Oligomerization of Olefins Catalyzed by New Cationic Palladium(II) Complexes Containing an Unsymmetrical α-Diimine Ligand

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Summary: The palladium complexes [(Py-2-CMe=NAr)-PdMe(MeCN)]⁺BAr′₄⁻ ($2^+BAr'_4{}^-$) and [Pd(Py-2-CMe=NAr)₂]²⁺(BAr′₄⁻)₂ [Ar = 2,6-(i-Pr)₂−C₆H₃, Ar′ = 3,5-(CF₃)₂−C₆H₃)] have been synthesized from (Py-2-CMe=NAr)PdMeCl, and their crystal and molecular structure has been determined by X-ray analysis. $2^+BAr'_4{}^-$ is an efficient catalyst for the oligomerization of ethylene, propylene, and 1-hexene, as well as for the cooligomerization of ethylene with alkyl acrylates.

Palladium(II) complexes containing symmetrical 1,4-diazabutadiene ligands with bulky substituents such as the 2,6-diisopropylphenyl group at the nitrogen atoms were shown recently to behave as efficient catalysts for the polymerization of ethylene and α-olefins.[1] On the other hand, related complexes with sterically less demanding ligands such as 2,2′-dipyridyl or 1,10-phenanthroline can activate the dimerization of ethylene.[2] We now report our studies on neutral and cationic palladium(II) complexes of 2-(acetyl-2,6-diisopropylphenylimine)pyridine, an unsymmetrical bidentate ligand possessing both the pyridyl and the bulky 2,6-diisopropylphenylimine functions.

The pyridinimine Py-2-CMe=NAr [Ar = 2,6-(i-Pr)₂−C₆H₃] was synthesized following classical condensation methods[1] and reacted with (COD)PdMeCl[3] in diethyl ether to yield a yellow precipitate of air-stable (Py-2-CMe=NAr)PdMeCl (**1**, yield 96%), which can be recrystallized from CH₂Cl₂/hexane (Scheme 1). This compound is analogous to previously synthesized derivatives possessing a different substituent at the imino nitrogen.[4] A single isomer is detected for **1** on the ¹H and ¹³C NMR spectra,[5] most probably adopting the expected square-planar geometry. A NOESY experiment[7] established that the methyl ligand is cis to the imino function. This configuration was also found to be the most favorable

Scheme 1
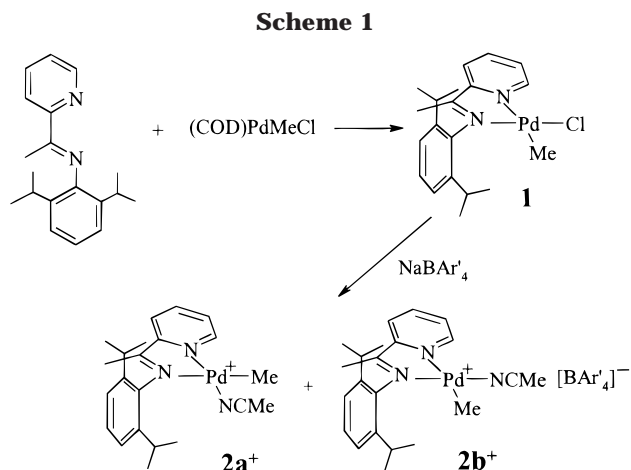
for the majority of methyl(chloro)palladium complexes of this type.[4,8]

Treatment of **1** with 1 equiv of NaBAr′₄ (Ar′ = 3,5-(CF₃)₂−C₆H₃)[9] in acetonitrile[1b] leads to slow formation of the cationic complex [(Py-2-CMe=NAr)PdMe-(MeCN)]⁺BAr′₄⁻ (**2**⁺BAr′₄⁻) as an air-stable yellow-brown solid (yield 80%). Recrystallization from cold CH₂Cl₂ affords orange crystals which were suitable for X-ray analysis (vide infra). The ¹H and ¹³C NMR spectra of **2**⁺ in CD₂Cl₂ show two sets of resonances in an approximate ratio 2/1, arising from the presence of the two isomers **2a**⁺ (major isomer) and **2b**⁺ (minor isomer), depicted in Scheme 1, in which the methyl ligand is respectively trans and cis to the imino nitrogen, as deduced from NOESY correlation measurements.[10] Hence, replacement in **1** of the chloro ligand by an

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(1) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514.
(2) (a) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661. (b) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894. (c) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137.
(3) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier: C. J.; Van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.
(4) Rülke, R. E.; Delis, J. G. P.; Groot, A. M.; Elsevier, C. J.; Van Leeuwen, P. W. N. M.; Vrieze, K.; Goubitz, K.; Schenk, H. *J. Organomet. Chem.* **1996**, *508*, 109.

(5) ¹H NMR for **1** (CDCl₃): δ 9.32 (dd, 1H, py H-6), 8.07 (dt, 1H, py H-4), 7.90 (dd, 1H, py H-3), 7.75 (ddd, 1H, py H-5), 7.3−7.2 (m, 3H, m- and p-Ar), 3.08 (sept, 2H, C*H*Me₂), 2.21 (s, 3H, *Me*C=N−), 1.29 (d, 6H, CH*Me*Me′), 1.10 (d, 6H, CHMe*Me′*), 0.48 (s, 3H, *Me*−Pd). ¹³C{¹H} NMR (CDCl₃): δ 174.13 (*C*=N−), 152.70 (py C-2), 149.59 (py C-6), 141.87 (ipso-Ar), 139.22 (o-Ar), 138.80 (py C-4), 128.58 (p-Ar), 127.68 (py C-3), 124.92 (py C-5), 124.03 (m-Ar), 28.23 (*C*HMe₂), 23.95, 23.39 (CH*Me*Me′, CHMe*Me′*), 19.13 (*Me*C=N−), 0.90 (*Me*−Pd).[6]
(6) The ¹³C NMR assignments were ascertained by DEPT experiments.
(7) Selected ¹H−¹H NOESY correlations: δ 9.32 (py H-6) with δ 7.75 (py H-5) and no other signal, δ 0.48 (*Me*−Pd) with δ 3.08 (C*H*Me₂) and 1.29 (CH*Me*Me′).
(8) With the present ligand, a significant shielding effect of the Ar group on the protons of the neighbouring ligand gives rise to remarkable low ¹H NMR chemical shifts: δ 0.48 for Me in **1**, 1.78 for MeCN in **2a**⁺, 0.51 for Me in **2b**⁺, and 6.22 for py H-6 in **3**²⁺. The unusually high frequency of the IR ν(C−H) absorption observed at 3140 cm⁻¹ for **3**²⁺ (BAr′₄⁻)₂ probably has the same origin.
(9) Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.
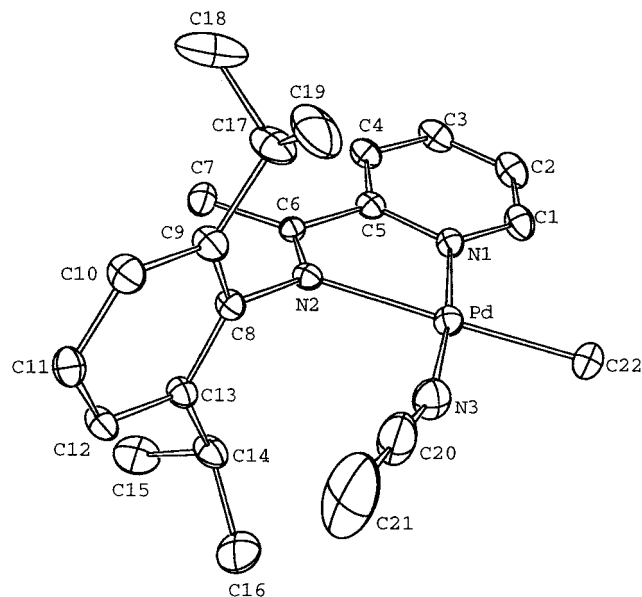
Figure 1. ORTEP diagram of **2a**$^+$BAr$'_4$$^-$. The counteranion and all hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−N(1) = 2.038(5), Pd−N(2) = 2.093(5), Pd−N(3) = 1.971(7), Pd−C(22) = 2.015(6), N(1)−Pd−N(2) = 78.8(2), N(3)−Pd−C(22) = 90.3-(3), Pd−N(3)−C(20) = 163.6(7).

acetonitrile molecule inverts the relative stability of the two expected configurations.[8]

The isomer present in the solid state is **2a**$^+$, as shown by a single-crystal X-ray structure determination (Figure 1).[12,13] As expected, the geometry about palladium is nearly ideally square-planar, and the chelating angle N(1)−Pd−N(2) is less than 90°. The MeCN ligand is slightly twisted toward the facing Ar group, whose plane is perpendicular to the plane of the complex. This confirms for the solid state the main structural features
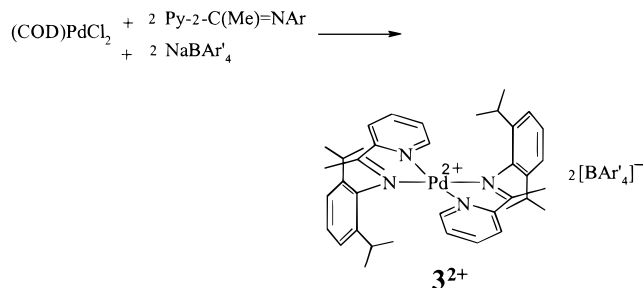
Scheme 2

found for **2a**$^+$ in solution. On dissolution of **2a**$^+$BAr$'_4$$^-$ in CD$_2$Cl$_2$, its isomerization into **2b**$^+$BAr$'_4$$^-$ could be followed by ^{1}H NMR, the equilibrium mixture of 2/1 being reached after ca. 15 min.

A further complex could be detected in the reaction mixture when **1** was treated with more than 1 equiv of NaBAr$'_4$. This is best obtained by addition of 2 equiv of NaBAr$'_4$ to (COD)PdCl$_2$,[14] in the presence of 2 equiv of Py-2-CMe=NAr (Et$_2$O, 24 h), and was identified as the dicationic complex [Pd(Py-2-CMe=NAr)$_2$]$^{2+}$(BAr$'_4$$^-$)$_2$ [**3**$^{2+}$(BAr$'_4$$^-$)$_2$, Scheme 2].[15] Pale green single crystals of **3**$^{2+}$(BAr$'_4$$^-$)$_2$ were obtained by recrystallization from cold methylene chloride and analyzed by X-ray diffraction (Figure 2).[13,16] Besides the expected square-planar geometry, **3**$^{2+}$ shows a mutually trans arrangement of the two imino and of the two pyridyl nitrogens, the palladium atom lying on a crystallographic symmetry center. The other structural parameters are similar to those of **2a**$^+$BAr$'_4$$^-$, the differences between the Pd−N(1) or Pd−N(2) bond distances of **2a**$^+$ (Figure 1) and **3**$^{2+}$ (Figure 2) reflecting the trans effect of the opposite ligands. The ^{1}H and ^{13}C NMR data[15] for **3**$^{2+}$ are consistent with the molecular structure found for the solid state.[8]

Complex **2**$^+$BAr$'_4$$^-$ is an efficient long-lived catalyst for the oligomerization of ethylene (Figure 3).[17] The catalytic reaction was carried out under various conditions of temperature (10−60 °C) and pressure (2−6 bar), which showed that its rate increases markedly at higher temperatures (the average activity reaches for instance

(10) Data for **2**$^+$ BAr$'_4$$^-$: Anal. Calcd for C$_{54}H_{43}N_3BF_{24}$Pd: C, 49.61; H, 3.29; N, 3.21. Found: C, 49.09; H, 3.26; N, 2.97. ^{1}H NMR (CD$_2$Cl$_2$) for **2a**$^+$: δ 8.60 (dd, 1H, py H-6), 8.21 (dt, 1H, py H-4), 8.00 (dd, 1H, py H-3), 7.76 (dt, 1H, py H-5), 7.32 (s, 3H, m- and p-Ar), 2.92 (sept, 2H, C*H*Me$_2$), 2.31 (s, 3H, *Me*C=N−), 1.78 (s, 3H, *Me*CN), 1.30 (d, 6H, CH*Me*Me′), 1.16 (d, 6H, CHMe*Me*′), 1.03 (s, 3H, *Me*−Pd). **2b**$^+$: δ 8.54 (dd, 1H, py H-6), 8.17 (dt, 1H, py H-4), 8.00 (dd, 1H, py H-3), 7.76 (dt, 1H, py H-5), 7.32 (s, 3H, m- and p-Ar), 2.87 (sept, 2H, C*H*Me$_2$), 2.41 (s, 3H, *Me*C=N−), 1.27 (d, 6H, CH*Me*Me′), 1.11 (d, 6H, CHMe*Me*′), 0.51 (s, 3H, *Me*−Pd).[11] Selected ^{1}H−^{1}H NOESY correlations for **2a**$^+$: δ 8.60 (py H-6) with δ 1.03 (*Me*−Pd) and 7.76 (py H-5), δ 1.78 (*Me*CN) with δ 1.30 CH*Me*Me′) and 7.32 (Ar), δ 1.03 (*Me*−Pd) with δ 8.60 (py H-6). **2b**$^+$: δ 8.54 (py H-6) with δ 7.76 (py H-5), δ 2.41 (*Me*CN) with no other signal, δ 0.51 (*Me*−Pd) with δ 2.87 (C*H*Me$_2$) and 1.27 (CH*Me*Me′). A chemical exchange process between the acetonitrile ligands of the two isomers (δ 1.78 and 2.41) is moreover revealed by this method. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) for **2a**$^+$: δ 171.92 (*C*=N−), 156.88 (py C-2), 149.96 (py C-6), 141.09 (py C-4), 140.41 (ipso-Ar), 138.58 (o-Ar), 129.35, 128.07 (py C-3 and p-Ar), 127.56 (py C-5), 124.31 (m-Ar), 28.79 (*C*HMe$_2$), 23.63, 23.49 (CH*Me*Me′, CHMe*Me*′), 18.16 (*Me*C=N−), 3.22, 2.03 (*Me*CN, *Me*-Pd). **2b**$^+$: δ 179.20 (*C*=N−), 152.08 (py C-2), 148.84 (py C-6), 140.72 (py C-4), 140.60 (ipso-Ar), 139.13 (o-Ar), 129.97, 128.77 (py C-3 and p-Ar), 126.82 (py C-5), 124.59 (m-Ar), 28.56 (*C*HMe$_2$), 23.77, 23.04 (CH*Me*Me′, CHMe*Me*′), 19.62 (*Me*C=N−), 6.09, 3.60 (*Me*CN, *Me*-Pd);[6,11] the Me*C*N signals of **2a**$^+$ and **2b**$^+$ could not be detected.

(11) The ^{1}H and ^{13}C NMR data for BAr$'_4$$^-$ are identical to those reported previously.[1b]

(12) Selected crystal and X-ray experimental data for **2a**$^+$BAr$'_4$$^-$ (full data are reported in the Supporting Information): C$_{54}$H$_{42}$BF$_{24}$N$_3$Pd, MW = 1306.13, monoclinic, space group P12$_1$/n1, a (Å) = 12.3620(4), b (Å) = 24.9100(7), c (Å) = 18.6450(6), β (deg) = 100.234(2), Z = 4, 173 K. The structure was solved using direct methods and the Enraf-Nonius Molen package for all calculations; R = 0.070, R$_w$ = 0.084.

(13) The X-ray structure determination was carried out by the Service Commun de Rayons X de la Faculté de Chimie de Strasbourg.

(14) Chatt, L.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 34.

(15) Yield: 65%. Anal. Calcd for C$_{102}$H$_{72}$N$_4$B$_2$F$_{48}$Pd: C, 51.10; H, 3.00; N, 2.34. Found: C, 51.16; H, 3.11; N, 2.36. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.21 (dt, 2H, py H-4), 8.06 (dd, 2H, py H-3), 7.74 (t, 2H, p-Ar), 7.49 (d, 4H, m-Ar), 7.42 (dt, 2H, py H-5), 6.22 (dd, 2H, py H-6), 3.01 (sept, 4H, C*H*Me$_2$), 2.54 (s, 6H, *Me*C=N−), 1.21 (d, 12H, CH*Me*Me′), 1.02 (d, 12H, CHMe*Me*′).[11] ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 184.71 (*C*=N−), 155.22 (py C-2), 149.89 (py C-6), 144.60 (py C-4), 141.72 (o-Ar), 137.65 (ipso-Ar), 133.12 (py C-3), 130.39, 129.99 (py C-5 and p-Ar), 127.26 (m-Ar), 29.83 (*C*HMe$_2$), 23.53, 23.09 (CH*Me*Me′, CHMe*Me*′), 20.83 (*Me*C=N−).[6,11]

(16) Selected crystal and X-ray experimental data for **3**$^{2+}$(BAr$'_4$$^-$)$_2$ (full data are reported in the Supporting Information): C$_{102}$H$_{72}$B$_2$F$_{48}$N$_4$-Pd, MW = 2393.68, orthorhombic, space group Pbca, a (Å) = 20.3950-(6), b (Å) = 20.3970(6), c (Å) = 24.8420(6), Z = 4, 173 K. The structure was solved using direct methods and the Enraf-Nonius Molen package for all calculations; R = 0.049, R$_w$ = 0.069.

(17) In a typical experiment, 0.04 mmol of **2**$^+$BAr$'_4$$^-$ was dissolved in 60 mL of 1,2-dichloroethane, before ethylene was introduced into the thermostated (30 °C) glass reactor. The ethylene pressure was maintained at 6 atm, while the solution was vigorously stirred at a controlled rate (450 rpm). After 18 h, the volume of the clear solution had reached 83 mL, allowing us to estimate that 23 mL of oligomers had been obtained at this stage. The catalytic reaction was then quenched by addition of methanol, and the crude reaction mixture was analyzed by GC. Evaporation of the volatiles under reduced pressure (1 mmHg) was then followed by renewed GC analysis of the resulting liquid (this showed that only the C$_4$−C$_8$ fractions initially present were significantly lost during evaporation), which was further characterized by size extrusion chromatography (SEC) and ^{1}H NMR.
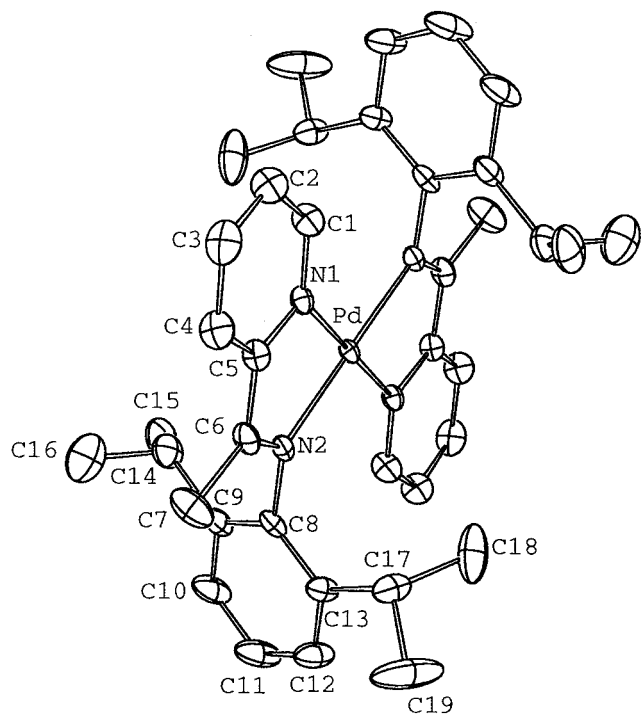
Figure 2. ORTEP diagram of $3^{2+}(BAr'_4{}^-)_2$. The counteranions and all hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–N(1) = 2.054(4), Pd–N(2) = 2.052(4), N(1)–Pd–N(2) = 78.3(2), N(1)–Pd–N(1') = N(2)–Pd–N(2') = 180.00.
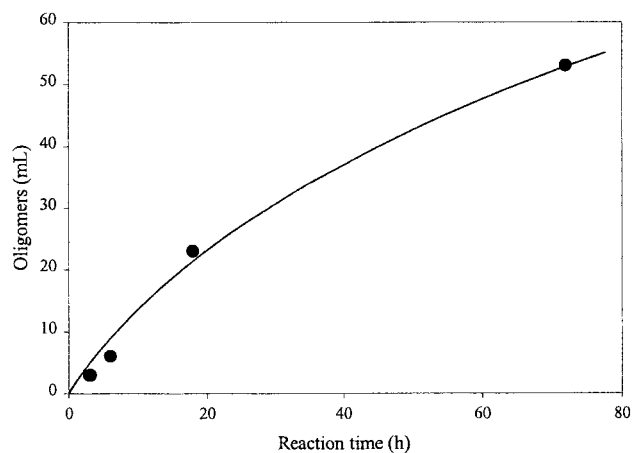
Figure 3. Ethylene oligomerization (30 °C, 6 bar) in the presence of $2^+BAr'_4{}^-$ (0.04 mmol in 1,2-dichloroethane).

105 kg oligomer mol^{-1} h^{-1} after 6 h at 60 °C and 6 bar), but is only slightly sensitive to pressure at 30 °C. The nature of the oligomeric products does not change significantly with the reaction conditions. GC and GC/MS analysis of the crude reaction mixtures shows that hydrocarbons containing as expected[18] even numbers of carbon atoms have been obtained. A large number of isomers is distinguished for each C_{2n} ($n = 2-10$) fraction (for instance 9 isomers for the C_{10} fraction), the integration of which yields $M_n = 155$ (± 5). These values increase to $M_n = 190$ (± 15) after evaporation of the volatiles,[17] whereas SEC analysis of the resultant liquids leads to higher values ($M_n = 275 \pm 20$).[19]

In the ^{1}H NMR spectra of these liquids, five distinct chemical groups can be distinguished,[20] whose integration leads to overall 2.15 (± 0.1) Me groups for 10

carbons, among which ca. 1.6 should correspond to chain end methyl groups,[21] and the other 0.55 to methyl or longer branches. This confirms a certain degree of branching already suspected on the basis of the numerous isomers detected by GC. About 0.4 of the terminal methyl groups belong to MeCH=CH– functions, and the other type of internal carbon–carbon double bonds, –CH=CH–, is present in approximately equal proportions (0.4/10C). The high amount of such internal double bonds contrasts with the surprising rarity of the vinyl end groups which represent less than 1% of the total number of double bonds.[22,23] One can assume that each oligomer contains one carbon–carbon double bond since this leads to $M_n = 180$ (± 20), a value which is near to that found by GC.

Catalyst $2^+BAr'_4{}^-$ remains active in the presence of 1500 equiv of methyl or benzyl acrylates, although only respectively 3 and 5 mL of oligomers were obtained from ethylene under otherwise identical reaction conditions.[17] The GC and SEC patterns of the products, the resultant M_n values, and the main features of their ^{1}H NMR spectra are only slightly different from those obtained in the absence of acrylates. However, the ^{1}H NMR spectra exhibit additional and relatively intense signals,[24] indicating that the acrylates have cooligomerized with ethylene. The acrylate incorporation[25] reaches 9.3 and 8.2%, respectively. The initial acrylate insertion products appear to have subsequently isomerized as in preceding cases,[1b] suggesting that analogous mechanisms[1b] are involved.

Also α-olefins such as propylene (6 bar) and 1-hexene (30 mL) are oligomerized in the presence of $2^+BAr'_4{}^-$ (0.04 mmol) at 30 °C, affording respectively 12 and 1 mL of products after 18 h reaction time. The GC and SEC profiles for these oligomers are similar to those of the ethylene oligomers, the successive oligomerization degrees being even better distinguished by both methods. They show that the average oligomerization degrees are lowered (DP = 3.5 and 2.9, respectively) and lead to respective M_n values of 146 and 242 (by GC) or 237 and 333 (by SEC).[19a] The occurrence of slower olefin insertion steps, with respect to ethylene, is hence clearly indicated. Interestingly, three isomers of hexene are

(18) In the case of initial insertion of ethylene into palladium–hydride bonds.

(19) (a) The SEC values were measured vs polystyrene standards and are probably overestimated. (b) Each plot exhibits six maxima corresponding to the shortest well-separated C_{2n} ($n = 2-7$) fractions.

(20) Beside the main chain CH_2 and the Me resonances at δ 1.28 and δ 0.90, respectively, several more or less broad multiplets are characteristic of three types of unsaturations: CH_2=CH– (δ 5.81 and 4.96), cis and trans MeCH=CH– (δ 1.65, 1.60, and 5.41), and cis and trans –CH=CH– (δ 5.41). The methylene protons adjacent to these three double bonds give rise to a further signal at δ 1.98.

(21) This number is based on the value of M_n and on the fact that each oligomer should possess almost exclusively methyl groups at both chain ends, almost no terminal carbon–carbon double bonds being detected (vide infra).

(22) Except at 60 °C, where up to 4% of vinyl end groups were found, or at very long reaction times.

(23) The fact that the –CH=CH– bonds may occupy diverse positions in the oligomer chains certainly contributes further to the large number of isomers.

(24) These signals show up at δ 3.67 (s) and 2.29 (t) for methyl acrylate and at δ 5.12 (s) and 2.36 (t) for benzyl acrylate and are assigned respectively to –$CH_2CH_2CO_2Me$, –$CH_2CH_2CO_2Me$, –CH_2-$CH_2CO_2CH_2$Ph, and –$CH_2CH_2CO_2CH_2$Ph groups.

(25) Actual insertion of benzyl acrylate into all C_{2n} fractions of the ethylene oligomer has been proven by determining that UV detection (benzyl acrylate shows an absorption maximum at 254 nm, at which wavelength the UV detector was set) affords the same SEC trace as the refractive index detection.

found in comparable proportions in the crude reaction mixture obtained from 1-hexene, suggesting the partial conversion of 1-hexene into 2- and 3-hexene and the existence of double bond shift reactions in the present catalytic systems.[26] The ^{1}H NMR spectra lead to a methyl content of 3.6 Me/10C for oligopropylene and 1.9 Me/10C for oligohexene, which is lower than expected for these monomers (ca. 4.3 and 2.2, respectively),[21] as reported for analogous catalysts as a result of chain isomerization reactions[1a,b] occurring also in the present case.

Overall, these results can be reconciled with conventional mechanistic assumptions.[1,27] β-H transfer from the growing oligomer chains to the palladium catalytic centers would be followed either by the reverse but regioselectively different reaction (leading to chain branching) or by displacement of the olefin of the resultant palladium−olefin−hydride complex (leading to chain transfer and to the formation of one double bond per oligomer molecule). The significant branch content (which results also, however, from the reincorporation into further growing chains of the α-olefinic oligomers produced in the early stage of the reactions)[28] and the low molecular weight of the oligomeric products show that these three steps are all relatively fast with respect to the olefin insertion step. This enables easy

chain-end analysis and allowed us to determine in particular that the expected vinyl groups CH_2=CR− (R = H, R′) are present in only very low amount. We suggest that $\mathbf{2}^+BAr'_4{}^-$ readily isomerizes the α-olefinic oligomers into internal olefins, although less frequent chain transfer after an olefin insertion step than after one or several isomerization steps may also seem a plausible explanation. Such a conclusion can probably be extended to the higher molecular weight polymers obtained in the presence of similar palladium(II) diimine catalysts.[1]

Supporting Information Available: Tables of crystal and X-ray experimental data, positional parameters, general displacement parameter expressions, and bond distances and bond angles for $\mathbf{2a}^+BAr'_4{}^-$ and $\mathbf{3}^{2+}(BAr'_4{}^-)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) These are further confirmed by the detection on the ^{1}H NMR spectra of oligopropylene and oligohexene of a broad multiplet assigned to RR′C=CHR″ groups (δ 5.13, respectively 20% and 4% of the total amount of double bonds), besides the weak signals due to the expected RR′C=CH_2 groups (δ 4.70, 10% of the total amount of double bonds in the oligopropylene). The other ^{1}H NMR resonances of both oligomers were already found for oligoethylenes.

(27) Desjardin, S. Y.; Way, A. A.; Murray, M. C.; Adirim, D.; Baird, M. C. *Organometallics* **1998**, *17*, 2382.

(28) This could be clearly proven by running ethylene oligomerization (25 °C, 4 atm, 18 h)[17] in the presence of 1-pentene (20 mL), which led to the GC observation of approximately equal proportions of even- and odd-carbon (in particular C_7 to C_{13}) oligomers.