Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 23–25
Mendeleev Communications

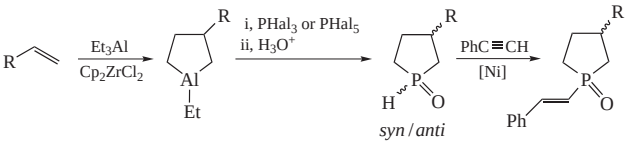
Zirconium-catalyzed cycloalumination of alkenes in the one-pot synthesis of 3-substituted 1*H*-phospholane oxides

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

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russian Federation. Fax: +7 347 284 2750; e-mail: DyakonovVA@gmail.com

DOI: 10.1016/j.mencom.2017.01.006

A new one-pot synthesis of 3-R-1*H*-phospholane oxides (57–65% yield) was implemented by reaction of phosphorus tri- or pentahalides with 3-R-1-aluminacyclopentanes (*in situ* generated by Zr-catalyzed cycloalumination of alkenes). The products are readily P-vinylated by Cu-promoted reaction with alkynes.



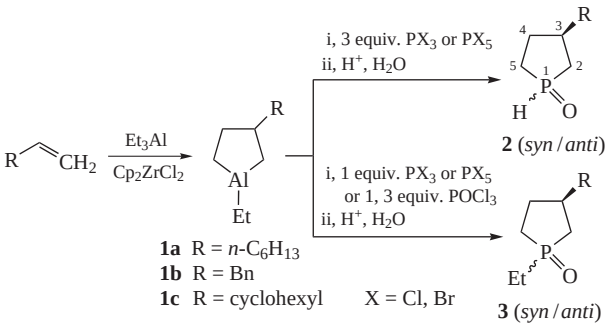
Tertiary phosphines, 1*H*-phosphines and 1*H*-phosphine oxides are very useful in organic and organometallic synthesis, in hydrophosphinylation of alkenes and alkynes and are employed as ligands and analogues of known biologically active compounds.[1–28]

The known syntheses of secondary phosphine oxides are mainly limited to diaryl(alkyl)phosphine oxides.[20–22,29,30] A bounded number of syntheses of cyclic 1*H*-phosphine oxides are described.[11,12,31–33] Due to high reactivity they are used in the hydrophosphinylation of alkynes[30,34,35] to prepare 1-alkenylphospholanes of specified structure. In addition, these cyclic 1*H*-phosphine oxides are of exceptional interest as key monomers to produce new reagents in organic synthesis and efficient ligands for catalytic systems.

Recently, we have developed an original one-pot synthesis of alkyl(aryl)phospholanes and phospholenes based on the catalytic cycloalumination as the key step giving rise to cyclic organoaluminums with subsequent replacement of aluminum by phosphorous atoms using alkyl(aryl)phosphorous(III) dichlorides.[36–40]

We hypothesized that the use of phosphorus halides such as PCl_3, PBr_3, or PCl_5 in this reaction after hydrolysis of the reaction mixture, and keeping in mind their feature to undergo hydrolysis without changing the oxidation state, would allow one to develop a new one-pot process giving access to five-membered cyclic hard-to-reach and previously undescribed phosphine oxides containing a P–H bond.

Our studies have shown that 3-substituted aluminacyclopentanes (ACP)[41] **1** *in situ* generated in the cycloalumination of alkenes with Et_3Al in the presence of 5 mol% Cp_2ZrCl_2 as the catalyst react with phosphorus trihalide or pentahalide in inert-gas atmosphere (CH_2Cl_2, room temperature, 6 h) to afford 3-alkyl(aryl)-1*H*-phospholane oxides **2** with *syn*/*anti* ratio of 1 : 1, after hydrolysis of the reaction mixture (Scheme 1).



Scheme 1

The experiments revealed that three equivalents of PCl_3 or PBr_3 are required for the selective formation of 1*H*-phospholane oxides. When this molar ratio was 1 : 1, the predominant formation of 3-alkyl-1-ethylphospholane oxides **3** occurred. Apparently, they resulted from interaction of intermediate 1-chlorophospholanes with excess of Et_3Al. 1-Ethylphospholane oxides **3** were also formed on using 1 or 3 equiv. of phosphorus oxychloride $POCl_3$.

The structure of the synthesized cyclic organophosphorus compounds was proved by mass spectrometry and ^1H, ^{13}C, ^{31}P NMR spectroscopy as well as homo- and heteronuclear 2D correlation experiments (COSY ^1H-^1H, HSQC, HMBC).†

The ^1H, ^{13}C, and ^{31}P NMR spectra of **2a–c** gave expectedly signals for *syn*- and *anti*-stereoisomers. Their ^1H NMR spectra

† All reactions were carried out under dry argon atmosphere. Dichloromethane was dried and distilled immediately prior to use. Commercially available phosphorus halides, Cp_2ZrCl_2 and Et_3Al (Aldrich) were used without additional purification. 1D (^1H, ^{13}C, ^{31}P) and 2D homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were measured in $CDCl_3$ on a Bruker Avance-400 spectrometer (400.13 MHz for ^1H, 100.62 MHz for ^{13}C, 161.97 MHz for ^{31}P). Elemental analysis was performed on a Karlo Erba model 1106 instrument. The mass spectrum was obtained using a Shimadzu instrument; the ionization energy was 70 eV.

*3-Substituted 1*H*-phospholane oxides* **2a–c** *(general procedure).* A round-bottomed flask was charged with stirring in dry argon atmosphere at 0 °C with Cp_2ZrCl_2 (0.073 g, 0.25 mmol), alkene (5 mmol), and $AlEt_3$ (0.75 ml, 5 mmol). The temperature was brought to 40 °C and the mixture was stirred for 12 h. Then CH_2Cl_2 (15 ml) was added, the reaction mixture was cooled to –(5–10) °C, phosphorus trihalide (15 mmol, 3 equiv.) was added portionwise, and the mixture was stirred at room temperature for additional 6 h. Then the mixture was hydrolyzed with a minimum of water, the reaction products were extracted with CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2 (2×10 ml). The combined extracts and organic layer were dried over $MgSO_4$. The solvent was evaporated and the residue was vacuum distilled to afford 1*H*-phospholane oxides **2a–c** as colourless oils.

Adding 1 equiv. of phosphorus trihalide as well as 1 or 3 equiv. of phosphorous oxychloride under the above reaction conditions caused formation of 1-ethylphospholane 1-oxide **3**.

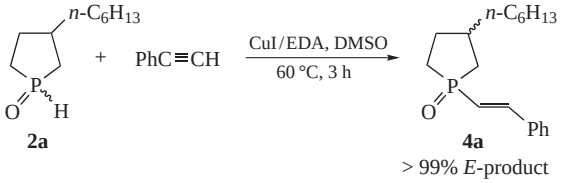
*3-Hexyl-1-[(*E*)-2-phenylvinyl]phospholane 1-oxide* **4a** was prepared as described.[43]

exhibit characteristic high-frequency doublet signals for the P–H protons at δ 7.3–7.4 ppm ($^1J_{PH}$ ~ 462–466 Hz).[7] The phosphorus chemical shift values (δ 46–49 ppm) in the ^{31}P NMR spectra are in good agreement with the published data.[7,30]

For the correct determination of the phosphorus chemical shifts, the ^{13}C NMR spectra were recorded in a broadband decoupling mode. The ^{13}C spectra of compounds **2a**–**c** show first, second, and third order splittings, whereas compounds **2a**,**b** also exhibit fourth order splittings. In addition, the C(2) and C(5) atoms in the cyclic moiety of each isomer have maximum phosphorus–carbon constants J_{PC} 64–67 Hz and J_{PC} 63–65 Hz, respectively.

In accordance with the published data,[6,30,42] secondary phosphine oxides exist in solution as a tautomeric equilibrium between pentavalent (phosphine oxide form) and trivalent (phosphonic form) structures. Phosphine oxide form is more stable at room temperature. The examination of 3-substituted 1*H*-phospholane oxide solutions using ^{1}H, ^{13}C, ^{31}P NMR spectroscopy showed that phosphonic form was absent. Hence, in the solution the tautomeric equilibrium was completely shifted towards phosphine oxide form.

On the example of 3-hexyl-1*H*-phospholane oxide **2a** as a mixture of *syn*- and *anti*-isomers, we have studied the reactivity of this class of compounds in the hydrophosphinylation with 1.5-fold excess of phenylacetylene in the presence of a catalyst system consisting of CuI (10 mol%) and ethylenediamine (15 mol%) as a ligand in DMSO at 60 °C for 3 h (Scheme 2).[43]



2a **4a**

> 99% *E*-product

Scheme 2

The process was highly regio- and stereoselective (>99%) to afford anti-Markovnikov β-adduct **4a** as a mixture of *syn*- and *anti*-isomers (1 : 1) in 97% yield. The structure of **4a** was identified by 1D multinuclear (^{1}H, ^{13}C, ^{31}P) and 2D NMR spectroscopy and mass spectrometry.

In conclusion, we have developed a simple original synthesis of five-membered cyclic secondary phosphine oxides of type **2** by coupling of phosphorus tri- and pentahalides (PCl_3, PBr_3, PCl_5) and aluminacyclopentanes, generated *in situ* from alkenes and Et_3Al in the presence of Cp_2ZrCl_2. The new 1*H*-phospholane oxides can be successfully subjected to hydrophosphinylation of alkynes. Presently we are investigating the catalytic cycloaluminations of various hydrocarbons to extend this procedure to more complex compounds.

This work was supported by the Russian Foundation for Basic Research (grant nos. 15-33-20043 and 16-33-00310) and the President of the Russian Federation (grant nos. NSh-6651.2016.3 and MD-6293.2016.3).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.006.

*3-Hexyl-1*H*-phospholane 1-oxide* **2a**. Two isomers, yield 62%, bp 102–103 °C (1 Torr). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 48.68, 49.08. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.73–0.75 [m, 6H, C(11^1)H$_3$, C(11^2)H$_3$], 1.14–1.35 [m, 21H, C(10^1)H$_2$, C(10^2)H$_2$, C(9^1)H$_2$, C(9^2)H$_2$, C(8^1)H$_2$, C(8^2)H$_2$, C(7^1)H$_2$, C(7^2)H$_2$, C(6^1)H$_2$, C(6^2)H$_2$, C(2^1)H$_a$], 1.49–1.56 [m, 2H, C(4^2)H$_2$], 1.65–1.75 [m, 2H, C(3^1)H, C(5^2)H$_a$], 1.83–1.99 [m, 5H, C(5^1)H$_2$, C(4^1)H$_a$, C(4^1)H$_b$, C(2^1)H$_b$], 2.09 [m, 1H, C(3^2)H], 2.20–2.28 [m, 3H, C(5^2)H$_b$, C(2^2)H$_2$], 7.36 (d, PH, $^1J_{PH}$ 464.4 Hz), 7.39 (d, PH, $^1J_{PH}$ 465.6 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ: 13.93 [C(11^{1,2})], 22.45 [C(10^{1,2})], 25.45 [d, C(5^1), $^1J_{CP}$ 64.8 Hz], 26.95 [d, C(5^2), $^1J_{CP}$ 63.4 Hz], 27.56 [C(7^{1,2})], 29.08 [C(8^{1,2})], 29.40 [d, C(4^1), $^2J_{CP}$ 8.55 Hz], 29.68 [d, C(4^2), $^2J_{CP}$ 6.2 Hz], 31.58 [C(9^{1,2})], 31.99 [d, C(2^1), $^1J_{CP}$ 66.2 Hz], 32.77 [d, C(2^2), $^1J_{CP}$ 64.7 Hz], 35.71 [d, C(6^1), $^3J_{CP}$ 13.2 Hz], 35.95 [d, C(6^2), $^3J_{CP}$ 12.5 Hz], 37.00 [d, C(3^1), $^2J_{CP}$ 10.9 Hz], 38.22 [d, C(3^2), $^2J_{CP}$ 7.6 Hz]. HRMS, *m*/*z*: 189 [M+H]$^+$. Found (%): C, 63.77; H, 11.09. Calc. for $C_{10}H_{21}PO$ (%): C, 63.80; H, 11.24.

*3-Benzyl-1*H*-phospholane 1-oxide* **2b**. Two isomers, yield 65%, bp 123–124 °C (1 Torr). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 46.70, 47.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15–1.24 [m, 1H, C(4^1)H$_a$], 1.46–1.51 [m, 2H, C(2^1)H$_a$, C(2^2)H$_a$], 1.64–1.69 [m, 1H, C(4^2)H$_a$], 1.74–2.03 [m, 7H, C(5^2)H$_a$, C(5^1)H$_2$, C(4^2)H$_b$, C(2^1)H$_b$, C(3^1)H, C(4^1)H$_b$], 2.19–2.26 [m, 2H, C(2^2)H$_b$, C(5^2)H$_b$], 2.46–2.52 [m, 1H, C(3^2)H], 2.60–2.69 [m, 4H, C(6^1)H$_2$, C(6^2)H$_2$], 7.07–7.24 (m, 10H, Ph), 7.36 (d, PH, $^1J_{PH}$ 462.5 Hz), 7.42 (d, PH, $^1J_{PH}$ 463.0 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ: 25.57 [d, C(5^1), $^1J_{CP}$ 64.4 Hz], 27.07 [d, C(5^2), $^1J_{CP}$ 63.1 Hz], 29.13 [d, C(4^1), $^2J_{CP}$ 7.8 Hz], 29.45 [d, C(4^2), $^2J_{CP}$ 5.4 Hz], 31.96 [d, C(2^1), $^1J_{CP}$ 66.2 Hz], 32.71 [d, C(2^2), $^1J_{CP}$ 64.5 Hz], 38.87 [d, C(3^1), $^2J_{CP}$ 11.4 Hz], 39.93 [d, C(3^2), $^2J_{CP}$ 8.4 Hz], 41.76 [d, C(6^1), $^3J_{CP}$ 13.4 Hz], 41.87 [d, C(6^2), $^3J_{CP}$ 13.0 Hz], 126.41 [C(4$'^{1,2}$)], 128.49 [C(3$'^{1,2}$), C(5$'^{1,2}$)], 128.78 [d, C(2$'^{1,2}$), C(6$'^{1,2}$), $^2J_{CP}$ 5.0 Hz], 139.33 [d, C(1$'^{1,2}$), $^1J_{CP}$ 21.5 Hz]. HRMS, *m*/*z*: 195 [M+H]$^+$. Found (%): C, 63.04; H, 7.65. Calc. for $C_{11}H_{15}PO$ (%): C, 63.08; H, 7.78.

*3-Cyclohexyl-1*H*-phospholane 1-oxide* **2c**. Two isomers, yield 57%, bp 109–110 °C (1 Torr). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 48.53, 48.96. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.70–0.90 [m, 8H, C(7^1)H$_2$, C(7^2)H$_2$, C(11^1)H$_2$, C(11^2)H$_2$], 0.97–1.22 [m, 14H, C(10^1)H$_2$, C(10^2)H$_2$, C(9^1)H$_2$, C(9^2)H$_2$, C(8^1)H$_2$, C(8^2)H$_2$, C(3^1)H, C(6^1)H], 1.26–2.21 [m, 14H, C(2^1)H$_a$, C(6^2)H, C(5^1)H$_2$, C(4^1)H$_2$, C(4^2)H$_2$, C(2^2)H$_a$, C(3^2)H, C(2^1)H$_b$, C(5^2)H$_2$, C(2^2)H$_b$], 7.30 (d, PH, $^1J_{PH}$ 465.6 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ: 25.49 [d, C(5^1), $^1J_{CP}$ 64.7 Hz], 27.12 [d, C(5^2), $^1J_{CP}$ 65.5 Hz], 25.97 [C(8^{1,2}), C(10^{1,2})], 26.16 [C(9^{1,2})], 29.71 [d, C(2^1), $^1J_{CP}$ 66.9 Hz], 30.64 [d, C(2^2), $^1J_{CP}$ 65.1 Hz], 30.70 [C(4^1)], 30.78 [C(4^2)], 31.13 [C(7^{1,2}), C(11^{1,2})], 42.46 [C(6^1)], 42.64 [d, C(3^1), $^2J_{CP}$ 10.7 Hz], 42.82 [C(6^2)], 43.99 [d, C(3^2), $^2J_{CP}$ 7.2 Hz]. HRMS, *m*/*z*: 187 [M+H]$^+$. Found (%): C, 64.45; H, 10.13. Calc. for $C_{10}H_{19}PO$ (%): C, 64.49; H, 10.28.

References

1 *Transition Metals for Organic Synthesis*, 2nd edn., eds. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 2004, vol. 1.
2 *Phosphorus Ligands in Asymmetric Catalysis*, ed. A. Börner, Wiley-VCH, Weinheim, 2008.
3 Y. Wei and M. Shi, *Acc. Chem. Res.*, 2010, **43**, 1005.
4 L. Kollár and G. Keglevich, *Chem. Rev.*, 2010, **110**, 4257.
5 Y. Xiao, Z. Sun, H. Guo and O. Kwon, *Beilstein J. Org. Chem.*, 2014, **10**, 2089.
6 N. V. Dubrovina and A. Börner, *Angew. Chem.*, 2004, **116**, 6007 (*Angew. Chem. Int. Ed.*, 2004, **43**, 5883).
7 N. V. Dubrovina, H. Jiao, V. I. Tararov, A. Spannenberg, R. Kadyrov, A. Monsees, A. Christiansen and A. Börner, *Eur. J. Chem. Org.*, 2006, 3412.
8 A. Galland, C. Dobrota, M. Toffano and J.-C. Fiaud, *Tetrahedron: Asymmetry*, 2006, **17**, 2354.
9 A. Galland, J.-M. Paris, T. Schlama, R. Guillot, J.-C. Fiaud and M. Toffano, *Eur. J. Org. Chem.*, 2007, 863.
10 X.-B. Jiang, A. J. Minnaard, B. Hessen, B. L. Feringa, A. L. L. Duchateau, J. G. O. Andrien, J. A. F. Boogers and J. G. de Vries, *Org. Lett.*, 2003, **5**, 1503.
11 W. Braun, B. Calmuschi, J. Haberland, W. Hummel, A. Liese, T. Nickel, O. Stelzer and A. Salzer, *Eur. J. Inorg. Chem.*, 2004, 2235.
12 M. Ostermeier, J. Prieß and G. Helmchen, *Angew. Chem.*, 2002, **114**, 625 (*Angew. Chem. Int. Ed.*, 2002, **41**, 612).
13 T. Hayashi, *Acc. Chem. Res.*, 2000, **33**, 354.
14 K. Fuji, M. Sakurai, T. Kinoshita and T. Kawabata, *Tetrahedron Lett.*, 1998, **39**, 6323.
15 P.-A. Jaffrès, N. Bar and D.Villemin, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2083.
16 I. P. Beletskaya and M. A. Kazankova, *Russ. J. Org. Chem.*, 2002, **38**, 1391 (*Zh. Org. Khim.*, 2002, **38**, 1447).
17 V. P. Ananikov, L. L. Khemchyan and I. P. Beletskaya, *Russ. J. Org. Chem.*, 2010, **46**, 1269 (*Zh. Org. Khim.*, 2010, **46**, 1273).
18 V. P. Ananikov, A. V. Makarov and I. P. Beletskaya, *Chem. Eur. J.*, 2011, **17**, 12623.

19 V. P. Ananikov, J. V. Ivanova, L. L. Khemchyan and I. P. Beletskaya, *Eur. J. Org. Chem*., 2012, 3830.
20 V. P. Ananikov, L. L. Khemchyan, Yu. 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, Yu. N. Luponosov, A. A. Rempel, A. A. Valeeva, A. Yu. Stakheev, O. V. Turova, I. S. Mashkovsky, S. V. Sysolyatin, V. V. Malykhin, G. A. Bukhtiyarova, A. O. Terent'ev and I. B. Krylov, *Russ. Chem. Rev.*, 2014, **83**, 885.
21 L. Coudray and J.-L. Montchamp, *Eur. J. Org. Chem.*, 2008, 3601.
22 O. Delacroix and A. C. Gaumont, *Curr. Org. Chem.*, 2005, **9**, 1851.
23 S. Abbas, R. D. Bertram and C. J. Hayes, *Org. Lett.*, 2001, **21**, 3365.
24 K.-Y. Jung, R. J. Hohl, A. J. Wiemer and D. F. Wiemer, *Bioorg. Med. Chem.*, 2000, **8**, 2501.
25 D. M. Cermak, D. F. Wiemer, K. Lewis and R. J. Hohl, *Bioorg. Med. Chem*., 2000, **8**, 2729.
26 M. R. Harnden, A. Parkin, M. J. Parratt and R. M. Perkins, *J. Med. Chem.*, 1993, **36**, 1343.
27 A. V. Artem'ev, N. K. Gusarova, S. F. Malysheva, N. A. Belogorlova, O. N. Kazheva, G. G. Alexandrov, O. A. Dyachenko and B. A. Trofimov, *Mendeleev Commun.*, 2015, **25**, 196.
28 A. V. Artem'ev, N. K. Gusarova, A. O. Sutyrina, Yu. V. Gatilov and B. A. Trofimov, *Mendeleev Commun.*, 2016, **26**, 314.
29 Q. Xu, R. Shen, Y. Ono, R. Nagahata, S. Shimada, M. Goto and L.-B. Han, *Chem. Commun.*, 2011, **47**, 2333.
30 J. Kanada and M. Tanaka, *Adv. Synth. Catal.*, 2011, **353**, 890.
31 R. A. Aitken, P. N. Clasper and N. J. Wilson, *Tetrahedron Lett.*, 1999, **40**, 5271.
32 F. Guillene, M. Rivard, M. Toffano, J.-Y. Legros, J.-C. Daran and J.-C. Fiaud, *Tetrahedron*, 2002, **58**, 5895.
33 M. Toffano, C. Dobrota and J.-C. Fiaud, *Eur. J. Org. Chem.*, 2006, 650.
34 L.-B. Han, F. Mirzaei, C.-Q. Zhao and M. Tanaka, *J. Am. Chem. Soc*., 2000, **122**, 5407.
35 A. Duraud, M. Toffano and J.-C. Fiaud, *Eur. J. Org. Chem.*, 2009, 4400.
36 V. A. D'yakonov, A. L. Makhamatkhanova, T. V. Tyumkina and U. M. Dzhemilev, *Russ. Chem. Bull., Int. Ed.*, 2012, **61**, 1556 (*Izv. Akad. Nauk, Ser. Khim*., 2012, 1540).
37 V. A. D'yakonov, A. L. Makhamatkhanova, R. A. Agliullina, T. V. Tyumkina and U. M. Dzhemilev, *Tetrahedron Lett*., 2014, **55**, 3913.
38 V. A. D'yakonov, A. L. Makhamatkhanova, L. K. Dil'mukhametova, T. V. Tyumkina and U. M. Dzhemilev, *Russ. Chem. Bull., Int. Ed.*, 2013, **62**, 2467 (*Izv. Akad. Nauk, Ser. Khim.*, 2013, 2467).
39 V. A. D'yakonov, A. L. Makhamatkhanova, L. K. Dil'mukhametova, R. A. Agliullina, T. V. Tyumkina and U. M. Dzhemilev, *Organometallics*, 2015, **34**, 221.
40 V. A. D'yakonov, A. L. Makhamatkhanova, R. A. Agliullina, T. V. Tyumkina and U. M. Dzhemilev, *Russ. Chem. Bull., Int. Ed*., 2015, **64**, 2493 (*Izv. Akad. Nauk, Ser. Khim*., 2015, 2494).
41 T. V. Tyumkina, D. N. Islamov, L. V. Parfenova, L. M. Khalilov and U. M. Dzhemilev, *Magn. Reson. Chem.*, 2016, **54**, 62.
42 I. Schlemminger, Y. Saida, H. Gröger, W. Maison, N. Durot, H. Sasai, M. Shibasaki and J. Martens, *J. Org. Chem.*, 2000, **65**, 4818.
43 M. Niu, H. Fu, Y. Jiang and Y. Zhao, *Chem. Commun.*, 2007, 272.

Received: 4th May 2016; Com. 16/4929