The use of carboranylphosphite ligands in Rh-catalyzed hydroformylation of alkenes in supercritical carbon dioxide

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Novel carborane-containing phosphites were synthesized. The efficiency of the ligands was tested in the Rh-catalyzed hydroformylation of styrene, hept-1-ene, and oct-1-ene in supercritical carbon dioxide ($scCO_2$) and toluene. The use of $scCO_2$ as the reaction medium allows one to attain higher conversions and regioselectivities compared to toluene.

Key words: carboranylphosphites, hydroformylation, supercritical carbon dioxide, rhodium.

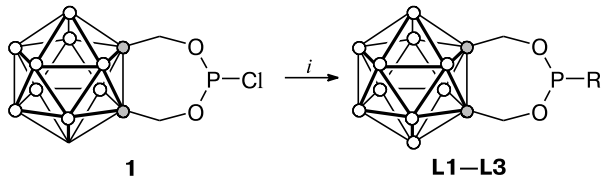
The study of regularities of chemical reactions catalyzed by transition metal complexes is an important aspect of development of modern chemistry. Presently, considerable attention of researchers is concentrated on the search for new efficient metallocomplex catalysts containing sterically bulky organophosphorus ligands.[1—3] Icosahedral carboranes ($C_2B_{10}H_{12}$) with a high steric factor are promising objects for the development of metallocomplex catalysts.[4] We have recently shown that the use of ligands of the phosphite type containing carborane substituents results in high conversions and enantioselectivity in reactions of Rh-catalyzed hydrogenation,[5—11] Pd-catalyzed allyl substitution,[12—14] and Suzuki—Miyaura Pd-catalyzed cross-coupling.[15]

One of the important processes of organometallic catalysis is hydroformylation of alkenes, which gives aldehydes used in fragrance, food, and pharmaceutical industry and in manufacturing vanishes, paints, detergents, and plasticizers.[16—18] Since these reactions are carried out in organic solvents in combination with with flammable and explosive substances, the search for alternative media for the process is needed. One of the most appropriate media is supercritical carbon dioxide ($scCO_2$) due to accessibility as well as environmental and fire safety of carbon dioxide.[19] The use of $scCO_2$ as a medium provides a unique possibility of handling of low-boiling reactants and products: carbon dioxide can readily be removed from the synthesis products, whereas the isolation of products when using organic solvents poses difficulties and requires further fractionation. Despite the advantages of $scCO_2$, there have been few reports on its use in the metallocomplex hydroformylation of alkenes.[20—26] In this work, we present for the first time the results of studies of novel carboranylphosphite ligands in the Rh-catalyzed hydroformylation of alkenes in $scCO_2$.

Results and Discussion

Novel carborane-containing phosphite ligands **L1—L3** were synthesized by the one-step reaction of phosphorylating agent **1** with propan-2-ol, 1,1,1,3,3,3-hexafluoropropan-2-ol, and 2,6-dimethylphenol (Scheme 1).

Scheme 1



1 **L1—L3**

R = Pr^iO (**L1**), $(CF_3)_2CHO$ (**L2**), 2,6-$Me_2C_6H_3O$ (**L3**)

i. RH, NEt_3, PhMe

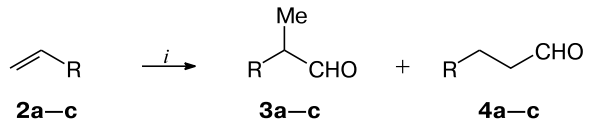
The protons of the methylene groups of carboranylphosphites **L1—L3** are not equivalent (see Experimental) because of a large size of the seven-membered heterocycle, which is also characteristic of a series of ligands similar in structure.[27,28]

The efficiency of carboranylphosphites **L1—L3** was first studied in the Rh-catalyzed hydroformylation of styrene **2a** in toluene with the formation of the catalysts *in situ* from [(acac)$Rh(CO)_2$] (acac is acetylacetonate) and 1 equiv. of the ligand (Scheme 2).

At the mole ratio substrate : catalyst = 200 : 1 it was shown that for styrene **2a** the maximum conversion within 4 h at 40 °C is observed when ligand **L1** is used (Table 1, entries *1—3*). All ligands exhibit fairly high regioselectivity towards the formation of branched product **3a** (see Scheme 2). When carboranylphosphite **L1** is used, the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2037—2040, October, 2011.

Scheme 2



2a—c **3a—c** **4a—c**

R = Ph (**a**), n-C_5H_{11} (**b**), n-C_6H_{13} (**c**)

i. H_2/CO (1 : 1, 35 atm), $[(acac)Rh(CO)_2]$/L.

temperature increase from 40 to 60 °C increases conversion but considerably decreases regioselectivity (see Table 1, entries *1* and *4*). The replacement of toluene by $scCO_2$ (total pressure 200 atm, 40 °C) and the use of the same pressure of synthesis gas (35 atm) make it possible to attain a high or even complete conversion, and in the case of ligand **L1** the regioselectivity can be increased from 88 to 96% (see Table 1, entries *1—3* and *5—7*). We also investigated the influence of the reaction temperature and CO_2 pressure on the conversion and regioselectivity. When higher temperatures (60 °C) are used, the regioselectivity in $scCO_2$ decreases (see Table 1, entries *7* and *8*), although this decrease is not so significant as in toluene (see Table 1, entries *1* and *4*). The decrease in the total pressure from 200 to 150 atm at the same pressure of synthesis gas (35 atm) decreases both conversion and regioselectivity (see Table 1, entries *5* and *9*). The reaction carried out at the total pressure 200 and 250 atm gives nearly the same regioselectivity (see Table 1, entries *5* and *10*), and the use of the increased pressure results in the complete conversion of styrene **2a**.

Hydroformylation of hept-1-ene (**2b**) involving ligand **L1** revealed that this process is insensitive to the reaction conditions. The variation of temperature and carbon dioxide pressure changes the content of linear isomer (**4b**, see Scheme 2); however, the same regioselectivity is observed in all cases (see table 1, entries *11—13*). Carboranylphosphites **L2** and **L3** allow one to obtain close selectivity in the formation of the linear product (see Table 1, entries *14—15*). In all cases, the complete conversion is achieved within 3 h. The close result was obtained for the hydroformylation of oct-1-ene (**2c**, see Table 1, entries *16—18*). So, ligands **L1**—**L3** allow one to attain quantitative conversion within 3 h, and the regioselectivity with respect to linear isomer **4c** is 62—66%.

Thus, carborane-containing phosphites were used for the first time in the Rh-catalyzed hydroformylation of terminal alkenes. These ligands can provide high conversion in hydroformylation at low temperature (40 °C) within 3—4 h. It was shown that higher values of regioselectivity and conversion can be attained in a medium of $scCO_2$ compared to toluene.

Experimental

^1H, ^{11}B, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker Avance 400 instrument (working frequencies 400.13,

Table 1. Rh-catalyzed hydroformylation of compounds **2a—c**[a]

Entry	Compound	Ligand	Medium	Total pressure, P/atm	T/°C	t/h	Conversion of compound **2** (%)	Ratio of products **3** : **4**
1	**2a**	**L1**	Toluene[b]	35	40	4	74	88 : 12
2	**2a**	**L2**	Toluene[b]	35	40	4	52	89 : 11
3	**2a**	**L3**	Toluene[b]	35	40	4	50	89 : 11
4	**2a**	**L1**	Toluene[b]	35	60	4	95	69 : 31
5	**2a**	**L1**	$skCO_2$	200	40	4	95	96 : 4
6	**2a**	**L2**	$skCO_2$	200	40	4	100	89 : 11
7	**2a**	**L3**	$skCO_2$	200	40	4	100	93 : 7
8	**2a**	**L1**	$skCO_2$	200	60	4	100	90 : 10
9	**2a**	**L1**	$skCO_2$	150	40	4	80	91 : 9
10	**2a**	**L1**	$skCO_2$	250	40	4	100	95 : 5
11	**2b**	**L1**	$skCO_2$	200	40	3	100	40 : 60
12	**2b**	**L1**	$skCO_2$	250	40	3	100	40 : 60
13	**2b**	**L1**	$skCO_2$	200	60	3	100	40 : 60
14	**2b**	**L2**	$skCO_2$	200	40	3	100	34 : 66
15	**2b**	**L3**	$skCO_2$	200	40	3	100	36 : 64
16	**2c**	**L1**	$skCO_2$	200	40	3	100	38 : 62
17	**2c**	**L2**	$skCO_2$	200	40	3	100	34 : 66
18	**2c**	**L3**	$skCO_2$	200	40	3	100	36 : 64

[a] The mole ratio [Rh] : L : substrate is 1 : 1 : 200, and the pressure of synthesis gas is 35 atm ($P_{H_2} : P_{CO} = 1 : 1$).
[b] The volume is 2 mL.

128.4, 376.5, and 161.98 MHz, respectively) relative to Me_4Si, $BF_3 \cdot OEt_2$, CF_3COOH, and 85% H_3PO_4 in D_2O. Elemental analysis was carried out at the Laboratory of Organic Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. 2-Chloro-5,6-carborano-1,3,2-dioxaphosphepane (**1**) and [Rh(acac)$(CO)_2$] were synthesized according to published procedures.[29,30]

Synthesis of ligands L1—L3 (general procedure). Triethylamine (0.28 mL, 2.0 mmol) and the corresponding alcohol or phenol (2.0 mmol) were added to a solution of 2-chloro-5,6-carborano-1,3,2-dioxaphosphepane (0.537 g, 2.0 mmol) in toluene (15 mL). The mixture was stirred for 5 min at 20 °C, heated to boiling, and cooled to room temperature. A precipitate of $NEt_3 \cdot HCl$ was filtered off. The products were purified by flash chromatography on a column with silica gel (benzene as eluent).

2-Isopropyloxy-5,6-carborano-1,3,2-dioxaphosphepane (L1). Viscous colorless oil. The yield was 0.49 g (84%). Found (%): C, 28.86; H, 7.29; P, 10.52. $C_7H_{21}PO_3B_{10}$. Calculated (%): C, 28.76; H, 7.24; P, 10.60. $^{31}P\{H\}$ NMR ($CDCl_3$), δ: 135.11. ^1H NMR ($CDCl_3$), δ: 1.27 (d, 6 H, $(CH_3)_2$, J = 6.2 Hz); 1.50—3.46 (m, 10 H, BH, carb.); 4.20 (dd, 2 H, CH_2, J = 13.0 Hz, J = 9.0 Hz); 4.20 (m, 1 H, CHO); 4.73 (t, 2 H, CH_2, J = 13.1 Hz). ^{11}B {H} NMR ($CDCl_3$), δ: −3.88 (s, 2 B); −(9.04—13.25) (m, 8 B).

2-(1,1,1,3,3,3-Hexafluoroisopropyloxy)-5,6-carborano-1,3,2-dioxaphosphepane (L2). Viscous colorless oil. The yield was 0.688 g (86%). Found (%): C, 21.08; H, 3.87; P, 7.65. $C_7H_{15}PO_3B_{10}F_6$. Calculated (%): C, 21.00; H, 3.78; P, 7.74. $^{31}P\{H\}$ NMR ($CDCl_3$), δ: 134.03. ^1H NMR ($CDCl_3$), δ: 1.44—3.48 (m, 10 H, BH, carb.); 4.32 (dd, 2 H, CH_2, J = 13.3 Hz, J = 10.3 Hz); 4.67 (m, 1 H, CH); 4.84 (t, 2 H, CH_2, J = 13.2 Hz). ^{11}B {H} NMR ($CDCl_3$), δ: −3.26 (s, 2 B); −(7.84—12.7) (m, 8 B). ^{19}F NMR ($CDCl_3$), δ: −74.46 (d, J = 6.9 Hz).

2-(2,6-Dimethylphenoxy)-5,6-carborano-1,3,2-dioxaphosphepane (L3). Viscous colorless oil. The yield was 0.573 g (81%). Found (%): C, 40.74; H, 6.63; P, 8.67. $C_{12}H_{23}PO_3B_{10}$. Calculated (%): C, 40.67; H, 6.54; P, 8.74. $^{31}P\{H\}$ NMR ($CDCl_3$), δ: 132.39. ^1H NMR ($CDCl_3$), δ: 1.43—3.49 (m, 10 H, BH, carb.); 2.23 (s, 6 H, CH_3); 4.32 (dd, 2 H, CH_2, J = 13.0 Hz, J = 8.9 Hz); 4.93 (t, 2 H, CH_2, J = 13.12 Hz); 6.93—7.05 (m, 3 H, Ar). ^{11}B {H} NMR ($CDCl_3$), δ: −3.82 (s, 2 B); −(8.21—12.63) (m, 8 B).

Rh-Catalyzed hydroformylation. A mixture containing [Rh(acac)$(CO)_2$] (2.5 mg, 0.01 mmol) and the corresponding ligand (0.01 mmol) was placed in a 10-mL autoclave and dissolved in toluene (0.2 mL). The mixture was stirred for 5 min, the solvent was removed *in vacuo*, and the corresponding substrate (2 mmol) was added. The autoclave was filled with synthesis gas (35 atm, $P_{H_2} : P_{CO} = 1 : 1$) and then with carbon dioxide to the required pressure (see Table 1) with a manually operated pump (High Pressure Equipment). The reactor was heated to the temperature indicated in Table 1 within 5 min, and experiments were carried out with magnetic stirring. After some time (see Table 1) the autoclave was cooled to 5 °C within 10 min, the pressure was discharged to atmosphere, and the reaction mixture was analyzed by ^1H NMR spectroscopy. The spectral characteristics of the hydroformylation products, 2-phenylpropanal (**3a**), 3-phenylpropanal (**4a**),[31] octanal (**4b**), 2-methylheptanal (**3b**),[32,33] nonanal (**4c**), and 2-methyloctanal (**3c**),[34,35] correspond to the published data. Experiments in toluene were carried out similarly using 2 mL of the solvent.

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Received June 1, 2011;
in revised form June 27, 2011