Articles

Cationic Methallylnickel and (Meth)allylpalladium 2-Phosphinophenol Complexes: Synthesis, Structural Aspects, and Use in Oligomerization of Ethylene

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Reactions of methallylnickel bromide with 2-$R_2PC_6H_4OH$ **1a**,**b** (R = Ph, *c*Hex) and $AgSbF_6$ furnish methallylnickel phosphinophenol hexafluoroantimonates **2a**,**b**, which are not very stable and decay in solution at room temperature within an hour (**2a**) or days (**2b**) to tetranuclear nickel complexes **3a**,**b**. The related cationic allylpalladium complex **4a** is more stable. A crystal structure analysis gives evidence of the monomeric nature, the typical η^3-coordination of the allyl group, and the coordination of the phenolic hydroxyl group to palladium. In solution the OH group is uncoordinated and underlines the hemilabile character of the phosphinophenol ligands. The allylpalladium phosphinophenol tetrafluoroborate **5a**, stable as a solid, slowly decomposes in $CDCl_3$ solution to give a dinuclear complex **6a** and in THF/water as the solvent the palladium bis(phosphinophenolate) **7a**. Methallylpalladium phosphinophenol acetates **8a**,**b**, existing as phosphinophenolate acetic acid conjugates, are uncommonly stable and lose the acid on heating in a vacuum without cleavage of the methallyl group to give neutral methallylpalladium phosphinophenolates **9a**,**b**. The labile complexes **2a** and **2b** proved to be highly active single-component catalysts for the conversion of ethylene to isomer mixtures of butenes, hexenes, and lower amounts of higher olefins at ambient temperature. The C_6 fraction consists mainly of branched and internal olefins. **5a** is less active but converts ethylene on heating under pressure to a mixture of butenes and smaller amounts of hexenes, while **8** and **9** are inactive.

Introduction

Late transition metal chelate complexes are well-known catalysts for the oligomerization[1] and polymerization[2] of ethylene. After the early work on neutral nickel chelate catalysts cationic nickel and palladium complexes with bidentate or multidentate ligands find increasing interest,[3] in particular since the discovery of bulky cationic nickel diimine catalysts, which convert ethylene to strongly branched high molecular weight polymers.[4] Cationic organonickel and organopalladium chelate complexes with $Ph_2P^{\frown}C(O)R'$ ligands and noncoordinating anions[5−10] are reported to afford mixtures of linear and branched low oligomers[6] or 1- and *E*/*Z*-2-butenes,[7−10] while neutral organonickel $P^{\frown}O^-$-chelate

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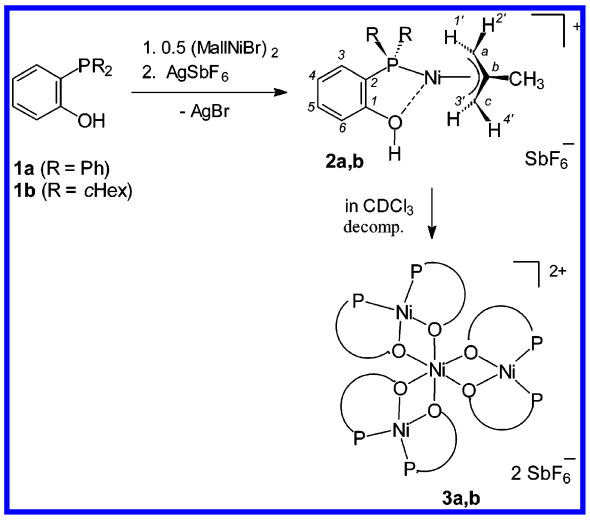
catalysts with 2-phosphinoenolate[11−15] and 2-phosphinophenolate ligands[15−17] give rise to linear oligomers or polymers, and related palladium complexes are usually inactive. Cationic methallylnickel β-phosphinoketone chelate complexes with bulky *tert*-butyl substituents at phosphorus, retarding the chain transfer reactions, turn the conversion of ethylene to nearly linear polymers with modest molecular weights and 6−8 methyl branches per 1000 carbon atoms. Related cationic methylpalladium complexes become modestly active only at 80 °C and give rise to oligomers in which the degree of branching decreases with increasing ethylene pressure.[18] Cationic organonickel and -palladium complexes with phosphinophenol ligands, differing from cationic β-ketophosphine complexes in a hydroxyl group in β-position, have not yet been reported in the literature to our knowledge. In the course of our investigations on phosphinophenols and its use in coordination chemistry and catalysis we were interested in such compounds and report here on the results.

Results and Discussion

Synthesis. Reaction of 2-diphenyl- or 2-dicyclohexylphosphinophenols **1a** and **1b** with methallylnickel bromide in methylene chloride and treatment with $AgSbF_6$ to exchange bromide by the noncoordinating hexafluoroantimonate anion provides the cationic methallylnickel phosphinophenol complex **2a** or **2b**, respectively, isolated from methylene chloride/hexane as dark red solids (Scheme 1). Compared to the corresponding neutral methallylnickel phosphinophenolate complexes[17] the cationic complexes exhibit much lower stability and decay at room temperature, slowly in the solid state and within an hour (**2a**) or days (**2b**) in solution. The decomposition in $CDCl_3$ leads to cleavage of the methallyl group from nickel(II) and formation of paramagnetic nickel complexes **3a**,**b**, which proved to be tetranuclear clusters of the type $[Ni_4(R_2PC_6H_4O)_6](SbF_6)_2$ and will be reported in more detail separately.[19] It is assumed that the decomposition is started by slow intermolecular protolysis of the methallyl group by the phenolic OH group, indicated by small singlets of isobutene in the ^{1}H NMR spectra (δ = 1.73, 4.66). The resulting instable cationic nickel complexes react via unknown intermediates, in the case of **2a** detected by small broad ^{31}P NMR signals (δ = −5.5 and −1.0), to nickel hexafluoroantimonate and nickelbis(phosphinophenolates), which due to lack of more suitable ligands are trapped by nickel(II) to form the μ-O-bridging complexes **3a**,**b**.

Scheme 1. Synthesis of Cationic Methallylnickel Phosphinophenol Complexes



Cationic allylpalladium complexes **4a** and **5a** were synthesized by reaction of **1a** with allylpalladium chloride and subsequent treatment with either $AgSbF_6$ or $AgBF_4$ to replace chloride by noncoordinating anions (Scheme 2). In solution **4a** is much more stable at room temperature than the related nickel complex **2a** and also somewhat more stable than **5a** with the smaller BF_4^- anion. It allows slow crystallization without marked decomposition from THF/hexane (see crystal structure below), while the tetrafluoroborate **5a** undergoes slow degradation and provides crystals of the dinuclear palladium complex **6a**.[19] As a solid, **5a** loses the allyl group detectably only above 120 °C (DTA). The NMR spectra of freshly prepared solutions of **5a** give evidence of the clean monomer complex, but spectra measured after some days display decomposition. After 2 weeks the allyl signals are no longer detectable, and the phosphorus resonance appeared at δ = 46.4. The ^{1}H NMR signals of H-6 and H-3 occur noticeably downfield from the signals of the known bis(chelate) *cis*-[(2-$Ph_2C_6H_4O)_2$Pd] (δ 44.5) **7a**,[20] obtained on crystallization of **5a** from THF/water. It is assumed that the decom-

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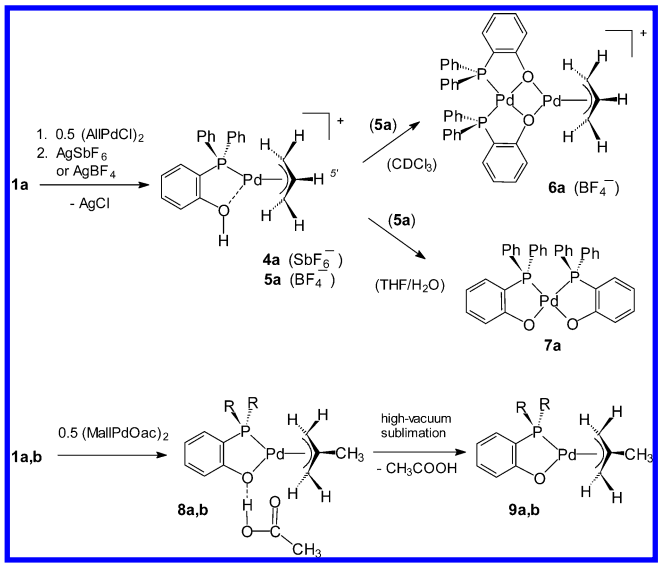
Scheme 2. Synthesis of Cationic (Meth)allylpalladium Phosphinophenol Complexes



position, similar to that for **2a**,**b**, is due to primary protolytic Pd−allyl bond cleavage and that the resulting cation is trapped by a second molecule of **5a** to give **6a**. The rather limited stability of the latter leads to further decomposition to **7a** when the crystallization is continued. The destiny of the HBF_4 liberated was not studied; possibly it reacts with THF. Elimination of propene was detected by mass spectra. Even the more stable solid **4a** displays cleavage of traces of propene at 25 °C by the $C_3H_6^+$ cation that forms the by far most abundant peak.

Finally, it should be mentioned that a cationic methallylpalladium 2-di-*tert*-butylphosphinophenol complex, the acetate, was reported as a highly stable compound that sublimes in a vacuum with loss of acetic acid but without cleavage of the methylallyl group.[20] This prompted us to investigate similar reactions of **1a** and **1b** with methallylpalladium acetate. These provide the complexes **8a** and **8b** in good yields. However, **8a** as well as **8b**, with the more basic dialkylphosphino group, proved to be phosphinophenolate chelate complexes, in particular by unambiguous ^{13}C NMR data (see below). The acetic acid is loosely bound via a hydrogen-bridging bond to the oxygen anion, indicated by the broad and strongly bathochromically shifted ν_{OH} vibration (2500 cm^{-1}) in the infrared spectra. For the di-*tert*-butylphosphinophenol complex the same structure is anticipated because of similar IR and aryl proton NMR data. On heating in a vacuum, better by high-vacuum sublimation, acetic acid is liberated, and the neutral methallylpalladium complexes **9a** and **9b** are obtained.

Structures. The structure elucidation of the compounds is based on satisfying elemental analyses and consistent ^1H, ^{13}C, and ^{31}P NMR data or crystal structure analysis. The phosphinophenol(ate) ligands are indicated by the characteristic proton and ^{13}C chemical shifts and coupling patterns. Neutral and cationic complexes are easily distinguished by the absence or the presence of the acidic hydroxyl proton. This appears for the hexafluoroantimonates **2a**, **2b**, and **4a** at δ = 9.4−9.8, for the tetrafluoroborate **5b** at δ = 11.2 (each in $CDCl_3$), and for the hydrogen-bridging acetates **8a** and **8b** at δ = 11.2 (C_6D_6) and 13.1 ($CDCl_3$). The

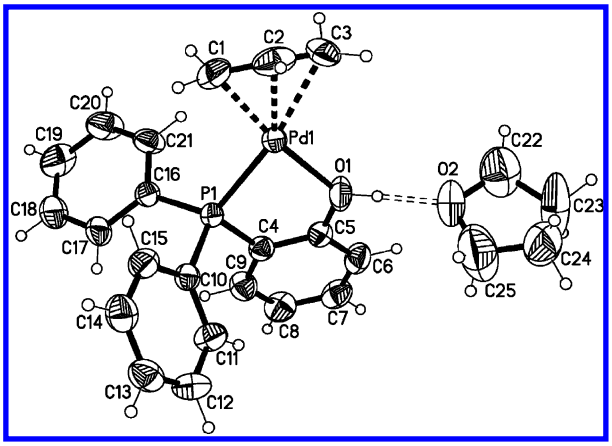


Figure 1. Molecular structure of the cation hydrogen-bonded to the THF molecule with the atom-numbering scheme in crystals of **4a**·THF (thermal ellipsoids with 50% probability).

downfield shift as compared to the OH resonance in **1a**,**b** indicates interactions with the metal. The P∩O⁻-chelate nature of **8a**,**b** like in **9a**,**b** follows unambiguously from the downfield chemical shifts of the $^{13}C(1)$ nuclei (δ = 176.4−177.8) as compared to those of the $^{13}C(1)$ nuclei with a free or weekly coordinated hydroxyl group (**1a**,**b** δ = 159, 163; **2a**,**b**, **4a**, and **5a** $\delta \approx 160$). The δ-values of the $^{13}C(2)$ nuclei are less characteristic since their upfield coordination chemical shifts are similar for neutral and cationic methallylnickel or -palladium complexes. The $^{31}P-^{13}C(2)$ one-bond coupling constants, dependent also on the nature of the P-substituents, are more indicative and smaller for the cationic than for the corresponding neutral chelate complexes ($^1J(P-C(2)$ = 31.2 Hz in **2b** versus 42.4 Hz in the corresponding neutral chelate;[17] 43.0 and 44.0 in **4a** and **5a** versus 51.0 and 52.1 in **8a** and **9a**). The same is valid for the phosphorus coordination chemical shifts ($\Delta\delta$ = 52.3, 73.4 in **2a**,**b** versus 58.2, 78.1 in the corresponding neutral chelates;[17] 25.3 and 25.5 in **4a** and **5a** versus 31.7 and 33.2 in **8a** and **9a**). The assignment of the allyl protons of **4a** and **5a** is based on the larger coupling constants of the protons H(1′) and H(3′) in *trans*-configuration as compared to H(2′) and H(4′) in *cis*-configuration and the larger P−H coupling of H(3′) and H(4′) in *trans*-position to phosphorus,[21] the local proximity of H(3′-5′) by cross-peaks in the NOESY spectrum, and the correlation with the ^{13}C resonances by CH-COSY. The allyl protons H(1′-4′) of **4a** and **5a** except H(1′) of **4a** appear at ambient temperature as broad singlets, but as shown for **5a**, at −30 °C the expected splitting is observed and the coupling constants did not change significantly on cooling to −65 °C. Selective ^{31}P-decoupling distinguished H−H and P−H coupling. The proton and carbon nuclei H(1′-4′) and C(a) and C(c) of the methallyl groups are assigned analogously.

More detailed structural information is provided by the crystal structure analysis of **4a**·THF (Figure 1). The compound crystallizes in orthorhombic cells, space group $P2_12_12_1$, with four molecules per unit cell and racemic twinning with a ratio of 0.88/0.22 for the two components. The most striking feature is the coordination of palladium by the oxygen atom, which contrasts with the

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Table 1. Selected Bond Lengths and Angles in 4a·THF

atoms	length (Å)	atoms	length (Å)
Pd-cation		anion	
Pd1−C1	2.056(3)	Sb1−F1	1.866(2)
Pd1−C2	2.134(3)	Sb1−F2	1.858(2)
Pd1−C3	2.217(3)	Sb1−F3	1.858(2)
Pd1−O1	2.161(2)	Sb1−F4	1.873(3)
Pd1−P1	2.2849(7)	Sb1−F5	1.848(2)
P1−C4	1.812(3)	Sb1−F6	1.843(3)
P1−C10	1.814(3)		
P1−C16	1.809(2)	cocrystallized THF	
O1−C5	1.369(3)	O2−C22	1.419(6)
C1−C2	1.427(5)	O2−C25	1.405(6)
C2−C3	1.316(5)	C22−C23	1.482(7)
		C23−C24	1.470(7)
average C−C in phenyl rings	1.386	C24−C25	1.396(7)
range	1.355−1.400		

atoms	angle (deg)	atoms	angle (deg)
C1 Pd1 C2	39.8(1)	C3−C2−C1	119.9(3)
C1−Pd1−C3	67.4(1)	C4−P1−Pd1	100.43(9)
C2−Pd1−C3	35.1(1)	C10−P1−Pd1	117.44(8)
C1−Pd1−O1	170.6(1)	C16−P1−Pd1	119.34(9)
C2−Pd1−O1	136.9(1)	C1−C2−Pd1	66.89(19)
O1−Pd1−C3	106.0(1)	C2−C1−Pd1	73.1(2)
C1−Pd1−P1	104.0(1)	C2−C3−Pd1	69.0(2)
C2−Pd1−P1	139.7(1)	C3−C2−Pd1	75.9(2)
O1−Pd1−P1	81.86(6)	O1−C5−C4	118.7(2)
C3−Pd1−P1	169.77(9)	O1−C5−C6	120.9(3)
C4−P1−C16	105.5(1)	C4−C5−C6	120.4(3)
C4−P1−C10	106.1(1)	C5−O1−Pd1	118.8(2)
C16−P1−C10	106.4(1)		

chemical shift of $^{13}C(1)$ in solution indicating rather a free phenol and suggests that the solution and crystal structures are different and that the Pd−O coordination in solution is labile. In the crystal the Pd1−O1 distance (Table 1) is comparable to the μ-O−Pd bond lengths of the allyl-Pd unit of **6a** (2.176(17), 2.180(4) Å)[19] or dinuclear μ-O−Pd complexes [(2-R_2P-4-MeC_6H_4O-*P*,*O*)-PdCl]$_2$ (2.146(2), 2.168(2) Å)[22] but longer than the Pd−O bonds within the P∩O$^-$-chelate units of **6a** (2.035(8), 2.037(8) Å),[19] [(2-R_2P-4-MeC_6H_4O-*P*,*O*)PdCl]$_2$ (2.022(2) Å)[22] or the Pd-mono(P∩O$^-$-chelate) [PdCl-(2-*t*BuPhPC_6H_4O)(2-*t*BuPhPC_6H_4OH)] (1.9972(16) Å).[16d] This indicates clearly the coordination of the hydroxyl group to the metal. To our knowledge this is the first structurally characterized P∩OH-chelate complex with a single phosphinophenol ligand. To date only a Rh(III)(Cl)[phosphinobis(phenolate)]phosphinobis-(phenol) complex is known to display a P∩OH-chelate coordination pattern.[23] The Pd···OH coordination shows hemilabile properties of free phosphinophenol ligands similar to those known for phosphinophenol ethers.[24] Cationic C_5Ph_5Ni phosphinoenolate[5] and methallylnickel phosphinobenzoate[6,7b] as well as cationic allyl-[9] and methylpalladium phosphinoenolate complexes[10,18b] with hemilabile coordination of oxygen to the metal have already been reported, but in all these complexes the oxygen belongs to a carbonyl group, is double bonded, and is a stronger Lewis base than the oxygen atom of a phenolic OH group.

A further feature of the structure of **4a**·THF is the remarkable difference of the Pd−C bond lengths to the allyl carbon atoms. The C1 atom in *trans*-position to oxygen (O−Pd−C1 170.4(1)°) is closer by 0.168 Å at the metal than C3, which is located opposite of phosphorus (P−Pd−C3 169.5(1)°). This reflects the different coordination properties and *trans*-influence of the hard and soft donor atoms as well as a bond strengthening of Pd−C1 on account of Pd−C3. It correlates with the strong upfield shift for the resonance of ^{13}C-*a* (i.e., C1) as compared to ^{13}C-*c* (i.e., C3), indicating a higher σ-character of the Pd−C1 as compared to the Pd−C3 bond and may be expressed by an increased weight of a classical resonance structure with σ-CH_2 and π-CH=CH_2 coordination of the allyl group. The Pd−P bond lengths are in the same range as in the phosphinophenolate chelates, while the P−Pd−O angle is substantially smaller in **4a**·THF.

Oligomerization of Ethylene. The easy loss of the methallyl groups of **2a**,**b** even at room temperature suggests that these complexes might be efficient catalysts for conversions of olefins. Indeed, suspensions of the cationic nickel phosphinophenol complexes **2a** and **2b** in toluene were found to be highly active single-component catalysts for the oligomerization of ethylene. In contrast to neutral methallylnickel phosphinophenolate catalysts, which require heating to polymerize ethylene,[17] the exothermic reaction starts without a perceptible induction period already at room temperature during pressurizing the autoclave and proceeds nearly quantitatively without external heating. The turnover numbers are limited by the ethylene/catalyst ratio used in the batch procedure, and decomposition of the catalyst to metallic nickel was not observed. The products were analyzed by GC and found to be mainly butenes, hexenes, and low amounts of higher olefins. The high selectivity for linear α-olefins (>90−95%) observed in the polymerization of ethylene with neutral methallylnickel phosphinophenolate catalysts[17] is lost. GC analyses display mainly *trans*- and *cis*-butene-2 in the C4 fraction (Table 2) and formation of branched (ca. 64%) along with linear internal (ca. 35%) olefins in the C6 fraction but only low amounts of 1-hexene (Table 3). The average chain lengths are somewhat higher on use of the dicyclohexylphosphino catalyst **2b**, but the effect of the higher P-basicity on the molecular weights of the oligomerization products is much lower than in the case of neutral phosphinophenolate catalysts. The preferred branching is also different for the diphenyl- and the dicyclohexylphosphinophenol nickel catalysts. With **2a** the most abundant C6 isomer is *cis*-3-methylpentene-2 followed by *trans*-hexene-2 and 2-ethylbutene-1, while with **2b** 2-ethylbutene-1 is the main component (ca. 50%) followed by *trans*-hexene-2.

The cationic allylpalladium complex **5a** also acts as catalyst but is less active than the related nickel complex **2a**. Heating was found necessary. At 70 or 100 °C ethylene is converted with rates comparable to those of neutral nickel phosphinophenolate catalysts. The maximum turnover frequencies are 2.300 mol/mol h at 70 °C and 12.000 mol/mol h at 100 °C and were estimated from the steepest nearly linear pressure drop

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Table 2. Oligomerization of Ethylene with Cationic Methallylnickel and Allylpalladium Phosphinophenol Single-Component Catalysts

expt no.	catalyst[a] (μmol)	ethylene (g (mmol))	conditions T (°C), p (bar)	conversion (%) (TON (mol/mol))	products (% of oligomer)[c]
1	**2a** (100)	14.3 (510)	>20, 1 to <10[b]	99 (5050)	$C_4\Sigma = 68.0$ (1.4, 49.4, 17.2), $C_6\Sigma = 27.8$, $C_8\Sigma = 4.0$, $C_{10}\Sigma = 0.2$
2	**2b** (100)	16.4 (585)	>20, 1 to <10[b]	100 (5850)	$C_4\Sigma = 44.8$ (4.3, 27.7, 12.8), $C_6\Sigma = 38.8$, $C_8\Sigma = 12.8$, $C_{10}\Sigma = 3.1$, $C_{12}\Sigma = 0.5$
3	**5a** (105)	15.7 (560)	70, 50	80 (4280)	$C_4\Sigma = 90.9$ (13.7, 52.9, 24.4), $C_6\Sigma = 9.0$, $C_{\geq 8}\Sigma = 0.1$
4	**5a** (95)	14.8 (528)	100, 50	77 (4290)	$C_4\Sigma = 87.4$ (16.8, 45.5, 25.1), $C_6\Sigma = 12.5$, $C_{\geq 8}\Sigma = 0.1$

[a] Catalyst suspended in 20 mL of toluene. [b] The exothermic oligomerization started at room temperature when ethylene was added, and the pressure did not exceed 10−15 bar; workup after 1 h. [c] C4 isomers in the order of retention times (reference at 5 °C isotherm): 1-butene, *trans*-butene-2, *cis*-butene-2.

Table 3. C_6-Isomer Distribution, Mass % of Oligomers (of C_6-isomers)

olefin	1/**2a**	2/**2b**	3/**5a**	4/**5a**
3-methylpentene-1	trace	1.1 (2.8)	0.1 (1.1)	trace
1-hexene/ 2-methylpentene-1	0.1 (0.4)	1.0 (2.6)	0.2 (2.2)	0.4 (3.2)
2-ethylbutene-1	5.6 (20.1)	19.5 (50.3)	2.1 (23.3)	1.4 (11.2)
trans-hexene-3	2.3 (8.3)	3.0 (7.7)	1.7 (18.8)	2.3 (18.4)
cis-hexene-3				
trans-hexene-2	6.1 (22.0)	7.3 (18.8)	2.3 (25.6)	3.2 (25.6)
trans-3-methylpentene-2	3.2 (11.5)	1.6 (4.1)	0.6 (6.7)	1.2 (9.6)
cis-hexene-2	1.5 (5.4)	2.3 (5.9)	0.5 (5.6)	0.8 (6.4)
cis-3-methylpentene-2	9.0 (32.4)	3.0 (7.7)	1.5 (16.7)	3.2 (25.6)

of the pressure−time plots (Figure 2). The products are mainly butenes, accompanied by roughly 10% of hexenes and trace amounts of octenes. The C6 isomer composition is similar to that in the experiment with the catalyst **2a** except for a markedly stronger content of *cis*/*trans*-hexene-3 (18−19% of C_6) (Tables 2, 3). The methallylpalladium phosphinophenolate acetic acid conjugates **8a** and **8b** do not catalyze the oligomerization of ethylene, nor do the neutral complexes **9a** and **9b**.

The loss of selectivity for linear α-olefins observed in the polymerization of ethylene with neutral nickel phosphinophenolate catalysts clearly indicates a different mechanism of the ethylene oligomerization by cationic nickel (and palladium) phosphinophenol catalysts. The only structural difference between cationic methallylnickel phosphinophenol and neutral phosphinophenolate complexes that may cause the different catalytic properties is the hemilabile OH-coordination in the cationic as compared to the quite stable O^--coordination in the neutral complexes. By the *trans*-influence this has a strong impact on the stability and reactivity of the metal−C bond. Strong O^--coordination strengthens the metal−C bond and limits the insertion more or less to ethylene, while the weak OH-coordination strongly facilitates the insertion and allows also unselective insertion of other olefins. Thus, the product composition observed with the cationic nickel catalyst **2a** and with nonfunctional PR_3 catalysts [methallylnickel(PPh_3)]$^+PF_6^-$ or [mesitylnickel(PR_3)]$^+PF_6^-$ is similar (C_4 2.5/68.4/29.1, C_6 26.8, C_8 2.3 mass %)[25] and suggests that the influence of the OH-coordination on the catalysts derived from **2** is quite limited. As concluded from the NMR data, the OH group may have a placeholder function and stabilize the catalyst as is typical for hemilabile transition metal complex catalysts.[24] Even as compared to cationic β-ketophosphine nickel or palladium catalysts, the cationic 2-phosphinophenol catalysts are less selective. Thus, the amount of 1-butene (58 mass %) is much higher than that of *trans*- and *cis*-butene-2 (23 and 19 mass %) in the ethylene dimerization with [MePd($Ph_2PCH_2C(Ph)$=O-(PPh_3)]$^+PF_6^-$,[10] while it is low with the catalyst **2a**, **2b**, or **5a**. The bulky P-substituted cationic allylnickel- or methylpalladium-t-$Bu_2PCH_2C(Ph)$=O catalysts even form mainly linear polyethylenes.[18]

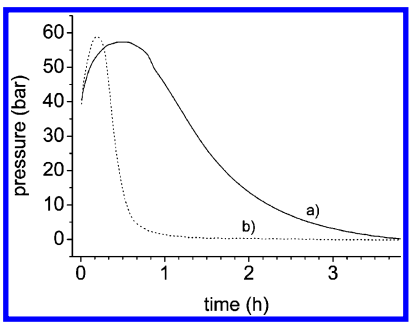

Figure 2. Pressure−time plots for batch oligomerization of ethylene with **5a** in toluene (a) at 70 °C and (b) at 100 °C.

The formation of the observed branched hexenes can be understood in terms of preferred coordination and unselective insertion of butene-1. This explains, for example, the high content of 2-ethylbutene-1 in the oligomerization with **2a** (20% of C_6) and in particular **2b** (50% of C_6) by insertion of butene into the Ni−C bond of primarily formed Ni-ethyl intermediates (Scheme 3). *cis*- and *trans*-3-methylpentene-2 can easily be formed from 2-ethylbutene-1 or 3-methylpentene-1 by metal- or acid-catalyzed isomerization. The *cis*/*trans* ratio with diphenylphosphinophenol catalysts **2a** and **5a** is ca. 3:1, with the more P-basic dicyclohexylphosphinophenol catalyst **2b** ca. 2:1. Butenes-2 and hexenes-2 and -3 can be formed directly as proposed in Scheme 3 or by metal-

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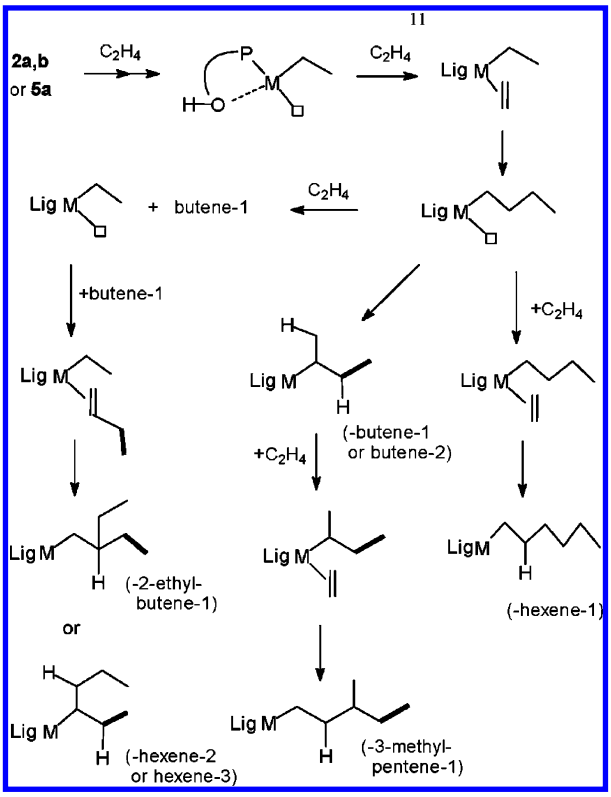
Scheme 3. Proposed Mechanism to Explain the Products Formed



or acid-catalyzed migration of the thermodynamically less favorable terminal double bond. The much lower amounts of hexenes in catalysis with the palladium complex **5a** as compared to **2a** and **2b** is due to significantly lower activity even at elevated temperatures, in particular a slow relative insertion rate of butene-1 (residual content in the C_4 fraction 13.7−16.8% versus 1.4−4.3% with Ni catalysts, Table 2) into the Pd−C bond of primarily formed Pd-ethyl species. The ability of the nickel catalysts to coordinate, isomerize, and insert α-olefins into Ni−C bonds was demonstrated by the formation of hexene isomers (60.7% *trans*-hexene-2, 23.0% *cis*-hexene-2) and dodecenes (6.6%) from 1-hexene by reflux in the presence of catalytic amounts of **2a**. Even *cis*-hexene-2 was isomerized (1.4% 1-hexene, 73.4% *trans*-hexene-2, 15.5% *cis*-hexene) and dimerized (8.2% dodecenes) under these conditions. However, no branching was observed so that this must be attributed to the chain growing, not to isomerization reactions. An attempt to co-oligomerize ethylene with 1-hexene (solvent) provided mainly butenes but also small amounts of co-dimers. The latter follows from the higher content of octenes as compared to the additional amount of hexenes formed from ethylene. The less active palladium catalyst **5a** does not convert ethylene in the presence of 1-hexene.

Conclusions

Cationic (meth)allylnickel and -palladium phosphinophenol complexes with noncoordinating anions are easily available from phosphinophenols, (meth)allylnickel halides, and silver salts with fluoro complex anions. The crystal structure analysis of **4a**·THF gives evidence of coordination of the OH group to palladium, while the chemical shift of the $^{13}C(1)$ nucleus in the solution ^{13}C NMR spectrum indicates a rather free aryl-OH group. This explains the higher stability of the solid complexes as compared to the solutions. The nickel complexes **2a**,**b**, at a slower rate also the palladium complex **5a**, decompose in $CDCl_3$ solution at room temperature via dismutation to $M^{2+}X^{-}{}_2$ salts (E = Ni, Pd; $X^- = SbF_6^-$, BF_4^-) and nickel or palladium bis($P^{\cap}O^-$ -chelates), which by lack of suitable ligands may coordinate to M^{2+} as bidentate $(\mu\text{-O})_2$-chelate ligands. The much higher thermal stability of methallylpalladium phosphinophenol acetates is due to tautomeric structures (methallylpalladium phosphinophenolate acetic acid conjugates). Solutions of the cationic (meth)allylnickel and -palladium phosphinophenol complexes with noncoordinating anions are more (Ni^{II}) or less (Pd^{II}) active catalysts converting ethylene to lower olefins or butenes, respectively. The selectivity is lower than in the case of cationic β-ketophosphine nickel or palladium catalysts and can be compared with that of the oxygen-free methallylnickel(triphenylphosphine) hexafluorophosphate catalyst, indicating that oxygen of the OH group is a weaker donor than carbonyl-oxygen. The labile O-coordination destabilizes the Ni−C bond and allows much faster insertions, even insertion of 1-butenes, which gives rise to branched olefins, in particular 2-ethyl-butene-1 and small amounts of 3-methylpentene-1. The formation of butenes-2 and hexenes-2 or -3 may also be explained in this way, but the formation of larger amounts of 3-methylpentene-2, probably by catalytic isomerization of 2-ethyl-butene-1 and 3-methylpentene-1, accounts also for a considerable contribution of metal- or proton-catalyzed double-bond migrations of 1-butene and 1-hexene to the thermodynamically more stable internal olefins, finally confirmed by the double-bond isomerization of 1-hexene and *cis*-hexene-2 by heating in the presence of **2a**.

Experimental Section

General Considerations. All reactions were carried out under dry argon, using Schlenk techniques and freshly distilled ketyl-dried solvents. The phosphinophenols **1a**,**b**,[17,26] methallylnickel bromide,[27] and methallylpalladium acetate[28] were prepared according to known procedures; other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. NMR spectra were recorded on a ARX300 multinuclear FT-NMR spectrometer (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz unless indicated otherwise. Shift references are tetramethylsilane for ^1H and ^{13}C and H_3PO_4 (85%) for ^{31}P. Coupling constants refer to J_{HH} in ^1H and J_{PC} in ^{13}C NMR data, and τ means a pseudotriplet appearance of ^{13}C signals for **7a** by coupling with two phosphorus nuclei, $N = |J + J'|$. Assignment numbers are given in Schemes 1 and 2. Proton or carbon nuclei of phenyl or cyclohexyl groups are denoted i, o, m, p and α, β, γ, δ, respectively. Assignments are supported by DEPT and CH-COSY experiments, and allyl proton coupling constants in **5a** were determined by ^{31}P decoupling and low-temperature measurements. IR spectra were measured on a System 2000 FTIR spectrometer (Perkin-Elmer), mass spectra on a AMD40 single-focusing mass spectrometer (Intectra). Melting points were determined by use of a Sanyo Gallenkamp melting point apparatus. TG/DTA

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were carried out with SETARAM TGDTA 92-16 (5 K/min) under argon and elemental analyses with a CHNS-932 analyzer from LECO using standard conditions. Analyses of oligomers were performed by GC (Siemens Sichromat 1-4), using a 50 m Cp-Sil-Pona-CP column, vaporization temperature of 250 °C, and temperature program of 30−250 °C, 20 min isotherm, 20 °C/min, and comparison with a reference mixture or a Hewlett-Packard 5890 gas chromatograph, 30 m HP-5 column (cross-linked 5% PhMe silicone), 30−180 °C, 20 min isotherm, 6 °C/min. Percentages given refer to mass % (uncorrected).

Nickel Complexes. (2-Diphenylphosphinophenol)(2-methylallyl)nickel Hexafluoroantimonate, 2a. A solution of **1a** (835 mg, 3.0 mmol) in CH_2Cl_2 (15 mL) was added to the red solution of $(methallylNiBr)_2$ (580 mg, 1.50 mmol) in CH_2Cl_2 (15 mL) and stirred for 1 h at about 20 °C. The resulting orange solution was added to a suspension of $AgSbF_6$ (1.035 g, 3.0 mmol) in CH_2Cl_2 (15 mL), stirred for 10 min, and filtered after cooling to −20 °C. The solvent of the filtrate was removed in a vacuum, and the residue was crystallized from CH_2Cl_2/hexane, yielding 950 mg (61%) of **2a** as a dark red solid, mp 70° C (dec). IR (Nujol): $\bar{\nu}$ 3468 (s br), 3208 (s br) OH, 1579 (m), 1443 (s), 1100 (s), 666 (vs), 639 cm^{-1} (s). The substance decomposes at 25 °C in solution within an hour and displays broadened NMR signals. ^1H NMR ($CDCl_3$): δ 2.12 (br) and 2.19 (s, 4 H, CH_3, 1′-H), 3.00 (br, 1 H, 2′-H), 3.34 (br, 1 H, 3′-H), 4.72 (br, 1 H, 4′-H), 7.18 (t, J = 7.3 Hz, 1 H, aryl), 7.37−7.60 (m, aryl), 9.78 (vbr, 1 H, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8 (after decomposition δ 19.1). Anal. Calcd for $C_{22}H_{22}F_6NiOPSb$ (627.82): C, 42.09; H, 3.53. Found: C, 41.91; H, 3.84.

(2-Dicyclohexylphosphinophenol)(2-methylallyl)nickel Hexafluoroantimonate, 2b. Solutions of **1b** (581 mg, 2.0 mmol) and of $(methallylNiBr)_2$ (387 mg, 1.0 mmol) in CH_2Cl_2 (each 15 mL) were united and stirred for 1 h at ambient temperature. The resulting orange solution was added to a suspension of $AgSbF_6$ (690 mg, 2.0 mmol) in CH_2Cl_2 (15 mL), stirred for 10 min, and worked up as reported for **2a** to give 550 mg (52%) of **2b** as a dark red powder. IR (Nujol): $\bar{\nu}$ 3461 (m br), 3265 (s br), 1597 (w), 1578 (m), 761 (s), 667 (vs), 639 cm^{-1} (s). ^1H NMR ($CDCl_3$): δ 0.80−2.35 (m, 26 H, Cy, CH_3, 1′-H), 2.90 (s, br, 1 H, 2′-H), 3.29 (s, br, 1 H, 3′-H), 4.65 (s, br, 1 H, 4′-H), 7.00−7.55 (m, 4 H, aryl), 9.39 (s, br, 1 H, OH). ^{13}C NMR (DEPT, $CDCl_3$): δ 23.2 (C-*d*), 25.9 (2 C-δ), 26.3−26.7 (4 C-γ,γ'), 28.4, 28.6 (2 C-β), 29.3 (d, ^2J = 3.8 Hz, C-β'), 29.5 (d, ^2J = 4.2 Hz, C-β'), 33.1 (d, ^1J = 26.1 Hz, C-α), 33.5 (d, ^1J = 26.0 Hz, C-α), 42.6 (d, J = 4.1 Hz, C-*a*), 74.9 (d, J = 16.4 Hz, C-*c*), 112.6 (d, ^1J = 31.2 Hz, C-2), 116.0 (d, ^3J = 5.4 Hz, C-6), 124.4 (d, J = 4.5 Hz, C-4), 128.4 (C-*b*), 131.9, 134.1 (C-3, C-5), 160.3 (d, ^2J = 14.3 Hz, C-1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.7. Anal. Calcd for $C_{22}H_{34}F_6NiOPSb$ (639.91): C, 41.29, H, 5.36. Found: C, 41.41; H, 5.34.

{Tris[*μ*-*O*,*O*′-*cis*-bis(2-diphenylphosphinophenolato-*P*,*O*)nickel(II)]}nickel(II) Hexafluoroantimonate $CDCl_3$ Solvate, 3a, and {Tris[*μ*-*O*,*O*′-*cis*-bis(2-dicyclohexylphosphinophenolato-*P*,*O*)nickel(II)]}nickel(II) Hexafluoroantimonate $CDCl_3$ Solvate, 3b. The solution of **2a** or **2b** in $CDCl_3$ decomposes slowly at room temperature. Slow diffusion of the solvent through a septum provided single crystals of **3a** and **3b**, respectively, which are stable to air and moisture; yield not determined.[19]

Palladium Complexes. (2-Diphenylphosphinophenol)(allyl)palladium Hexafluoroantimonate, 4a. A solution of **1a** (343 mg, 1.234 mmol) in CH_2Cl_2 (10 mL) was added at −40 °C to a solution of $(allylPdCl)_2$ (226 mg, 1.235 mmol) in CH_2Cl_2 (15 mL) and was then allowed to warm to room temperature (ca. 1.5 h). The yellow solution was cooled to −60 °C, and a suspension of $AgSbF_6$ (424.5 mg, 1.235 mmol) in CH_2Cl_2 (5 mL) was added. The resulting colorless turbid mixture was kept overnight at −60 °C, then it was allowed to warm to room temperature and filtered. Hexane was added to the filtrate until precipitation was starting. The mixture was placed in a fridge (−30 °C) overnight, then it was filtered and the solid dried in a vacuum to give 0.53 g (65%) of **4a**·0.5CH_2Cl_2, soluble in CH_2Cl_2 or THF. A single crystal taken from the mother liquor was found to include 1 CH_2Cl_2/**4a**, allyl group strongly disordered. Recrystallization from THF/hexane provided single crystals of **4a**·THF, which allowed the crystal structure analysis. ^1H NMR ($CDCl_3$/CD_2Cl_2, 25 °C): δ 3.05 (d br, J = 8.7 Hz, 1 H, 1′-H), 4.02 (s br, 1 H, 2′-H), 4.23 (vbr, 1 H, 3′-H), 5.42 (s br, 1 H, 4′-H), 5.82 ("sept", 1 H, 5′-H), 7.14 (tm, 1 H, aryl), 7.30−7.40 (m, 2 H, aryl), 7.43−7.58 (m, 11 H, aryl), 9.68 (s br, 1 H, OH). ^{13}C NMR (CD_2Cl_2): δ 51.7 (br, C-*a*), 86.3 (d br, $J \approx$ 12 Hz, C-*c*), 115.3 (d, ^1J = 43.0 Hz, C-2), 117.0 (d, ^3J = 6.0 Hz, C-4), 120.8 (br, C-*b*), 124.7 (d, ^3J = 5.5 Hz, C-6), 129.9 (d, ^3J = 11.4 Hz, C-*m*), 132.2 (d, ^4J = 2.6 Hz, C-*p*), 133.4 (d, ^2J = 14.0 Hz, C-*o*), 134.6 (s, C-3), 135.1 (d, ^4J = 1.6 Hz, C-5), 159.5 (d, ^2J = 15.3 Hz, C-1); C-*i* uncertain. $^{31}P\{^1H\}$ NMR ($CDCl_3$/CD_2Cl_2): δ 25.3. Anal. Calcd for $C_{21}H_{20}OPPdSbF_6$·0.5CH_2Cl_2 (703.99): C, 36.68; H, 3.01. Found: C, 36.60; H, 3.05.

(2-Diphenylphosphinophenol)(allyl)palladium Tetrafluoroborate, 5a, and Decomposition Products. The compound was prepared by the same procedure as **4a** using 562 mg (2.02 mmol) of **1a** and 370 mg (2.02 mmol) of $(allylPdCl)_2$ but followed by reaction with $AgBF_4$ (393 mg, 2.02 mmol) instead of $AgSbF_6$. Workup gave 0.65 g (63%) of **5a**. (A second, somewhat less pure slightly gray and oily portion (0.35 g) was isolated from the concentrated mother liquor; total yield 96%.) The compound is soluble in CH_2Cl_2 or THF with deposition of a thin layer of black palladium at the glass wall. Recrystallization from THF/hexane furnished the dinuclear complex **6a**·THF.[19] Solid **5a** decomposes at 153−165 °C (at 165 °C dark oil). DTA/TG: endothermic peaks at 175 (s), 210, 230 (m) °C, exothermic peak 192/195 °C, mass loss 50−120 1.8%, 120−175 9% (-allyl calc 8%), >175 °C further decay. ^1H NMR (CH-COSY, $CDCl_3$, 25 °C): δ 3.00 (s, $br_{1/2}$ = 32 Hz, 1 H, 1′-H), 3.97 (s, $br_{1/2}$ = 35 Hz, 1 H, 2′-H), 4.25 (dd, $^3J_{trans}$ = 14.4, J_{PH} = 8.5 Hz, 1 H, 3′-H), 5.53 (dd, $^3J_{cis}$ = 7.8, J_{PH} = 5.8 Hz, 1 H, 4′-H), 5.79 (m, 1 H, 5′−H), 7.11 (m, $^3J \approx$ 7.7, 5.8, 2.4 Hz, 1 H, 6-H), 7.31 (tm, $^3J_{PH}$ = 8.9 Hz, ^3J = 7.7, ^4J = 1.4, J = 0.6 Hz, 1 H, 3-H), 7.36−7.58 (m br, 12 H, aryl), 11.16 (s br, 1 H, OH). ^1H NMR ($CDCl_3$, −30 °C, [{^{31}P}]): δ 3.04 (d, $^3J_{trans}$ = 11.7 [11.9] Hz, 1 H, 1′-H), 4.03 (d, $^3J_{cis}$ = 5.5 [6.4] Hz, 1 H, 2′-H), 4.24 (dd, $^3J_{trans}$ = 14.2 [14.3], J_{PH} = 8.5 Hz, 1 H, 3′-H), 5.52 ("t", $^3J_{cis}$ = [7.8], J_{PH} = 3.8 Hz, 1 H, 4′-H). ^{13}C NMR (CH-COSY, $CDCl_3$): δ 50.5 (C-*a*), 86.9 (d, J = 26.3 Hz, C-*c*), 114.6 (d, ^1J = 44.0 Hz, C-2), 117.4 (d, ^3J = 6.1 Hz, C-4), 119.9 (d, J = 4.1 Hz, C-*b*), 123.8 (d, ^3J = 5.7 Hz, C-6), 129.5 (d, ^3J = 11.4 Hz, C-*m*), 131.8 (d, ^4J = 2.6 Hz, C-*p*), 132.9 (d, ^2J = 14.0 Hz, C-*o*), 133.7 (d, ^2J = 1.7 Hz, C-3), 134.7 (d, ^4J = 1.8 Hz, C-5), 159.93 (d, ^2J = 15.9 Hz, C-1); C-*i* uncertain. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.5. Anal. Calcd for $C_{21}H_{20}OPPdBF_4$ (512.58): C, 49.21; H, 3.93. Found: C, 48.91; H, 4.06.

Decomposition product (after 2 weeks) ^1H NMR ($CDCl_3$): δ 6.83 (m, 1 H, aryl), 7.04 (dd br, 1 H, aryl), 7.21 (m, 1 H, aryl), 7.23−7.55 (m, 11 H, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.4.

Crystallization of **5a** from THF/water gave **7a**, containing THF. ^1H NMR ($CDCl_3$): δ 6.45 (tm, ^3J = 6.8, 7.8, $^4J + {}^4J_{PH}$ < 2 Hz, 1 H, 4-H), 6.78 (ddd, $^3J_{PH}$ = 9.3, ^3J = 7.8, ^4J = 1.4 Hz, 1 H, 3-H), 7.02 (dd, ^3J = 8.5, $^4J_{PH}$ = 4.5 Hz, 1 H, 6-H), 7.05−7.12 (m, 4 H, Ph), 7.19 (tm, ^3J = 8.5, 6.8, $^4J_{PH}$ = 2.6, ^4J = 1.4 Hz, 1 H, 5-H), 7.24−7.35 (m, 6 H, Ph). ^{13}C NMR (CD_2Cl_2): δ 116.2 (τ, N = 8.0 Hz, C-4), 117.5 (m_{ABX}, N = 55.4 Hz, C-2), 119.3 (τ, N = 18.1 Hz, C-6), 128.7 (m_{ABX}, N = 57.0 Hz, C-*i*), 129.1 (τ, N = 10.7 Hz, C-*m*), 131.5 (s, C-*p*), 132.4 (s, C-3), 133.3 (τ, N = 12.5 Hz, C-*o*), 134.4 (s, C-5), 176.7 (τ, N = 13.7 Hz, C-1). ^{31}P NMR ($CDCl_3$): δ 44.5. The NMR data agree with those of **7a** synthesized according to ref 20 from **1a**, Na_2PdCl_4, and soda in methanol.

(2-Diphenylphosphinophenolate)(2-methylallyl)palladium(II) Acetic Acid, 8a. A solution of di-*μ*-acetatobis[2-

methylallylpalladium(II)] (317 mg, 0.72 mmol) in benzene (5 mL) was added to a solution of **1a** (400 mg, 1.44 mmol) in benzene (10 mL) and heated for 3 h to 40 °C, and **8a** was precipitated by addition of *n*-hexane (15 mL). Separation and drying in a vacuum gave 264.4 mg (73%) of a yellow powder of **8a**, mp >220 °C. ^{1}H NMR (C_6D_6): δ 1.50 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3CO), 2.50 (s vbr, 2 H, 1′-H, 2′-H), 3.39 (d, J_{PH} = 8.9 Hz, 1 H, 3′-H), 4.65 (d, J_{PH} = 5.9 Hz, 1 H, 4′-H), 6.50 (tm, ^3J = 7.4, 7 Hz, 1 H, 4-H), 6.95−7.05 (m, 6 H, Ph), 7.10−7.25 (m, 2 H, 3-H, 5-H), 7.40−7.50 (m, 4 H, Ph), 7.63 (dd, $J \approx 7$, 5 Hz, 1 H, 6-H), 13.09 (s br, O−H···O). ^{13}C NMR (C_6D_6): δ 22.0, 174.0 (acetic acid); 24.0 (CH_3), 48.9 (C-*a*), 77.0 (d, J = 31.1 Hz, C-*c*), 116.6 (d, ^1J = 51.0 Hz, C-2), 117.2 (d, ^3J = 6.6 Hz, C-4), 121.5 (d, ^3J = 8.2 Hz, C-6), 129.6 (d, ^3J = 10.6 Hz, C-*m*), 131.0 (d, ^4J = 1.9 Hz, C-*p*), 133.4 (d, J = 4.7 Hz, C-*b*), 133.9 (d, ^2J = 13.1 Hz, C-*o*), 134.1 (C-3), 134.4 (d, ^1J = 46.0 Hz, C-*i*), 134.9 (C-5), 177.2 (d, ^2J = 21.2 Hz, C-1). ^{31}P{^{1}H} NMR: δ (C_6D_6) 31.7.

(2-Dicyclohexylphosphinophenolate)(2-methylallyl)-palladium(II) Acetic Acid, 8b. A solution of di-μ-acetatobis-[2-methylallylpalladium(II)] (403 mg, 0.91 mmol) in benzene (5 mL) was added to a solution of **1b** (530 mg, 1.83 mmol) in benzene (10 mL), heated for 3 h, and allowed to cool to room temperature. Petroleum ether (15 mL) was added, and after 2 h the precipitate was separated, washed with recondensed solvent, and dried in a vacuum (8 h, 10^{-4} Torr) to give 332 mg (71%) of a yellow powder of **8b**, mp > 220 °C. IR (Nujol): $\bar{\nu}$ ca. 2500 (br w), 1749 (w), 1707 (s) cm^{-1} (m). ^{1}H NMR ($CDCl_3$): δ 1.02−1.41 (m, 10 H, Cy), 1.62−1.87 (m, 8 H, Cy), 1.90−2.20 (m, 4 H, Cy), 1.95 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3CO), 2.33 (s vbr, 1 H, 1′−H), 3.30 (s vbr, 1 H, 2′-H), 3.51 (d, J_{PH} = 8.5 Hz, 1 H, 3′-H), 4.55 (d, J_{PH} = 5.5 Hz, 1 H; 4′-H), 6.57 (tm, ^3J = 7.5, 7.1, $^4J_{PH}$ = 1.4, ^4J = 0.9 Hz, 1 H, 4-H), 6.97 (ddd, ^3J = 8.4, $^4J_{PH}$ = 4.9, ^4J = 0.9 Hz, 1 H, 6-H), 7.12−7.23 (m, 2 H, 3-H, 5-H), 12.35 (br, 1 H, OH). ^{13}C NMR ($CDCl_3$, CH-COSY): δ 21.2, 174.8 (acetic acid); 23.9 (CH_3), 26.1 (C-δ), 26.7 (d, ^3J = 11.2 Hz, C-γ), 26.8 (d, ^3J = 14.0 Hz, C-γ'), 28.6 (C-β), 29.8 (d, ^2J = 5.2 Hz, C-β'), 34.5 (d br, ^1J = 23 Hz, C-α), 43.0 (C-*a*), 76.4 (d, J = 31.3 Hz, C-*c*), 114.0 (d, ^1J = 43.3 Hz, C-2), 115.3 (d, ^3J = 5.9 Hz, C-4), 119.4 (d, ^3J = 7.2 Hz, C-6), 130.8 (d, J = 4.4 Hz, C-*b*), 131.7 (C-3), 132.9 (d, ^4J = 1.5 Hz, C-5), 176.4 (d, ^2J = 17.7 Hz, C-1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 52.5. Anal. Calcd for $C_{24}H_{37}O_3PPd$ (510.95): C, 56.42; H, 7.30. Found: C, 57.13; H, 7.46.

(2-Diphenylphosphinophenolate)(2-methylallyl)palladium(II), 9a. 8a (260 mg, 0.52 mmol) was heated for 6 h to 130 °C at 2 × 10^{-4} Torr, and the residue was extracted with toluene. Removal of the solvent (8 h, 10^{-4} Torr) furnished 153 mg (67%) of pale yellow **9a**, mp >220 °C. DTA/TG: exothermic peak at 206.5 °C, decomposition begins at 130 °C, strongly at 175−206.5 °C, mass loss 12.5% (C_4H_7), further decay > 270 °C. ^{1}H NMR (C_6D_6): δ 1.39 (s, 3 H, CH_3), 2.03 (s br, 1 H, 1′-H), 2.93 (s br, 1 H, 2′-H), 3.22 (d, J_{PH} = 8.9 Hz, 1 H, 3′-H), 4.27 (d, J_{PH} = 5.8 Hz, 1 H, 4′-H), 6.54 (tm, 1 H, 4-H), 6.90−7.08 (br, 6 H, Ph), 7.18 (td, 1 H, 3-H), 7.24 (ddt, 1 H, 5-H), 7.42 (dd br, 1 H, 6-H), 7.45−7.60 (br, 4 H, Ph). ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3 H, CH_3), 2.48 (s br, 1 H, 1′-H), 3.39 (s br, 1 H, 2′-H), 3.57 (d, J_{PH} = 9.0 Hz, 1 H, 3′-H), 4.59 (d, J_{PH} = 5.6 Hz, 1 H, 4′-H), 6.54 (tt, ^3J = 7.6, 6.8, $^4J_{PH}$ = 1.6, ^4J = 0.9 Hz, 1 H, 4-H), 6.98 (ddd, ^3J = 8.5, $^4J_{PH}$ = 6.2, ^4J = 0.9 Hz, 1 H, 6-H), 7.10 (ddd, $^3J_{PH}$ = 9.5, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, 3-H), 7.21 (ddt, ^3J = 8.5, 6.8, ^4J = 1.6, $^5J_{PH}$ = 1.4 Hz, 1 H, 5-H), 7.32−7.43 (vbr, 6 H, Ph), 7.47−7.60 (vbr, 4 H, Ph). ^{13}C NMR ($CDCl_3$): δ 23.9 (CH_3), 48.3 (d, J = 3.1 Hz, C-*a*), 74.8 (d, J = 31.7 Hz, C-*c*), 115.2 (d, ^3J = 6.0 Hz, C-4), 115.3 (d, ^1J = 52.1 Hz, C-2), 120.1 (d, ^3J = 8.3 Hz, C-6), 128.65 (d, ^3J = 10.9 Hz, C-*m*), 128.7 (d, ^3J = 10.7 Hz, C-*m*′), 130.25 (d, ^4J = 2.6 Hz, C-*p*), 130.34 (d, ^4J = 2.6 Hz, C-*p*′), 132.8 (partly superimposed, d, $^1J \approx 45$ Hz, C-*i*), 132.9 (d, J = 4.8 Hz, C-*b*), 133.8 (d, ^2J = 13.1 Hz, C-*o*), 133.9 (d, ^2J = 13.8 Hz, C-*o*′), 133.1 (C-3), 133.6 (d, ^4J = 1.8 Hz, C-5), 177.4 (d, ^2J = 21.9 Hz, C-1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.2. Anal. Calcd for $C_{22}H_{21}OPPd$ (438.80): C, 60.22; H, 4.82. Found: C, 60.81; H, 5.27.

(2-Dicyclohexylphosphinophenolate)(2-methylallyl)-palladium(II), 9b. 8b (200 mg, 0.39 mmol) was heated to 120 °C at 2.5 × 10^{-4} Torr for 6 h. The residue was extracted with toluene (10 mL), and the solvent was removed (8 h, 10^{-4} Torr) to give 108 mg (61%) of pale yellow **9b**, mp >220 °C. DTA/TG: endothermic peaks at 149.2, 181.9 (m), 242.2 (vs) °C, exothermic peak ca. 215 °C, mass loss starting > 185 °C, at 250 °C ca. 7.8%, further decay >255 °C. ^{1}H NMR ($CDCl_3$): δ 1.05−1.40 (m, 12 H, Cy), 1.60−2.15 (m, 10 H, Cy), 1.94 (s, 3 H, CH_3), 2.31 (s br, 1 H, 1′-H), 3.27 (s br, 1 H, 2′-H), 3.49 (d, J_{PH} = 8.5 Hz, 1 H, 3′-H), 4.51 (dd, J_{PH} = 5.4, J = 1.6 Hz, 1 H, 4′-H), 6.52 (tt, $^3J \approx 7.3$, $^4J_{PH}$ = 1.4, ^4J = 0.9 Hz, 1 H, 4-H), 6.91 (ddd, ^3J = 8.5, $^4J_{PH}$ = 4.9, ^4J = 0.9 Hz, 1 H, 6-H), 7.10−7.21 (m, 2 H, 3-H, 5-H). ^{13}C NMR ($CDCl_3$): δ 23.9 (CH_3), 26.1 (C-δ), 26.7 (d, ^3J = 10.9 Hz, C-γ), 26.8 (d, ^3J = 14.0 Hz, C-γ'), 28.6 (C-β), 29.8 (d br, ^2J = 9.2 Hz, C-β'), 34.4 (d br, ^1J = 29.4 Hz, C-α), 34.7 (d br, ^1J = 26.8 Hz, C-α′), 42.8 (C-*a*), 75.8 (d, J = 30.3 Hz, C-*c*), 113.8 (d, ^1J = 43.4 Hz, C-2), 114.5 (d, ^3J = 5.9 Hz, C-4), 119.6 (d, ^3J = 7.8 Hz, C-6), 130.8 (d, J = 4.7 Hz, C-*b*), 131.7, 132.9 (2s, C-3, C-5), 177.8 (d, ^2J = 17.8 Hz, C-1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.3. Anal. Calcd for $C_{22}H_{33}OPPd$ (450.90): C, 58.60; H, 7.38. Found: C, 59.15; H, 8.03.

Crystal Data and Structure Determination of 4a·THF. A suitable colorless crystal of **4a**·THF was mounted under argon inside a thin-wall glass capillary, transferred onto a Bruker/Nonius Apex-X8 diffractometer, and cooled in a stream of cold dinitrogen to −60 °C. Diffraction data were measured using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection, cell refinement, and data reduction were made using APEX2, Smart, Saint, and SADABS software.[29] The cell was established to be primitive orthorhombic with a = 8.7047(2), b = 11.4662(2), and c = 27.3342(7) Å; space group $P2_12_12_1$: The structure was solved by direct methods (SHELXS-97[30]) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97).[30] The positions of the H atoms were calculated assuming idealized geometries and refined using riding models with U(H) = 1.2·U(C). During the refinement process, racemic twinning became evident with a ratio of 0.88/0.22 for the two components. Anisotropic refinement of all the atoms but H yielded R1(F) = 0.0315 (7914 data with $I_o > 2\sigma(I_o)$) and wR2(F^2) = 0.0778 (all data).

Crystallographic data are given in Table 4, and selected bond lengths and angles in Table 1.

Oligomerization of Ethylene. The single-component (pre)-catalyst (quantities of **2a**, **2b**, or **5a**, see Table 2) was added to toluene (20 mL), and the suspension was transferred to a steel autoclave (75 mL), equipped with a Teflon-coated magnetic stirrer, gas (argon or C_2H_4) and sample inlet valves, a safety diaphragm, and a manometer or HEJU pressure sensor (1−100 bar, Juchheim) for pressure registration. Then ethylene was added. In the case of **2a** and **2b** the strongly exothermic reaction of ethylene started during pressurizing the autoclave. Addition of ethylene was stopped after about 2.5 min, and the mixture was allowed to stir for 1 h without heating. The maximum pressure observed after 2 min was ca. 15 bar; the final pressure was ca. 3 bar. In the case of **5a** ethylene was added until a pressure of 50 bar, then the autoclave was closed, placed into a preheated bath, and heated overnight to 70 or 100 °C (see Table 2). The autoclave was cooled to 0 °C, unconverted ethylene was allowed to escape, and gaseous products were condensed in a cooling trap (−78 °C). After cooling to −50 °C the contents of the autoclave were transferred to a flask. The oligomers were flash distilled (80−

(29) *Apex2, Smart, Saint,* and *SADABS*; Bruker AXS Inc.: Madison, WI, 2003.

(30) (a) Sheldrick, G. M. *SHELXS-97*, *Program for the Solution of Crystal Structures*; Universität Göttingen, 1997. (b) Sheldrick, G. M. *SHELXL-97*, *Program for Crystal Structure Refinement*; Universität Göttingen, 1997.

Table 4. Selected Data Collection, Refinement, and Crystallographic Data for 4a·THF

empirical formula	$C_{25}H_{28}F_6O_2PPdSb$
fw/g·mol^{-1}	733.59
color, habit	colorless, plate
temp/K	213(2)
cryst size/mm	0.31 × 0.17 × 0.10
cryst syst	orthorhombic
space group	$P2_12_12_1$
a/Å	8.7047(2)
b/Å	11.4662(2)
c/Å	27.3342(7)
V/Å^3	2728.2(1)
Z	4
density(calc)/g·cm^{-3}	1.786
absorb coeff μ/mm^{-1}	1.770
range of data collection/deg	$4.8 \le 2\theta \le 60.0$
index range	$-13 \le h \le 12$ $-17 \le k \le 9$ $-40 \le l \le 41$
no. of reflns collected	43 142
no. of indep reflns, R_{int}	10 105; 0.0312
reflections $I_o \ge 2\sigma(I_o)$	7918
no. of params/restraints	326/0
R1(F)[a] (7918 data)	0.0315
wR2(F^2)[b]	0.0778
GOF	1.054
largest residual electron-density peaks/e Å^{-3}	+0.716/−0.425

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w(|F_o^2| - |F_c^2|/\sum w(F_o^2)^2)^{-1/2}$ with $w = 1/[(\sigma^2(F_o^2) + (0.0395P)^2]^2$; $P = (F_o^2 + 2F_c^2)/3$.

100 °C/1 Torr) into a cooling trap (−196 °C) and analyzed by GC. Results are given in Tables 2 and 3. (The maximum turnover frequency (TOF_{max}) in experiments 3 and 4 was determined from the slope of the range with the steepest roughly linear pressure decrease.)

Isomerization and Dimerization of Hexene-1. 2a (54.8 mg, 100 μmol) was added to hexene-1 (10 mL), and the mixture was refluxed for 15 h and flash distilled. The mixture was composed of hexene isomers (total 93.4%), mainly *trans*-hexene-2 (60.7%), *cis*-hexene-2 (23.0), *cis*- and *trans*-hexene-3 (5.6%), and hexene-1 (3.9%), and of 12 dodecene isomers (total 6.6%, thereof two isomers each 1.2% and six isomers each ca. 0.6%).

Isomerization and Dimerization of *cis*-Hexene-2. Treatment of hexene-2 (10 mL) with **2a** (55 mg, 100 μmol) as above afforded mainly *trans*-hexene-2 (73.6%) along with residual *cis*-hexene-2 (15.5%), with hexene-1 or 2-methylpentene-1 (1.4%) and 25 dodecene isomers (total 8.2%).

(Co)Oligomerization of Ethylene in Hexene-1. The reaction was performed as described above for the oligomerization of ethylene (14.6 g) with **2a** (100 μmol) except that a mixture of toluene and hexene-1 (each 10 mL) was used as solvent. The total conversion of ethylene was 59%. GC analysis of the flash distillate and correction by C4 trapped at −78 °C revealed 45.8% butenes (15.2, 21.5, 9.1%), 51.4% hexenes (33.5% hexene-1, 9.6% *trans*-hexene-2, 2.7% *cis*-hexene-2), corresponding to an increase by 1.3%, 2.1% octenes, 0.3% decenes, 0.1% dodecenes, and 0.3% tetradecenes.

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Supporting Information Available: Tables of crystal structure parameters and details of data collection, structure solution and refinement, atomic coordinates, isotropic as well as anisotropic displacement parameters, and bond lengths and angles of **4a**·THF, figure of the molecular structure with anion, and figure of the package of **4a**·THF in the crystal. This material is available free of charge via the Internet at http://pubs.acs.org.

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