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Cationic palladium(II)–acetylacetonate complexes containing phosphine and aminophosphine ligands and their catalytic activities in telomerization of 1,3-butadiene with methanol

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Keywords: palladium, acetylacetonate, 1,3-butadiene, telomerization, methanol

CONTENTS

1 Introduction

Telomerization, linear dimerization of 1,3-dienes with simultaneous addition of a nucleophile in a catalytic reaction, is a very efficient organic transformation. The telomerization process which allows the synthesis of functionalized octadienyl substrate with a potentially 100% atom efficiency [1,2], fulfils most of the principles of the green chemistry. Complexes of palladium are known to effectively catalyze the reaction of dienes with a variety of nucleophiles. Since its discovery 45 years ago [3,4], telomerization has attracted significant interest by many industrial and academic laboratories due to its robustness and versatility in the production of a wide variety of valuable products. The resulting products of telomerization have been used as intermediates in the total synthesis of several natural products, as well as precursors for plasticizer alcohols, industrial monomers, solvents, corrosion inhibitors, and non-volatile herbicides [1,2]. Pd-catalyzed telomerization is also explored as a potential route for the valorization of biomass-derived feedstock [5,6].

Telomerization of 1,3-butadiene (**BD**) with methanol developed by Dow Chemical represent a commercial route to produce 1-octene [7] (Figure 1). The telomerization of 1,3-butadiene with methanol in the presence of a palladium catalyst modified with triarylphosphine, yields 1-methoxy-2,7-octadiene, which is hydrogenated and cracked to give 1-octene and methanol [7]. It is also known that apart from telomerization (products: 1-methoxy-2,7-octadiene, 3-methoxy-2,7-octadiene) the palladium catalyzed dimerization or Diels-Alder reaction of butadiene can take place, leading to 1,3,7-octatriene and 4-vinylcyclohexene, with chemoselectivity depending on the nature of nucleophiles and ligands coordinated to the reactive palladium center (Figure 2) [1,2,8–10].

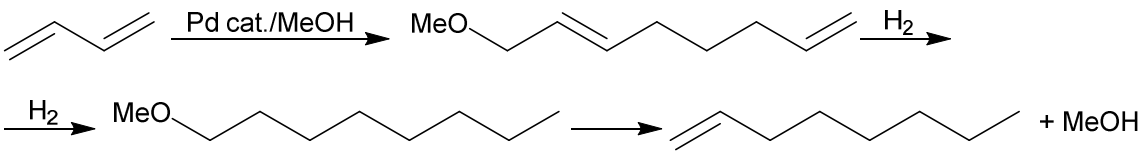

Figure 1 – Simplified Scheme of the Dow Process

A series of palladium complexes with various monodentate phosphines [11–16], diphosphines [17], zwitterionic phosphonium alkylsulfonate ligands [18] and NHC (NHC — N-heterocyclic carbene) ligands [19–21] were reported for the telomerization of BD with methanol. Nevertheless, the search still continues for new ligands and catalysts, due to the high requirements in terms of the stability, reactivity and selectivity of the resulting catalyst [2].

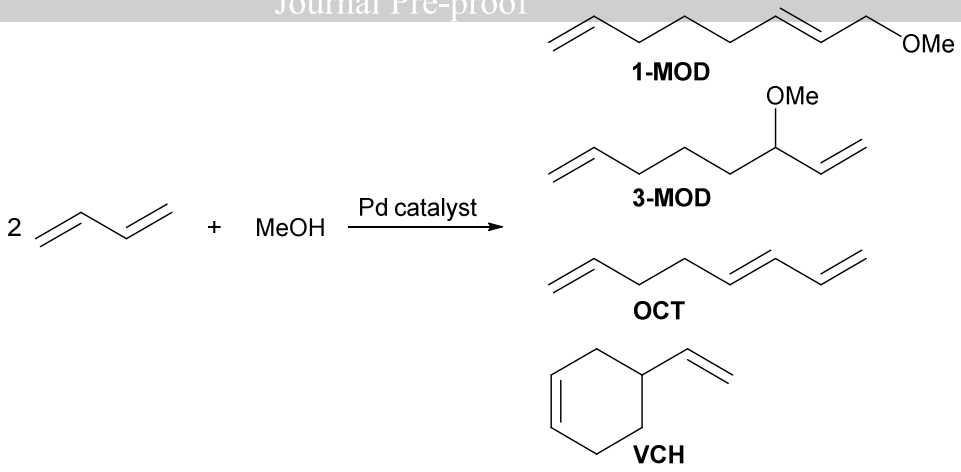

Figure 2 – Telomerization of 1,3-Butadiene with Methanol

We reported synthesis of cationic acetylacetonate palladium complexes with phosphine ligands as well as the results of their usage as efficient precursors (usually activated with $BF_3 \cdot OEt_2$) for the polymerization of norbornene and its derivatives [22–25], polymerization of phenylacetylene [26], selective dimerization or hydroamination of vinylarenes [25,27], telomerization of butadiene and isoprene with diethylamine [28,29]. It should be noted, that application of $[Pd(acac)(PPh_3)_2]BF_4$ as precatalyst for the telomerization of isoprene with amines was reported by Röper et al [30].

In this work we report the results of synthesis of the novel palladium complexes as well as results of $[Pd(acac)(L)_n]BF_4$-catalyzed telomerization of 1,3-butadiene with methanol under base-free conditions (n = 2: L = PPh_3, $PCyPh_2$, PCy_2Ph, PCy_3, $P(NMe_2)_3$, $P(NEt_2)_3$, tri-2-furylphosphine, tri-2-thienylphosphine, *tris*(2-methoxyphenyl)phosphine; n = 1: L = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl). The eight new compounds have been fully characterized, and crystal structures of $[Pd(acac)(L)_2]BF_4$ (L = $PCyPh_2$, PCy_2Ph) have been determined by means of X-ray diffraction. NMR spectroscopy features of the prepared cationic complexes are discussed.

2 Experimental Section

2.1 General procedures and materials

All air- and/or moisture-sensitive compounds were manipulated by using standard high-vacuum line, Schlenk, or cannula techniques under an argon atmosphere. Argon (Arnika-Prom-Service) was purified before feeding to the reactor by passing through columns packed with oxygen scavenger and molecular sieve 4A (Aldrich), respectively. Diethyl ether, petroleum ether, toluene (ZAO Vekton) were distilled from sodium−benzophenone. CH_2Cl_2 (ZAO Vekton), CH_3CN (ZAO Vekton), methanol (ZAO Vekton) were distilled from CaH_2. Solvents were stored over molecular sieves. Other chemicals were purchased from Acros Organic, Sigma-Aldrich, ABCR and employed without drying or any further purification. All glassware and steel reactors was dried for at least 3 h in a 150°C oven and cooled under an argon atmosphere. $Pd(acac)_2$ was synthesized according to a literature procedure [31] and recrystallized from acetone. Complexes $[Pd(acac)(PPh_3)_2]BF_4$ (**1**), $[Pd(acac)(PCy_3)_2]BF_4$ (**4**), $\{Pd(acac)[P(o\text{-}MeOC_6H_4)_3]_2\}BF_4$ (**9**), $[Pd(acac)(MeCN)_2]BF_4$ (**12**) were prepared according to literature procedures [25,26,28]. All other reagents were obtained commercially and used as received. All NMR spectra were recorded at room temperature on Bruker DPX-400 spectrometer. IR spectra were recorded on a Simex Infralum FT 801 spectrometer. GC-FID and GC–MS analyses were performed on Chromatec Crystall 5000.2 (SGE BPX-5 capillary column, internal standard benzene) and Shimadzu QP2010 Ultra (GSBP-5MS capillary column), respectively.

2.2 Telomerization experiments

All reactions were performed in a 20 mL custom-made stainless steel autoclave. The 1,3-butadiene (39 mmol) was condensed to the reactor and controlled volumetrically. The catalyst was added as solution in CH_2Cl_2 directly into the reactor pot. Then methanol (39 mmol) was added via syringe. Afterwards the reactor was closed and placed in an oil bath at 70 °C. The reaction was magnetically stirred at 900 rpm. After 2 h the reaction was stopped using an ice-bath. Analyses of the catalytic reactions have been performed on a GC-FID

2.3 Synthesis of Palladium Complexes

2.3.1 Preparation of (acetylacetonate-κ^2*O,O′*)bis[cyclohexyl(diphenyl)phosphine-κ*P*]palladium(II) tetrafluoroborate, [Pd(acac)($PCyPh_2$)$_2$]BF_4 (**2**)

$PCyPh_2$ (0.2147 g, 0.800 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)$(MeCN)_2$]BF_4 (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 1.5 h at room temperature. The resulting yellow solution was concentrated to 2 mL under vacuum. Addition of diethyl ether (10 mL) formed an lemon precipitate, which was collected, washed with diethyl ether (2×10 mL), and dried (8 h) under vacuum to afford complex **2** as a yellow powder (300 mg, 90.6%). Vapor diffusion of mixture of petroleum ether and diethyl ether (1:1 v/v) into a 1,2-dichloroethate solution of **2** afforded yellow crystals suitable for single-crystal X-ray analysis. Anal. Calcd for $C_{41}H_{49}BF_4O_2P_2Pd$: C, 59.40; H, 5.96. Found: C, 58.17; H, 6.00. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 7.63 – 7.55 (m, 4H, H_{Phi}), 7.40 –7.13 (m, 16H, H_{Phi}), 5.64 (s, 1H, H_{acac}), 2.74 – 2.59 (m, 2H, H_{Cyi}), 2.02 (s, 6H, H_{Me}), 1.91 – 1.79 (m, 4H, H_{Cyi}), 1.75 – 1.65 (m, 4H, H_{Cyi}), 1.65 – 1.54 (m, 2H, H_{Cyi}), 1.29 – 1.12 (m, 4H, H_{Cyi}), 1.11 – 0.82 (m, 6H, H_{Cyi}).^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ 186.69 (s, $C_{CO\text{-}acac}$), 133.74 (observed as virtual triplets (vt) due to virtual coupling [32,33], J = 5.0 Hz, $C_{Ph,ortho}$), 132.39 (s, $C_{Ph,para}$), 129.08 (vt, J = 5.3 Hz, $C_{Ph,meta}$), 124.42 (d, ^1J(P,C_{ipso}) = 51.9 Hz), 101.10 (s, $C_{CH\text{-}acac}$), 35.99 – 35.54 (m, C_{Cyi}), 29.21 (s, C_{Cyi}), 27.51 – 27.29 (m, C_{Cyi}), 27.26 – 27.00 (m, C_{Cyi}), 25.70 (s, C_{Me}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ 35.78 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O′*)-group: 1570 ν(C⋯O and C⋯C); 1516 ν(C⋯C and C⋯O); 1282 (sh) and 1274 (sh) ν_s(C–CH_3) and chelate deformations; 1196 δ(C–H from CH, plane) and chelate deformations; 1004 chelate deformations and δ(C–CH_3, rocking); 938 ν_{as}(C–CH_3) and chelate deformations; 843 (sh) δ(C–H from CH, off-plane); 668 chelate deformations and ν_s(Pd–O); 665 π(CH_3–C(O)⋯C); 604 chelate deformations. ($PCyPh_2$)-group: 3068, 3047, 3033 ν(C–H from CH, Ph); 1589, 1550, 1482, 1438, 1432 ν_{as}(C=C, Ph) and phenyl ring deformations; 1448 (sh) δ(C–H from CH_2, scissoring); 1344, 1340 (sh), 1329, 1314, 1300, 1289, 1269, 1252, 1208 δ(C–H from CH_2, Cy, wagging); 1321 δ(C–H from CH_2, Cy, wagging) and δ(C–H from CH, Cy); 1190, 1165, 1160 (sh), 1119, 1113, 1085, 1077, 1062 δ(C–H from CH_2, Cy, twisting); 1185, 1178, 1101 δ(C–H, Ph, plane); 1049 ν(C–C, Cy) and cyclohexyl ring deformations and δ(C–H from CH_2, Cy, twisting); 1027 ν_s(C=C, Ph) and ring deformations; 998 ν(C–C, Cy) and ν_s(C=C, Ph), with cyclohexyl and phenyl rings deformations; 974, 918, 892, 885, 850 δ(C–H from CH_2, Cy, rocking); 933, 888 δ(C–H, Ph, off-plane); 858, 806 phenyl ring deformations; 816 δ(C–H from CH_2, Cy, rocking) and cyclohexyl ring deformations; 743, 721, 695 δ(C–H, Ph, off-plane);

752 ν_{as}(P–C_{Ar}, Ph); 705 ν_{s}(P–C_{Ar}, Ph); 687 ν(P–C, Cy); 655, 651, 648, 644, 639, 635, 631, 630, 622, 615, 609, 607 cyclohexyl and phenyl rings deformations. (BF_4)-group: 1093, 1054, 1035 ν_{as}(B–F); 782 partially resolved in the IR bands of the symmetric ν_{s}(B–F) vibrations, which appear in the spectrum due to violation of the symmetry of the environment.

2.3.2 Preparation of (acetylacetonate-κ^2*O,O′*)bis[dicyclohexyl(phenyl)phosphine-κ*P*]palladium(II) tetrafluoroborate, [Pd(acac)(PCy_2Ph)$_2$]BF_4 (**3**)

PCy_2Ph (0.2195 g, 0.800 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)($MeCN$)$_2$]BF_4 (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 1.5 h at room temperature. The resulting yellow solution was concentrated to 2 mL under vacuum. Addition of diethyl ether (10 mL) formed an lemon precipitate, which was collected, washed with diethyl ether (2×10 mL), and dried (8 h) under vacuum to afford complex **3** as a yellow powder (276 mg, 82.0%). Vapor diffusion of mixture of petroleum ether and diethyl ether (1:1 v/v) into a 1,2-dichloroethate solution of **3** afforded yellow crystals suitable for single-crystal X-ray analysis. Anal. Calcd for $C_{41}H_{61}BF_4O_2P_2Pd$: C, 58.55; H, 7.31. Found: C, 57.89; H, 7.14. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 7.47 (t, *J* = 7.6 Hz, 2H, H_{Phi}), 7.32 (t, *J* = 7.7 Hz, 4H, H_{Phi}), 7.14 (m, 4H, H_{Phi}), 5.64 (s, 1H, H_{acac}), 2.43 – 2.28 (m, 4H, H_{Cyi}), 2.12 – 1.95 (m, 4H, H_{Cyi}), 2.04 (s, 6H, H_{Me}), 1.94 – 1.67 (m, 18H, H_{Cyi}), 1.55 – 1.10 (m, 18H, H_{Cyi}). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ 186.12 (s, $C_{CO\text{-}acac}$), 132.36 (vt, *J* = 4.1 Hz, $C_{Ph,ortho}$), 131.95 (s, $C_{Ph,para}$), 129.08 (vt, *J* = 4.9 Hz, $C_{Ph,meta}$), 123.65 (d, ^1J(P,C_{ipso}) = 47.4 Hz), 100.83 (s, $C_{CH\text{-}acac}$), 34.53 – 33.84 (m, C_{Cyi}), 30.60 – 29.94 (m, C_{Cyi}), 27.90 – 27.46 (m, , C_{Cyi}), 27.27 – 27.00 (m, C_{Cyi}), 25.84 (s, C_{Me}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ 41.95 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O′*)-group: 1571 ν(C⋯O and C⋯C) and ν_{as}(C=C, Ph from PCy_2Ph); 1525 ν(C⋯C and C⋯O); 1281 (sh) and 1273 (sh) ν_{s}(C–CH_3) and chelate deformations; 1197 δ(C–H from CH, plane) and chelate deformations; 1006 (sh) chelate deformations and δ(C–CH_3, rocking); 938 ν_{as}(C–CH_3) and chelate deformations; 840 δ(C–H from CH, off-plane); 668 chelate deformations and ν_{s}(Pd–O); 663 π(CH_3–C(O)⋯C); 602 chelate deformations. (PCy_2Ph)-group: 3084, 3067, 3042 ν(C–H from CH, Ph); 1550, 1485 (sh), 1436 ν_{as}(C=C, Ph) and phenyl ring deformations; 1449 (sh) δ(C–H from CH_2, scissoring); 1350, 1342, 1330, 1316, 1307, 1293, 1269, 1264, 1211, 1204 (sh) δ(C–H from CH_2, Cy, wagging); 1189, 1170, 1122 (sh), 1115, 1085, 1072, 1038 δ(C–H from CH_2, Cy, twisting); 1181, 1162, 1154, 1099 δ(C–H, Ph, plane); 1051 ν(C–C, Cy) and cyclohexyl ring deformations and δ(C–H from CH_2, Cy, twisting); 1026 ν_{s}(C=C, Ph) and ring deformations; 998 ν(C–C, Cy) and ν_{s}(C=C, Ph), with cyclohexyl and phenyl rings deformations; 981, 914, 892, 851 δ(C–H from CH_2, Cy,

rocking); 932, 920, 887 δ(C–H, Ph, off-plane); 859, 806 phenyl ring deformations; 817 δ(C–H from CH_2, Cy, rocking) and cyclohexyl ring deformations; 735, 692 δ(C–H, Ph, off-plane); 748 ν(P–C_{Ar}, Ph); 723 ν_{as}(P–C, Cy); 705 ν_s(P–C, Cy); 660, 653, 650, 646, 642, 638, 633, 631, 629, 625, 622, 616, 610, 607 cyclohexyl and phenyl rings deformations. (BF_4)-group: 1093, 1054, 1033 ν_{as}(B–F).

2.3.3 Preparation of (acetylacetonate-κ^2*O,O′*)bis[tris(dimethylamino)phosphine-κ*P*]palladium(II) tetrafluoroborate, [Pd(acac){$P(NMe_2)_3$}$_2$]BF_4 (**5**)

$P(NMe_2)_3$ (0.16 mL, 0.800 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)$(MeCN)_2$]BF_4 (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 1.5 h at room temperature. The resulting yellow solution was concentrated to 2 mL under vacuum. Addition of diethyl ether (10 mL) formed an lemon precipitate, which was collected, washed with diethyl ether (2×10 mL), and dried (8 h) under vacuum to afford complex **5** as a yellow powder (218 mg, 88.0%). Anal. Calcd for $C_{17}H_{43}BF_4N_6O_2P_2Pd$: C, 33.00; H, 7.00; N, 13.58. Found: C, 32.41; H, 6.77; N, 13.15. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.51 (s, 0.3H, H_{acac}), 5.48 (s, 0.7H, H_{acac}), 2.80 (vt, *J* = 5.1 Hz, 6H, NC*H*$_3$), 2.76 (d, ^{2}*J*(P,H) = 9.6 Hz, 30H, NC*H*$_3$), 2.05 (s, 1H, H_{Me}), 1.99 (s, 5H, H_{Me}). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ 187.45 (s, $C_{CO\text{-}acac}$), 100.69 (s, $C_{CH\text{-}acac}$), 39.35 (vt, weak, *J* = 3.8 Hz, N*C*H$_3$), 38.76 (vt, *J* = 3.8 Hz, N*C*H$_3$), 26.30 (vt, *J* = 5.7 Hz, C_{Me}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ 90.81 (s), 85.04 (s, weak). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O′*)-group: 1582 ν(C⋯O and C⋯C); 1520 ν(C⋯C and C⋯O); 1185 δ(C–H from CH, plane) and chelate deformations, and ν_s(C–N–C from $P(NMe_2)_3$); 998 chelate deformations and δ(C–CH_3, rocking) and ν_{as}(P–N from $P(NMe_2)_3$); 934 ν_{as}(C–CH_3) and chelate deformations; 820 δ(C–H from CH, off-plane); 673 chelate deformations and ν_s(Pd–O); 665 π(CH_3–C(O)⋯C). ($P(NMe_2)_3$)-group: 2817, 2805 ν(C–H from N$(CH_3)_2$); 1298 (sh) δ_s(C–H from N$(CH_3)_2$, plane); 1280 and 1268 ν_{as}(C–N–C from N$(CH_3)_2$), overlapping ν_s(C–CH_3 from acac) and acac-chelate deformations; 1185 ν_s(C–N–C from N$(CH_3)_2$) and δ(C–H from CH from acac) and acac-chelate deformations; 1160 and 1141 (sh) ν_s(C–N–C from N$(CH_3)_2$); 1065 (sh) δ(N–CH_3, rocking); 998 ν_{as}(P–N) and acac-chelate deformations and δ(C–CH_3, from acac); 972, 957 ν_{as}(P–N); 717 ν_s(P–N); 734, 703 δ(N–CH_3) and δ(C–N–C); 652 δ(C–N–H) and δ(P–N–C). (BF_4)-group: 1095, 1052, 1035 ν_{as}(B–F); 788 and 779 partially resolved in the IR bands of the symmetric ν_s(B–F) vibrations, which appear in the spectrum due to violation of the symmetry of the environment.

2.3.4 Preparation of (acetylacetonate-κ^2*O,O′*)bis[tris(diethylamino)phosphine-κ*P*]palladium(II) tetrafluoroborate, [Pd(acac){P(NEt$_2$)$_3$}$_2$]BF$_4$ (**6**)

P(NEt$_2$)$_3$ (0.23 mL, 0.800 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)(MeCN)$_2$]BF$_4$ (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 2 h at room temperature. The resulting yellow solution was concentrated to 2 mL under vacuum. Addition of petroleum ether (30 mL) formed an oily precipitate. The reaction mixture was cooled to −18°C and stored for 24 h. The crude product was then filtered, and the yellow solid was washed twice with petroleum ether (2×10 mL), and dried (8 h) under vacuum to afford complex **6** as a yellow powder (263 mg, 83.6%). Anal. Calcd for $C_{29}H_{67}BF_4N_6O_2P_2Pd$: C, 44.25; H, 8.58; N, 10.68. Found: C, 44.05; H, 8.54; N, 9.45. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.45 (s, 1H, H_{acac}), 3.53 – 2.92 (m, 24H, NC*H*$_2$CH$_3$), 1.98 (s, 6H, H_{Me}), 1.24 (t, ^3J(H,H) = 7.1 Hz, 3H, NCH$_2$C*H*$_3$), 1.16 (t, ^3J(H,H) = 7.1 Hz, 33H, NCH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ 186.52(s, $C_{CO\text{-}acac}$), 101.19 (s, $C_{CH\text{-}acac}$), 41.80 (weak, N*C*H$_2$CH$_3$), 40.89 (vt, *J* = 4.6 Hz, N*C*H$_2$CH$_3$), 25.63 (vt, *J* = 5.9 Hz, C_{Me}), 13.32 (s, NCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ 99.56 (s, weak), 93.69 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O′*)-group: 1576 ν(C···O and C···C); 1514 ν(C···C and C···O); 955 ν_{as}(C–CH$_3$) and chelate deformations; 820 δ(C–H from CH, off-plane); 677 chelate deformations and ν_s(Pd–O); 668 π(CH$_3$–C(O)···C). (P(NEt$_2$)$_3$)-group: 1348 (sh) δ_s(C–H from CH$_3$); 1295, 1265 ν_{as}(C–N–C), overlapping ν_s(C–CH$_3$ from acac) and acac-chelate deformations; 1199 ν_s(C–N–C); 1171 ν_s(C–N–C) and δ(C–H from CH from acac, plane) and acac-chelate deformations; 1024 (sh) and 1013 ν_{as}(P–N), overlapping acac-chelate deformations and δ(C–CH$_3$ from acac, rocking); 938, 922, 916 ν_{as}(P–N); 808, 800, 793, 770 δ(C–H from CH$_2$, rocking); 721, 690, 686 ν_s(P–N); 654 and 639 δ(P–N–C) and δ(N–C–C). (BF$_4$)-group: 1090, 1052, 1034 ν_{as}(B–F); 787 and 780 partially resolved in the IR bands of the symmetric ν_s(B–F) vibrations, which appear in the spectrum due to violation of the symmetry of the environment.

2.3.5 Preparation of (acetylacetonate-κ^2*O,O′*)bis(tri-2-furylphosphine-κ*P*)palladium(II) tetrafluoroborate, [Pd(acac)(TFP)$_2$]BF$_4$ (TFP = tri-2-furylphosphine) (**7**)

TFP (0.2000 g, 0.800 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)(MeCN)$_2$]BF$_4$ (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 2 h at room temperature. The resulting yellow solution was concentrated to 2 mL under vacuum. Addition of diethyl ether (7 mL) formed an yellow oily precipitate, which was dissolved in toluene (10 mL). The reaction mixture was cooled to −18°C

and stored for 24 h. The crude product was then filtered, and the yellow solid was washed twice with Et_2O (2×10 mL), and dried (8 h) under vacuum to afford complex **7** as a yellow powder (279 mg, 92.4%). Anal. Calcd for $C_{29}H_{25}BF_4O_8P_2Pd$: C, 46.03; H, 3.33. Found: C, 46.69; H, 3.20. ^{1}H NMR (400 MHz, Acetone-d_6, 25°C): δ 7.98 (s, 6H, H_{Fur5}) (**Fur** – furyl ring), 7.19 (d, J = 3.6 Hz, 6H, H_{Fur3}), 6.67 (s, 6H, H_{Fur4}), 5.69 (s, 1H, H_{acac}), 1.83 (s, 6H, H_{Me}). ^{13}C NMR (101 MHz, Acetone-d_6, 25°C): δ 186.93 (s, $C_{CO\text{-}acac}$), 151.00 (vt, J = 3.6 Hz, C_{Fur5}), 137.54 (d, ^1J(P,C) = 99.2 Hz, C_{Fur2}), 126.20 (vt, J = 10.2 Hz, C_{Fur3}), 112.24 (vt, J = 4.3 Hz, C_{Fur4}), 100.64 (s, $C_{CH\text{-}acac}$), 25.14 (vt, ^4J(P,C) = 5.9 Hz, C_{Me}). ^{19}F NMR (376 MHz, Acetone-d_6, 25°C): δ −151.14, −151.19 (intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{31}P{^{1}H} NMR (162 MHz, Acetone-d_6, 25°C): δ −18.63 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O′*)-group: 1575 ν(C···O and C···C); 1517 ν(C···C and C···O); 1281 (sh) and 1272 ν_s(C–CH_3) and chelate deformations; 1196 δ(C–H from CH, plane) and chelate deformations; 1006 (sh) chelate deformations and δ(C–CH_3, rocking); 937 ν_{as}(C–CH_3) and chelate deformations; 847 δ(C–H from CH, off-plane); 687 chelate deformations and ν_s(Pd–O); 668 π(CH_3–C(O)···C); 602 chelate deformations. TFP-group: 3147, 3124, 3084 ν(C–H from Fur); 1549 ν(C=C from Fur) and ring deformations, 1580 ν(C=C from Fur) overlapped by ν(C···O and C···C) from acac-group; 1226, 1216 and 1169 δ(C–H from Fur, plane) and ring deformations, including ν(C–O–C, quasi ν_{as}); 1138 and 1128 ν(C–O–C, quasi ν_{as}) with ring deformations and δ(C–H from Fur, plane); 1067 δ(C–H from Fur, plane) and ring deformations including ν(C–O–C, quasi ν_s); 1009 ring deformations and δ(C–H from Fur, plane); 911 ν(C–C from Fur) and δ(C–H from Fur, off-plane); 907, 883, 859 ring deformations and δ(C–H from Fur, off-plane); 768 ν(P–C); 786 (sh), 756 (sh), 723 δ(C–H from Fur, off-plane); 655, 643, 637 ring deformations, 589 ring deformations with δ(C–O–C). (BF_4)-group: 1079, 1053, 1035 ν_{as}(B–F).

2.3.6 Preparation of (acetylacetonato-κ^2*O,O′*)bis(tri-2-thienylphosphine-κ*P*)palladium(II) tetrafluoroborate, [Pd(acac)(TTP)$_2$]BF_4 (TTP = tri-2-thienylphosphine) (**8**)

TTP (0.411 mmol, 3.2 mL of solution in 1,2-dichloroethane) was diluted in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)(MeCN)$_2$]BF_4 (0.0770 g, 0.206 mmol. The reaction mixture was then stirred for 2 h at room temperature. The resulting yellow solution was concentrated to 2 mL under vacuum. Addition of diethyl ether (7 mL) formed oily precipitate, which was filtered and dried (1 h) under vacuum. The obtained powder was washed with toluene (2×10 mL), Et_2O (1×10 mL) and dried (8 h) under vacuum to afford complex **8** as a brown powder (146 mg, 83.5%). Anal. Calcd for $C_{29}H_{25}BF_4O_2P_2PdS_6$: C, 40.83; H, 2.95 Found: C,

40.86; H, 3.02. ^{1}H NMR (400 MHz, Acetone-d_6, 25°C): δ 8.12 – 8.05 (m, 6H, H_{Thi5}) (**Thi** – thienyl ring), 7.64 – 7.56 (m, 6H, H_{Thi3}), 7.28 – 7.22 (m, 6H, H_{Thi4}), 5.67 (s, 1H, H_{acac}), 1.74 (s, 6H, H_{Me}). ^{13}C NMR (101 MHz, Acetone-d_6, 25°C): δ 186.96 (s, $C_{CO\text{-}acac}$), 139.73 (vt, J = 6.5 Hz, C_{Thi5}), 136.79 (s, C_{Thi4}), 128.99 (vt, J = 7.0 Hz, C_{Thi3}), 127.21 (d, J = 70.5 Hz, C_{Thi2}), 100.94 (s, $C_{CH\text{-}acac}$), 25.41 (vt, ^{4}J(P,C) = 5.5 Hz, C_{Me}). ^{19}F NMR (376 MHz, Acetone-d_6, 25°C): δ −151.25, −151.30 (intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{31}P{^{1}H} NMR (162 MHz, Acetone-d_6, 25°C): δ 3.83 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O′*)-group: 1563 ν(C···O and C···C); 1519 ν(C···C and C···O); 1282 (sh) and 1272 ν_s(C–CH_3) and chelate deformations; 1200 δ(C–H from CH, plane) and chelate deformations; 1011 chelate deformations and δ(C–CH_3, rocking) and thienyl ring deformations; 937 ν_{as}(C–CH_3) and chelate deformations; 845 (sh) δ(C–H from CH, off-plane); 684 chelate deformations and ν_s(Pd–O); 668 π(CH_3–C(O)···C); 602 chelate deformations. TTP-group: 3107, 3092, 3077 ν(C–H from Thi); 1494 and 1401 ν(C=C from Thi) and ring deformations; 1332 δ(C–H from Thi, plane); 1226 (sh), 1218 and 1110 (sh) δ(C–H from Thi, plane) and ring deformations; 1011 ring deformations and δ(C–H from Thi, plane) and acac-chelate deformations; 914 δ(C–H from Thi, off-plane); 854 ν(C–S–C, quasi ν_{as}) with ring deformations and δ(C–H from Thi, off-plane); 806 ν(C–S–C, quasi ν_s) with ring deformations and δ(C–H from Thi, off-plane); 743, 698 δ(C–H from Thi, off-plane); 734 δ(C–H from Thi, off-plane) and ν(C–S) with ν(P–C); 721 ν(P–C) with ν(C–S), 665, 648, 641, 637, 621, 618, 611, 596, 587 ring deformations; 572 ring deformations with ν(C–S–C). (BF_4)-group: 1100, 1052, 1036 ν_{as}(B–F).

2.3.7 Preparation of (acetylacetonate-κ^2*O,O′*)(2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl-κ*P*)palladium(II) tetrafluoroborate, [Pd(acac)(SPhos)]BF_4, (SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) (**10**)

SPhos (0.1693 g, 0.400 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)$(MeCN)_2$]BF_4 (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 2 h at room temperature. The resulting yellow solution was concentrated to 4 mL under vacuum. Addition of diethyl ether (10 mL) followed by addition of petroleum ether (6 mL) formed a precipitate, which was collected, washed with diethyl ether (2×10 mL), and dried (8 h) under vacuum to afford complex **10** as a orange powder (274 mg, 97.3%). Anal. Calcd for $C_{31}H_{42}BF_4O_4PPd$: C, 52.97; H, 6.02. Found: C, 51.57; H, 5.98. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.28 – 8.15 (m, 1H, H_{Ari}), 7.62 – 7.40 (m, 3H, H_{Ari}), 6.80 – 6.66 (m, 1H, H_{Ari}), 6.57 – 6.47 (m, 2H, H_{Ari}), 5.26 – 5.22 (two peaks, 1H, H_{acac}), 3.85 – 3.70 (two peaks,

6H, H_{OMe}), 2.27 – 2.16 (m, 2H, H_{Cyi}), 2.13 – 2.04 (m, 2H, H_{Cyi}), 1.93 (s, 3H, H_{Me}), 1.89 (s, 3H, H_{Me}), 1.85 – 1.62 (m, 9H, H_{Cyi}), 1.60 – 1.06 (m, 9H, H_{Cyi}). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C) δ 189.23 (d, ^3J(C,P) = 3.5 Hz, $C_{CO\text{-}acac}$), 183.10 (s, $C_{CO\text{-}acac}$), 170.55, 147.77, 145.77, 145.60, 133.68, 133.20, 132.71, 131.28, 131.17, 128.71, 128.64, 105.03, 100.07 (s, $C_{CH\text{-}acac}$), 56.99, 35.69, 35.43, 29.72, 29.64, 28.32, 28.11, 27.16, 27.02, 26.99, 26.87, 25.79, 25.63, 25.60 [observed complexity due to C−P coupling]. ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): δ −153.94, −154.03 (intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ 66.20 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O*,*O*′)-group: 1573 ν(C···O and C···C); 1509 ν(C···C and C···O); 1273 (sh) and 1281 (sh) ν_s(C–CH_3) and chelate deformations; 1183 (sh) δ(C–H from CH, plane) and chelate deformations; 1012 chelate deformations and δ(C–CH_3, rocking); 958 ν_{as}(C–CH_3) and chelate deformations; 841 δ(C–H from CH, off-plane); 668 chelate deformations and ν_s(Pd–O); 663 π(CH_3–C(O)···C); 604 chelate deformations. (SPhos)-group: 3095, 3071, 3034 ν(C–H from CH, Ar); 1592, 1576, 1559, 1550, 1487, 1437 (sh), 1416 δ_s(O–CH_3) and ν_{as}(C=C, Ar) and aryl rings deformations; 1449 (sh) δ(C–H from CH_2, scissoring); 1341, 1337, 1330, 1296, 1208 δ(C–H from CH_2, Cy, wagging); 1258 ν_{as}(C–O–C_{Ar}); 1189 (sh) δ(C–H, Ar, plane) and δ(O–CH_3, rocking); 1172, 1115 (sh), 1110 (sh) δ(C–H from CH_2, Cy, twisting); 1161 δ(C–H, Ar, plane); 1140 δ(O–CH_3, rocking); 1057 ν_{as}(C–O–C_{Ar}) and δ(C–H from CH_2, Cy, twisting) with ν(C–C, Cy) and cyclohexyl ring deformations; 1002 ν(C–C, Cy) and ν_s(C=C, Ar), with cyclohexyl and aryl rings deformations; 989, 917, 896, 892, 886, 869 δ(C–H from CH_2, Cy, rocking); 934 δ(C–H, Ar, off-plane) and δ(C–H from CH_2, Cy, rocking); 824, 767 (sh) aryl rings deformations; 821 cyclohexyl ring deformations; 778, 765, 757, 753, 746 δ(C–H, Ar, off-plane); 760 ν_{as}(P–C_{Ar}, Ar); 737 ν_{as}(P–C, Cy); 725 ν_s(P–C, Cy); 699, 695, 690, 686, 684, 681, 677, 674, 657, 655, 649, 645, 642, 638, 636, 632, 628, 623, 620, 613, 606 cyclohexyl and aryl rings deformations. (BF_4)-group: 1097, 1053, 1036 ν_{as}(B–F).

2.3.8 Preparation of (acetylacetonate-κ^2*O*,*O*′)(2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl-κ*P*)palladium(II) tetrafluoroborate, [Pd(acac)(XPhos)]BF_4, (XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) (**11**)

XPhos (0.1966 g, 0.400 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution was added [Pd(acac)$(MeCN)_2$]BF_4 (0.1497 g, 0.400 mmol), forming a yellow solution. The reaction mixture was then stirred for 2 h at room temperature. The resulting yellow solution was concentrated to 4 mL under vacuum. Addition of diethyl ether (15 mL) formed a precipitate, which was collected, washed with diethyl ether (2×10 mL), and dried (8 h) under vacuum to

afford complex **11** as a orange powder (270 mg, 87.7%). Anal. Calcd for $C_{38}H_{56}BF_4O_2PPd$: C, 59.35; H, 7.34. Found: C, 58.84; H, 7.54. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 7.84 – 7.74 (m, 1H, H_{Ari}), 7.63 – 7.48 (m, 2H, H_{Ari}), 7.09 (s, 2H, H_{Ari}), 6.72 – 6.65 (m, 1H, H_{Ari}), 5.19 (s, 1H, H_{acac}), 3.03 (dq, ^3J(H,H) = 6.7 Hz, 1H, $(CH_3)CH$), 2.46 – 2.27 (m, 4H, H_{Cyi}+$(CH_3)CH$), 2.25 – 2.15 (m, 2H, H_{Cyi}), 2.11 – 1.99 (m, 2H, H_{Cyi}), 1.93 (s, 3H, H_{Me}), 1.87 – 1.77 (m, 4H, H_{Cyi}), 1.74 (s, 3H, H_{Me}), 1.70 – 1.56 (m, 6H, H_{Cyi}), 1.53 (d, ^3J(H,H) = 6.8 Hz, 6H, $(CH_3)CH$), 1.33 (d, ^3J(H,H) = 6.9 Hz, 6H, $(CH_3)CH$), 1.45 – 1.03 (m, 6H, H_{Cyi}), 0.90 (d, ^3J(H,H) = 6.7 Hz, 6H, $(CH_3)CH$). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ 189.11 (d, ^3J(C,P) = 3.5 Hz, $C_{CO\text{-}acac}$), 183.19 (s, $C_{CO\text{-}acac}$), 163.95, 158.25, 145.23, 145.07, 133.29, 132.91, 132.24, 132.09, 131.90, 131.44, 129.50, 129.43, 124.83, 104.37, 104.34, 100.24 (s, $C_{CH\text{-}acac}$), 39.92, 39.66, 37.78, 37.53, 34.60, 32.85, 29.08, 29.06, 28.82, 28.79, 27.78, 27.70, 27.31, 27.21, 27.18, 27.09, 25.71, 25.49, 25.17, 23.10 [observed complexity due to C−P coupling]. ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): δ −154.32, −154.37 (intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ 61.43 (s). IR (nujol, NaCl plates, cm^{-1}): (acetylacetonate-κ^2*O,O'*)-group: 1564 ν(C⋯O and C⋯C); 1514 ν(C⋯C and C⋯O); 1270 ν_s(C–CH_3) and chelate deformations and ν_s(C–CH_3, i-Pr from XPhos); 1193 δ(C–H from CH, plane) and chelate deformations; 1007 chelate deformations and δ(C–CH_3, rocking) and δ(C–CH_3, rocking, i-Pr from XPhos); 938 ν_{as}(C–CH_3) and chelate deformations and ν_s(C–CH_3, i-Pr from XPhos); 843 δ(C–H from CH, off-plane); 670 chelate deformations and ν_s(Pd–O); 663 π(CH_3–C(O)⋯C); 602 chelate deformations. (XPhos)-group: 3056, 3045 ν(C–H from CH, Ar); 1604, 1571, 1540, 1490, 1422 (sh), 1419 (sh) ν_{as}(C=C, Ar) and aryl rings deformations; 1447 (sh) δ(C–H from CH_2, scissoring); 1356 δ(C–CH_3, i-Pr); 1326, 1316, 1303, 1296, 1248, 1242, 1228 δ(C–H from CH_2, Cy, wagging); 1213 ν(C–C from i-Pr) and δ(C–H from CH_2, Cy, wagging); 1183, 1162, 1136, 1115, 1087 δ(C–H from CH_2, Cy, twisting); 1176, 1153 δ(C–H, Ar, plane); 1047 ν(C–C, Cy) and cyclohexyl ring deformations and δ(C–H from CH_2, Cy, twisting); 1028 ν_s(C=C, Ar) and ring deformations; 1002 ν(C–C, Cy) and ν_s(C=C, Ar), with cyclohexyl and aryl rings deformations; 995, 905, 895, 889, 880, 853 δ(C–H from CH_2, Cy, rocking); 931, 920 δ(C–H, Ar, off-plane) and δ(C–H from CH_2, Cy, rocking); 874 δ(C–H, Ar, off-plane); 822, 797 aryl rings deformations; 840, 816 cyclohexyl ring deformations; 772, 754 δ(C–H, Ar, off-plane); 746 ν(P–C_{Ar}, Ar); 732 ν_{as}(P–C, Cy); 722 ν_s(P–C, Cy); 710, 707, 702, 693, 688, 684, 681, 677, 659, 656, 652, 648, 642, 638, 630, 622, 616, 613, 608 cyclohexyl and aryl rings deformations. (BF_4)-group: 1091, 1051, 1034 ν_{as}(B–F).

2.4 Calculations

All density functional theory calculations were performed with the ORCA program [34]. All geometry optimizations were run with tight convergence criteria, using the BP86 functional [35,36], making use of the resolution of the identity technique [37]. The applicability of gradient-corrected functionals as BP86 for the structural prediction of transition metal compounds and reliable determination of the kinetic balance are well documented [38–43]. The basis sets that were used were the Weigend−Ahlrichs basis sets [44,45]. Triple-ξ-quality basis sets with one set of polarization functions (def2-TZVP) were used for the palladium and phosphorus in connection with effective core potentials for Pd. The remaining atoms were described by slightly smaller def2-SVP basis sets.

2.5 X-ray crystallographic studies

Data were collected on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_{α} radiation (λ = 0.71073 Å) using the φ and ω scans technique. The structures were solved and refined by direct methods using the SHELX [46]. Data were corrected for absorption effects using the multi-scan method (SADABS) [47]. All non-hydrogen atoms were refined anisotropically using SHELX [46]. The coordinates of the hydrogen atoms were calculated from geometrical positions. Crystal data and experimental details are given in Table 1. Selective bond lengths, bond angles and torsion angles are given in Table S.1 and S.2 (Electronic Supplementary Information). Table 1 contains CCDC reference number of the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk

Table 1 – X-ray crystallographic data for compounds **2** and **3**.

CCDC number	1997255	1997258
Empirical formula	$C_{41}H_{49}O_2P_2Pd, BF_4$	$C_{41}H_{61}O_2P_2Pd, BF_4$
Formula weight / g·mol^{-1}	828.95	841.04
Crystal system	Orthorhombic	monoclinic
Space group	Pbca	P 2(1)/n
a / Å	12.6876(5)	11.6277(7)
b / Å	18.0564(8)	15.6915(10)
c / Å	34.6284(13)	23.0400(15)
α, *β*, *γ* / °	90.00, 90.00, 90.00	90.00, 98.984(2), 90.00
Volume / Å^3	7933.1(6)	4152.2(5)
Z	8	4
Density (calculated) / g·cm^{-3}	1.388	1.345
Absorptions coefficient / mm^{-1}	0.601	0.575
Radiation (*λ* / Å)	MoKα (0.71073)	MoKα (0.71073)
Temperature / K	296(2)	296(2)
2*Θ* range / °	2.29 – 28.31	2.27 – 27.00
Crystal size / mm	0.36 × 0.31 × 0.14	0.28 × 0.11 × 0.10
Crystal habit	yellow, prism	yellow, prism
F(000)	3424	1760
Index ranges	-16<=h<=16, -24<=k<=23, -46<=l<=46	-14<=h<=14, -19<=k<=20, -29<=l<=29
Reflections collected	74643	92634
Independent reflections	9847 [R(int) = 0.0488]	9042 [R(int) = 0.0747]
Number of ref. parameters	462	462
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0498 / 0.1131	0.0617 / 0.1260
R_1 / wR_2 (all data)	0.0760 / 0.1253	0.0837 / 0.1345
Goodness-of-fit on F^2	1.086	1.267
Completeness [%]	99.8	99.9
Largest diff. peak and hole / e·Å^{-3}	0.752/ -0.875	0.463/ -0.674
Weight scheme	$w=1/[\sigma^2(F_o^2)+(0.0504P)^2+11.5385P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0000P)^2+15.2241P]$ where $P=(F_o^2+2F_c^2)/3$

3 Results and Discussion

3.1 Synthesis of Palladium(II) Complexes.

The Pd-complexes used as precatalysts are shown in Figure 3. We report here the synthesis of the new cationic acetylacetonate palladium complexes **2**, **3**, **5**–**8**, **10**, **11**, while **1**, **4**, **9** are a known compounds. The new compounds were fully characterized by NMR and FTIR spectroscopy as well as elemental analysis.

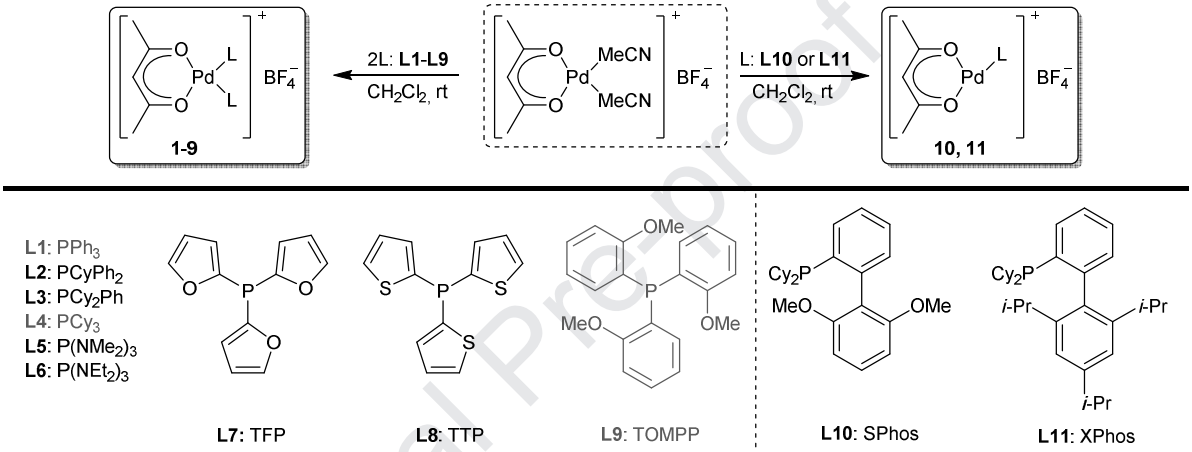

Figure 3 – Top: synthesis of cationic acetylacetonate palladium complexes (**1**–**11**) with phosphine ligands (L). Bottom: phosphine ligands used (**L1**–**L11**)

The synthesis of the complexes **1**–**9** was achieved by reacting bis(acetonitrile)(acetylacetonate)palladium(II) tetrafluoroborate with two equivalents of **L1**–**L9** in dichloromethane which led to the formation of $[Pd(acac)(L)_2][BF_4]$ (**1**–**9**) as depicted in Figure 3. Two phosphines coordinate to the palladium(II) centre, replacing the labile acetonitrile ligands. In the case of bulky XPhos and SPhos ligands $[Pd(acac)(MeCN)_2][BF_4]$ reacted with 1 equiv of the $PArCy_2$ giving monophosphine complexes $[Pd(acac)(L)][BF_4]$ (**10**, **11**). It is most likely that in these molecules the *ipso*-carbon of the diisopropylphenyl or dimethoxyphenyl rings from **L10**, **L11** occupies the fourth coordination site of the Pd atom [48–50]. In particular, δ ^{19}F NMR signals for $[BF_4]^-$ in **10** and **11** are −154.0 and −154.3 ppm, respectively, indicating that tetrafluoroborate anion is non-coordinating in $CDCl_3$ solutions of the complexes [51–53].

In most cases coordination of the phosphines caused a downfield shift $\Delta(\delta_{complex} - \delta_{ligand})$ of the $^{31}P\{^1H\}$ NMR signals in the range of 39.2 to 74.8 ppm (Table 2). In contrast, complexes **5**, **6** with $P(NMe_2)_3$ and $P(NEt_2)_3$ have $^{31}P\{^1H\}$ NMR chemical shifts at higher field, by about 30 ppm, compared with the signals of the free ligands. As was observed for platinum complexes

with κ*P* ligands bearing electronegative substituents [54], this effect reflects the increase in electron density at the phosphorus atoms, which is presumably due to the p_{π}(N)-σ*(P) interaction as well as the palladium-phosphorus backbonding, which is expected to increase with increasing electronegativity of the substituents at phosphorus.

Table 2 – $^{31}P\{^{1}H\}$ Chemical Shift of the Cationic Phosphine-Pd-acac Complexes and Coordination Induced Shifts Δ for the Complexes

Free ligand	δ $^{31}P\{^{1}H\}$ chemical shift, ppm	Complex	δ $^{31}P\{^{1}H\}$ chemical shift, ppm	Δ($^{31}P\{^{1}H\}$) ($\delta_{complex} - \delta_{ligand}$), ppm
$PCyPh_2$	−3.9 [55]	**2**	35.8	39.7
PCy_2Ph	2.7 [55]	**3**	41.9	39.2
$P(NMe_2)_3$	122.7 [56]	**5**	90.8	−31.9
$P(NEt_2)_3$	118.0 [57]	**6**	93.7	−24.3
TFP	−75.2 [58]	**7**	−18.3	56.9
TTP	−45.6 [59]	**8**	3.8	49.4
SPhos	−8.6 [49]	**10**	66.2	74.8
XPhos	−11.5 [60]	**11**	61.4	72.9

Generally, the δ values obtained from ^{1}H and ^{13}C NMR spectra of **2**, **3**, **5**–**8**, **10**, **11** are consistent with NMR data for the ligands or the corresponding transitions metal complexes [49,55–58,60–63]. The ^{1}H NMR spectra of **2**, **3** show signals at 2.02 and 2.04 ppm for the methyl-group of the acac ligand non-shielded by phenyl aromatic ring current, indicating the location of phenyl substituents mainly within ∠P-Pd-P. In contrast, for **7** and **8** the acac-methyl groups signals in ^{1}H NMR spectra are at 1.83 and 1.74 ppm (shielded by heteroaromatic rings, cf. the same group signal for $[Pd(acac)(PPh_3)_2]A$ (A = BF_4, CF_3SO_3, ClO_4) is around 1.5 ppm [52,64]).

The formation of the monophosphine complexes **10**, **11** was evident from the distinctive proton signal resonances at 1.93 (**10**), 1.93 (**11**) and 1.89 (**10**), 1.74 (**11**) ppm (the last two shielded by aromatic ring current) from CH_3-group of acac ligand in the ^{1}H NMR spectrum. In addition, the $^{13}C\{^{1}H\}$ NMR spectrum revealed the appearance of diagnostic carbon peaks of acac ligand [189.23 or 189.11 (d, ^{3}J= 3.5 Hz)] and [183.10 or 183.19 (s)] for carbonyl, which were split by the adjacent PCy_2 moiety of SPhos or XPhos ligand in the *trans*- and *cis*-position, respectively.

The NMR spectra of compounds **5** and **6** suggest that it exist in two isomeric forms in solution. In particular, the ^{1}H and ^{13}C NMR spectra of **5** display two distinct set of resonances in methyl group region. The resonances at δ 2.76 (d, *J* = 9.6 Hz, NC*H*$_3$) and 38.76 (vt, *J* = 3.8 Hz, N*C*H$_3$) are due to the major isomer while those at δ 2.80 (vt, *J* = 5.1 Hz, NC*H*$_3$) and 39.35 (vt, *J* = 3.8 Hz, N*C*H$_3$) are assigned to the minor isomer. Consistent with this the $^{31}P\{^{1}H\}$ NMR spectrum of **5** displays a singlet at δ 90.81 for the major isomer and singlet δ 85.04 for the minor

isomer in 5:1 intensity ratio. We assume that the isomers observed in solution are due to two different coordination geometries at nitrogen (pyramidal and planar) in the six NMe_2 groups in two coordinated molecules of $P(NMe_2)_3$. Previously it was shown that the ground state of $P(NMe_2)_3$ has C_s symmetry, with two different coordination geometries at the nitrogen atoms [65,66].

3.2 X-ray Crystal Structures of **2** and **3**

Single crystals of **2** and **3** suitable for X-ray crystallography were obtained by slow diffusion of mixture of petroleum ether and diethyl ether into 1,2-dichloroethane solutions of the complexes. Complexes **2** and **3** contain a four-coordinate palladium(II) centre with a non-coordinating $[BF_4]^-$ anion.

The solid-state molecular structure of **2** is depicted in Figure 4 with selected inter-atomic distances and angles listed in the figure caption. The Pd–P bond lengths of 2.2835(8) and 2.2766(9) Å are typical for cationic palladium(II) acetylacetonate complexes [22,28,64,67,68], but slightly shorter when compared to *trans*-$[PdCl_2(PPh_2Cy)_2]$, having a Pd–P bond length of 2.3256(10) Å [69].

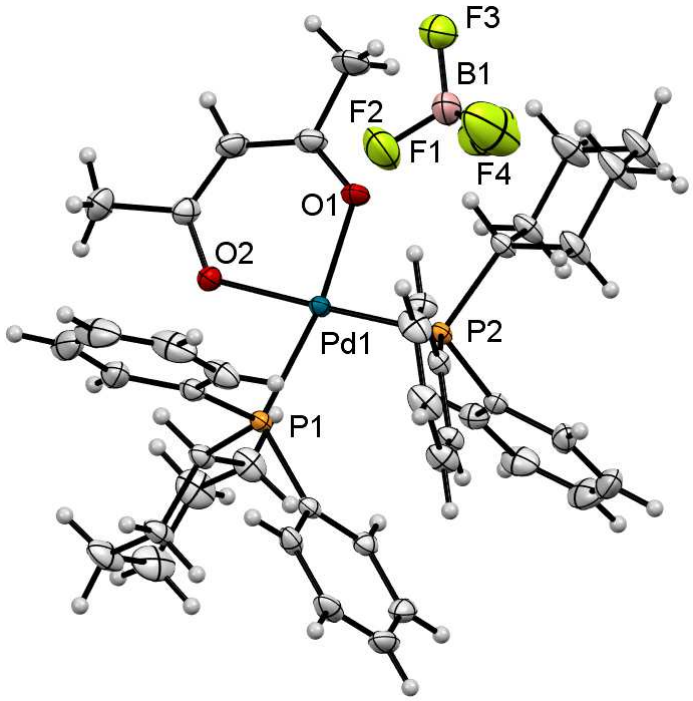

Figure 4 – Molecular structure of $[Pd(acac)(PCyPh_2)_2]BF_4$ (**2**) with atoms represented by thermal vibration ellipsoids of 50% probability. Details of the structure refinement are given in Table 1. Selected bond distances (Å) and angles (°):Pd1-O1 = 2.050(2), Pd1-P1 = 2.2835(8), Pd1-O2 = 2.051(2), Pd1-P2 = 2.2766(9), ∠O2-Pd1-O1 = 89.97(10), ∠P2-Pd1-P1 = 98.97(3).

The complex **2** has a distorted square planar geometry for palladium, shown by the ∠O2-Pd1-O1, ∠P2-Pd1-P1, ∠O1-Pd1-P2 and ∠O1-Pd1-P1 bond angles of 89.97(10)°, 98.97(3)°, 89.23(8)° and 170.25(8)° respectively. The average P-C bond distance of 1.845 Å (cyclohexyl moiety) is somewhat longer than the bond distances for the phenyl moieties, where *l*(P-C) = 1.814 Å. The C-C bond distances in the phenyl rings agree well with the expected value; the cyclohexyl ring has a normal chair conformation. Analysis of the bond lengths and angles of $[BF_4]^-$ ion (Table S.1) showed distortion of the idealized tetrahedral geometry (e.g. *l*(B1-F*i*) = 1.305…1.376Å). In addition short contacts between the fluorine atoms of $[BF_4]^-$ and the hydrogens of the phenyl rings (F…H-C, 2.5Å) are observed in the crystallographic packing of **2**, thus presumably forming weak C-H...F hydrogen bonds. Such short contacts between $[BF_4]^-$ ions and the hydrogen atoms of the phenyl rings in the crystal structures of transition metal complexes are known in the literature [70]. Moreover, distortion of idealized tetrahedral geometry of the anion $[BF_4]^-$ leads to appearance in the IR spectrum of **2** the symmetric stretching vibration at 782 cm^{-1}, forbidden in the infrared absorption spectrum. The same infrared spectral feature was reported for the cationic palladium complexes with coordinated secondary amines, where hydrogen bonding between the NH group of morpholine ligand and $[BF_4]^-$ anion was observed [29].

The results of the X-ray crystal structure analysis of **3** are shown in Figure 5. The main structural features of **3** appear close to those for **2**. The structure of **3** is a four-coordinate palladium(II) complex with two phosphines and one acetylacetonate ligand coordinated to the palladium centre. The complex has a distorted square planar geometry as shown by the ∠O2-Pd1-O1, ∠P2-Pd1-P1, ∠O1-Pd1-P2 and ∠O1-Pd1-P1 bond angles of 89.96(14)°, 102.94(5)°, 172.15(11)° and 84.60(11)° respectively; the P2-Pd1-P1 angle is larger than in complex **2**. To gain more insight into the structure of the cationic species, we performed DFT (BP86) calculations for the ions $[Pd(acac)(PCyPh_2)_2]^+$ and $[Pd(acac)(PCy_2Ph)_2]^+$ in gas phase, hence, free from the influence of crystal packing or intermolecular interactions. Within the limits of the basis set employed, the optimized geometries were good representation of the structures obtained from the crystallographic studies. Calculated molecular models showed ∠P-Pd-P of 100.52° and 106.04° for the cationic species **2** and **3**, respectively. Consequently, the P2-Pd1-P1 angle for **3** is larger than in complex **2** mainly due to the steric bulk of the cyclohexyl groups.

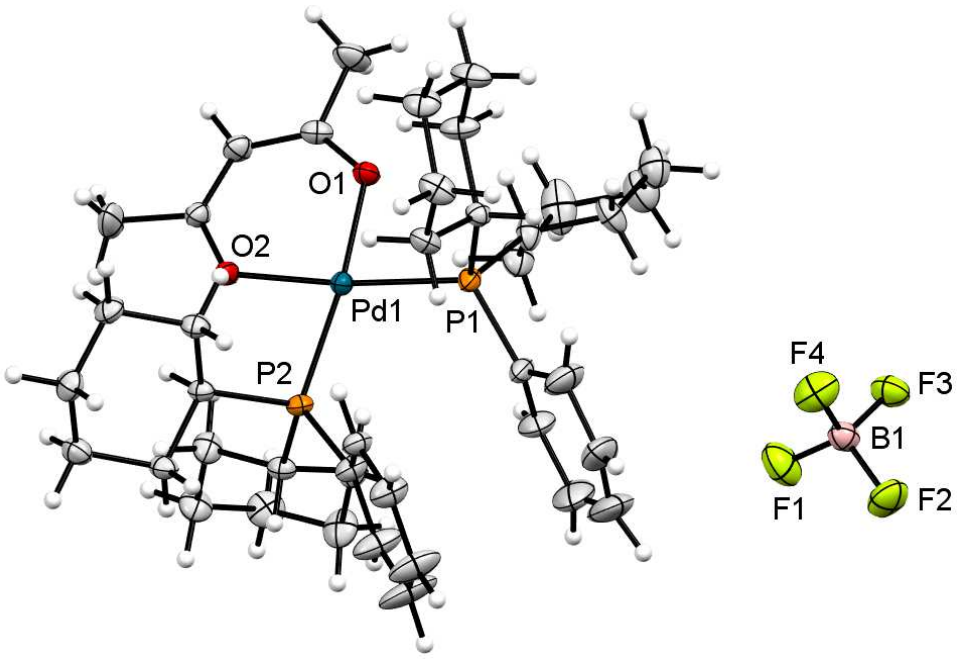

Figure 5 – Molecular structure of $[Pd(acac)(PCy_2Ph)_2]BF_4$ (**3**) with atoms represented by thermal vibration ellipsoids of 50% probability. Details of the structure refinement are given in Table 1. Selected bond distances (Å) and angles (°): Pd1-O1 = 2.068(3), Pd1-P1 = 2.2805(13), Pd1-O2 = 2.053(3), Pd1-P2 = 2.2927(13), ∠O2-Pd1-O1 = 89.96(14), ∠P1-Pd1-P2 = 102.94(5).

3.3 Catalytic Studies

The cationic palladium complexes **1-11** (Figure 3) with monodentate phosphine ligands varying steric bulk at the coordinating atoms, and their electronic properties were tested in the telomerization of 1,3-butadiene with MeOH. The conditions used are 70°C, 2 h, 0.0167 mol% of catalyst vs butadiene to evaluate their overall productivity and selectivity to the linear product. The reaction was performed in the presence of an excess of nucleophile relative to the diene ($[MeOH]_0$:$[BD]_0$ = 1), so *TON* is based on butadiene conversion. As shown in Table 3, the selectivity and BD conversion largely depended on the nature of the catalyst. As might be expected from published telomerization results by Beller et al. [11] using an *in situ* catalyst mixture [$Pd(OAc)_2$/*n*PPh_3], the addition of triethylamine as base has no positive influence on the product selectivity or on the catalyst productivity with complex **1** as precatalyst (entries 1–3, Table 3). So the other complexes were tested using base-free conditions.

Table 3 – Influence of the Nature of Catalyst on Conversion and Selectivity.

Entry[a]	Pd	Conv. BD %[b]	Selectivity, mol%			Chemo, mol%[c]	*n/iso*[d]	*E/Z*[e]	*TON*[f]
			OCT	3-MOD	1-MOD				
1	**1**	96.2	16.3	6.1	77.6	83.7	13	12	5800
2	**1**[g]	68.4	16.0	5.2	78.8	84.0	15	11	8200
3	**1**[h]	72.7	14.5	5.5	80.0	85.5	15	12	8700
4	**2**	96.7	18.5	5.6	75.9	81.5	13	18	5800
5	**3**	95.1	15.8	5.8	78.3	84.1	13	**55**	5700
6	**4**	0.1	95.3	0.2	4.5	4.8	18	9	5
7	**5**	0.3	97.3	0.0	2.7	2.7	—	11	20
8	**6**	0.1	71.8	1.6	26.7	28.2	17	10	10
9	**7**	17.0	6.1	4.3	89.5	93.9	21	12	1000
10	**8**	36.3	6.6	4.9	88.6	93.4	18	10	2200
11	**9**	86.2	1.8	3.8	94.5	**98.2**	25	39	5200
12	**10**	6.0	26.6	8.3	65.2	73.5	8	13	400
13[i]	**10**	94.7	16.0	7.8	76.2	84.0	10	24	5700
14	**11**	0.1	48.1	9.1	42.7	51.9	5	8	5
15[j]	**11**	14.3	3.4	7.7	88.9	96.6	12	14	900
16[k]	**12**	0.5	68.0	0.7	31.2	32.0	42	11	30

[a] Reaction conditions: t = 70 °C, 0.0167 mol% of Pd, $[BD]_0/[Pd]_0$ = 6000, $[MeOH]_0/[Bd]_0$ = 1, n_{Pd} = 6.5 μmol, dichloromethane, V_{DCM} = 0.5 mL, reaction time – 2 h. [b] 1,3-Butadiene conversion. [c] Chemoselectivity = (1-MOD + 3-MOD)(1-MOD + 3-MOD + OCT + VCH)$^{-1}$. [d] Regioselectivity = (1-MOD)(3-MOD)$^{-1}$. [e] Stereoselectivity = (*trans*-1-MOD)(*cis*-1-MOD)$^{-1}$. [f] In units of (mol of BD) (mol of Pd)$^{-1}$. [g] 0.0087 mol% of Pd, n_{Pd} = 6.5 μmol, $[BD]_0/[Pd]_0$ = 12000. [h] 0.0087 mol% of Pd, n_{Pd} = 6.5 μmol, $[BD]_0/[Pd]_0$ = 12000, 133 eq. of NEt_3 per Pd was added. [i] 1 eq. of SPhos per **10** was added. [j] 1 eq. of XPhos per **11** was added. [k]Catalyst mixture $[Pd(acac)(MeCN)_2]BF_4$ (**12**)/1PPh_3 were used

As one can see from Table 3, for phosphine-ligated complexes catalytic productivity under the same conditions decreased in the following order: **1**, **2**, **3**, **9** > **8** > **7** > **10** > **4**, **5**, **6**, **11**. The order of decreasing catalytic productivity by these catalysts can be attributed to decreasing steric bulk in the coordination sphere of the metal and reducing basicity of the phosphine ligands containing (hetero)aryl moieties (by means of Tolman's parameters, see Table 4). Complexes **4**–**6** with tricyclohexylphosphine and triaminophosphines were not suitable for this telomerization reaction (entries 6–8, Table 3). For **5** and **6 t**he presence of phosphorus and nitrogen as chelating atoms might entail too strong coordination to the metal, inhibiting the catalytic activity [71]. Low conversion was also observed in the presence of **10** and **11** containing "Buchwald-type" phosphines (entries 12 and 14). However, when 1 eq. of SPhos or XPhos was added to the reaction mixture, conversion of BD was observed with concomitant formation of products (entries 13, 15; Table 3). It should be noted that complexes **10** and **11** contain one phosphorus atom in the coordination sphere of the transition metal and direct comparison of their catalytic activity with those for complexes **1**–**9** is not entirely correct. Moreover the catalyst prepared *in situ* from the $[Pd(acac)(MeCN)_2]BF_4$ and 1 eq. of PPh_3 was also not active (entry 16, Table 3).

Thus, it seems that in order to obtain effective telomerization catalysts based on cationic acetylacetonate palladium (II) complexes, it is required to use $[P]_0$:$[Pd]_0 \geq 2$.

Table 4 – Tolman's Steric (Cone Angle) and Electronic (ν_{CO}) Properties of Phosphines.

Complex	Phosphine ligand (L)	Cone angle [°][a]	ν(CO) [cm^{-1}][b]
1	PPh_3	145	2068.9
2	$PCyPh_2$	153	2064.8
3	PCy_2Ph	162	2060.6
4	PCy_3	170	2056.4
5	$P(NMe_2)_3$	157	2061.9
6	$P(NEt_2)_3$	108	2060.3
7	TFP	133 [72]	2078.3
8	TTP	–	–
9	TOMPP	176 [73]	2058.3
10	SPhos	204 [74]	–
11	XPhos	173 [74]	2059 [75]

[a] Ref. [76]. [b] The stretching frequencies ν(CO) of the terminal CO of $[Ni(CO)_3L]$ in CH_2Cl_2, directly measured or estimated values using Tolman's equation from ref. [76]

By contrast, complexes **1**, **2**, **3**, and **9** are the most productive catalysts of the series, showing nearly complete conversions. Among the various complexes tested **9** is the more chemoselective catalyst (entry 11, Table 3), yielding 98% of telomers (with 96% of 1-MOD, the linear to branched telomers ratio is *n*/*iso* = 25/1, *trans*-/*cis*- telomers ratio is 39). The results for **9** are close to those found by van Leeuwen et al [15] using Pd(TOMPP)$(dvd)_2$ (dvd — tetramethyldivinyldisiloxane). Under identical conditions, the catalyst prepared from precursor **2** yielded 81.5% of octadienyl ethers (linear to branched telomers ratio is 13, *trans*-/*cis*- telomers ratio is 18). Remarkably, in the presence of **3** significantly improved *trans*- to *cis*-1-methoxyocta-2,7-diene ratio (98.2% of *trans*-1-MOD) was obtained (entry 3, Table 3). Catalytic mechanism of the palladium/phosphine-catalyzed telomerization of 1,3-butadiene with methanol has been carefully studied by Jolly [77–79] and extended by mechanistic [14,16,80] and DFT studies [81,82]. It is supposed that under telomerization conditions, active Pd(0) species can be formed from cationic complexes (Figure 6). In our opinion the observed stereoselectivity in favor of the *trans*-linear product is determined by the stability of the intermediates **II**, **III** or **V** obtained after oxidative coupling of two 1,3-butadiene molecules at the palladium to form the bisallyl complex or after protonation of **II** to form η^3-allylpalladium methoxide complexes (Figure 6).

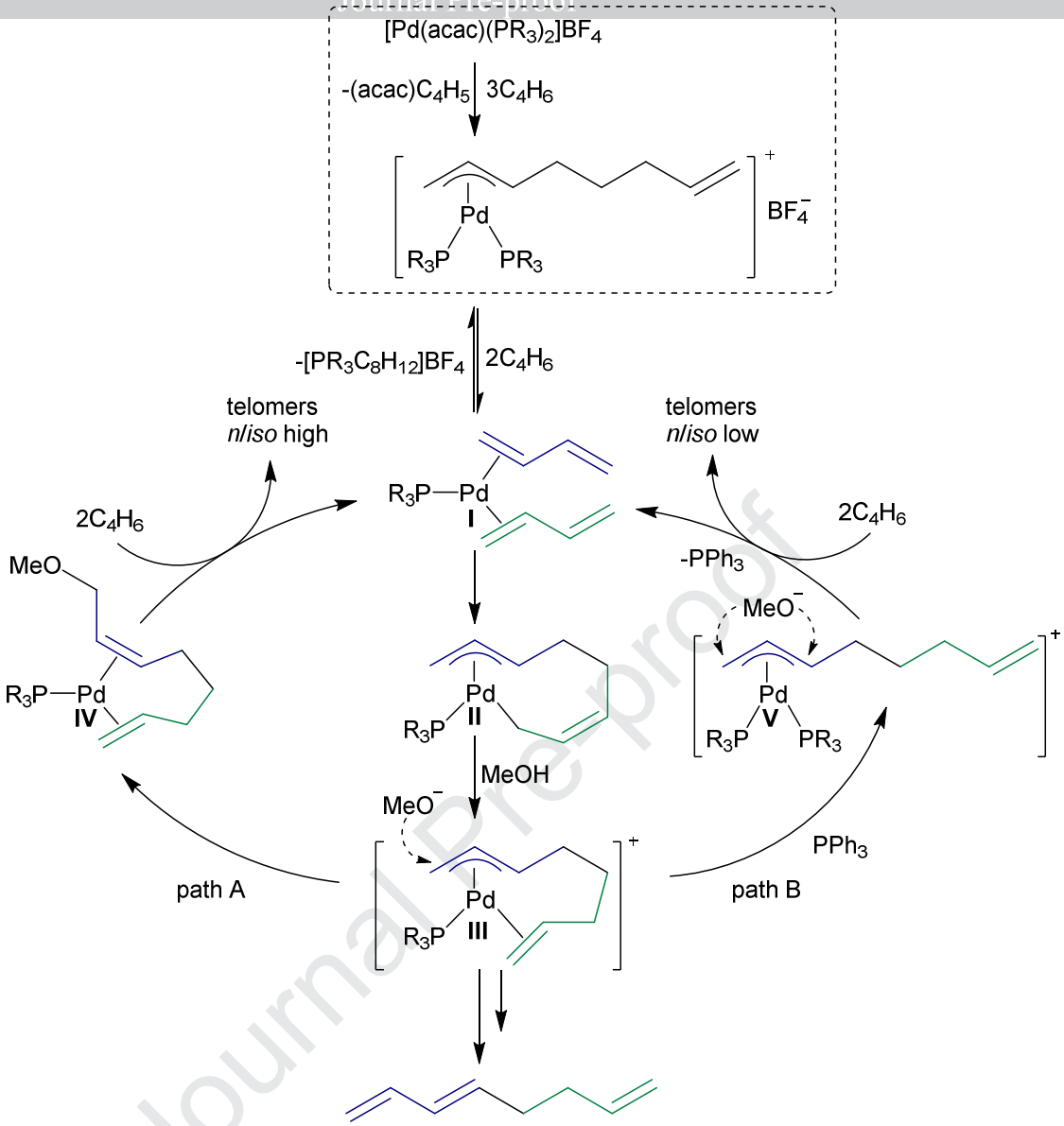

Figure 6 – Mechanism of the Telomerization Reaction

Next, the most interesting precatalysts **3** and **9** were studied under different reaction conditions, such as palladium concentration, $[MeOH]_0/[BD]_0$ ratio, and temperature. Whatever the reaction conditions, some amounts of vinylcyclohexene as a result of Diels-Alder reaction were detected (>1%). In the case of **3** at 50°C, when only 0.0021 mol% of Pd loading is used, higher selectivity is obtained compared to the results at higher temperatures, but turnovers do not exceed 18200 (chemoselectivity up to 94%; entry 18, Table 5). When Pd loading was decreased, the conversion of BD as well as selectivity substantially droped (entries 19, 20; Table 5). But in the case of low $[MeOH]_0/[BD]_0$ ratios (0.5 instead of 1.0) BD conversion and the selectivity enhanced (*TON* = 4400 with $[MeOH]_0/[BD]_0$ = 1.0 and *TON* = 38500 with $[MeOH]_0/[BD]_0$ = 0.5; entries 19 and 22, Table 5). Better catalyst performance was observed at lower substrate:catalyst ratio. In this case, a high catalyst productivity (TON up to 60 000) is achieved

with 0.0017 mol% of Pd vs BD (entry 21, Table 5). Improvement of catalyst performance at low methanol concentration have been previously reported for Pd-based catalyst systems containing triarylphosphines [15,16]. However at 90°C, the conversion of butadiene and the selectivity decreases, showing that the catalyst formed from **3** is unstable at high temperatures. Similar trends were observed in the presence of isolated cationic complex **9**. Remarkably, in the presence of **9** improved linear to branched telomers ratios and chemoselectivities were obtained. Using **9** *n/iso* ratios >27:1 were achieved. Finally, with a $[BD]_0/[Pd]_0$ ratio of 96000:1 a modest conversion was achieved (entry 26, *TON* = 20 200).

Table 5 – Influence of the Catalyst Concentration and Temperature on Conversion and Selectivity.

Entry[a]	Pd	$[BD]_0/[Pd]_0$	*t*, °C	Conv. BD %[b]	Selectivity, mol%			Chemo, mol%[c]	*n/iso*[d]	*E/Z*[e]	*TON*[f]
					OCT	3-MOD	1-MOD				
17	**3**	24000	50	88.5	5.9	5.3	88.8	94.1	17	109	21200
18	**3**	48000	50	38.0	4.7	5.2	89.1	94.3	17	87	18200
19	**3**	96000	70	4.6	9,7	4,9	71,2	76,1	14	25	4400
20[g]	**3**	960000	70	7.7	0.1	0,4	0,7	1,1	2	16	74000
21[h]	**3**	60000	70	99.9	23,8	5,2	71,0	76,2	14	46	60000
22[h]	**3**	96000	70	40,1	25,1	5,1	67,6	72,7	13	35	38500
23	**3**	48000	90	64,1	28,3	5,3	62,1	67,4	12	32	30800
24	**9**	48000	70	24,1	7,6	2,9	84,1	87,0	29	22	11600
25	**9**	96000	70	11,0	10,1	3,1	86,8	89,9	28	19	10600
26[h]	**9**	96000	70	21,0	9,2	3,0	81,4	84,4	27	19	20200

[a] Reaction conditions: n_{BD} = 78 mmol, $[MeOH]_0/[Bd]_0$ = 1, dichloromethane, V_{DCM} = 0.5 mL, reaction time – 16 h. [b] 1,3-Butadiene conversion. [c] Chemoselectivity = (1-MOD + 3-MOD)(1-MOD + 3-MOD + OCT + VCH)$^{-1}$. [d] Regioselectivity = (1-MOD)(3-MOD)$^{-1}$. [e] Stereoselectivity = (*trans*-1-MOD)(*cis*-1-MOD)$^{-1}$. [f] In units of (mol of BD) (mol of Pd)$^{-1}$. [g]Reaction time – 160 h. [h]$[MeOH]_0/[Pd]_0 = 48 \cdot 10^3$.

4 Conclusions

We have synthesized eight new cationic acetylacetonate palladium complexes $[Pd(acac)(L)_n][BF_4]$ (*n* = 2: L = $PCyPh_2$, PCy_2Ph, $P(NMe_2)_3$, $P(NEt_2)_3$, tri-2-furylphosphine, tri-2-thienylphosphine; *n* = 1: L = SPhos, XPhos) by the reaction of $[Pd(acac)(MeCN)_2][BF_4]$ with 2 equiv. or 1 equiv. of L. Two palladium(II) complexes have been characterized by X-ray crystallography. The catalytic potential of $[Pd(acac)(L)_n][BF_4]$ (L – monodentate phosphine ligands) is demonstrated in the industrially important telomerization of 1,3–butadiene with methanol under base-free conditions. Complexes with phosphines containing (hetero)aryl moieties catalyzed formation of methoxyocta-2,7-dienes. The other studied palladium complexes showed substantially lower activities. Complexes $[(acac)Pd(PCy_2Ph)_2]BF_4$ and $[(acac)Pd(TOMPP)_2]BF_4$ is highly active for catalytic telomerization. Under optimal conditions

in the presence of only 0.001–0.0025 mol% palladium loading the desired telomers were obtained with chemoselectivities of 76–98 % and *TON* up to 60000 mol BD per mol Pd. Though the present research were limited to the telomerization of 1,3-butadiene with methanol, we believe these novel precatalyst have a broad potential for a variety of other catalytic applications, too.

Electronic Supplementary Information available: XRD, NMR, FTIR spectral data and results.

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Highlights

- Cationic palladium complexes $[Pd(acac)(PR_3)_2]BF_4$ and $[Pd(acac)(L)]BF_4$ were obtained
- PR_3 = $PCyPh_2$, PCy_2Ph, $P(NMe_2)_3$, $P(NEt_2)_3$; L = SPhos, XPhos
- The synthesized complexes were characterized through NMR and FTIR spectroscopy
- Complexes $[Pd(acac)(L)_2]BF_4$ (L = $PCyPh_2$, PCy_2Ph) were characterized by XRD
- Complexes were tested as catalysts for telomerization of 1,3-butadiene with methanol

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: