ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 4, pp. 779–780. © Pleiades Publishing, Ltd., 2011. Original Russian Text © D.S. Suslov, V.S. Tkach, M.V. Bykov, M.V. Belova, O.I. Mis'ko, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 4, pp. 689–690.

> LETTERS TO THE EDITOR

## Synthesis of New Mixed-Ligand Cationic Complexes of Palladium [(acac)Pd(PPh<sub>3</sub>)(L)]BF<sub>4</sub>

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Received April 22, 2010

## **DOI:** 10.1134/S107036321104030X

A selection of ligands, including mono-, bi-, and tridentate ones containing phosphorus, nitrogen, sulfur, oxygen, or a combination of them, is an important part of the practice of homogeneous catalysis of the reactions of unsaturated hydrocarbons by the transition metal complexes [1, 2]. While comparing the reactivity of neutral and cationic complexes, the preference was given to the latter [3, 4]. In a series of the transition metals, the palladium complexes are extensively used as active and selective catalysts for conversion of the unsaturated hydrocarbons over 50 years [5]. A common characteristic of the known synthetic methods of the cationic palladium complexes used as catalysts or components of catalytic systems is a multistage process and the use of expensive starting reagents including the silver salt of AgA type (where A is

anion), thallium salts, or triphenylmethyl tetrafluoroborate [2, 6, 7]. In [8–10] we described a method for the synthesis of cationic palladium complexes [(acac) Pd(PAr\_3)\_2]BF\_4 in one stage by the reaction of Pd(acac)\_2, PAr\_3, and BF\_3OEt\_2 in 1:2:2 molar ratio. The testing of the catalytic system [(acac)Pd(PAr\_3)\_2]BF\_4/BF\_3OEt\_2 showed its high activity and selectivity (100%) in the process of styrene dimerization [8] and additive polymerization of norbornene [11].

This publication presents the results of the synthesis of a new series of cationic palladium complexes  $[(acac)Pd(PPh_3)(L)]BF_4$ , where L is HNEt<sub>2</sub>, HNBu<sub>2</sub>, or PBu<sub>3</sub>. The proposed approach expands essentially the potential of the synthesis of mixed-ligand cationic complexes of palladium.



(Acetylacetonato- $k^2 O$ ,O')diethylamino(triphenylphosphine)palladium tetrafluoroborate (I). To a mixture of 0.4355 g (0.768 mmol) of Pd(Acac)<sub>2</sub>PPh<sub>3</sub> and 0.0562 g (0.08 ml) of NHEt<sub>2</sub> in toluene was added dropwise 1 ml of 10 vol % of HBF<sub>4</sub>·OEt<sub>2</sub> solution in CH<sub>3</sub>NO<sub>2</sub> at room temperature under argon. The mixture was stirred for 2–3 h. The yellow precipitate formed. The solution was decanted, the precipitate was washed thrice with toluene. Yield 0.2323 g (48%). IR spectrum, v, cm<sup>-1</sup>: 1526, 1567 (C=O+C=C, acac), 689, 706, 745 (C–H, PPh<sub>3</sub>), 1047, 1092 (B–F, BF<sub>4</sub>), 3200 (N–H), 2953, 2986 (C–H, NHEt<sub>2</sub>). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 10 (CH<sub>3</sub>), 26 (CH<sub>3</sub>), 43 (CH<sub>2</sub>), 100 (CH), 126–135 (Ph), 186 (C=O). Found, %: C 50.63; H 6.26. C<sub>27</sub>H<sub>33</sub>BF<sub>4</sub>NO<sub>2</sub>PPd. Calculated, %: C 51.66; H 5.30.

(Acetylacetonato- $k^2 O, O'$ )dibutylamino(triphenylphosphine)palladium tetrafluoroborate (II) was prepared similarly. Yield 0.1600 g (32%). IR spectrum, v, cm<sup>-1</sup>: 1523, 1565 (C=O+C=C, acac), 685, 715, 740 (C–H, PPh<sub>3</sub>), 1050, 1090 (B–F, BF<sub>4</sub>), 3200–3300 (N–H), 2967, 2942, 2880 (C–H, NHBu<sub>2</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 11 (CH<sub>3</sub>), 19 (CH<sub>2</sub>), 26 (CH<sub>3</sub>), 48 (CH<sub>2</sub>), 100 (CH), 126-135 (Ph), 186 (C=O). Found, %: C 54.47; H 6.94. C<sub>31</sub>H<sub>41</sub>BF<sub>4</sub>NO<sub>2</sub>PPd. Calculated, %: C 54.45; H 6.04.

(Acetylacetonato- $k^2 O, O'$ )tributylphosphino(triphenylphosphine)palladium tetrafluoroborate (III). To a solution of 0.48 g (0.846 mmol) of Pd(acac)<sub>2</sub>PPh<sub>3</sub> in 15 ml of toluene was added 0.78 ml of 1 M tributylphosphine solution in toluene at room temperature under argon. Then to this mixture was added dropwise 1 ml of 10 vol % HBF<sub>4</sub>·OEt<sub>2</sub> solution in OEt<sub>2</sub>. The reaction mixture was stirred for 1 h and concentrated at 40°C in a vacuum. The precipitate was washed with diethyl ether and dried in a vacuum. Yield 0.3 g (52%). IR spectrum, v, cm<sup>-1</sup>: 1520, 1558 (C=O+C=C, acac), 687, 742 (C–H, PPh<sub>3</sub>), 1048, 1090 (B–F, BF<sub>4</sub>), 3200– 2870, 2927, 2959 (C–H, PBu<sub>3</sub>). <sup>31</sup>P NMR spectrum,  $\delta$ , ppm: 26.5 (PBu<sub>3</sub>), 35.7 (PPh<sub>3</sub>). Found, %: C 54.47; H 6.94. C<sub>35</sub>H<sub>49</sub>BF<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Pd. Calculated, %: C 54.54; H 6.52.

The <sup>13</sup>C and <sup>31</sup>P were registered on a Varian VXR-500S spectrometer in CH<sub>3</sub>NO<sub>2</sub>. The IR spectra were recorded on a Infralum FT-801 instrument.

## ACKNOWLEDGMENTS

This work was supported by the Russian Federation Ministry of Education and Science (the Federal Target Program "Scientific and scientific-pedagogical stuff on the innovational Russia" on the 2009–2013 years, state contract no. P1488).

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