Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 939–944. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 1004–1010.

Formation of π-Allyl Palladium Complexes from Tertiary Alcohols

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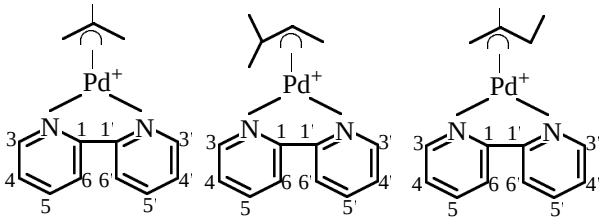
Received November 15, 2000

Abstract — Reactions of 2-methyl-2-propanol, 2-methyl-2-butanol, 2-methyl-2-pentanol, 1-methyl-1-cyclohexanol, and 1-ethyl-1-cyclohexanol with palladium(II) tetraaqua complex in a perchloric acid medium give carbonyl and aromatic compounds, as well as the corresponding palladium π-allyl complexes. The complexes were isolated from the reaction mixtures by way of formation of 2,2'-bipyridine complexes and characterized by the elemental analyses and ^{1}H and ^{13}C NMR spectra. The main direction of transformation of acyclic alcohols is formation of complexes with no alkyl substituents at the central carbon atom of the allyl ligand; with cyclic alcohols, exocyclic complexes are formed.

Earlier we studied reactions of 2-methyl-2-propanol, 2-methyl-2-butanol, 2-methyl-2-pentanol, 1-methyl-1-cyclohexanol, and 1-ethyl-1-cyclohexanol with the palladium complex $[Pd(H_2O)_4](ClO_4)_2$ (**I**) in a perchloric acid medium [1,2]. Spectrophotometrically (by absorbance at λ_{max} 320 nm), it was found that the reactions give palladium π-allyl complexes in yields varying from 41 to 100%, depending on the reaction conditions and the structure of the alcohol. The yield of the complexes is substantially increased by iron(III) ions. The palladium π-allyl complexes formed by 2-methyl-2-propanol and 2-methyl-2-butanol were isolated from the reaction mixtures by treatment with 2,2'-bipyridine and characterized by ^{1}H and ^{13}C NMR spectroscopy. It was proposed that the syntheses involve intermediate formation of olefins.

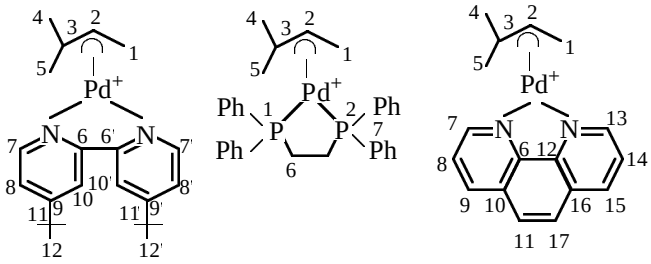
To elucidate the path of reaction of tertiary alcohols with complex **I**, we should determine the structure of both the palladium π-allyl complexes and the organic products forming in the course of the reaction.

The reaction of complex **I** with 2-methyl-2-propanol resulted in isolation of complex **II**, while the reaction with 2-methyl-2-butanol gave a mixture of isomers **III** and **IV** (5 : 1).



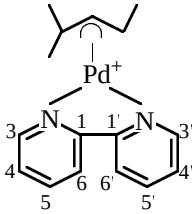
II **III** **IV**

The π-allyl palladium complex obtained from 2-methyl-2-butanol was also isolated from the reaction mixture with use of 4,4'-di(*tert*-butyl)-2,2'-bipyridine, 1,2-bis(diphenylphosphino)ethane, and 1,10-phenanthroline (complexes **IIIa**–**IIIc**, respectively).



IIIa **IIIb** **IIIc**

The reaction between 2-methyl-2-pentanol and complex **I** gave palladium π-allyl complex **V**.



V

It follows from the above results that the dominating reaction direction with aliphatic alcohols is formation of π-allyl palladium complexes with no substituents at the central carbon atom of the allyl ligand. This feature distinguish the synthesis of η^3-allyl complexes we propose in the present work from those described earlier [3–5].

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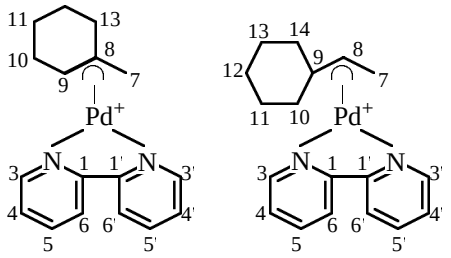
The reactions of complex **I** with 1-methyl-1-cyclohexanol and 1-ethyl-1-cyclohexanol resulted in isolation of compounds **VI** and **VII**, respectively.



VI **VII**

The reactions of 2-methyl-2-butanol, 2-methyl-2-pentanol, and cyclic alcohols with palladium tetraaqua complex can conceivably provide η^3-allyl complexes isomeric to compounds **V**–**VII**. No such complexes were found in the present study, but their presence cannot be ruled out. The palladium π-allyl complexes obtained from 2-methyl-2-pentanol, 1-methyl-1-cyclohexanol, and 1-ethyl-1-cyclohehanol were isolated by treatment with 2,2'-bipyridine (bipy) after the reactions in the presence of iron(III) ions, because under other conditions the yields of these complexes were low. The palladium complexes were isolated from their mixtures with $[Fe(bipy)_3]^{2+}$ by repeated reprecipitation, so there is a possibility that the identified complexes are those formed in the highest yield. Accumulation of iron(III) ions in the solution is the result of the catalytic reaction of tertiary alcohols with complex **I** in the presence of iron(III) ions.

To test the proposal, based on the results of kinetic investigations [1, 2], that the reactions of tertiary alcohols with complex **I**, yielding palladium π-allyl complexes, involve intermediate formation of olefins, we reacted the corresponding olefins with complex **I**. The resulting π-allyl complexes were isolated from the reaction mixtures by treatment with 2,2'-bipyridine. Analysis of the NMR spectra showed that the structure of these complexes is identical to that of compounds **III**–**VI** isolated in the reactions of palladium(II) tetraaqua complex with tertiary alcohols. The reaction times and yields of the π-allyl palladium complexes obtained by the reactions of olefins with complex **I** (C^0_{ol} 0.1, $C^0_{Pd^{2+}}$ 5.5×10^{-3} and $C^0_{HClO_4}$ 0.6 M; 20°C) are given below.

Olefin	2-Methyl-2-butene	2-Methyl-2-pentene	1-Methyl-1-cyclohexene
Reaction time, min	30	15	10
Yield, %	90	56	15

Reaction conditions and yields of palladium π-allyl complexes obtained by the reactions of tertiary alcohols with palladium(II) tetraaqua complex; C^0_{alc} 0.1, $C^0_{Pd^{2+}}$ 5.5×10^{-3}, and $C^0_{HClO_4}$ 0.6 M

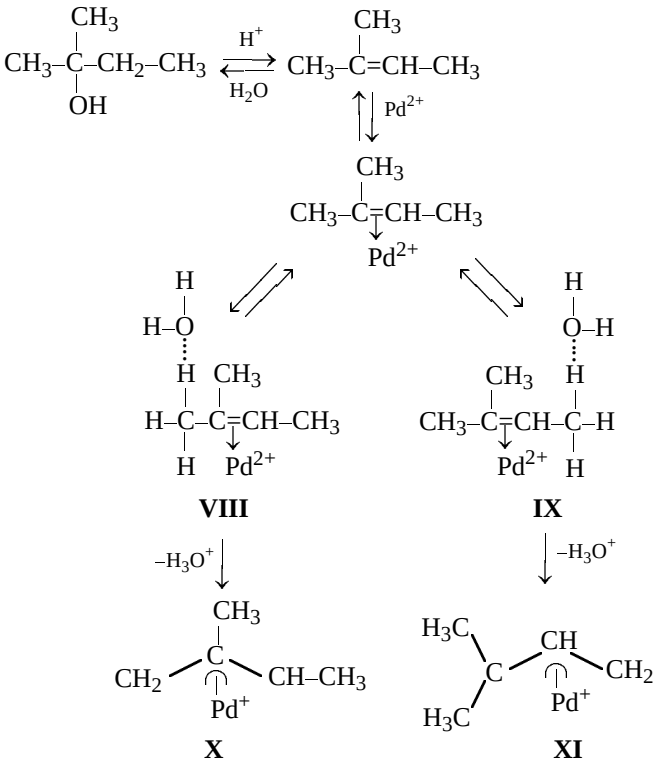
Alcohol	*T*, °C	Reaction time, min	Yield, %
2-Methyl-2-propanol	55	180	57
2-Methyl-2-butanol	45	100	51
2-Methyl-2-pentanol	40	40	17
1-Methyl-1-cyclohexanol	35	80	—
1-Ethyl-1-cyclohexanol[a]	35	80	1

[a] C_{alc} 0.05 M.

The results obtained for the reactions of tertiary alcohols with palladium(II) tetraaqua complex are given in the table. As seen, the reactions of complex **I** with olefins give higher yields of palladium π-allyl complexes. The increased reaction rate is due to the lack of the slow stage of alcohol dehydration. The yields of the complexes increases with increasing substrate concentration. These facts are evidence in favor of the proposed intermediate formation of olefins.

It is significant that the reactivity order of olefins toward palladium(II) tetraaqua complex is opposite to the trends in variation of their reaction rates with palladium(II) chloride or acetate along the homologous series of olefins. The rates of the latter reactions drop with increasing olefin hydrocarbon chain length, especially as concerns olefins with an internal double bond [6, 7].

Thus, on the basis of the present results and published data, the scheme of formation of palladium π-allyl complexes from tertiary alcohols, with the reaction of complex **I** with 2-methyl-2-butanol as an example, can be presented by the following scheme.



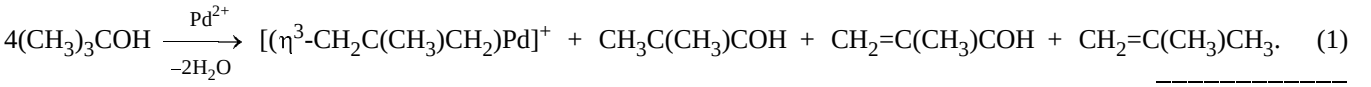
Acid-catalyzed dehydration of an alcohol gives the correposonding alkene which then fastly reacts palladium(II) tetraaqua complex. It is known that the initial product of reaction of an alkene with a palladium salt is a π-olefin complex [8, 9]. Then the reaction may proceed by several paths. The π-olefin complex can convert either to a π-allyl complex or to a saturated carbonyl compound. When direct oxidation of alkene double bonds is hindered by steric reasons, i.e. in reactions of palladium(II) compounds with branched olefins, palladium π-allyl complexes are formed faster than carbonyl compounds by oxidation of π-olefin complexes [10].

It is suggested [4] that π-olefin complexes undergo π–σ rearrangement to give σ-bonded organopalladium compounds whose subsequent transformations result in predominant formation of complexes like **IV** containing a methyl substituent at the central carbon atom of the allyl ligand. However, in reactions between branched olefins and complex **I**, the palladium π-olefin complex does not rearrange to a tertiary carbenium ion, probably, because of the high rate of the π–σ rearrangement. It is also known [6] that the principal role in formation of olefin π-complexes belongs to the donor–acceptor metal–substrate bond which induces effective positive charges on the carbon atoms of the double bond and, consequently, on groups adjacent to the double bond. Therefore, the nucleophilic molecule of water can abstract proton from the methyl group either at a tertiary (intermediate compound **VIII**) or at a secondary carbon atom (intermediate compound **IX**). In the first case, π-allyl complex **X** can be formed, while in the second, π-allyl complex **XI**. However, since the C^2 and C^3 carbon atoms in 2-methyl-2-butene bear different electron densities, on account of the inductive effect of the methyl groups, methyl protons at C^2 than at C^3. As a result, the major product of the reaction between 2-methyl-2-butanol and palladium(II) tetraaqua complex will be complex **XI**.

The formation of π-allyl complexes **VI** and **VII** from the corresponding palladium π complexes with 1-methyl-1-cyclohexene or 1-ethyl-1-cyclohexene as ligands, involves methyl proton cleavage. Here, probably, steric factors play a decisive role in the mechanism of complex formation.

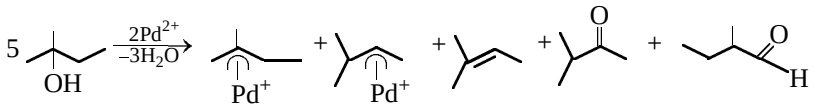
The reactions of tertiary alcohols with palladium(II) tetraaqua complex provide, along with palladium π-allyl complexes, various carbonyl compounds. Their yields vary from 4 to 14% (per taken palladium) and increase up to 20% when the reactions are carried out in the presence of iron(III) ions. With cyclic alcohols, aromatic compounds are formed in 50% yields (per converted alcohol).

Among products of the reaction of 2-methyl-2-propanol with complex **I** by means of GS–MS we found, along with 2-methyl-2-propene, 2-methylpropanal [*m/z* 72 (9), 43 (100), 41 (84), 27 (64), 15 (9)], and the ^{1}H NMR spectrum of an aqueous reaction solution revealed the presence of 2-methyl-2-propenal, δ, ppm: 6.13 s (1H, H_E), 5.85 s (1H, H_Z), 1.41 s (3H, CH_3), 9.08 s (1H, COH. The overall reaction scheme is as follows.



The reaction of 2-methyl-2-butanol with palladium(II) tetraqua complex yields, along with palladium π-allyl complexes and the corresponding olefins, 2-methylbutenal [*m/z* 86 (12), 57 (76), 41 (100), 39 (48), 27 (69), 15 (7)] and 3-methyl-2-butanone [*m/z* 86 (14), 71 (4), 59 (4), 43 (100), 39 (9), 27 (9), 15 (4)] (scheme 2).

In the reaction of 2-methyl-2-pentanol with complex **I** we could detect no other products than

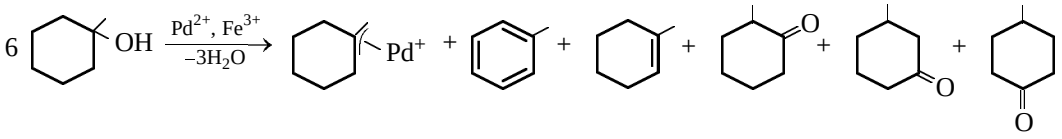


(2)

2-methyl-2-pentene [*m/z* 84 (31), 69 (91), 55 (13), 41 (100), 7 (22), 15 (7)]. In the reaction with 1-methyl-1-cyclohexanol we detected, along with the corresponding olefins, methylbenzene [*m/z* 93 (4), 91 (100), 81 (8), 65 (15), 39 (20), 28 (18), 14 (3)], while in the reaction with 1-ethyl-1-cyclohexanol, ethylbenzene [*m/z* 106 (28), 91 (100), 77 (7), 65 (9), 51 (12), 39 (7), 28 (5)].

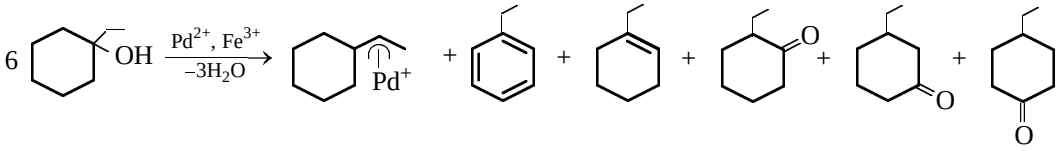
The amounts of carbonyl compounds formed in the systems comprising palladium(II) and 1-methyl-1-cyclohexanol or 1-ethyl-1-cyclohexanol, found with use of 2,4-dinitrophenylhydrazine, were 7 and 14%, respectively.

The reactions of cyclic alcohols with palladium(II) tetraaqua complex in the presence of Fe(III) give, along with the above products, a number of ketones. With 1-methyl-1-cyclohexanol, 2-methyl-1-cyclohexanone [*m/z* 112 (60), 97 (10), 84 (36), 68 (100), 55 (88), 41 (96), 39 (60), 28 (48), 15 (6)], 3-methyl-1-cyclohexanone [*m/z* 112 (31), 97 (11), 69 (100), 56 (42), 41 (46), 28 (46), 18 (8)], and 4-methyl-1-cyclohexanone [*m/z* 112 (33), 105 (6), 83 (24), 69 (16), 55 (100), 41 (53), 39 (33), 28 (29), 15 (6)] are formed [scheme (3)].



(3)

In the reaction of 1-ethyl-1-cyclohexanol [scheme (4)] the following products were found: 2-ethyl-1-cyclohexanone [*m/z* 126 (25), 111 (10), 99 (6), 83 (42), 71 (21), 67 (21), 55 (92), 43 (100), 27 (42)], 3-ethyl-1-cyclohexanone [*m/z* 126 (29), 97 (53), 83 (65), 70 (24), 55 (94), 41 (100), 27 (69)], and 4-ethyl-1-cyclohexanone [*m/z* 126 (6), 97 (37), 69 (25), 55 (100), 41 (67), 27 (58)].



(4)

The saturated carbonyl compounds all are probably formed by oxidation of the corresponding olefin π-complexes, and 2-methyl-2-pronenal, by oxidation of palladium η^3-methallyl complex **II**. In the course of formation of carbonyl compounds from cyclic alcohols, precipitation of palladium metal is observed, which is likely to catalyze aromatization of cyclic olefins [11].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer. Residual signals of solvents were used as internal references. The formation of palladium π-allyl complexes was monitored spectrophotometrically on an SF-56 instrument by the absorbance at λ_{max} 320 nm. Elemental analysis of precipitated π-allyl palladium complexes was made on CHNS-932 and Vario EL instruments.

All reactions were carried out in a temperature-controlled bubble reactor equipped with a sampler.

Complex **I** was prepared by the procedure in [2]. 2-Methyl-2-propanol and 2-methyl-2-pentanol were of chemically pure grade. 2-Methyl-2-butanol was prepared by the procedure in [13], and 1-methylcyclo-

hexanol and 1-ethylcyclohexanol, by the procedure in [14]. The concentration of perchloric acid in the starting solution of complex **I** was found by acid–base titration. The concentration of palladium(II) in reaction mixtures was determined spectrophotometrically by the absorbance of the palladium–tin complex (λ_{max} 635 nm) [15], and the concentration of palladium in π-allyl complexes was found from the difference of the concentrations of palladium(II) determined with and without aqua regia added to the sample to be analyzed. The optical densities was measured on an FEK-56 photoelectrocolorimeter. In all cases, palladium metal was removed from the solution by centrifuging.

Palladium π-allyl complexes were synthesized at the following initial concentrations of the reactants, M: palladium(II) tetraaqua complex 5.0×10^{-3}, alcohol 0.1 (the concentration of 1-ethyl-1-cyclohexanol was 0.05 M because of its poor solubility in water), and perchloric acid 0.5. The reaction with 2-methyl-2-propanol was carried out at 55°C for 3 h, and with 2-methyl-2-butanol, at 45°C for 2 h. Palladium π-allyl complexes based on other tertiary alcohols were isolated after reactions in the presence of Fe(III) ions under the following conditions [concentration of ferric sulfate (M), temperature (°C), reaction time (min)]: 2-methyl-2-pentanol 1×10^{-2}, 40, 80; 1-methyl-1-cyclohexanol 5×10^{-2}, 35, 240; and 1-ethyl-1-cyclohexanol 5×10^{-2}, 35, 220.

Palladium π-allyl complexes were isolated by adding excess 2,2'-bipyridine to the reaction mixture after reaction completion. The white precipitates of 2-methyl-2-propanol and 2-methyl-2-butanol complexes were filtered off, washed with water and diethyl ether to remove excess precipitant, and dried in vacuo. The complexes of other tertiary alcohols, obtained in the presence of iron(III) ions, were isolated from the reaction mixtures containing red precipitates of $Fe(bipy)_3^{2+}$ and white precipitates of palladium π-allyl complexes by repeated reprecipitation from methylene chloride solutions with diethyl ether. The procedure is based on different solubilities of these complexes in the system used (η^3-allyl complexes precipiate first).

Organic reaction products were isolated by extraction from 25 ml of the reaction mixture with 1 ml of dodecane or pentane and then analyzed by GC–MS on a Hewlett–Packard MSD-5972 system (stationary phase DB-5MS).

Analysis of the reaction products was carried out at the laboratory of Prof. Steinborn (Martin-Luther-University, Halle, Germany)

Complex **II**. ^{1}H NMR spectrum (400 MHz, acetone-d_6), δ, ppm: 2.3 s (3H, CH_3), 3.5 s (2H, H_{anti}), 4.3 s (2H, H_{syn}), 7.3–8.9 m (8H, bipy). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 23.7 (CH_3), 62.1 ($2CH_2$), 137.8 (C), 156.1 (C^1), 124.7 (C^3), 142.2 (C^4), 128.9 (C^5), 155.6 (C^6). Found, %: C 40.32; H 3.80; N 6.69. $C_{14}H_{15}N_2Pd$. Calculated, %: C 40.31; H 3.63; N 6.72.

Complex **III**. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2), δ, ppm (*J*, Hz): 1.39 s (3H, CH_{3anti}), 1.76 s (3H, CH_{3syn}), 3.7 d.d (1H, H_{anti}, ^3J 13, ^2J 1.17), 4.1 d.d (1H, H_{syn}, ^3J 7.6, ^2J 1.17), 5.55 d.d (1H, $^3J_{HHanti}$ 13, $^3J_{HHsyn}$ 7.6), 7.6–8.9 m (8H, bipy). ^{13}C NMR spectrum (CD_2Cl_2), δ_C, ppm: 22 (CH_{3anti}), 25.8 (CH_{3syn}), 58.5 (CH_2), 91.8 (C), 113.6 (CH), 155.5, 154.6 ($C^{1,1'}$), 124, 123.9 ($C^{3,3'}$), 141.6, 141.4 ($C^{4,4'}$), 128.4, 128.2 ($C^{5,5'}$), 150.2, 154.8 ($C^{6,6'}$).

Complex **IV**. ^{1}H NMR spectrum (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 3.4 s (1H, H_{anti}), 4.25 s (1H, H_{syn}), 2.24 s (3H, CH_{3centr}), 4.13 q (1H, H, ^3J 6.25), 1.65 d (3H, CH_3, ^3J 6.25), 7.8–9.2 m (8H, bipy). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 73.1 (CH), 78.5 (C), 62.5 (CH_2), 14.1 (CH_{3centr}), 19.1 (CH_3). Found, %: C 41.82; H 4.21; N 6.38. $C_{15}H_{17} \cdot N_2Pd$ (mixture of isomers **III** and **IV**). Calculated, %: C 41.78; H 3.97; N 6.50.

Complex **IIIa**. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 3.64 d.d (1H, H^1_{anti}, ^3J 13.1, ^2J 1.16), 4.17 d.d (1H, H^1_{syn}, ^3J 7.7, ^2J 1.27), 5.45 d.d (1H, H^2, $^3J_{H^1_{syn}H^2}$ 7.7, $^3J_{H^1_{anti}H^2}$ 13.3), 1.72 s (3H, CH^3_4), 1.34 s (3H, CH^5_3), 1.44, 1.42 s (2×9H, $CH^{12,12'}_3$), 7.6–8.8 m (6H, bipy). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 58.2 (C^1), 112.8 (C^2), 90.3 (C^3), 25.6 (C^4), 21.8 (C^5), 154, 155.1 ($C^{6,6'}$), 119.5, 119.7 ($C^{7,7'}$), 125.1, 125.2 ($C^{8,8'}$), 165.6, 165.9 ($C^{9,9'}$), 149.5, 154.5 ($C^{10,10'}$), 30.2 ($C^{12,12'}$).

Complex **IIIb**. ^{1}H NMR spectrum (400 MHz, DMF-d_7), δ, ppm: 3.5 (1H, H^1_{anti}), 4.6 broad signal (1H, H^1_{syn}), 5.8 t (1H, H^2), 1.9 m (3H, CH^4_3), 1.1 m (3H, CH^5_3), 3.2 m (4H, C^6), 7.3–8.0 m (20H, H^7). ^{31}P NMR spectrum (DMF-d_7), δ_P, ppm (*J*, Hz): 56.4 (P^1), 51.9 (P^2, ^{2+3}J 33.9). ^{13}C NMR spectrum (DMF-d_7), δ_C, ppm: 62.2 m (C^1), 116.6 t (C^2), 108.5 d (C^3), 26.8 d (C^4), 20.2 d (C^5), 28.4, 28.7 d ($C^{6,6'}$).

Complex **IIIc**. ^{1}H NMR spectrum (400 MHz, DMF-d_7), δ, ppm (*J*, Hz): 4.03 d (1H, H^1_{anti}, ^3J 13.1), 4.57 d (1H, H^1_{syn}, ^3J 7.7), 5.84 d.d (1H, H^2, $^3J_{H^2H^1_{syn}}$ 7.7, $^3J_{H^2H^1_{anti}}$ 13.1, H^2), 1.94 s (3H, CH^4_3), 1.53 s (3H, CH^5_3), 8.2–9.6 m (8H, $C^{7–9,11,13–15,17}$). ^{13}C NMR spectrum (DMF-d_7), δ_C, ppm: 59.3 (C^1), 114.2 (C^2), 92.2 (C^3), 25.6 (C^4), 21.7 (C^5), 155.6 ($C^{6,12}$), 140.9 ($C^{7,13}$),

128.5 ($C^{8,14}$), 131.2 ($C^{9,15}$), 134.2 ($C^{10,16}$), 131.1 ($C^{11,17}$).

Complex **IV**. ^{1}H NMR spectrum (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 1.4 s (3H, CH_{3anti}), 1.65 d (3H, CH_3, ^3J 6.1), 1.76 s (3H, CH_{3syn}), 4.55 d.q (1H, H, $^3J_{HCH}$ 6.1, $^3J_{HH}$ 12.2), 5.49 d (1H, H_{centr}, ^3J 12.2), 7.9–8.9 m (8H, bipy). ^{13}C MMR spectrum (acetone-d_6), δ_C, ppm: 17.2 (CH_{3anti}), 22.7 (CH_{3syn}), 26.0 (CH_3), 72.4 (CH), 89.5 (C), 113.6 (CH_{centr}), 154.9, 155.0 ($C^{1,1'}$), 123.9 ($C^{3,3'}$), 141.4, 141.5 ($C^{4,4'}$), 128.1, 128.3 ($C^{5,5'}$), 150.2, 151.6 ($C^{6,6'}$). Found, %: C 43.19; H 4.52; N 6.23. $C_{16}H_{19}N_2Pd$. Calculated, %: C 43.16; H 4.30; N 6.29.

Complex **V**. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.28 s (1H, H^7_{anti}), 3.88 s (1H, H^7_{syn}), 4.38 m (1H, H^9), 0.9–2.8 m (8H, $H^{10–13}$), 7.6–9.0 m (8H, bipy). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 59.7 (C^7), 91.2 (C^8), 107.8 (C^9), 19.7 (C^{10}), 28.1 (C^{11}), 35.6 (C^{12}), 23.9 (C^{13}), 154.1, 154.8 ($C^{1,1'}$), 123.8, 124.0 ($C^{3,3'}$), 141.0, 141.2 ($C^{4,4'}$), 127.8, 127.9 ($C^{5,5'}$), 149.8, 153.4 ($C^{6,6'}$).

Complex **VI**. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2), δ, ppm (*J*, Hz): 1.26–2.18 m (10H, $5CH_2$), 3.8 d.d (1H, H^7_{anti}, ^3J 13.2, ^2J 1.14), 4.17 d.d (1H, H^7_{syn}, ^3J 7.7, ^2J 1.14), 5.5 d.q (1H, H^8, $^3J_{HHanti}$ 13.2, $^3J_{HHsyn}$ 7.7), 7.6 – 9.1 m (8H, bipy). ^{13}C NMR spectrum (CD_2Cl_2), δ_C, ppm: 60.3 (C^7), 112.7 (C^8), 101.7 (C^9), 34.2 (C^{10}), 31.7 (C^{11}), 27.8 (C^{12}), 32.6 (C^{13}), 39.0 (C^{14}), 156.1, 155.1 ($C^{1,1'}$), 124.4, 124.6 ($C^{3,3'}$), 141.9, 142.2 ($C^{4,4'}$), 128.7, 128.8 ($C^{5,5'}$), 150.8, 155.2 ($C^{6,6'}$). Found, %: C 45.92; H 4.51; N 5.88. $C_{18}H_{21}N_2Pd$. Calculated, %: C 45.88; H 4.49; N 5.94.

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