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LETTERS TO THE EDITOR

Preparation of Novel Cationic Acetylacetonate Complexes of Palladium with Diimine Ligands

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Catalytic systems based on palladium and nickel complexes with α-diimine ligands are known as the Brookhart catalysts [1, 2]; they are well known in modern practice of laboratory and industrial homogeneous catalysis of oligo- and polymerization of lower alkenes. The strong point of such catalysts is their stability towards polar functional groups of the monomer, allowing preparation of hyperbranched polyolefines. Significant part of palladium complexes with α-diimine ligands described in the literature are neutral (halogenide or alkyl) complexes of palladium that generally require activation with organoaluminum compounds to initiate the active cationic sites [2]. A common feature of preparations of the known cationic palladium complexes is that they are multi-stage processes. On top of that, expensive starting materials are normally used (salts of silver and thallium) as well as magnesium- or- tin- containing chemicals [1]. There have been no examples of preparation of cationic acetylacetonato complexes of palladium with α-diimine ligands.

Earlier [4–7] we presented a series of single-stage syntheses of cationic palladium complexes [Pd(acac)·$(PAr_3)_2$]BF_4, [Pd(acac)(PPh_3)(L)]BF_4, [Pd(acac)(P^P)]·BF_4 (acac, acetylacetonate; L, secondary amine; P^P, bidentate organophosphorus ligand). Catalytic systems based on the listed complexes and BF_3·OEt_2 revealed high activity and selectivity (> 99%) in reactions of styrene dimerization [8], additive polymerization of norbornene [5], and telomerization of butadiene and isoprene with diethylamine [7].

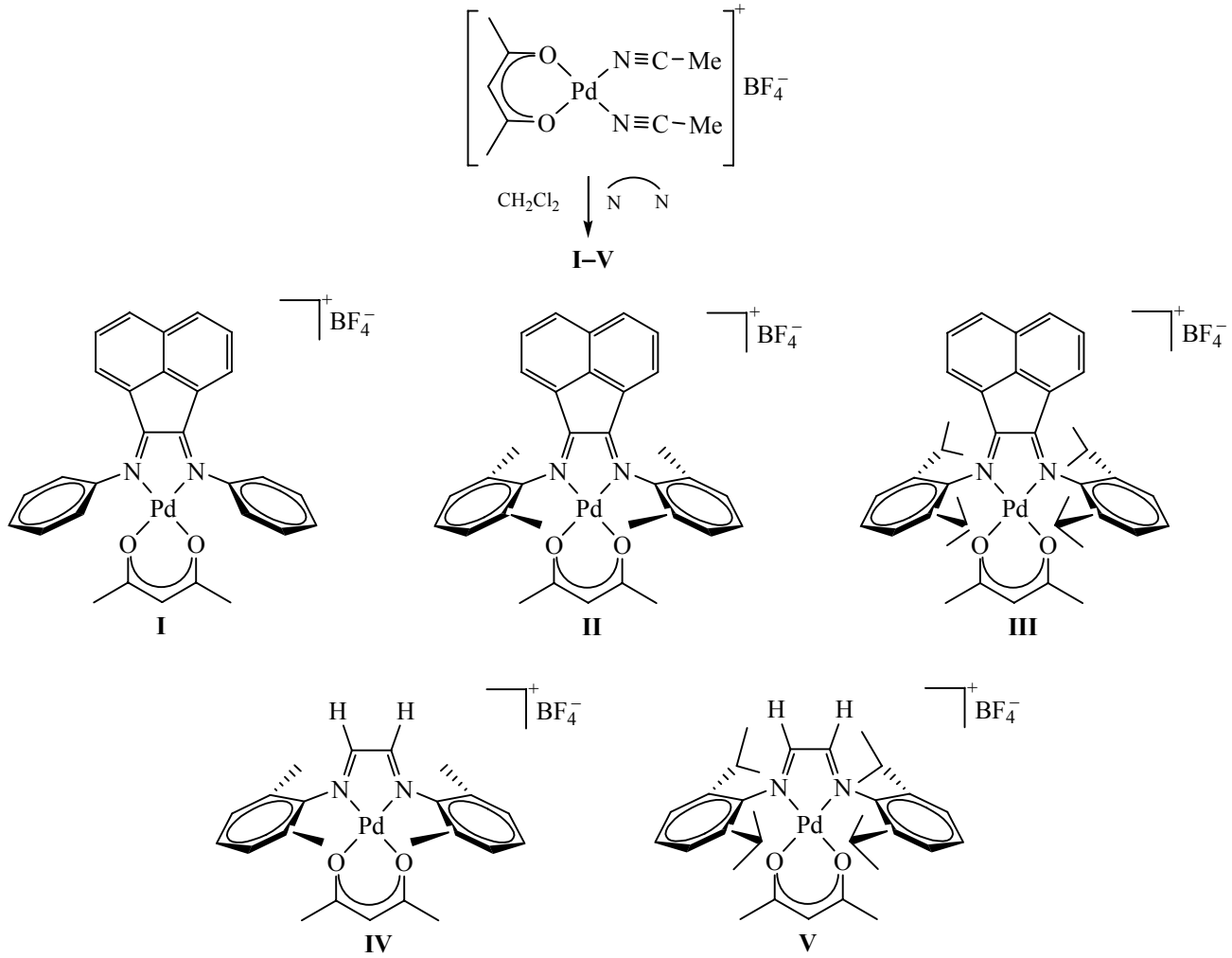
Herein we report on preparation of a new series of cationic palladium complexes [Pd(acac)(N^N)]BF_4, with N^N being α-diimine ligands. The suggested procedure considerable extends the possibility to prepare novel palladium complexes with such ligands (Scheme 1).

Acetylacetonato-k^2*O*,*O*')(1,2-bis[*N*-(phenyl)-imino]-1,2-dihydroacenaphthene)palladium tetrafluoroborate (I). Synthesis was performed under argon atmosphere. The [Pd(acac)$(MeCN)_2$]BF_4 (0.5 g, 1.34 mmol) was added at room temperature in small portions to a solution of 1,2-bis[*N*-(phenyl)imino]-1,2-dihydroacenaphthene (bian) (0.444 g, 1.34 mmol) in 20 mL of dichloromethane. The mixture was stirred during 1 h and evaporated. The formed orange precipitate was washed with cold hexane and dried in vacuum. Yield 0.8235 g (98.0%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.88 s (6H, CH_3, acac), 5.68 s (1H, CH, acac), 6.55 d (2H, bian, *J* 7.6 Hz), 7.10–7.50 m (10H, CH, Ar), 8.07–8.31 m (4H, bian). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.3 (CH_3, acac), 101.3 (CH, acac), 122.0 (bian), 124.0 (H^m, Ar), 126.0 (H^p, Ar), 128.6 (H^o, Ar), 129.2 (CH, bian), 130.8 (CH, bian), 133.0 (bian), 133.6 (CH, bian), 139.4 (bian), 147.2 (C–N), 186.0 (C=N), 188.2 (C=O). Found, %: C 55.33; H 3.74; N 4.48. $C_{29}H_{23}BF_4N_2O_2Pd$. Calculated, %: C 55.75; H 3.71; N 4.48.

Complexes **II**–**V** were prepared similarly.

(Acetylacetonato-k^2*O*,*O*')(1,2-bis[*N*-(2,6-dimethylphenyl)imino]-1,2-dihydroacenaphthen)-palladium tetrafluoroborate (II). Yield 0.889 g (97.8%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.81 s (6H, CH_3, acac), 2.44 s (12H, CH_3), 5.31 s (1H, CH, acac), 6.89 d (2H, bian, *J* 7.2 Hz), 7.33 d (4H, H^m, *J*

Scheme 1.



7.6 Hz), 7.67 t (2H, H^p, *J* 7.6 Hz), 8.11 d (2H, bian, *J* 7.6 Hz), 8.35 d (2H, bian, *J* 8.4 Hz). ^{13}C NMR spectrum ($CHCl_3$), δ_C, ppm: 18.1 (CH_3Ph), 24.9 (CH_3, acac), 101.8 (CH, acac), 123.3 (bian), 125.7 (H^p, Ar), 127.1 (CH, bian), 129.2 (H^m, Ar), 129.4 (CH, bian), 129.8 (CH, bian), 133.8 (bian), 135.1 (bian), 140.2 (H^o, Ar), 148.3 (C–N), 176.5 (C=N), 187.2 (C=O). Found, %: C 58.26; H 4.62; N 4.41. $C_{33}H_{31}BF_4N_2O_2Pd$. Calculated, %: C 58.22; H 4.59; N 4.11.

(Acetylacetonato-k^2*O*,*O*')(bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene)palladium tetrafluoroborate (III). Yield 0.743 g (93.8%). ^1H NMR spectrum ($CDCl_3$), δ, ppm:1.27 d (24H, CH_3, *i*-Pr, *J* 6.8 Hz), 1.81 s (6H, CH_3, acac), 3.37 m (4H, CH, *i*-Pr), 5.30 s (1H, CH, acac), 6.82 d (2H, bian, *J* 7.2 Hz), 7.43 d (4H, H^m, *J* 7.6 Hz), 7.66 (2H, bian, *J* 8.0 Hz), 7.67 t (2H, H^p, *J* 8.0 Hz), 8.46 d (2H, bian, *J* 8.4 Hz). ^{13}C NMR spectrum ($CHCl_3$), δ_C, ppm: 23.5 (CH_3, *i*-Pr), 25.1 (CH_3, acac), 29.8 (CH, *i*-Pr), 102.0 (CH, acac), 122.0 (bian), 124.9 (H^m, Ar), 126.8 (H^p, Ar), 129.9 (CH, bian), 130.3 (CH, bian), 132.1 (bian), 134.4 (CH, bian), 138.8 (bian), 141.4 (H^o, Ar),149.1 (C–N), 178.3 (C=N), 188.2 (C=O). Found, %: C 62.26; H 5.37; N 3.65. $C_{41}H_{47}BF_4N_2O_2Pd$. Calculated, %: C 62.09; H 5.97; N 3.53.

(Acetylacetonato-k^2*O*,*O*')[*N*,*N*-(ethenediylidene) bis(2,6-dimethylaniline)]palladium tetrafluoroborate (IV). Yield 0.73 g (98.2%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.71 s (6H, CH_3, acac), 2.35 s (12H, CH_3, Ar), 5.36 s (1H, CH, acac), 7.50–7.00 m (CH, Ar), 8.36 (2H, CH). ^{13}C NMR spectrum ($CHCl_3$, CH_3NO_2, 1 : 1), δ_C, ppm: 18.0 (CH_3Ph), 24.7 (CH_3, acac), 102.0 (CH, acac), 127.9 (H^o, Ar), 129.4 (H^p, Ar), 129.9 (H^m, Ar), 142.9 (C–N), 171.4 (C=N), 187.7 (C=O). Found, %: C 50.18; H 4.72; N 5.29. $C_{23}H_{27}N_2 \cdot O_2BF_4Pd$. Calculated, % : C 49.62; H 4.89; N 5.03.

(Acetylacetonato-k^2*O*,*O*')[*N*,*N*-(ethanediylidene) bis(2,6-diisopropylaniline)]palladium tetrafluoroborate (V). Yield 0.829 g (92.8%). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 1.37 d (24H, CH_3, *i*-Pr, *J* 7.2 Hz), 1.73 s (6H, CH_3, acac), 3.24 m (4H, CH, *i*-Pr, *J* 6.8 Hz), 5.41 s (1H, CH, acac), 7.25 d (4H, H^m, *J* 7.6 Hz,), 7.43 t (2H, H^p, *J* 7.6 Hz,), 8.50 d (2H, CH, *J* 8.0 Hz). ^{13}C NMR spectrum ($CHCl_3$), δ_C, ppm: 22.8 (CH_3, *i*-Pr), 23.2 (CH_3, *i*-Pr), 24.7(CH_3, acac), 28.94 (CH, *i*-Pr), 102.2 (CH, acac), 123.5 (H^m, Ar), 129.8 (H^n, Ar), 139.9 (C–N), 140.6 (H^o, Ar), 171.8 (C=N), 187.2 (C=O). Found, %: C 55.04; H 7.0; N 4.42. $C_{31}H_{43}N_2O_2BF_4Pd$. Calculated, %: C 55.66; H 6.48; N 4.19.

^{13}C and ^{1}H ($CDCl_3$) spectra were recorded using Varian VXR-500S and Bruker Avance 400 instruments.

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