and the same level of enantioselectivity (91% ee) in CH_2Cl_2 (Table 1, entries 5 and 7). In the case of THF as solvent, the use of BSA or K_2CO_3 (under phase-transfer conditions) showed the same level of enantioselectivity (90% ee, Table 1, entries 6 and 8), but only 56% conversion of **5** was observed in 18 h, compared to the reaction in CH_2Cl_2 under phase-transfer conditions (Table 1, entries 7 and 8). The use of $scCO_2$ as solvent and the inorganic base – K_2CO_3 in the presence of 18-crown-6 gave moderate enantioselectivity (64% ee) and conversion 75%. A simple change of the inorganic base to Cs_2CO_3 strongly increased the enantioselectivity from 64% to 81% ee and moreover the reaction proceeded without addition of the crown ether.

3. Conclusions

In conclusion, we have prepared a novel carborane-containing diamidophosphite ligand for the use in asymmetric catalysis. The ligand proved to be efficient in the Pd-catalysed allylic alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate (up to 95% ee). We have shown also that the ligand can catalyze actively the allylic alkylation process in the presence of a simple base – K_2CO_3 under phase-transfer conditions with a complete conversion and high enantioselectivity (91% ee). No less important, the ligand has provided for the first time a very good enantioselectivity (up to 81% ee) in $scCO_2$ with the use of inorganic bases.

4. Experimental

4.1. General

^{31}P, ^{13}C, and ^{11}B spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 128.4 MHz for ^{11}B). Chemical shifts (ppm) are given relative to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P NMR) and $BF_3 * Et_2O$ (^{11}B). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Conversion of substrate **5** and optical purity of product **6** were determined using HPLC (Daicel Chiralcel OD-H column) as described previously [11]. Phosphorylating reagent **1** – (*2R,5S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane [12] and 9-hydroxy-1,2-dimethylcarborane **2** [13] were prepared as published. Cationic palladium complex **4** was synthesised analogously to the known procedure [12].

Table 1
Pd-catalyzed enantioselective allylic alkylation of **5** with dimethyl malonate.

Entry	Catalyst	L/Pd	Solvent	Base	*T* (h)	Conversion (%)	ee (%)
1	$[Pd(allyl)Cl]_2$/**3**	1/1	CH_2Cl_2	BSA	36	100	93 (*S*)
2	$[Pd(allyl)Cl]_2$/**3**	1/1	THF	BSA	36	100	91 (*S*)
3	$[Pd(allyl)Cl]_2$/**3**	2/1	CH_2Cl_2	BSA	36	100	95 (*S*)
4	$[Pd(allyl)Cl]_2$/**3**	2/1	THF	BSA	36	100	92 (*S*)
5	**4**	2/1	CH_2Cl_2	BSA	36	100	92 (*S*)
6	**4**	2/1	THF	BSA	36	100	90 (*S*)
7	**4**	2/1	CH_2Cl_2	K_2CO_3[a]	18	100	91 (*S*)
8	**4**	2/1	THF	K_2CO_3[a]	18	56	90 (*S*)
9	**4**	2/1	$scCO_2$	K_2CO_3[b]	18	75	64 (*S*)
10	**4**	2/1	$scCO_2$	Cs_2CO_3	18	60	81 (*S*)

[a] Phase-transfer conditions – Bu_4NBr.
[b] Phase-transfer conditions – 18-crown-6.

*4.2. Synthesis of (2R,5S)-2-(1,2-dimethyl-ortho-carboran-9-yloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (**3**)*

The corresponding hydroxycarborane **2** (0.188 g, 1.0 mmol) was added to a vigorously stirred solution of the phosphorylating agent **1** (0.240 g, 1.0 mmol) and NEt_3 (0.135 mL, 1.0 mmol) in benzene (25 mL). The mixture was stirred for 10 min. The reaction mixture was then heated at reflux for 10 min, cooled, and filtered. The resulting solution was passed through a short silica gel plug and the solvent was evaporated at reduced pressure. Yield – 0.275 g (70%), colourless oil. $^{31}P\{H\}$ NMR ($CDCl_3$): = 130.01 (q, $J_{P,B}$ = 74 Hz). ^{11}B NMR ($CDCl_3$): −13.55–9.68 (m, 8B), −6.42 (d, J = 148.4 Hz, 1B), 11.48 (s, 1B). ^{13}C {H}NMR ($CDCl_3$): 145.7 (d, J = 15.5 Hz, Ar), 128.5 (s, Ar), 118.1 (s, Ar), 115.5 (d, J = 12.6 Hz), 68.0 (s, carb), 62.3 (d, J = 8.4 Hz, C_5), 57.7 (s, carb), 53.2 (d, J = 6.8 Hz, C_4), 47.5 (d, J = 35.9 Hz, C_8), 31.4 68.0 (s, C_6), 26.1 (d, J = 4.2 Hz, C_7), 23.6 (s, CH_3), 20.6 (s, CH_3). Anal. Calc. for $C_{15}H_{29}B_{10}N_2OP$: C, 45.90; H, 7.45; N, 7.14. Found: C, 46.07; H, 7.56; N, 7.10%.

*4.3. Palladium complex **4** [Pd(allyl)(3)$_2$]BF_4*

Yield: 92%, white solid; m.p.: 152 (dec.). $^{31}P\{H\}$ NMR ($CDCl_3$): = 105.10. Anal. Calc. for $C_{33}H_{63}B_{21}F_4N_4O_2P_2Pd$: C, 38.89; H, 6.23; N, 5.50. Found: C, 38.95; H, 6.35; N, 5.68%.

4.4. Pd-catalysed allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate

Method A: A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and ligand **3** (0.02 or 0.04 mmol, depending on desired Pd/L ratio) in 3 mL of the appropriate solvent was stirred for 10 min [alternatively, the pre-synthesised complex **4** (0.02 mmol) was dissolved in the appropriate solvent (3 mL)]. (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added and the solution stirred for 10 min, then dimethyl malonate (0.1 mL, 0.87 mmol), BSA (0.22 mL, 0.87 mmol) were added and the reaction mixture stirred for further 36 h. The resulting solution was filtered through silica gel. The solvent was removed under vacuum to give dimethyl [(*E*)-1,3-diphenyl-prop-2-en-1-yl]malonate (**6**) as a yellow oil slowly crystallizing on storage.

Method B: A solution of complex **4** (0.02 mmol) was dissolved in the appropriate solvent (5 mL). (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added and the solution stirred for 10 min, then dimethyl malonate (0.1 mL, 0.87 mmol), K_2CO_3 (87 mg, 0.75 mmol) and Bu_4NBr were added and the reaction mixture stirred for a further 18 h. The resulting solution was diluted with water (5 mL), three times extracted with benzene (3 mL), the organic solvents were separated, dried with $CaCl_2$ and the solvents removed under vacuum.

Method C: The pre-formed catalysts **4** (0.02 mmol), dimethyl malonate (0.07 mL, 0.6 mmol), substrate **5** (0.1 mL, 0.5 mmol), K_2CO_3 or Cs_2CO_3 (0.75 mmol) and 18-crown-6 (25 mg, in the case of K_2CO_3) were placed open to air into a 10 mL autoclave. The vessel was filled with $scCO_2$ by means of a syringe-press to a total pressure of 170 atm. The mixture was allowed to equilibrate to the reaction temperature of 70 °C (20 min) and stirred for 18 h. After this, the vessel was slowly depressurised. The resulting solution was diluted with water (5 mL), three times extracted with benzene (3 mL), the organic solvents was separated, dried with $CaCl_2$ and concentrated under reduced pressure.

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