Journal of Organometallic Chemistry 824 (2016) 73–79

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Zirconium-catalyzed alkene cycloalumination for the synthesis of substituted phosphines and their transition metal (Mo, Pd) complexes

Leisan K. Dil'mukhametova, Vladimir A. D'yakonov*, Tat'yana V. Tyumkina**, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa 450075, Russian Federation

ARTICLE INFO

Article history:
Received 5 March 2016
Received in revised form
29 September 2016
Accepted 5 October 2016
Available online 6 October 2016

Keywords:
Cycloalumination
Aluminacyclopentane
Phosphine oxide
Phosphine
Molybdenum complex
Palladium complex

ABSTRACT

An original method for the synthesis of substituted phosphines $R_2P(X)BuR'$ (R′ = n-Hex, Bn, napht, *cyclo*-Hex) and $R_2P(X)EtR'$ (R′ = 2-bycyclo[2.2.1]hept-2-yl) (R = Et, Ph, X = O, S), in 65–72% yield has been developed via the interaction between halophosphines R_2PCl (R = Et, Ph) and aluminacyclopentanes, generated *in situ* from alkenes and Et_3Al in the presence of Cp_2ZrCl_2. The synthesized phosphines were found to react with $Mo(CO)_6$ giving rise to molybdenum complexes $Mo(CO)_5L$ (L = **4a**; **3b**; **3c**). The interaction between (2-bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine and $Pd(COD)Cl_2$ leads to compound of the type L_2PdCl_2. Structures of new compounds were determined using X-ray diffraction techniques and multinuclear (^1H, ^{13}C, and ^{31}P) NMR spectroscopy.

1. Introduction

Organophosphorous compounds (OPC) continue to be attractive due to diverse applications thereof in organic and elementoorganic chemistry as the reagents for organic synthesis, precursors of biologically active compounds [1–4], and components of catalytic systems for homogeneous metal complex catalysis [5–18]. The nature and structure of the ligand as a part of the catalytic system is one of the most important factors, which define stereo- and regioselectivity of the reaction. Therefore, the development of the new and efficient approaches to the synthesis of phosphines (phosphine ligand) of specified structure is an actual problem.

Among the wide variety of approaches to the carbon-phosphorous bond formation [8,19–26], the interaction between organometallics and phosphorous halides is one of the simple and convenient methods. We have recently shown that the *in situ* interaction of aluminacarbocycles, being synthesized through the catalytic cycloalumination of α-olefins, norbornenes, and acetylenes-, with alkyl(phenyl)phosphorus(III) dihalides led to the corresponding cyclic five-membered OPC with high yields (80–90%) [27–31].

In the development of these investigations we have put forward a one-pot synthetic strategy to prepare substituted 1,4-bis(phosphino)butanes by the reaction between di-substituted organophosphorous(III) monohalides and aluminacyclopentanes involving both Al–C bonds [32,33].

In this paper, we report on our efforts to produce new types of phosphines and transition metal complexes thereof as promising ligands for metal complex catalysis [8,10,14].

2. Results and discussion

2.1. Synthesis and structure of substituted phosphineoxides, phosphinesulfides and phosphines

Our studies have shown that the reaction of dialkyl- or diphenylphosphorus chlorides R_2PCl (R = Ph, Et) with aluminacyclopentanes **1** provides phosphines **3** involving exclusively the Al–C bond located at C(5) carbon atom.

Thus, the interaction between diphenylphosphine chloride and 3-hexylaluminacyclopentane **1a** *in situ* generated in the cycloalumination reaction of 1-octene with $AlEt_3$ in the presence of Cp_2ZrCl_2 (~20–22 °C, 6 h), after hydrolysis of the reaction mixture,

* Corresponding author.
** Corresponding author.
E-mail address: DyakonovVA@gmail.com (V.A. D'yakonov).

http://dx.doi.org/10.1016/j.jorganchem.2016.10.012
0022-328X/

was found to afford (3-methylnonyl)diphenylphosphine **3a.** Subsequent oxidation of **3a** with H_2O_2 led to (3-methylnonyl)diphenylphosphine oxide **5a** in 80% yield. Elemental sulfur reacted with phosphorus under mild conditions (toluene, 40 °C, 8 h) to form (3-methylnonyl)diphenylphosphine sulfide **5a** in 71% yield (Scheme 1).

In an analogous fashion, (3-methyl-4-phenylbutyl)diphenylphosphine oxide **5b**, (2-bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine oxide **5c**, (3-(2-naphthyl)butyl)diphenylphosphine oxide **5d**, (3-cyclohexylbutyl)diphenylphosphine oxide **5e**, (3-methylnonyl)diethylphosphine oxide **5f**, a number of deutero-substituted derivatives **6a,c,f,** and also (2-(3-deuterobicyclo[2.2.1]hept-2-ylethyl)diethylphosphine oxide **6g** have been obtained from aluminacyclopentanes **1** and corresponding diphenyl- and diethylphosphorus chlorides (Table 1).

This study has shown that attachment of dialkyl(aryl)phosphorus(III) chloride to aluminacarbocycle **1** occurs by the more sterically accessible Al–C bond. It should be noted that all attempts to involve the second molecule of R_2PCl (R = Ph, Et) in the above reaction altering other reaction parameters (*eg.* the use of the three-fold or five-fold excess of halophosphine, the elevated temperatures within the interval 50–110 °C, and also catalytic amounts of CuCl, CuI [34,35], were unsuccessful.

Apparently, the strong donating bond P → Al in the *in situ* generated six-membered intermediate [(hexyl-, 2-bycyclo[2.2.1]hept-2-yl)(diethylphosphino- or diphenylphosphino)ethyl] or [(benzyl-, cyclohexyl)(diethylphosphino- or diphenylphosphino)butyl] ethylaluminum chloride **2** causes the relative inertness of the Al–C(2) bond thus preventing incorporation of the second molecule of dialkyl(aryl)phosphine chloride that implies preliminary coordination of organophosphorus reagent to aluminum in the initial aluminacyclopentane. In this way, owing to the preferred intramolecular interactions between aluminum and phosphorus as compared to intermolecular, the second Al–C bond remains inert.

Regioselective formation of diphenyl(diethyl)substituted phosphine oxides **5, 6** and phosphine sulfide **7** has been unambiguously confirmed by the data of multinuclear ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Thus, the signals assigned to the methyl group on the C(3) carbon atom at ~18–19 ppm in the ^{1}H and ^{13}C NMR spectra of phosphine oxides **5a-b**, **5d-f,** and phosphine sulfide **7a** indicate the activity of only one Al–C bond. In addition, the triplet C(10) signals detected in the NMR spectra of products after deuterolysis of diphenyl- or diethylphosphine oxides **6a** and **6f** as well as the signals from the C(8) carbon atoms in the norbornene skeleton in compounds **6c** and **6g**, may serve as the further support for this fact.

As the three-substituted phosphine oxides have the only single phosphorus atom in the molecule, heteronuclear constants $J(^{31}P\text{-}^{13}C)$ were measured only for three C(1), C(2) and C(3) carbon atoms, in this case, the maximum value of SSCC (J_{PC} ~ 64–76 Hz) corresponds to the carbon atom located in the α position relative to the heteroatom. It has been noticed that chemical shift of phosphorus in the diphenyl substituted phosphines occurs at low frequencies (δP ~ 32–33 ppm), whereas their diethyl analogs manifest themselves at much higher frequencies (δP 52–54 ppm) that corresponds to the literature data [36]. The intermediate value of chemical shift (δP = 43.44 ppm) was obtained for sulfide **7a**.

The individual phosphine oxides **5a-f**, **6a**, **6c**, **6f-g** and phosphine sulfide **7a** were isolated by column chromatography on SiO_2 with hexane:EtOAc:MeOH = 5:3:1 as the eluent. These compounds **5a-e** represent white crystals, **5f, 6f-g** - colorless oils, and phosphine sulfide **7a** was yellow oil. From a number of the phosphine oxides synthesized, (2-bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine oxide **5c** after crystallization from a mixture of methylene chloride and hexane has been additionally studied by X-ray method (Fig. 1).

Table 1
Reaction yields of the target substituted phosphines, phosphine oxides and phosphine sulfide.

Entry	Compound	R	R′	Yield (%)[a]
1	**3a**	Ph	*n*-Hex	69
2	**3b**	Ph	Bn	72
3	**3c**	Ph		70
4	**3d**	Ph		67
5	**3e**	Ph		68
6	**4a**	Ph	*n*-Hex	65[b]
7	**5a**	Ph	*n*-Hex	80
8	**5b**	Ph	Bn	82
9	**5c**	Ph		79
10	**5d**	Ph		73
11	**5e**	Ph		84
12	**5f**	Et	*n*-Hex	77
13	**6a**	Ph	*n*-Hex	78[b]
14	**6c**	Ph		76[b]
15	**6f**	Et	*n*-Hex	74[b]
16	**6g**	Et		72[b]
17	**7a**	Ph	*n*-Hex	71[c]

[a] Isolated yields.
[b] Deuterated products.
[c] Phosphine sulfide.

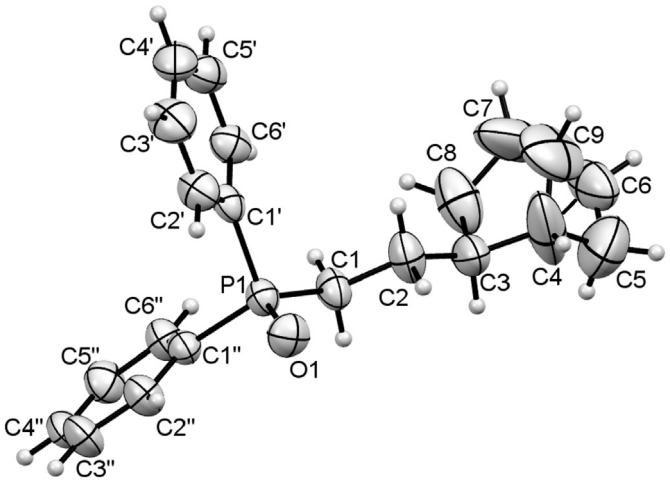


Fig. 1. Spatial structure of compound **5c**. The atoms are represented by thermal vibration ellipsoids (p = 50%). Main bond lengths (Å) and angles (deg): P1–C1′ = 1.808(4), P1–C1″ = 1.801(4), P1–C1 = 1.799(4), C1–C2 = 1.544(6), C2–C3 = 1.552(6), C3–C4 = 1.560(9), C4–C5 = 1.862(13), C4–C9 = 1.383(10), C5–C6 = 1.322(10), C6–C7 = 1.788(11), C7–C8 = 1.474(9), C7–C9 = 1.263(10), C8–C3 = 1.469(8), O–P1–C1′ = 111.63(17), O1–P1–C1″ = 110.91(17), O1–P1–C1 = 114.75(19), C1″–P1–C1′ = 106.04(17), C1–P1–C1′ = 107.02(18), C1–P1–C1″ = 105.96(17), C2–C1–P1 = 110.6(3), C1–C2–C3 = 112.0(4).

2.2. Synthesis of molybdenum and palladium complexes of substituted phosphines

It is well known that the majority of transition metals form stable phosphine complexes. In order to investigate binding properties of the synthesized OPC and the possibilities thereof as ligands, we have performed reduction of **5a-e** and **6a** using silicon hydride $HSiCl_3$ (benzene, 80 °C, 4 h) to obtain appropriate phosphines. Among them, **3a-c**,**e** and **4a** represent colorless paraffin-like substances, and compound **3d** is a white powder (Scheme 1). The shift of the ^{31}P phosphorus signals attributable to the said compounds toward extremely low frequency magnetic field ($\delta P = -15$ ppm) indicates the complete reduction of phosphines tested. The presence of a lone electron pair on phosphorus expectedly led to a decrease in the J_{PC} values corresponding to α-carbon atoms (to7–11 Hz) [36].

Complexes of the type $Mo(CO)_5L$ (L = (3-deuteromethylnonyl) diphenylphosphine, (3-methyl-4-phenylbutyl)diphenylphosphine, (2-bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine) **8a-c** have been obtained from the reaction of molybdenum hexacarbonyl with eqiumolar amounts of compounds **4a** and **3b,c** in tetrahydrofuran (80 °C, 5 h) (Scheme 2). The reaction of (2-bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine **3c** with $Pd(COD)Cl_2$ in methylene dichloride (30–35 °C, 5 h) provided bisphosphine complex (*bis*-[(2-bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphino]palladium dichloride) **9** (Scheme 2).

Control over the complexation reaction between phosphine and molybdenum carbonyl or (1,5-cyclooctadiene)palladium(II) dichloride was carried out by a shift of the phosphorus signal in the ^{31}P NMR spectra relative to the starting phosphine. Thus, phosphine complexes of molybdenum **8a-c** resonate in the region of ~27 ppm, whereas complex **9** showed a signal at δP 16.68 ppm. The molecular structures of these complexes have been confirmed by one- and two-dimensional NMR spectroscopy. The observed magnetic equivalence of the C(1) carbon signals of initial phosphines **4a**, **3b-c** in the ^{13}C spectra of compounds **8a-c** indicates that the phosphine ligand displaces only one molecule of CO in hexacarbonyl molybdenum. In the case of a structure having two phosphine ligands, the ^{13}C signals of α-carbon atoms of the said ligand appear as a triplet, due to aliasing [31,37]. The IR spectra of compounds **8a-c** contain the absorption CO bands at 2070 (s) and 1987 (s) cm^{-1}, characteristic for mono-phosphine complexes of the type $Mo(CO)_5L$. This also confirms the structure of complexes above [37]. The structure of complex **9** has been proposed on the basis of elemental analysis and the data of the ^{13}C NMR spectrum containing the triplet signals attributable to the α-carbon atoms [C(1) and C(1′)] of the phosphine ligand.

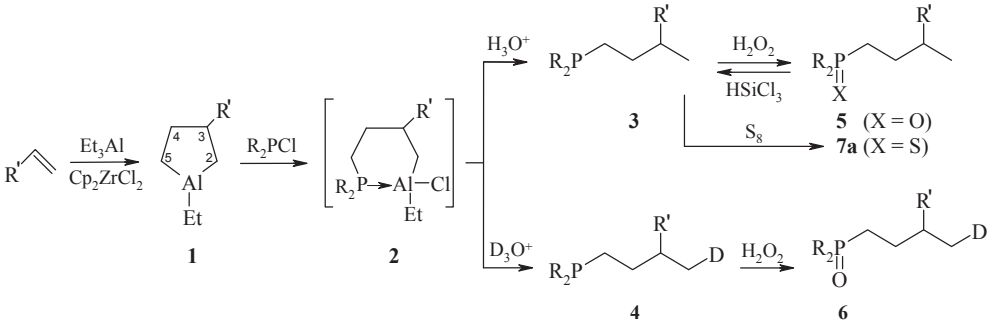
3. Conclusion

In conclusion, we have developed a new original method for the synthesis of acyclic phosphines via the interaction between diethyl(diphenyl)phosphorus halides and aluminacyclopentanes generated *in situ* from alkenes and Et_3Al in the presence of $CpZrCl_2$ as the catalyst. Based on phosphines synthesized, stable phosphine complexes of Mo and Pd previously undescribed have been obtained. The elaborated reaction opens up new ways for the direct synthesis of acyclic phosphines of a definite structure, promising as ligands for metal complex catalysts and precursors of potential biologically active compounds.

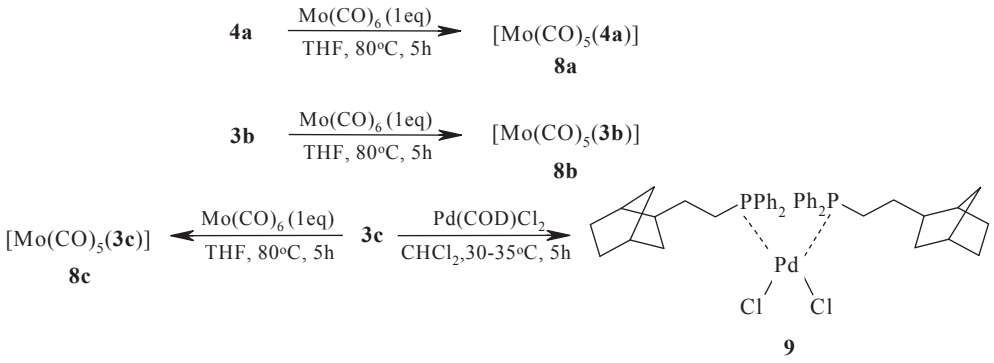
4. Experimental

4.1. General (instruments)

Chromatographic analysis was performed on a Shimadzu GC-9A instrument using a 2000 × 2 mm column, the SE-30 (5%) stationary phase on Chromaton N-AW-HMDS (0.125–0.160 mm), helium carrier gas (30 mL/min), temperature programming from 50 to 300 °C at a 8 °C/min rate. IR spectra were recorded on Bruker VERTEX 70V using KBr discs over the range of 400–4000 cm^{-1}. Melting points were recorded on Stuart SMP3. The ^1H, ^{13}C, and ^{31}P NMR spectra were measured in $CDCl_3$ on a Bruker Avance-400 spectrometer (100.62 MHz for ^{13}C, 400.00 MHz for ^1H, and 161.92 MHz for ^{31}P). Mass spectra were run on a MALDI TOF/TOF Autoflex-III Bruker instrument with 2,5-dihydroxybenzoic (2,5-DHB) and α-cyano-4-hydroxycinnanic acid (HCCA) matrix in the reflection, positive ion mode. Elemental analysis of the samples was determined by elemental analyzer firm Karlo Erba, model 1106. X-ray diffraction analysis was performed on an XCaliburEos four-circle automated diffractometer (graphite monochromator, MoKα radiation, λ = 0.71073 Å, $2\theta_{max} = 62°$). The data were collected and treated using the CrysAlis^{Pro} Oxford Diffraction Ltd. program package, version 1.171.36.20. The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were located on electron density maps and refined in the isotropic approximation. The refinement was done using SHELX97 program package [38]. TLC was performed on Silufol UV-254 plates with hexane–ethyl acetate–methanol (5:3:1) mixture as the eluent and I_2 for visualization. For column chromatography, Acros silica gel (0.060–0.200 mm) was used. Reactions with



Scheme 1.



Scheme 2.

organometallic compounds were performed in a dry argon flow. The solvents were dried and distilled immediately prior to use. Commercially available phosphines, Cp_2ZrCl_2 and Et_3Al (Aldrich) were used.

4.1.1. The synthesis of substituted dialkyl-diphenylphosphine oxide and deuterated analogs (general procedure)

A round-bottomed flask in a dry argon atmosphere was charged successively with stirring at 0 °C with Cp_2ZrCl_2 (0.0584 g, 0.20 mmol), alkene (4 mmol), and $AlEt_3$ (0.60 mL, 4 mmol). The temperature was brought to ~20 °C and the mixture was stirred for 8 h. Then toluene (10 mL) was added, the reaction mixture was cooled to −5−−10 °C, dialkyl(diphenyl) chlorophosphine (4 mmol) was added dropwise, and the mixture was stirred at room temperature for an additional 6 h. Then the reaction mixture was treated with a saturated aqueous solution of NH_4Cl or D_2O, the reaction products were extracted with diethyl ether, and the solvent was evaporated. Chloroform (10 mL) was added to the residue, then 30% hydrogen peroxide (0.35 mL, 3 mmol) was slowly added dropwise with vigorous stirring, and the mixture was stirred for 1 h. Then the reaction mixture was washed with water (3 × 5 mL) and the organic phase was dried with $MgSO_4$. The solvent was evaporated and the residue was chromatographed on silica gel (hexane: ethyl acetate: methanol = 5:3:1).

*4.1.1.1. (3-Methylnonyl)diphenylphosphine oxide (**5a**).* Yield 80%; Rf = 0.37, white solid, mp = 59−61 °C. 31P NMR (CDCl3): δ 33.28. ^{13}C NMR (CDCl3): δ 14.10 (C(9)), 19.15 (C(10)), 22.64 (C(8)), 26.85 (C(5)), 27.21 ($1J_{C\text{-}P}$ = 72.4, C(1)), 28.05 ($2J_{C\text{-}P}$ = 4.0, C(2)), 29.53 (C(6)), 31.85 (C(7)), 33.76 ($3J_{C\text{-}P}$ = 14.1, C(3)), 36.28 (C(4)), 128.61 ($3J_{C\text{-}P}$ = 11.1, Ph), 130.78 ($2J_{C\text{-}P}$ = 9.05, Ph), 130.80 ($2J_{C\text{-}P}$ = 9.05, Ph), 131.64 ($4J_{C\text{-}P}$ = 3.0, Ph), 133.10 ($1J_{C\text{-}P}$ = 97.6, Ph), 133.20 ($1J_{C\text{-}P}$ = 96.6, Ph). ^{1}H NMR(CDCl$_3$): δ 0.78−0.98 (m, 6H, (C(9)H3, C(10)H3), 1.00−1.35 (m, 10H, (C(4)Ha, C(4)Hb, C(7)H2, C(6)H2, C(5)H2, C(8) H2), 1.36−1.55 (m, 2H, C(3)H, C(2)Ha), 1.56−1.70 (м, 1H, C(2)Hb), 2.15−2.35 (m, 2H, C(1)H2), 7.40−7.58, 7.70−7.82 (m, 10H, Ph); MALDI TOF/TOF: [M + H]+found = 343.487, C22H31PO requires 342.455.

*4.1.1.2. (3-Deuteromethylnonyl)diphenylphosphine oxide (**6a**).* Yield 78%; R_f = 0.37, white solid, mp = 58−60 °C. ^{31}P NMR (CDCl$_3$): δ 33.19. ^{13}C NMR (CDCl$_3$): δ 14.14 (C(9)), 18.89 (t, $J_{C\text{-}D}$ = 19.0, C(10)), 22.67 (C(8)), 26.88 C((5)), 27.26 ($^1J_{C\text{-}P}$ = 72.5, C(1)), 28.07 ($^2J_{C\text{-}P}$ = 4.0, C(2)), 29.57 (C(6)), 31.89 (C(7)), 33.71 ($^3J_{C\text{-}P}$ = 14.0, C(3)), 36.30 (C(4)), 128.65 ($^3J_{C\text{-}P}$ = 11.1, Ph), 130.81 ($^2J_{C\text{-}P}$ = 9.05, Ph), 130.83 ($^2J_{C\text{-}P}$ = 9.05, Ph), 131.66 ($^4J_{C\text{-}P}$ = 3.0, Ph), 133.16 ($^1J_{C\text{-}P}$ = 97.6, Ph), 133.27 ($^1J_{C\text{-}P}$ = 97.7, Ph). ^{1}H NMR(CDCl$_3$): δ 0.80−0.87 (m, 5H, (C(9)H$_3$, C(10)H$_2$D), 1.04−1.14 (m, 1H, (C(4)H$_a$), 1.15−1.31 (m, 9H, C(4)H$_b$, C(7)H$_2$, C(6)H$_2$, C(5)H$_2$, C(8)H$_2$), 1.39−1.47 (m, 2H, C(3)H, C(2)H$_a$), 1.56−1.66 (m, 1H, C(2)H$_b$), 2.17−2.32 (m, 2H, C(1)H$_2$), 7.40−7.55, 7.70−7.80 (m, 10H, Ph); MALDI TOF/TOF: [M + H]$^+$found = 344.497, $C_{22}H_{31}PO$ requires 343.457.

*4.1.1.3. (3-Methyl-4-phenylbutyl)diphenylphosphine oxide (**5b**).* Yield 82%; Rf = 0.37, white solid, mp = 110−112 °C. 31P NMR (CDCl3): δ 33.02. ^{13}C NMR (CDCl3): 18.96 (C(5)), 27.34 (1JC-P = 72.0, C(1)), 28.03 (C(2)), 35.91 (3$J_{C\text{-}P}$ = 13.9, C(3)), 42.95 (C(4)), 125.83 (Ph), 128.20 (Ph), 128.64 (3JPh-P = 11.5, Ph), 129.05 (Ph), 130.69, 130.72, 130.78 (Ph), 131.68 (Ph), 132.91 (1JC-P = 98.1, Ph); 133.05 (1JC-P = 98.0, Ph), 140.66 (Ph).^{1}H NMR (CDCl3): δ 0.84−1.01 (d, 3H, (C(5)H3), 1.62−1.90 (m, 3H, C(3)H, C(2)H2), 2.10−2.45 (m, 4H, C(1)H 2, C(4)H2), 6.90−7.70, 7.70−7.80 (m, 15 H, Ph); MALDI TOF/TOF: [M + H]+found = 349.207, C23H25PO requires 348.417.

*4.1.1.4. (2-Bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine oxide (**5c**).* Yield 79%; R_f = 0.36, white solid, mp = 108−110 °C. ^{31}P NMR (CDCl$_3$): δ 32.85. ^{13}C NMR (CDCl$_3$): δ 27.78 ($^2J_{CP}$ = 2.4, C(2)), 28.16 ($^1J_{C\text{-}P}$ = 70.2, C(1)), 28.57 (C(6)), 29.85 (C(5)), 35.04 (C(9)), 36.38 (C (7)), 37.69 (C(8)), 40.63 (C(4)), 43.42 ($^3J_{C\text{-}P}$ = 14.4, C(3)), 128.50 ($^3J_{C\text{-}P}$ = 11.5, Ph), 130.64 ($^2J_{C\text{-}P}$ = 9.2, Ph), 131.51 ($^4J_{CP}$ = 2.4, Ph), 133.03 ($^1J_{C\text{-}P}$ = 98.0, Ph), 133.06 ($^1J_{C\text{-}P}$ = 97.0, Ph). ^{1}H NMR (CDCl$_3$): δ 0.77−0.98 (m, 4H, (C(9)H$_a$, C(8)H$_a$, C(6)H$_a$, C(5)H$_a$), 1.01−1.09 (m, 1H, (C(8)H$_b$), 1.18−1.36 (m, 5H, C(6)H$_b$, C(9)H$_b$, C(3)H, C(2)H$_a$, C(5)H$_b$), 1.37−1.51 (m, 1H, C(2)H$_b$), 1.76−1.82 (m, 1H, C(7)H), 1.95−2.03 (m, 1H, C(4)H), 2.04−2.17 (m, 2H, C(1)H$_2$), 7.20−7.40, 7.45−7.70 (m, 10H, Ph); MALDI TOF/TOF [M + H]$^+$found = 325.307, $C_{21}H_{25}PO$ requires 324.396.

*4.1.1.5. (2-(3-Deuterobicyclo[2.2.1]hept-2-yl)ethyl)diphenylphosphine oxide (**6c**).* Yield 76%; Rf = 0.36, white solid, mp = 107−109 °C. ^{31}P NMR (CDCl3): δ 32.78. ^{13}C NMR (CDCl3): δ 27.73 (2$J_{C\text{-}P}$ = 3.7, C(2)), 28.19 (1$J_{C\text{-}P}$ = 76.5, C(1)), 28.52 (C(6)), 29.85 (C(5)), 35.02 (C(9)), 36.28 (C(7)), 37.29 (t, $J_{C\text{-}D}$ = 19.4, C(8)), 40.61 (C(4)), 43.32 (3JC-P = 14.4, C(3)), 128.50 (3$J_{C\text{-}P}$ = 11.5, Ph), 130.64 (2$J_{C\text{-}P}$ = 9.2, Ph), 131.50 (4$J_{C\text{-}P}$ = 2.7, Ph), 133.05 (1$J_{C\text{-}P}$ = 97.7, Ph), 133.07 (1$J_{C\text{-}P}$ = 97.7, Ph). ^{1}H NMR (CDCl$_3$): δ 0.95−1.14 (m, 3H, (C(9)Ha, C(6)Ha, C(5)Ha), 1.16−1.26 (m, 1H, C(9)Hb), 1.34−1.65 (m, 6H, C(8)HD, C(3)H, C(2)Hb, C(6)Hb, C(5)Hb, C(2)Ha), 1.92−1.97 (m, 1H, C(7)H), 2.12−2.32 (m, 3H, C(4)H, C(1)H2), 7.42−7.56, 7.69−7.78 (m, 10H, Ph); MALDI TOF/TOF [M + H]+found = 326.441, C21H24DPO requires 325.398.

*4.1.1.6. (3-(2-Naphthyl)butyl)diphenylphosphine oxide (**5d**).* Yield 73%; R_f = 0.37, white solid, mp = 113−115 °C. ^{31}P NMR (CDCl$_3$): δ 32.89. ^{13}C NMR (CDCl$_3$): 22.54 (C(14)), 27.79 ($^1J_{C\text{-}P}$ = 72.4, C(1)), 29.33 ($^2J_{C\text{-}P}$ = 3.0, C(2)), 41.15 ($^3J_{C\text{-}P}$ = 14.1, C(3)), 125.44 (C(5)),

125.58 (C(9)), 125.62 (C(7)), 126.07 (C(13)), 127. 65 (C(8)), 127.67 (C(12)),128.36 (C(10)), 128.66 ($^3J_{Ph-P}$ = 12.1, Ph), 130.69 ($^2J_{C-P}$ = 10.1, Ph), 130.87 ($^2J_{C-P}$ = 9.05, Ph), 131.72 ($^4J_{C-P}$ = 3.0, Ph), 131.74 ($^4J_{C-P}$ = 2.0, Ph),132.42 (C(6)), 132.56 ($^1J_{C-P}$ = 97.5, Ph); 133.32 ($^1J_{C-P}$ = 98.5, Ph), 133.62 (C(11)), 143.19 (C(4)). ^{1}H NMR ($CDCl_3$): δ 1.33–1.35 (d, 3H, (C(14)H_3), 1.92–2.26 (m, 4H, C(2)H_2, C(1)H_2), 2.88–2.98 (m, 1H, C(3)H), 7.23–7.31, 7.34–7.97 (m, 17H, napht, Ph); MALDI TOF/TOF: $[M + H]^+_{found}$ = 385.337, $C_{26}H_{25}PO$ requires 384.450.

*4.1.1.7. (3-Cyclohexylbutyl)diphenylphosphine oxide (**5e**).* Yield 84%; Rf = 0.39, white solid, mp = 100–102 °C. ^{31}P NMR ($CDCl_3$): δ 33.23. ^{13}C NMR ($CDCl_3$): 15.65 (C(10)), 25.43 ($2J_{C-P}$ = 4.0, C(2)), 26.63 (C(6)), 26.67 (C(8)), 26.78 C((7)), 27.66 ($1J_{C-P}$ = 72.0, C(1)), 28.36 C((5)), 30.68 C((9)), 39.13 ($3J_{C-P}$ = 13.8, C(3)), 42.07 C((4)), 128.60 ($3J_{Ph-P}$ = 11.5, Ph), 130.75 ($2J_{C-P}$ = 9.1, Ph), 131.61 (4JC-P = 2.3, Ph), 133.13 (1JC-P = 97.7, Ph); 133.19 (1JC-P = 97.8, Ph). ^{1}H NMR ($CDCl_3$): δ 0.80–0.82 (d, 3H, (C(10)H3), 0.85–1.67 (m, 14H, C(5)Ha, C(9)Ha, C(7)H2, C(4)H, C(3)H, C(2)H2, C(9)Hb, C(5)Hb, C(6)H2, C(8)H2) 2.14–2.29 (m, 2H, C(1)H2), 7.44–7.48, 7.70–7.75 (m, 10H, Ph); MALDI TOF/TOF: [M + H]+found = 341.611, C22H29PO requires 340.439.

*4.1.1.8. (3-Methylnonyl)diethylphosphine oxide (**5f**).* Yield 77%; R_f = 0.38, colorless oil. ^{31}P NMR ($CDCl_3$): δ 54.16. ^{13}C NMR ($CDCl_3$): δ 5.73 ($^2J_{C-P}$ = 5.0, C(12)), 5.75 ($^2J_{C-P}$ = 5.0, C(12′)), 14.15 (C(9)), 19.11 (C(10)), 19.88 ($^1J_{CP}$ = 63.7, C(11), C(11′)), 22.62 (C(8)), 24.05 ($^1J_{C-P}$ = 65.3, C(1)), 26.87 (C(5)), 28.27 ($^2J_{C-P}$ = 4.0, C(2)), 29.53 (C(6)), 31.83 (C(7)), 33.87 ($^3J_{C-P}$ = 13.1, C(3)), 36.35 C(4). ^{1}H NMR ($CDCl_3$): δ 0.87–0.95 (m, 6H, (C(9)H_3, C(10)H_3), 1.13–1.83 (m, 25H, (C(4)H_a, C(12)H_3, C(12′)H_3, C(7)H_2, C(6)H_2, C(5)H_2, C(8)H_2, C(4)H_b, C(2)H_b, C(3)H, C(2)H_a, C(1)H_2, C(11)H_2, C(11′)H_2); MALDI TOF/TOF $[M + H]^+_{found}$ = 247.596, $C_{14}H_{31}PO$ requires 246.339.

*4.1.1.9. (3-Deuteromethylnonyl)diethylphosphine oxide (**6f**).* Yield 74%; Rf = 0.38, colorless oil. ^{31}P NMR ($CDCl_3$): δ 52.24. ^{13}C NMR ($CDCl_3$): δ 5.79 ($2J_{C-P}$ = 5.2, C(12), (C(12′)), 13.87 (C(9)), 18.63 (t, J_{C-D} = 18.6, C(10)), 19.86 ($1J_{C-P}$ = 66.2, C(11), C(11′)), 22.43 (C(8)), 24.04 ($1J_{C-P}$ = 65.1, C(1)), 26.68 (C(5)), 28.11 ($2J_{C-P}$ = 4.0, C(2)), 29.34 (C(6)), 31.64 (C(7)), 33.63 ($3J_{C-P}$ = 13.0, C(3)), 36.15 (C(4)).^{1}H NMR ($CDCl_3$): δ 0.75–0.85 (m, 5H, (C(9)H3, C(10)H2D), 1.00–1.73 (m, 25H, (C(4)Ha, C(12)H3, C(12′)H3, C(7)H2, C(6)H2, C(5)H2, C(8)H2, C(4)Hb, C(2)Hb, C(3)H, C(2)Ha, C(1)H2, C(11)H2, C(11′)H2); MALDI TOF/TOF [M + H]+found = 248.609, C14H31PO requires 247.371.

*4.1.1.10. (2-(3-Deuterobycyclo[2.2.1]hept-2-yl)ethyl)diethylphosphine oxide (**6g**).* Yield 72%; R_f = 0.37, colorless oil. ^{31}P NMR ($CDCl_3$): δ 52.02. ^{13}C NMR ($CDCl_3$): δ 5.85 ($^2J_{C-P}$ = 4.7, C(11)), (C(11′)), 20.17 ($^1J_{C-P}$ = 65.8, C(10), C(10′)), 25.31 ($^1J_{C-P}$ = 64.8, C(1)), 28.16 ($^2J_{C-P}$ = 3.1, C(2)), 28.67 (C(6)), 30.03 (C(5)), 35.24 (C(9)), 36.47 (C(7)), 37.52 (t, J_{C-D} = 19.3, C(8)), 40.86 (C(4)), 43.65 ($^3J_{C-P}$ = 13.5, C(3)). ^{1}H NMR ($CDCl_3$): δ 1.07–1.22 (m, 9H, (C(9)H_a, C(5)H_a, C(6)H_a, C(11)H_3, C(11′)H_3), 1.27–1.57 (m, 7H, C(9)H_b, C(2)H_2, C(3)H, C(8)HD, C(5)H_b, C(6)H_b), 1.63–1.77 (m, 6H, C(1)H_2, C(10)H_2, C(10′)H_2), 1.95–2.00 (m, 1H, C(4)H), 2.18–2.23 (m, 1H, C(7)H); MALDI TOF/TOF $[M + H]^+_{found}$ = 230.543, $C_{13}H_{24}$DPO requires 229.313.

4.1.2. Reduction of substituted phosphineoxides

Substituted phosphines **3a-c** were prepared as described earlier [27–30].

*4.1.2.1. (3-Methylnonyl)diphenylphosphine (**3a**).* Yield 69%, colorless oil. ^{31}P NMR ($CDCl_3$): δ -15.19. ^{13}C NMR ($CDCl_3$): δ 14.22 (C(9)), 19.51 (C(10)), 22.77 (C(8)), 25.40 ($^1J_{C-P}$ = 10.05, C(1)), 27.01 (C(5)), 29.69 (C(6)), 32.01 (C(7)), 32.96 ($^2J_{CP}$ = 16.1, C(2)), 34.12 ($^3J_{C-P}$ = 12.1, C(3)), 36.61 (C(4)), 128.41, 128.54 ($^3J_{C-P}$ = 7.0, Ph), 132.70, 132.82 ($^2J_{C-P}$ = 18.1, Ph), 138.70, 138.82, 138.93, 138.98 (Ph). ^{1}H NMR ($CDCl_3$): δ 0.78–0.98 (m, 6H, (C(9)H_3, C(10)H_3), 1.10–1.40 (m, 11H, C(2)H_a, (C(4)H_a, C(4)H_b, C(7)H_2, C(6)H_2, C(5)H_2, C(8)H_2), 1.44–1.61 (m, 2H, C(3)H, C(2)H_b), 2.00–2.19 (m, 2H, C(1)H_2), 7.40–7.58, 7.70–7.82 (m, 10H, Ph); MALDI TOF/TOF: $[M + H]^+_{found}$ = 327.463, $C_{22}H_{31}P$ requires 326.455.

*4.1.2.2. (3-Methyl-4-phenylbutyl)diphenylphosphine (**3b**).* Yield 72%; colorless oil. ^{31}P NMR ($CDCl_3$): δ -15.72. ^{13}C NMR ($CDCl_3$): 19.28 (C(5)), 25.60 ($2J_{C-P}$ = 9.05, C(2)), 32.76 ($1J_{C-P}$ = 7.00, C(1)), 36.29 ($3J_{C-P}$ = 10.1, C(3)), 43.23 (C(4)), 125.78 (Ph), 128.22, 128.43, 128.51, 129.23 (Ph); 132.73 ($2J_{C-P}$ = 18.1, Ph), 132.87 ($2J_{C-P}$ = 19.1, Ph), 138.91 ($1J_{C-P}$ = 24.1, Ph); 139.01 ($1J_{C-P}$ = 23.1, Ph), 141.21 (Ph)).^{1}H NMR ($CDCl_3$): δ 0.92–1.00 (d, 3H, (C(5)H3), 1.34–1.47 (m, 1H, (C(1) Ha), 1.53–1.68 (m, 1H, C(1)Hb), 1.87–1.98 (m, 1H, C(3)H), 2.05–2.25 (m, 2H, C(2)H2), 2.38–2.46 (m, 1H, C(4)Ha), 2.66–2.76 (m, 1H, C(4)Hb), 7.10–7.65, 7.70–7.80 (m, 15 H, Ph); MALDI TOF/TOF: [M + H]+found = 333.221, C23H25P requires 332.418.

*4.1.2.3. (2-Bicyclo[2.2.1]hept-2-ylethyl)diphenylphosphine (**3c**).* Yield 70%, colorless oil. ^{31}P NMR ($CDCl_3$): δ -15.55; ^{13}C NMR ($CDCl_3$): δ 26.50 ($^1J_{C-P}$ = 11.1, C(1)), 28.89 (C(6)), 30.15 (C(5)), 33.01 ($^2J_{C-P}$ = 16.1, C(2)), 35.31 (C(9)), 36.62 C((7)), 38.15 (C(8)), 40.96 (C(4)), 43.86 ($^3J_{C-P}$ = 12.1, C(3)), 128.40, 128.47 (Ph), 132.78 ($^2J_{C-P}$ = 18.1, Ph), 138.15, 138.08, 138.04, 138.00 (Ph). ^{1}H NMR ($CDCl_3$): δ 1.03–1.40 (m, 6H, (C(9)H_a, C(8)H_a, C(6)H_a, C(5)H_a, C(9)H_b, C(2)H_a), 1.46–1.62 (m, 5H, (C(8)H_b, C(2)H_b, C(5)H_b, C(6)H_b, C(3)H), 2.04–2.17 (m, 3H, C(4)H, C(1)H_2), 2.23–2.30 (m, 1H, C(7)H), 7.30–7.60, 7.80–7.98 (m, 10H, Ph); MALDI TOF/TOF $[M + H]^+_{found}$ = 309.312, $C_{21}H_{25}P$ requires 308.397.

*4.1.2.4. (3-(2-Naphthyl)butyl)diphenylphosphine (**3d**).* Yield 67%, white solid, mp = 109–111 °C. ^{31}P NMR ($CDCl_3$): δ -15.73; ^{13}C NMR ($CDCl_3$): δ 22.59 C(14)), 26.06 ($^1J_{C-P}$ = 11.1, C(1)), 34.22 ($^2J_{C-P}$ = 16.1, C(2)), 41.43 ($^3J_{C-P}$ = 12.1, C(3)), 125.30 (C(5)), 125.55 (C(9)), 125.88 (C(7)), 125.97 (C(13)), 127. 71 (C(8)), 128.17 (C(12)), 128.45 (Ph), 128.67 (C(10)), 132.41 (C(6)), 132.66 ($^2J_{C-P}$ = 18.1, Ph), 132.98 ($^2J_{C-P}$ = 18.5, Ph), 133.74 (C(11)), 138.44, 138.57, 139.02, 139.15 (Ph), 144.19 (C(4)).^{1}H NMR ($CDCl_3$): δ 1.40–1.48 (d, 3H, (C(14)H_3), 1.92–2.16 (m, 4H, (C(2)H_2, C(1)H_2), 3.06–3.13 (m, 1H, C(3)H), 7.37–7.62, 7.66–7.72, 7.88–7.97 (m, 17H, Ph, napht); MALDI TOF/TOF $[M + H]^+_{found}$ = 369.322, $C_{26}H_{25}P$ requires 368.450.

*4.1.2.5. (3-Cyclohexylbutyl)diphenylphosphine (**3e**).* Yield 68%; colorless oil. ^{31}P NMR ($CDCl_3$): δ -15.56. ^{13}C NMR ($CDCl_3$): 16.02 (C(10)), 26.05 ($^2J_{C-P}$ = 11.1, C(1)), 26.87 (C(6)), 27.01 (C(8)), 26.93 C((7)), 28.60 C((5)), 30.34 ($^1J_{C-P}$ = 16.1, C(2)), 30.90 C((9)), 39.49 ($^3J_{C-P}$ = 12.3, C(3)), 42.30 C((4)), 128.45, 128.51($^3J_{C-P}$ = 6.0, Ph), 132.75 ($^2J_{C-P}$ = 18.2, Ph), 132.85 ($^2J_{C-P}$ = 18.3, Ph),139.09, 139.22, 139.33 (Ph). ^{1}H NMR ($CDCl_3$): δ 0.94–0.96 (d, 3H, (C(10)H_3), 1.07–1.81 (m, 14H, C(5)H_2, C(9)H_2, C(7)H_2, C(4)H, C(3)H, C(1)H_2, C(6)H_2, C(8)H_2) 2.07–2.20 (m, 2H, C(2)H_2), 7.44–7.48, 7.70–7.75 (m, 10H, Ph); MALDI TOF/TOF $[M + H]^+_{found}$ = 325.601, $C_{22}H_{29}P$ requires 324.439.

*4.1.3. Synthesis of (3-methylnonyl)diphenylphosphine sulfide (**7a**)*

(3-Methylnonyl)diphenylphosphine sulfide **7a** was prepared as described earlier [27–30].

Yield 71%; R_f = 0.37, yellow oil; ^{31}P NMR ($CDCl_3$): δ 43.44; ^{13}C NMR ($CDCl_3$): δ 14.18 (C(9)), 19.38 (C(10)), 22.66 (C(8)), 26.83 (C(7)), 28.90 ($^2J_{C-P}$ = 2.0, C(2)), 29.53 (C(6)), 30.10 ($^1J_{C-P}$ = 45.5, C(1)), 31.86 (C(7)), 33.45 ($^3J_{C-P}$ = 12.1, C(3)), 36.36 (C(4)), 128.59 ($^3J_{C-P}$ = 9.5, Ph), 131.04 ($^2J_{C-P}$ = 7.9, Ph), 131.05 ($^2J_{C-P}$ = 7.8, Ph),

131.35, 131.37 (Ph), 132.99 ($^1J_{C-P}$ = 63.5, Ph), 133.07 ($^1J_{C-P}$ = 63.6, Ph). ^{1}H NMR ($CDCl_3$): δ 0.80–0.87 (m, 6H, (C(9)H_3, C(10)H_3), 1.00–1.30 (m, 10H, (C(4)H_a, C(4)H_b, C(7)H_2, C(6)H_2, C(5)H_2, C(8)H_2), 1.39–1.48 (m, 2H, C(3)H, C(2)H_a), 1.57–1.66 (m, 1H, C(2)H_b), 2.33–2.50 (m, 2H, C(1)H_2), 7.30–7.45, 7.76–7.86 (m, 10H, Ph); MALDI TOF/TOF $[M + H]^+_{found}$ = 359.501, $C_{22}H_{31}PS$ requires 358.521.

4.1.4. Synthesis of a Mo complex

Phosphine complexes of molybdenum **8** were prepared as previously described [30]. Then complexes **8** were purified by column chromatography on silica gel (hexane as eluent).

*4.1.4.1. Complex $Mo(CO)_5L^{4a}$ (**8a**).* Yield 53%; R_f = 0.40, dark blue oil; ^{31}P NMR ($CDCl_3$): δ 27.79; ^{13}C NMR ($CDCl_3$): δ 14.19 (C(9)), 19.08 (t, J_{C-D} = 19.0, C(10)), 22.72 (C(8)), 26.88 (C(5)), 29.56 (C(6)), 29.88 ($^1J_{C-P}$ = 22.0, C(1)), 30.73 (C(2)), 31.92 (C(7)), 33.94 ($^3J_{C-P}$ = 9.6, C(3)), 36.43 (C(4)), 128.71 (d, $^3J_{C-P}$ = 8.9, Ph), 129.97 (d, $^3J_{C-P}$ = 8.2, Ph), 131.86 (d, $^2J_{C-P}$ = 11.4, Ph), 132.03 (d, $^2J_{C-P}$ = 11.6, Ph), 136.83 (d, $^1J_{C-P}$ = 34.6, Ph); 137.14 (d, $^1J_{C-P}$ = 34.8, Ph), 205.85 (d, J_{C-P} = 8.7, CO), 210.22 (d, J_{C-P} = 22.3, CO);^{1}H NMR ($CDCl_3$): δ 0.89–1.01 (m, 5H, (C(9)H_3, C(10)H_2D), 1.17–1.43 (m, 10H, (C(4)H_a, C(4)H_b, C(7)H_2, C(6)H_2, C(5)H_2, C(8)H_2), 1.45–1.58 (m, 3H, C(2)H_2, C(3)H), 2.36–2.54 (m, 2H, C(1)H_2), 7.35–7.55, 7.60–7.66 (m, 10 H, Ph); IR ($CHCl_2$, cm^{-1}), (υCO): 2070 (s), 1987 (s). Found: C, 57.49; H, 5.40. $C_{27}H_{30}DMoO_5P$ requires: C, 57.55; H, 5.37.

*4.1.4.2. Complex $Mo(CO)_5L^{3b}$ (**8b**).* Yield 44%; Rf = 0.39, dark blue oil; ^{31}P NMR ($CDCl_3$): δ 27.77; ^{13}C NMR ($CDCl_3$): 19.21 (C(5)), 30.09 (1J_{C-P} = 21.9, C(1)), 30.63 (2J_{C-P} = 2.4, C(2)), 36.34 (3J_{C-P} = 13.5, C(3)), 43.22 (C(4)), 125.88, 128.24, 129.05, (Ph); 128.68, 128.70 (d, 3J_{C-P} = 9.05, Ph), 131.75 (d, 2J_{C-P} = 11.4, Ph), 131.96 (d, 2J_{C-P} = 11.5, Ph), 136.57 (d, 1J_{C-P} = 33.5, Ph), 136.90 (d, 1J_{C-P} = 33.9, Ph), 140.61 (Ph)), 205.74 (d, J_{C-P} = 8.8, CO), 210.20 (d, J_{C-P} = 22.4, CO); ^{1}H NMR ($CDCl_3$): δ. 0.90–0.95 (d, 3H, C(5)H3), 1.19–1.32 (m, 1H, C(2)H_a), 1.42–1.54 (m, 1H, C(2)Hb),1.78–1.87 (m, 1H, C(3)H), 2.29–2.63 (m, 4H, C(1)H2, C(4)H2), 7.07–7.13, 7.19–7.32, 7.41–7.58 (m, 15H, Ph). IR ($CHCl_2$, cm-1), (υCO): 2070 (s), 1987 (s). Found: C, 59.10; H, 4.44. C28H25MoO5P requires C, 59.17; H, 4.43.

*4.1.4.3. Complex $Mo(CO)_5L^{3c}$ (**8c**).* Yield 49%; R_f = 0.38, dark blue oil; ^{31}P NMR ($CDCl_3$): δ 27.21; ^{13}C NMR ($CDCl_3$): δ 28.70 (C(2)), 29.71 (C(6)), 29.96 (C(5)), 30.95 (d, $^1J_{C-P}$ = 21.5, C(1)), 35.14 (C(9)), 36.46 C((7)), 37.92 (C(8)), 40.78 (C(4)), 43.55 (d, $^3J_{CP}$ = 13.1, C(3)), 128.63 (d, $^3J_{C-P}$ = 9.2, Ph), 129.86 (Ph), 131.85 (d, $^2J_{C-P}$ = 11.5, Ph), 136.86 (d, $^1J_{CP}$ = 34.3, Ph), 136.92 (d, $^1J_{C-P}$ = 34.3, Ph), 205.76 (d, J_{C-P} = 9.0, CO), 210.18 (d, J_{C-P} = 22.3, CO); ^{1}H NMR ($CDCl_3$): δ 0.92–1.21 (m, 5H, (C(9)H_a, C(8)H_a, C(6)H_a, C(5)H_a, C(9)H_b), 1.25–1.52 (m, 5H, C(5)H_b, C(6)H_b, C(8)H_b, C(2)H_2), 1.93–1.98 (m, 1H, C(4)H), 2.11–2.15 (m, 1H, C(7)H), 2.30–2.40 (m, 2H, C(1)H_2), 7.40–7.60, 7.75–7.80 (m, 10H, Ph); IR ($CHCl_2$, cm^{-1}), (υCO): 2070 (s), 1987 (s). Found: C, 57.29; H, 4.90. $C_{26}H_{25}MoO_5P$ requires C, 57.36; H, 4.63.

*4.1.5. Synthesis of a complex $PdCl_2L^{3c}{}_2$ (**9**)*

Reactions was performed under argon using standard Schlenk techniques. A mixture of Pd(COD)Cl_2 (0.79 g, 3 mmol) and substituted phosphane **3c** (3 mmol) was stirred under reflux in 6 mL CH_2Cl_2 for 5 h. The yellow solution became red during this time. The solvent was removed under vacuum and the residue was chromatographed on silica gel (hexane: ethyl acetate = 7:1) to give **9** as yellow oil. Yield 41%; R_f = 0.40; ^{31}P NMR (MHz, $CDCl_3$): δ 16.67; ^{13}C NMR ($CDCl_3$): δ 23.90 (d, $^1J_{C-P}$ = 13.1, C(1)), 24.04 (d, $^1J_{C-P}$ = 14.1, C(1^1)), 28.79 (C(2)); 29.97 (C(6)), 30.94 (C(5)), 35.23 (C(9)), 36.53 ((C(4)), 37.78 (C(8)), 40.80 (C(7)), 43.70 (d, $^3J_{C-P}$ = 7.0, C(3)), 43.77 (d, $^3J_{C-P}$ = 7.0, C(3^1)), 128.17, 130.30, 133.70, 133.73 (Ph). ^{1}H NMR ($CDCl_3$): δ 0.95–1.19 (m, 10H, C(8)H_a, C(9)H_a, C(2)H_a, C(6)H_a, C(9)H_b, C(8^1)H_a, C(9^1)H_a, C(2^1)H_a, C(6^1)H_a, C(9^1)H_b), 1.27–1.50 (m, 12H, C(3)H, C(8)H_b, C(5)H_a, C(5)H_b, C(6)H_b, C(2)H_b, C(3^1)H, C(8^1)H_b, C(5^1)H_a, C(5^1)H_b, C(6^1)H_b, C(2^1)H_b), 1.93–1.98 (m, 2H, C(7)H, C(7^1)H), 2.10–2.16 (m, 2H, C(4)H, C(4^1)H), 2.40–2.48 (m, 4H, C(1)H_2, C(1^1)H_2), 7.39–7.50, 7.67–7.76 (m, 20H, Ph). Found: C, 63.58; H, 6.41. $C_{42}H_{50}P_2PdCl_2$ requires C, 63.62; H, 6.35.

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research (Grants nos. 15-33-20043, 16-33-00310) and Grants of RF President (MD-6293.2016.3, NSh-6651.2016.3). The structural studies of the synthesized compounds were performed with the use of Collective Usage Centre "Agidel" at the Institute of Petrochemistry and Catalysis of RAS.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.10.012.

References

[1] B.-B. Li, Y.-X. Jia, P.C. Zhu, R.J. Chew, Y. Li, N.S. Tan, P.-H. Leung, Eur. J. Med. Chem. 98 (2015) 250–255, http://dx.doi.org/10.1016/j.ejmech.2015.05.027.
[2] M. Yamada, M. Yamashita, T. Suyama, J. Yamashita, K. Asai, T. Niimi, N. Ozaki, M. Fujie, K. Maddali, S. Nakamura, K. Ohnishi, Bioorg. Med. Chem. Lett. 20 (2010) 5943–5946, http://dx.doi.org/10.1016/j.bmcl.2010.01.061.
[3] M. Yamashita, V.K. Reddy, L.N. Rao, B. Haritha, M. Maeda, K. Suzuki, H. Totsuka, M. Takahashi, T. Oshikawa, Tetrahedron Lett. 44 (2003) 2339–2341, http://dx.doi.org/10.1016/S0040-4039(03)00255-7.
[4] D.M. Cermak, D.F. Wiemer, K. Lewis, R.J. Hohl, Bioorg. Med. Chem. 8 (2000) 2729–2737, http://dx.doi.org/10.1016/S0968-0896(00)00212-1.
[5] A. Borner (Ed.), Phosphorus Ligands in Asymmetric Catalysis, Wiley-VCH, Weinheim, 2008.
[6] Y. Wei, M. Shi, Acc. Chem. Res. 43 (2010) 1005–1018, http://dx.doi.org/10.1021/ar900271g.
[7] Y. Xiao, Z. Sun, H. Guo, O. Kwon, Beilstein J. Org. Chem. 10 (2014) 2089–2121, http://dx.doi.org/10.3762/bjoc.10.218.
[8] L. Kollar, G. Keglevich, Chem. Rev. 110 (2010) 4257–4302, http://dx.doi.org/10.1021/cr900364c.
[9] B. Breit, E. Fuchs, Chem. Commun. (2004) 694–695, http://dx.doi.org/10.1039/B315709A.
[10] J. Klosin, C.R. Landis, Acc. Chem. Res. 40 (2007) 1251–1259, http://dx.doi.org/10.1021/ar7001039.
[11] M. Sawamura, Y. Ito, Chem. Rev. 92 (1992) 857–871, http://dx.doi.org/10.1021/cr00013a005.
[12] P.-H. Leung, Acc. Chem. Res. 37 (2004) 169–177, http://dx.doi.org/10.1021/ar030008o.
[13] R.A. Baber, M.F. Haddow, A.J. Middleton, A.G. Orpen, P.G. Pringle, Organometallics 26 (2007) 713–725, http://dx.doi.org/10.1021/om060912v.
[14] W. Tang, X. Zhang, Chem. Rev. 103 (2003) 3029–3070, http://dx.doi.org/10.1021/cr020049i.
[15] T.P. Clark, C.R. Landis, Tetrahedron Asymmetry 15 (2004) 2123–2137, http://dx.doi.org/10.1016/j.tetasy.2004.06.025.
[16] V.P. Ananikov, J.V. Ivanova, L.L. Khemchyan, I.P. Beletskaya, Eur. J. Org. Chem. 20 (2012) 3830–3840, http://dx.doi.org/10.1002/ejoc.201200342.
[17] J.L. Methot, W.R. Roush, Adv. Synth. Catal. 346 (2004) 1035–1050, http://dx.doi.org/10.1002/adsc.200404087.
[18] I.R. Ramazanov, R.N. Kadikova, Z.R. Saitova, U.M. Dzhemilev, Asian J. Org. Chem. 4 (11) (2015) 1301–1307, http://dx.doi.org/10.1002/ajoc.201500274.
[19] I.P. Beletskaya, M.A. Kazankova, Russ. J. Org. Chem. 38 (10) (2002) 1391–1430, http://dx.doi.org/10.1023/A:1022685801622.
[20] K.M. Pietrusiewicz, M. Zablocka, Chem. Rev. 94 (1994) 1375–1411, http://dx.doi.org/10.1021/cr00029a009.
[21] O. Delacroix, A.C. Gaumont, Curr. Org. Chem. 9 (2005) 1851–1882, http://dx.doi.org/10.2174/138527205774913079.
[22] L. Coudray, J.-L. Montchamp, Eur. J. Org. Chem. (2008) 3601–3613, http://dx.doi.org/10.1002/ejoc.200800331.
[23] I.P. Beletskaya, M.M. Kabachnik, Mendeleev Commun. 18 (2008) 113–120, http://dx.doi.org/10.1016/j.mencom.2008.05.001.
[24] C.S. Demmer, N. Krogsgaard-Larsen, L. Bunch, Chem. Rev. 111 (2011) 7981–8006, http://dx.doi.org/10.1021/cr2002646.
[25] A.A. Zagidullin, I.A. Bezkishko, V.A. Miluykov, O.G. Sinyashin, Focus article, Mendeleev Commun. 23 (2013) 117–130, http://dx.doi.org/10.1016/j.mencom.2013.05.001.
[26] V.P. Ananikov, L.L. Khemchyan, Y.V. Ivanova, V.I. Bukhtiyarov, A.M. Sorokin, I.P. Prosvirin, S.Z. Vatsadze, A.V. Medved'ko, V.N. Nuriev, A.D. Dilman,

V.V. Levin, I.V. Koptyug, K.V. Kovtunov, V.V. Zhivonitko, V.A. Likholobov, A.V. Romanenko, P.A. Simonov, V.G. Nenajdenko, O.I. Shmatova, V.M. Muzalevskiy, M.S. Nechaev, A.F. Asachenko, O.S. Morozov, P.B. Dzhevakov, S.N. Osipov, D.V. Vorobyeva, M.A. Topchiy, M.A. Zotova, S.A. Ponomarenko, O.V. Borshchev, Y.N. Luponosov, A.A. Rempel, A.A. Valeeva, A.Y. Stakheev, O.V. Turova, I.S. Mashkovsky, S.V. Sysolyatin, V.V. Malykhin, G.A. Bukhtiyarova, A.O. Terent'ev, I.B. Krylov, Russ. Chem. Rev. 83 (10) (2014) 885–985, http://dx.doi.org/10.1070/RC2014v083n10ABEH004471.

[27] V.A. D'yakonov, A.L. Makhamatkhanova, T.V. Tyumkina, U.M. Dzhemilev, Russ. Chem. Bull. 61 (2012) 1556–1559, http://dx.doi.org/10.1007/s11172-012-0205-4.

[28] V.A. D'yakonov, A.L. Makhamatkhanova, L.K. Dil'mukhametova, T.V. Tyumkina, U.M. Dzhemilev, Russ. Chem. Bull. 62 (2013) 2467–2471, http://dx.doi.org/10.1007/s11172-013-0357-x.

[29] V.A. D'yakonov, A.L. Makhamatkhanova, R.A. Kalimullina, T.V. Tyumkina, U.M. Dzhemilev, Tetrahedron Lett. 55 (2014) 3913–3915, http://dx.doi.org/10.1016/j.tetlet.2014.05.029.

[30] V.A. D'yakonov, A.L. Makhamatkhanova, L.K. Dil'mukhametova, R.A. Agliullina, T.V. Tyumkina, U.M. Dzhemilev, Organometallics 34 (1) (2015) 221–228, http://dx.doi.org/10.1021/om5010463.

[31] V.A. D'yakonov, A.L. Makhamatkhanova, R.A. Agliullina, L.K. Dilmukhametova, T.V. Tyumkina, U.M. Dzhemilev, Beilshtein J. Org. Chem. 12 (2016) 406–412, http://dx.doi.org/10.3762/bjoc.12.43.

[32] U.M. Dzhemilev, A.G. Ibragimov, J. Organomet. Chem. 695 (2010) 1085–1088, http://dx.doi.org/10.1016/j.jorganchem.2010.01.002.

[33] U.M. Dzhemilev, V.A. D'yakonov, Top. Organomet. Chem. 41 (2013) 215–244, http://dx.doi.org/10.1007/3418_2012_38.

[34] C. Xi, S. Huo, T.H. Afifi, R. Hara, T. Takahashi, Tetrahedron Lett. 38 (1997) 4099–4102.

[35] S. Doherty, J.G. Knight, E.G. Robins, T.H. Scanlan, P.A. Champkin, W. Clegg, J. Am, Chem. Soc. 123 (2001) 5110–5111, http://dx.doi.org/10.1021/ja010090n.

[36] O. Kuhl, Phosphoros ^{31}P NMR Spectroscopy: a Concise Introduction for the Synthetic Organic and Organometallic Chemist, Springer-Verlag Berlin Heidelberg, 2008.

[37] K.W. Muir, F.Y. Pétillon, R. Rumin, P. Schollhammer, J. Talarmin, J. Organomet. Chem. 622 (2001) 297–301, http://dx.doi.org/10.1016/S0022-328X(00)00874-3.

[38] G.M. Sheldrick, A short history of SHELX,, ActaCryst A64 (2008) 112–122, http://dx.doi.org/10.1107/S0108767307043930.