Articles

Ligand and Solvent Effects in the Alternating Copolymerization of Carbon Monoxide and Olefins by Palladium−Diphosphine Catalysis

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Received August 9, 2001

The substitution of two hydrogen atoms by methyl groups in the 1,2 positions of 1,2-bis(diphenylphosphino)ethane (dppe) gives *meso*- and *rac*-2,3-bis(diphenylphosphino)butane (*meso*-2,3-dppb and *rac*-2,3-dppb). The corresponding Pd(II) complexes $Pd(OTs)_2$(*meso*-2,3-dppb) and $Pd(OTs)_2$(*rac*-2,3-dppb) are effective catalyst precursors for the alternating copolymerization and terpolymerization of carbon monoxide with ethene and ethene/propene in MeOH with productivities that are higher than those of the unsubstituted dppe catalyst $Pd(OTs)_2$(dppe) even by a factor of 10 (OTs = *p*-toluenesulfonate). It has been found that the low productivity of the dppe-based catalyst in MeOH is due to the autoionization of the precursor $Pd(OAc)_2$(dppe) in MeOH to give the catalytically inactive bis-chelate species $[Pd(dppe)_2](OAc)_2$ and palladium acetate. In an attempt to evaluate and rationalize the effective ligand control on the intrinsic catalytic activity, the methyl complexes $[Pd(Me)(MeCN)(P-P)]PF_6$ have been synthesized and employed in CH_2Cl_2 to catalyze the alternating carbon monoxide/ethene copolymerization. The intrinsic activity of the three precursors decreases in the order [Pd(Me)(MeCN)(*meso*-2,3-dppb)]$^+$ > [Pd(Me)(MeCN)(*rac*-2,3-dppb)]$^+$ > $[Pd(Me)(MeCN)(dppe)]^+$. High-pressure NMR experiments and the determination of activation barriers of migratory insertions agree to indicate the relative stability of the β-chelate ring in $[Pd(CH_2CH_2C(O)Me)(P-P)]^+$ as the factor that controls the copolymerization rate in aprotic solvents. The impact of the different diphosphines on both productivity and intrinsic catalytic activity has been attributed to the different stereochemical rigidity of the Pd(P−P) five-membered metallarings. The β-chelate complexes $[Pd(CH_2CH_2C(O)Me)(P-P)]PF_6$ with diphosphine ligands containing two carbon atoms between the phosphorus donors have been isolated for the first time and employed to study the chain-transfer by protonolysis, which proceeds via the enolate mechanism. It has been shown that the chain-transfer products $[Pd(OH)(P-P)]_2^{2+}$ do not represent a dead end for the alternating CO/ethene copolymerization.

Introduction

Copolymers and terpolymers of carbon monoxide and ethene or ethene/propene are not only low-cost thermoplastics but also polymeric materials characterized by unique chemical and physical properties as well as environmentally friendly nature.[1] Perfectly alternating polyketones are actually photo- and biodegradable, completely impermeable to hydrocarbons, and easily modifiable by various chemical procedures; they can be processed by means of conventional techniques into films, sheets, plates, fibers, and shaped articles for domestic use and for parts in car industry. The rapid and widespread commercialization of polyketones (e.g., Carilon from Shell[1a] and Ketonex from BP[1b]) is hampered, however, by their still imperfect stability, in particular when exposed to high temperature for extended periods or subjected to repeated cycles of melting and solidification. Moreover, the exclusive use of palladium catalysts to achieve high productivity provides inherent drawbacks due to the high cost of this noble metal as well as its tendency to plate out during both catalyst preparation and copolymer workup. Both catalyst composition and material stability can therefore be improved, which is demonstrated also by the continuous discovery of more and more efficient catalysts in different phase variation systems as well as the increasing availability of detailed mechanistic information on the copolymerization process.[2]

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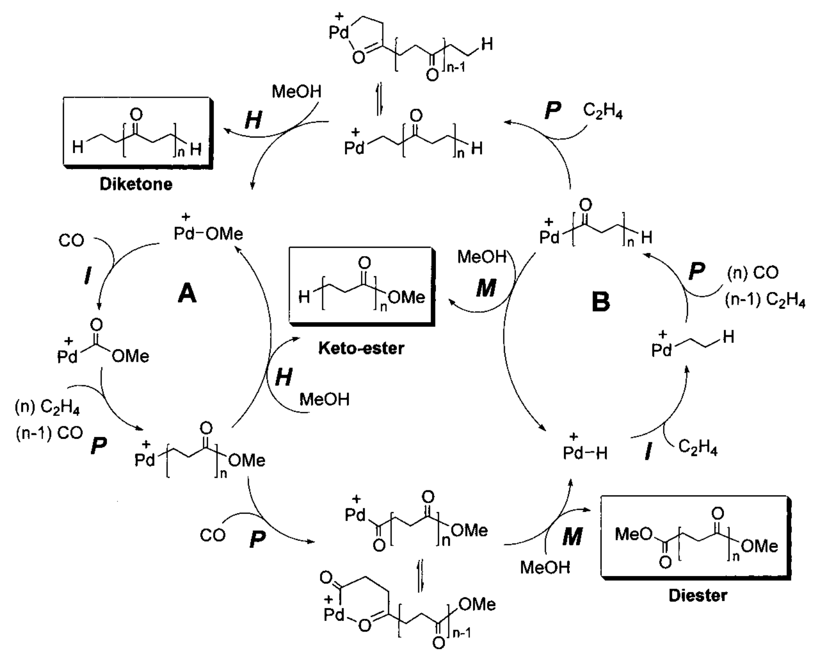
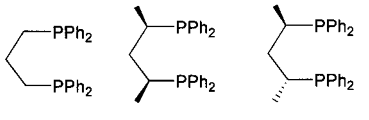
(1) (a) Shell, Carilon Thermoplastic Polymers, Information Sheet, 1994. (b) *Eur. Plast. News* **1995**, *October*, 57. (c) Ash, C. E. *Int. J. Polym. Mater.* **1995**, *30*, 1. (d) Ash, C. E.; Flood, J. E. *ACS Proc.* **1997**, *76*, 110.

10.1021/om010727b CCC: $22.00
Publication on Web 12/11/2001

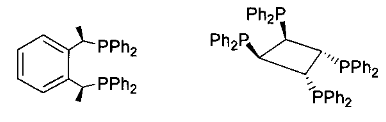
Scheme 1



Scheme 2



Scheme 3



Since the discovery of the effectiveness of palladium-1,3-bis(diphenylphosphino)propane (dppp) catalysts in 1984 at Shell Research,[3] many different types of diphosphine ligands have been designed and successfully employed to catalyze the alternating CO/ethene copolymerization in conjunction with palladium(II) salts through the general mechanism shown in Scheme 1.[2b,c]

Common ligand variations have generally involved substitution(s) at either the phenyl rings or the saturated carbon backbone.[4] With respect to the latter issue, it has been recently found that the introduction of alkyl substituents in the 2-position of the carbon backbone of dppp does not significantly improve the catalytic performance of the corresponding Pd(II) precursors.[4] In contrast, a considerable increase in productivity (kg of polyketone (g of Pd)$^{-1}$) has been obtained by introducing methyl groups in both 1-positions of the dppp backbone, particularly with *R*,*S* (*S*,*R*) stereochemistry as in *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-2,4-bdpp) (Scheme 2).[4] Under comparable experimental conditions, Pd(TFA)$_2$(dppp) (**1**), Pd(TFA)$_2$(*meso*-2,4-bdpp) (**2**), and Pd(TFA)$_2$(*rac*-2,4-bdpp) (**3**) have been found to catalyze the CO/ethene copolymerization in MeOH, yielding 16, 24, and 17 kg of polyketone (g of Pd)$^{-1}$ in 3 h, respectively (TFA = trifluoroacetate).[4]

It was suggested that both electronic and steric factors contribute to increase the productivity of the *meso*-2,4-bdpp **2**,[4a] but a clear-cut explanation of the activity trend exhibited by the palladium(II) precursors **1**−**3** was not given. Accordingly, it was not possible to rule out that the higher activity of **2** might simply be due to a fortuitous combination of electronic and steric effects. Recently, however, other reports have appeared in which palladium(II) catalysts with *meso*-diphosphines have been shown to give higher copolymerization activity as compared to catalysts bearing similar diphosphine ligands but devoid of *meso* structure. Consiglio and coworkers have communicated that cationic [Pd(solvent)$_2$(P−P)]$^{2+}$ complexes are much more active in both CO/propene and CO/ethene copolymerization when the P−P ligand contains methyl groups with either (*S*,*R*) or (*R*,*S*) stereochemistry as in *meso*-2,4-bdpp or *meso*-(C$_6$H$_4$)(CH(Me)PPh$_2$)$_2$ (Scheme 3).[5] It has also been reported that the ligand *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane (*cyclo*-tetraphos) with pseudo-*meso*-structure (Scheme 3) forms palladium(II) catalysts for CO/ethene copolymerization which are more efficient than those with 1,2-bis(diphenylphosphino)ethane (dppe) by 1 order of magnitude.[6]

Intrigued by the increasing evidence of a *meso effect* enhancing the productivity of palladium−diphosphine

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(2) (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (c) Drent, E.; van Broekhoven, J. A. M.; Budzelaar, P. H. M. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Vol. 1, p 333. (d) Sommazzi, A.; Garbassi, G. *Prog. Polym. Sci.* **1997**, *22*, 1547. (e) Nozaki, K.; Hijama, T. *J. Organomet. Chem.* **1999**, *576*, 248. (f) Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2001**, *225*, 35.

(3) (a) Drent, E. Eur. Pat. Appl. 121965A2, 1984; *Chem. Abstr.* **1985**, *102*, 46423. (b) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. *J. Organomet. Chem.* **1991**, *417*, 235.

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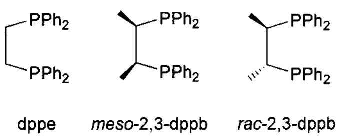
(6) Bianchini, C.; Lee, H. M.; Meli, A.; Oberhauser, W.; Vizza, F.; Brügeller, P.; Haid, R.; Langes, C. *J. Chem. Soc., Chem. Commun.* **2000**, 777.

Scheme 4



catalysts, we decided to verify the existence/generality of such a phenomenon and, if confirmed, to try to understand its chemical underpinnings. Our attention was immediately drawn by the dppe ligand, which differs from dppp by the presence of two CH_2 spacers separating the diphenylphosphino groups and also forms palladium(II) catalysts for the alternating CO/ethene copolymerization that are remarkably less active than those with dppp.[2] Then, we synthesized the diastereomeric ligands *meso*-2,3-bis(diphenylphosphino)butane (*meso*-2,3-dppb) and *rac*-2,3-bis(diphenylphosphino)butane (*rac*-2,3-dppb), which differ from dppe by the presence of two methyl groups in the 1,2 positions of the ligand backbone (Scheme 4).

Various palladium(II) precursors have been prepared with dppe, *rac*-2,3-dppb, and *meso*-2,3-dppb and have been employed to catalyze the copolymerization of CO and ethene in either MeOH or CH_2Cl_2. The existence of a ligand effect, particularly of a favorable *meso effect*, controlling the intrinsic catalytic activity was actually observed also for this series of ligands, and therefore a detailed in situ and model study of the copolymerization process was carried out.

Results

Synthesis and Characterization of $Pd(OAc)_2(P-P)$ (OAc = CH_3CO_2; P−P = dppe, 4; *meso*-2,3-dppb, 5; *rac*-2,3-dppb, 6). The bis-acetate complex $Pd(OAc)_2$(dppe) (**4**) has been synthesized by the reaction of Pd(II) acetate in CH_2Cl_2 with a stoichiometric amount of dppe, while the preparation of the *meso*-2,3-dppb and *rac*-2,3-dppb complexes $Pd(OAc)_2$(*meso*-2,3-dppb) (**5**) and $Pd(OAc)_2$(*rac*-2,3-dppb) (**6**) was best accomplished by scavenging the chloride ligands from the bis-chloride derivatives with silver acetate (Scheme 5). Pure samples of *meso*-2,3-dppb and *rac*-2,3-dppb were obtained by standard organic reactions; *rac*-$(CH_3CH(OMs))_2$ (OMs = mesyl) was isolated by fractional recrystallization of an isomeric mixture of $(CH_3CH(OMs))_2$ and then reacted with $KPPh_2$ to give *rac*-2,3-dppb.

The solid-state structures of **4**, **5**, and **6** have been determined by single-crystal X-ray analyses (Figures 1−3, Tables 1 and 2). In all compounds the palladium center is coordinated by a chelating diphosphine and by two *cis* acetate ions in an almost regular square-planar geometry. No major metrical and angular differences are apparent in the three structures, except for the dihedral angle defined by the atoms C1,1, P1, P2, and C1,3, which is significantly smaller (10.42(15)°) for the *meso* complex **5** than for the other two (**4**, 20.71(67)°; **6**, 19.15(40)°). No particular contact involving the hydrogen atoms of the phenyl rings and the palladium centers has been observed for all compounds. The chelate metallarings are puckered with one axial and one equatorial CMe group for the *meso* diasteromer and two equatorial for the *rac*.

All the bis-acetate complexes are quite stable in CH_2Cl_2, where no autoionization to bis-chelate species was observed (see below).[7] In this solvent, the $^{31}P\{^1H\}$ NMR spectra show singlets at δ 58.9 (**4**), 61.8 (**5**), and 60.5 (**6**) at room temperature. Chelate ring flipping in the *meso* complex is therefore quite rapid to interchange axial and equatorial CMe groups, so that a pseudo-symmetry plane makes the phosphorus and methyl groups magnetically equivalent down to −60 °C. Below this temperature, the dynamic process is frozen out and the molecule, like in the solid state, loses any symmetry (AM pattern with broad singlets at δ 65.6 and 60.4 for

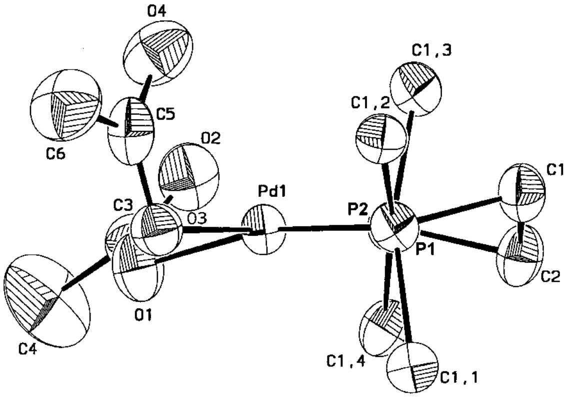


Figure 1. ORTEP drawing of **4**·CH_2Cl_2. Phenyl rings of dppe are omitted for clarity.

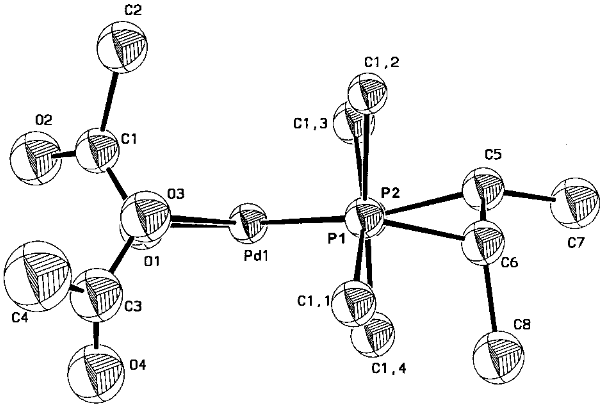


Figure 2. ORTEP drawing of **5**. Phenyl rings of *meso*-2,3-dppb are omitted for clarity.

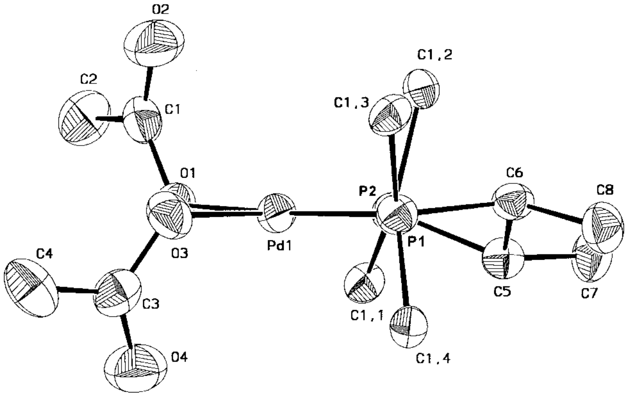


Figure 3. ORTEP drawing of **6**·H_2O. Phenyl rings of *rac*-2,3-dppb are omitted for clarity.

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[7] (a) Jarrett, P. S.; Sadler, P. J. *Inorg. Chem.* **1991**, *30*, 2098. (b) Angulo, I. M.; Bouwman, E.; Lutz, M.; Mul, W. P.; Spek, A. L. *Inorg. Chem.* **2001**, *40*, 2073. (c) Angulo, I. M.; Bouwman, E.; Lok, S. M.; Lutz, M.; Mul, W. P.; Spek, A. L. *Eur. J. Inorg. Chem.* **2001**, 1465.

Scheme 5

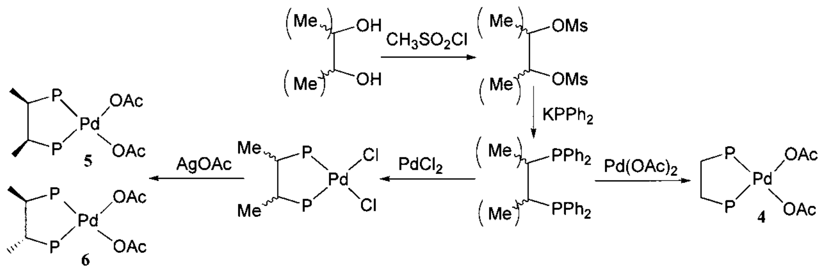

Table 1. Crystal Data and Structure Refinements for $4\cdot CH_2Cl_2$, 5, and $6\cdot H_2O$

	$4\cdot CH_2Cl_2$	5	$6\cdot H_2O$
empirical formula	$C_{31}H_{32}Cl_{2}0_{4}P_{2}Pd$	$C_{32}H_{34}0_{4}P_{2}Pd$	$C_{32}H_{36}0_{5}P_{2}Pd$
fw, g	707.85	650.93	668.99
cryst color	white	pale yellow	white
cryst size, mm	0.55 × 0.25 × 0.20	0.50 × 0.10 × 0.45	0.45 × 0.20 × 0.05
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
unit cell dimens			
a, Å	11.711(2)	8.191(5)	8.798(1)
b, Å	19.818(3)	13.173(2)	15.665(7)
c, Å	14.380(4)	14.404(4)	22.102(5)
α, deg		104.45(2)	
β, deg	112.80(1)	90.80(3)	100.32(1)
γ, deg		94.48(3)	
volume, Å^3	3076.7(19)	1499.5(12)	2996.8(15)
Z	4	2	4
density(calc), g/cm^3	1.528	1.442	1.482
abs coeff, mm^{-1}	0.906	0.760	0.753
F(000)	1440	668	1336
radiation/wavelength, Å	Mo Kα/0.71069	Mo Kα/0.71069	Mo Kα/0.71069
θ range, deg	1.85−22.97	2.85−24.97	2.28−22.97
index ranges	$-12 < h < 11$	$-9 < h < 9$	$-9 < h < 9$
	$0 < k < 21$	$-15 < k < 15$	$0 < k < 17$
	$0 < l < 15$	$0 < l < 17$	$0 < l < 24$
no. of reflns collected	4457	5473	4275
no. of unique reflns	4261 [*R*(int) = 0.0355]	5245 [*R*(int) = 0.0361]	4155 [*R*(int) = 0.0550]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	4261/0/302	5245/0/310	4155/0/314
goodness-of-fit on F^2	0.890	1.049	1.022
final *R* indices [$I > 2\sigma(I)$]			
R_1	0.0556	0.0462	0.0490
wR_2	0.1717	0.1087	0.0931
R indices (all data)			
R_1	0.0845	0.0860	0.1317
wR_2	0.1985	0.1237	0.1126
largest diff peak and hole, e/Å^3	0.936 and −1.331	0.888 and −1.313	0.574 and −0.444

Table 2. Selected Bond Distances (Å) and Angles (deg) for $4\cdot CH_2Cl_2$, 5, and $6\cdot H_2O$

	$4\cdot CH_2Cl_2$	5	$6\cdot H_2O$
Pd−P(1)	2.218(2)	2.221(2)	2.212(2)
Pd−P(2)	2.225(2)	2.221(2)	2.232(2)
Pd−O(1)	2.078(7)	2.072(3)	2.087(5)
Pd−O(3)	2.108(6)	2.075(4)	2.087(5)
P(1)−Pd−P(2)	85.24(9)	85.44(6)	84.81(7)
O(3)−Pd−P(2)	172.67(19)	173.66(10)	94.19(14)
O(1)−Pd−O(3)	89.7(3)	92.95(14)	91.68(19)
O(3)−Pd−P(1)	87.46(19)	89.86(11)	178.95(15)
O(1)−Pd−P(1)	167.8(2)	177.82(11)	89.34(15)
O(1)−Pd−P(2)	97.5(2)	92.42(11)	173.53(15)

P_A and P_M, respectively). The presence of a C_2 axis in the *rac* isomer **6** does not allow one to estimate its molecular flexibility by variable-temperature NMR spectroscopy. It is well known, however, that the presence of the methyl substituents makes the metallaring in **6** more rigid than in the dppe derivative **4**, in which the Pd(dppe) metallaring rapidly interconverts in solution from one chiral twisted conformation to the other.[8]

In conclusion, NMR spectroscopy shows the *meso* complex to adopt in ambient temperature solution a time-averaged preferred conformation containing a pseudo-symmetry plane with two axial and two equatorial phenyl groups located as shown in Scheme 6, while the Pd(*rac*-2,3-dppb) ring would be fixed into a twisted conformation with two pseudoaxial and two pseudo-equatorial phenyl substituents diagonally positioned with respect to the Pd(P−P) plane.[8,9]

To estimate the basicity of the palladium center in **4**, **5**, and **6**, the homologous series of bis-cyanide compounds $Pd(CN)_2$(P−P) (P−P = dppe, *meso*-2,3-dppb, *rac*-2,3-dppb) were prepared by reaction of $Pd(CN)_2$ with the corresponding P−P ligand.[10,11] IR spectroscopy showed

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(8) Fryzuk, M. D.; Bosnich B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

(9) (a) MacNeil, P. A.; Roberts, N. K.; Bosnich B. *J. Am. Chem. Soc.* **1981**, *103*, 2273. (b) Bakos, J.; Tóth, I.; Heil, B.; Szalontai, G.; Párkányi, L.; Fülöp, V. *J. Organomet. Chem.* **1989**, *370*, 263.

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(11) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

Scheme 6

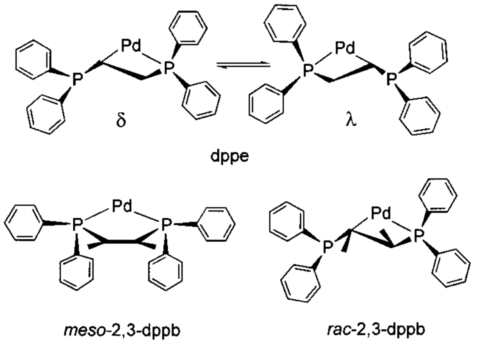

Table 3. $^{31}P\{^1H\}$ NMR and Selected IR Data for $Pd(CN)_2(P-P)$ Complexes

P−P	$^{31}P\{^1H\}$ NMR (δ)	ν (CN) (cm^{-1})[a]
dppe	53.8[b]	2139, 2134
meso-2,3-dppb	59.4[c]	2142, 2134
rac-2,3-dppb	57.6[c]	2138

[a] In KBr. [b] In $CDCl_3$. [c] In DMF-d_7.

the stretching frequency ν(CN) to be invariant within the bis-cyanide complexes (Table 3), which suggests that the electron density at palladium does not appreciably change by substituting either *rac*-2,3-dppb or *meso*-2,3-dppb for dppe.[10,11] This is also consistent with the close $^{31}P\{^1H\}$ NMR chemical shifts of **4**, **5**, and **6**.

Alternating Copolymerization (Terpolymerization) of Ethene (Ethene/Propene) and Carbon Monoxide Catalyzed by $Pd(OTs)_2(P-P)$ in MeOH. Autoclave Experiments. Compounds **4**, **5**, and **6** have been employed as catalyst precursors to copolymerize CO and ethene or ethene/propene in MeOH applying standard experimental conditions for this kind of reaction.[2] *p*-Toluenesulfonic acid (TsOH) and 1,4-benzoquinone (BQ) were employed as protic acid and oxidant, respectively.[2,3]

As shown in Table 4, both **5** and **6** give rise to efficient catalysts for the formation of copolymers and terpolymers with productivities (entries 3, 4 and 7, 8) that are slightly lower than those of the standard catalyst **1**[3,4] but higher than those obtained with the unsubstituted dppe derivative **4** up to *1 order of magnitude*. Notably, the catalyst derived from *meso* **5** is more efficient than that derived from the *rac* diasteromer **6**, in particular for the terpolymerization reaction (6.8 vs 4.5 kg of terpolymer (g of Pd)$^{-1}$).

The overall productivity trend exhibited by **4**, **5**, and **6** reflects a ligand-induced activity decreasing in the order *meso*-2,3-dppb > *rac*-2,3-dppb ≫ dppe, which is analogous to that observed for the dppp-like precursors **1**, **2**, and **3** under comparable conditions.[4]

The polyketones produced with **5** and **6** appeared as fluffy off-white solids, while a gray powder was obtained using **4**. Irrespective of the catalyst precursor, the ^1H and $^{13}C\{^1H\}$ NMR spectra of the copolymers showed the presence of both ketone and ester end groups, limiting viscosity numbers (LVN) in the range 0.25−0.35 dL g^{-1} and average molecular weights (M_n) in the range 6−8 kg mol^{-1} (Table 4).[2]

Alternating Copolymerization of Ethene and Carbon Monoxide Catalyzed by $Pd(OTs)_2(P-P)$ in MeOH. In Situ HPNMR Study. The CO/ethene copolymerization reactions catalyzed by **4**, **5**, and **6** were studied in situ by means of high-pressure NMR spectroscopy (HPNMR) in 10 mm OD sapphire tubes. Mass transfer of gases from the headspace of the 10 mm NMR tubes is generally efficient enough to replenish the solution which is being depleted of the reagents by the catalyst.[4,12] In the NMR experiments was employed a palladium concentration higher than that in the batch reactions (ca. 10^{-2} vs 10^{-4} M) in order to acquire well-resolved NMR spectra in a short residence time.[12] The amount of the gaseous reagents contained in the headspace of the tubes was large enough to maintain a relatively high concentration of gases in solution during and after each experiment (^1H NMR evidence for ethene, singlet at δ 5.3).[4,12]

A sequence of $^{31}P\{^1H\}$ NMR spectra relative to the reaction catalyzed by the dppe-based catalyst in MeOH-d_4 is shown in Figure 4.

The first spectrum, recorded after dissolving **4** in MeOH-d_4 at room temperature (trace a), showed the partial conversion of the precursor (δ 63.9) to the bis-chelate complex cation $[Pd(dppe)_2]^{2+}$ (**7**) (δ 58.8), which was identified by its independent synthesis.[13] The addition of the co-reagents TsOH (5 equiv) and BQ (10 equiv) resulted in the complete transformation of residual **4** into the bis-tosylate derivative $Pd(OTs)_2(dppe)$[4a] (**8**) (δ 75.4), while the concentration of **7** did not change (trace b). After 1 h at room temperature, no variation of the NMR picture was observed (trace c). The NMR tube was pressurized with 40 bar of carbon monoxide/ethene (1:1) at room temperature (trace d) and then heated to 85 °C for 1 h. As shown by the spectrum acquired at room temperature (trace e), the concentration of **8** decreased remarkably, while that of **7** increased. Black palladium metal and polyketone were found in the HPNMR tube.

Unlike the dppe precursor **4**, complexes **5** and **6** did not form any bis-chelate complex upon dissolution in MeOH-d_4 under either nitrogen or CO/ethene copolymerization conditions. The NMR behavior of **5** is illustrated in Figure 5. The only diphosphine−Pd complex seen by NMR spectroscopy under copolymerization conditions (i.e., in the presence of both comonomers) gave a singlet at δ 78.1 (traces b−d) that was observed also when isolated $Pd(OTs)_2$(*meso*-2,3-dppb)[4a] (**9**) was dissolved in MeOH. In line with previously reported studies with palladium precursors stabilized by dppp-like diphosphines,[4a] the resonance at δ 78.1 was attributed to a catalyst resting state containing “Pd(P−

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Table 4. Alternating Co- and Terpolymerization of Carbon Monoxide with Ethene and Ethene/Propene Catalyzed by $Pd(OTs)_2(P-P)$ in MeOH[a]

complex	P−P ligand	entry	copol. prod.[b]	LVN (dLg^{-1})	M_n ($kgmol^{-1}$)	mp (°C)	entry	terpol. prod.[b]	LVN ($dL\ g^{-1}$)	M_n ($kg\ mol^{-1}$)	mp (°C)	propene (%)[c]
1	dppp	1	16.2	0.61	14.2	256	5	16.0	0.60	14.1	224	6
4	dppe	2	1.1	0.25	6.7	251	6	1.0	0.27	7.2	227	5
5	*meso*-2,3-dppb	3	11.1	0.29	7.7	254	7	6.8	0.26	6.9	225	6
6	*rac*-2,3-dppb	4	8.8	0.28	7.7	252	8	4.5	0.31	8.0	227	5

[a] Conditions: catalyst (0.01 mmol), MeOH (100 mL), BQ (0.8 mmol), TsOH (0.2 mmol), initial $p(C_2H_4)$ (20 bar), initial p(CO) (20 bar), temperature (85 °C), time (3 h), stirring rate (1400 rpm). In the terpolymerization reactions 20 g of propene was introduced in the autoclave just before pressurizing with the C_2H_4/CO mixture. [b] Productivity expressed as kg of polymer (g of Pd)$^{-1}$. [c] Amount of propene incorporated in the polymeric chains as calculated by ^1H NMR integration. The units $CH_2C(O)CH(Me)CH_2$ and $CH_2C(O)CH_2CH(Me)$ are in 1:1 ratio in all polymeric samples ($^{13}C\{^1H\}$ NMR integration).

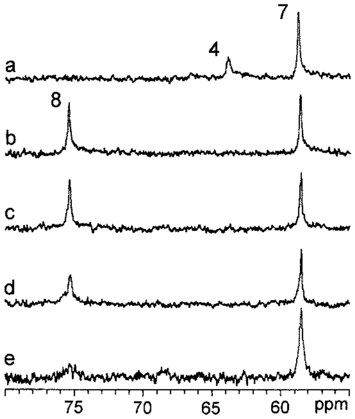


Figure 4. $^{31}P\{^1H\}$ NMR study (sapphire tube, MeOH-d_4, 20 °C, 81.01 MHz) of CO/C_2H_4 copolymerization assisted by **4**: (a) dissolving **4** in MeOH-d_4 under nitrogen; (b) immediately after the addition of both TsOH and BQ; (c) after 1 h; (d) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1); (e) spectrum acquired at room temperature after 1 h heating to 85 °C.

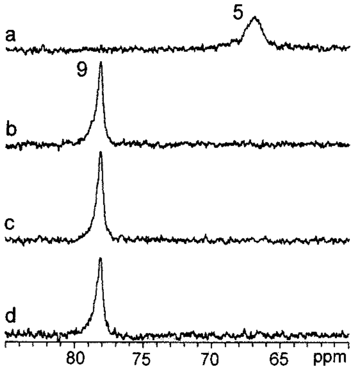
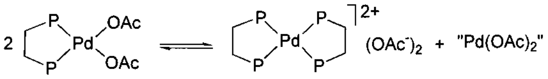


Figure 5. $^{31}P\{^1H\}$ NMR study (sapphire tube, MeOH-d_4, 20 °C, 81.01 MHz) of CO/C_2H_4 copolymerization assisted by **5**: (a) dissolving **5** in MeOH-d_4 under nitrogen; (b) immediately after the addition of both TsOH and BQ; (c) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1); (d) spectrum acquired at room temperature after 1 h heating to 85 °C.

P)$^{2+}$" moieties stabilized by OTs^- ligands, eventually in rapid exchange with solvent molecules.

On standing in solution at 85 °C, also the catalysts generated by **5** and **6** underwent degradation, but this was much slower than that of the dppe system and also different in nature. Indeed, after 3 h in copolymerization conditions, no bis-chelate complex analogous to **7** was seen, while traces of palladium metal were actually observed. Catalyst deactivation using Pd(II) precursors may occur through several pathways including spontaneous degradation of palladium hydrides[2] and, especially in the presence of oxygenated coligands, an inner-sphere metal reduction.[14]

Scheme 7



The deactivation of the dppe precursor proceeds via the autoionization mechanism illustrated in Scheme 7, which is well known for $Ni(OAc)_2$(dppe).[7] In a polar solvent such as MeOH ($\epsilon = 32.6$), $^{31}P\{^1H\}$ NMR has shown that the autoionization equilibrium is largely shifted to the right, namely, toward the formation of the catalytically inactive bis-chelate complex **7** and of palladium acetate (trace a in Figure 4). Consistent with a reversible autoionization reaction, when all MeOH-d_4 was removed in vacuo from a solution such as that giving trace a in Figure 4 and the solid residue was dissolved in CD_2Cl_2 ($\epsilon = 9.1$),[7] the precursor **4** was re-formed quantitatively.

The autoionization reaction of **4** in MeOH is very rapid and is not inhibited by the presence of BQ, TsOH, CO, C_2H_4, or CO/C_2H_4, as shown by batch reactions performed applying a different order of addition of the reagents. However, palladium acetate is not stable in methanol under copolymerization conditions in the absence of ligands and degrades to palladium metal,[2] which accounts for the fast and complete deactivation of the dppe-based catalyst.

Synthesis of the Methyl Acetonitrile Complexes [Pd(Me)(MeCN)(P−P)]PF_6 and their Use as Catalyst Precursors in the Alternating Copolymerization of Ethene and Carbon Monoxide in CH_2Cl_2. The new methyl acetonitrile palladium complexes [Pd(Me)(MeCN)(*meso*-2,3-dppb)]PF_6 (**11**) and [Pd(Me)(MeCN)(*rac*-2,3-dppb)]PF_6 (**12**) were synthesized following a procedure previously reported for the dppe derivative [Pd(Me)(MeCN)(dppe)]PF_6 (**10**).[15] This involves the treatment of the neutral methyl chloride complexes PdCl(Me)(P−P) dissolved in a CH_2Cl_2/MeCN solution (10:1, v:v) with $AgPF_6$ as chloride scavenger. Concentration under reduced pressure and addition of diethyl ether/n-hexane gave analytically pure samples of [Pd(Me)(MeCN)(P−P)]PF_6, whose unambiguous identification was achieved by both $^{31}P\{^1H\}$ (AM patterns) and ^1H

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Table 5. Alternating Copolymerization of Carbon Monoxide with Ethene Catalyzed by $[Pd(Me)(MeCN)(P-P)]PF_6$ and $[Pd(OH)(P-P)]_2(PF_6)_2$ in CH_2Cl_2[a]

			copolymer productivity[c]					
complex	P–P ligand	initial rate[b] (g h^{-1})	0.5 h	3 h	5 h	3 h[d]	M_n[e] (kg mol^{-1})	mp[e] (°C)
10	dppe	2.2	0.6	1.9	2.5	2.3	56	255
11	*meso*-2,3-dppb	3.3	1.0	3.0	3.9	3.6	53	253
12	*rac*-2,3-dppb	2.9	0.8	2.3	3.2	2.9	58	254
16	dppe		0.3					
cis/*trans*-**17**	*meso*-2,3-dppb	-	0.6					

[a] Conditions: catalyst (0.01 mmol), CH_2Cl_2 (100 mL), initial $p(C_2H_4)$ (20 bar), initial $p(CO)$ (20 bar), temperature (70 °C), stirring rate (1400 rpm). [b] Expressed as g of comonomers consumed per hour. [c] Expressed as kg of polymer (g of Pd)$^{-1}$. [d] In the presence of BQ (0.8 mmol). [e] Data for the copolymers obtained in the reactions lasting 3 h.

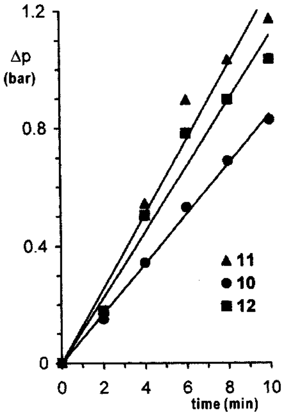

Figure 6. Gas uptake against time during the copolymerization reactions catalyzed by the methyl acetonitrile complexes **10**−**12** in CH_2Cl_2.

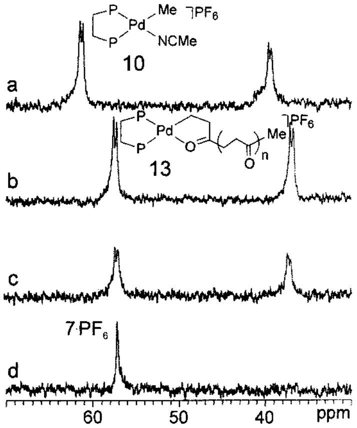

Figure 7. $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of CO/C_2H_4 copolymerization assisted by **10**: (a) dissolving **10** in CD_2Cl_2 under nitrogen at room temperature; (b) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1) at room temperature; (c) at 50 °C (first spectrum); (d) after 15 min at 70 °C.

NMR spectroscopy (singlets at ca. δ 2.2 for the coordinated MeCN ligand).

Complexes **10**−**12** were employed as catalyst precursors for the copolymerization of CO and ethene in CH_2Cl_2 (distilled over CaH_2) at 70 °C in the absence of both organic oxidant and protic acid, which are typical conditions for reactions catalyzed by initiators containing a Pd−alkyl moiety in aprotic solvents.[16] The results of reactions lasting 0.5, 3, and 5 h are reported in Table 5, which also contains data in the presence of organic oxidant as well as initial copolymerization rates. These have been estimated measuring the gas consumption within the first 10 min (Figure 6).

As is generally observed in copolymerization reactions in CH_2Cl_2,[2,16] the productivities were lower than those obtained in MeOH solution with comparable palladium precursors, while the molecular weights were much larger (50−60 vs 6−8 kg mol^{-1}) and almost independent of the diphosphine ligand (Tables 4 and 5). The large M_n's did not allow us to determine the nature of the end groups by ^1H NMR spectroscopy in 1,1,1,3,3,3-hexafluoropropan-2-ol-d_2 (HFIP-d_2). On the basis of previous studies on co-oligomers, it is likely that the polyketone material contains vinyl and ketone end groups, formed by β-H chain transfer and Pd−H initiation, respectively.[16]

A perusal of Table 5 reveals that the intrinsic activity, indicated by the initial rate values, decreased in the ligand order *meso*-2,3-dppb > *rac*-2,3-dppb > dppe. All the catalyst systems underwent slow deactivation with time as a result of palladium metal formation. Consistently, the addition of BQ increased the productivity as in the reactions in MeOH, which means that, also in CH_2Cl_2, catalyst deactivation occurs by palladium(II) reduction.

In Situ HPNMR Study of the Alternating Copolymerization of Ethene and Carbon Monoxide Catalyzed by $[Pd(Me)(MeCN)(P-P)]PF_6$ in Either Dry or Wet CD_2Cl_2. The CO/C_2H_4 copolymerization reactions catalyzed by **10**, **11**, and **12** were studied in situ by means of HPNMR spectroscopy in 10 mm OD sapphire tubes applying comparable experimental conditions to those of the batch reactions. Selected $^{31}P\{^1H\}$ NMR spectra relative to the reactions catalyzed by the dppe and *meso*-2,3-dppb precursors **10** and **11** in CD_2Cl_2 distilled over CaH_2 are reported in Figures 7 and 8, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of the precursor **10** is shown in Figure 7 (trace a). Immediately after pressurizing the tube to 40 bar with a 1:1 CO/C_2H_4 mixture at room temperature, polyketone formation occurred while **10** converted to the β-chelates $[Pd(CH_2CH_2C(O)\text{-chain})(dppe)]^+$ (**13**) (AM pattern at δ 57.7 and 37.0, $J(PP) =$ 29.2 Hz) where "chain" is the propagating copolymer (trace b) (Scheme 1). By ^1H NMR integration, the average repeating units of the chain have been esti-

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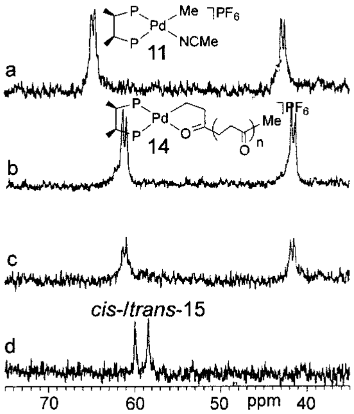

Figure 8. $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of CO/C_2H_4 copolymerization assisted by **11**: (a) dissolving **11** in CD_2Cl_2 under nitrogen at room temperature; (b) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1) at room temperature; (c) at 70 °C (first spectrum); (d) after 45 min at 70 °C.

mated to be **8**.[2,17] The β-chelates were the only phosphorus-containing compounds visible on the NMR time scale at 50 °C (trace c). With time, however, they slowly decomposed to give palladium metal and the catalytically inactive bis-chelate complex **7**·PF_6 (singlet at δ 57.2 overlapping the low-field resonance of the β-chelates). Increasing the temperature to 70 °C accelerated the decomposition of the β-chelates that disappeared completely after 15 min at 70 °C, leaving **7**·PF_6 as the predominant palladium complex (trace d). The large noise of the spectrum did not rule out the formation of other unidentified species, in fact.

The copolymerization reactions catalyzed by **11** (Figure 8) or **12** gave a similar NMR picture. The $^{31}P\{^1H\}$ NMR spectrum at room temperature under nitrogen of precursor **11** (AM pattern with δ 64.8 and 42.7) is shown in trace a. Pressurizing the tube to 40 bar with a 1:1 mixture of carbon monoxide/ethene at room temperature transformed **11** into the β-chelate complexes of the formula $[Pd(CH_2CH_2C(O)\text{-chain})(\textit{meso}\text{-}2,3\text{-dppb})]^+$ (**14**) (AM pattern with signals at δ 61.0 and 41.3 and $J(PP) = 35.1$ Hz, trace b; number of average repeating units = 9).[2,17] The appearance of the β-chelates at room temperature coincided with the formation of the copolymer product. When the temperature was increased to 70 °C, the intensity of the β-chelate signal decreased (trace c), which was essentially attributed to catalyst degradation.[2] The formation of the known bis-chelate complexes[13c] *cis*-$[Pd(\textit{meso}\text{-}2,3\text{-dppb})_2]^{2+}$ (*cis*-**15**) and *trans*-$[Pd(\textit{meso}\text{-}2,3\text{-dppb})_2]^{2+}$ (*trans*-**15**) (singlets at δ 59.7 and 58.2) became appreciable after ca. 10 min at 70 °C and coincided with the formation of palladium metal. The bis-chelate complexes were the predominant phosphorus-containing species after 45 min at 70 °C (trace d).

The β-chelates **13** and **14**[2,17−19] and the binuclear complexes **7**·PF_6,[13a] *cis*-**15**, and *trans*-**15**[13c] were identified by comparison with either authentic specimens or structurally similar compounds (vide infra) prepared by independent methods.

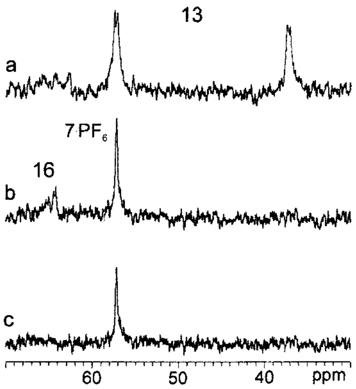

Figure 9. $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of CO/C_2H_4 copolymerization assisted by **10** in the presence of H_2O: (a) after heating a solution of **10** under 40 bar of CO/C_2H_4 (1:1) to 50 °C; (b) at 70 °C (first spectrum); (c) after 1 h at 70 °C.

The copolymerization reactions in CD_2Cl_2 catalyzed by **10**, **11**, and **12** were similarly followed by HPNMR spectroscopy in the presence of added water (10 μL) to study the chain-transfer mechanism by protonolysis and ultimately gain insight into the possible paths to catalyst deactivation in solution.

Figure 9 shows a sequence of spectra relative to the copolymerization reaction catalyzed by **10** in wet CD_2Cl_2. The first spectrum at 50 °C (trace a) was rather similar to that in dry solvent (Figure 7, trace c) except for the presence of some broad resonances in the 60−70 ppm region. The presence of water accelerated the degradation of the β-chelates, as no trace of the latter compounds was visible already in the first spectrum at 70 °C (trace b). Formed in their place were the bis-chelate **7**·PF_6 and other products, among which only the μ-OH binuclear complex $[Pd(OH)(dppe)]_2^{2+}$ (**16**) (singlet at δ 64.2) could be unambiguously identified. With time, **16** disappeared and the bis-chelate **7**·PF_6 remained the only well-defined palladium complex (trace c after 1 h at 70 °C).

The overall $^{31}P\{^1H\}$ HPNMR pictures obtained for the copolymerization reactions catalyzed by **11** and **12** in wet CD_2Cl_2 were similar to each other. The variable-temperature spectra for the reaction of **11** are reported in Figure 10. The most striking difference between the reaction catalyzed by **10** and that catalyzed by **11** is that the μ-OH binuclear complexes, *cis*- and *trans*-$[Pd(OH)(\textit{meso}\text{-}2,3\text{-dppb})]_2^{2+}$ (*cis*-**17,** *trans*-**17**) (broad resonance centered at δ 67.8 comprising two singlets, vide infra), were formed already at 50 °C before any trace of the bis-chelates *cis*- and *trans*-**15** appeared in the spectrum (trace a). With time, the β-chelates slowly converted into the μ-OH complexes (in a separate experiment, the HPNMR tube was removed from the probe-head at this stage: the formation of the unsoluble copolymer was confirmed, while no trace of palladium metal was seen). Increasing the temperature to 70 °C accelerated the conversion process. Indeed, in the first spectrum at 70 °C, the μ-OH complexes were the largely predominant palladium compounds in solution (trace b). At 70 °C, the μ-OH complexes started decomposing to give pal-

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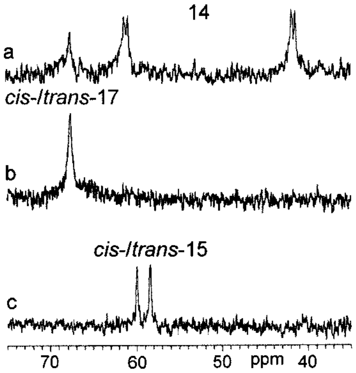
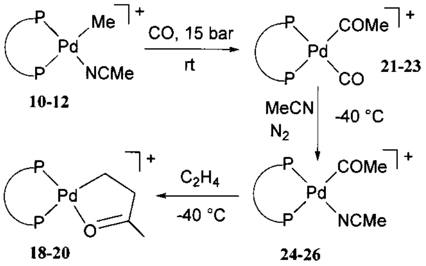
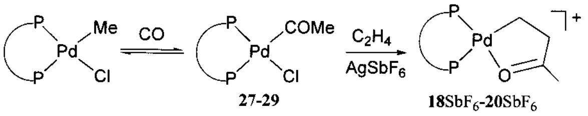


Figure 10. $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of CO/C_2H_4 copolymerization assisted by **11** in the presence of H_2O: (a) after heating a solution of **11** under 40 bar of CO/C_2H_4 (1:1) to 50 °C; (b) at 70 °C (first spectrum); (c) after 1 h at 70 °C.

Scheme 8



Scheme 9



ladium metal and the bis-chelates *cis*-**15** and *trans*-**15**, which were the only well-defined palladium products after 1 h (trace c).

Model Chain-Transfer Reactions Using the Palladium(II) *β*-Ketoalkyl Chelates. The *β*-chelate complexes $[Pd(CH_2CH_2C(O)Me)(P{-}P)]PF_6$ (P−P = dppe, **18**; *meso*-2,3-dppb, **19**; *rac*-2,3-dppb, **20**) were isolated in the solid state through the procedure illustrated in Scheme 8, and their thermal behavior in both dry and wet CH_2Cl_2 was studied. The synthesis involves the conversion of the methyl acetonitrile complexes **10**−**12** to the corresponding acyl carbonyl derivatives $[Pd(COMe)(CO)(P{-}P)]PF_6$ (P−P = dppe, **21**; *meso*-2,3-dppb, **22**; *rac*-2,3-dppb, **23**) by reaction with 15 bar CO in CH_2Cl_2 at room temperature. To the solution of each acyl carbonyl complex in a 10 mm OD sapphire NMR tube was added a small amount of MeCN (20 *μ*L) at −40 °C. After NMR spectroscopy showed the complete transformation of the acyl carbonyl complexes to the acyl acetonitrile derivatives $[Pd(COMe)(MeCN)(P{-}P)]PF_6$ (P−P = dppe, **24**; *meso*-2,3-dppb, **25**; *rac*-2,3-dppb, **26**), the NMR tube was purged with C_2H_4 at −40 °C until the *β*-chelate complexes were quantitatively obtained. At this point, all the solvent was removed under reduced pressure at −20 °C to give a solid product that was washed with *n*-pentane and dried.

Alternatively, the *β*-chelate complexes were prepared in situ as SbF_6^- salts following a procedure recently described by Brookhart and co-workers for $[Pd(CH_2CH_2C(O)Me)(dppp)]SbF_6$.[19] The chloride acyl complexes PdCl(COMe)(P−P) (P−P = dppe, **27**; *meso*-2,3-dppb, **28**; *rac*-2,3-dppb, **29**) were quantitatively generated in CD_2Cl_2 at room temperature by carbonylation (20 bar CO, 40 °C) of the chloride methyl precursors PdCl(Me)(P−P) in HPNMR tubes and then transformed into the desired *β*-chelates by treatment with $AgSbF_6$, as chloride scavenger, under a stream of C_2H_4 (Scheme 9).

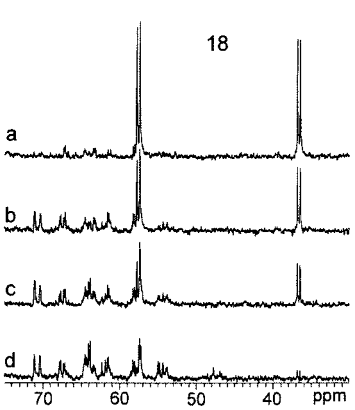


Figure 11. $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 20 °C, 81.01 MHz) on the stability of the *β*-chelate **18** in CD_2Cl_2 under nitrogen: (a) after dissolving **18** in CD_2Cl_2; (b) after 1.5 h; (c) after 3.5 h; (d) after 15 h.

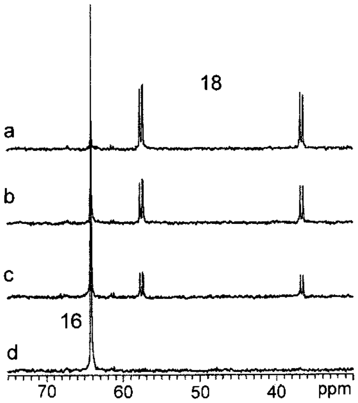


Figure 12. $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 20 °C, 81.01 MHz) on the stability of the *β*-chelate **18** in wet CD_2Cl_2 under nitrogen: (a) after dissolving **18** in wet CD_2Cl_2; (b) after 1.5 h; (c) after 3.5 h; (d) after 15 h.

All the new compounds (acyl acetonitrile, acyl carbonyl, chloride acyl, *β*-chelates) were straightforwardly identified by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (Tables 6 and 7). Comparisons with the spectra of similar or related complexes described in the literature have substantially contributed to validate our structural assignments.[2,15−20]

Irrespective of the synthetic procedure, $[Pd(CH_2CH_2C(O)Me)(dppe)]^+$ was found to be rather stable at room temperature in dry CD_2Cl_2, where it disappeared completely in ca. 15 h. Formed in its place were free vinyl methyl ketone and methyl ethyl ketone in a ca. 5:1 ratio (^1H NMR, GC/MS), traces of Pd metal, and several unknown palladium complexes (Figure 11).

When **18** was dissolved in wet CD_2Cl_2 (10 *μ*L water), its decomposition gave exclusively the *μ*-OH binuclear complex **16** and methyl ethyl ketone (Figure 12); traces of methyl vinyl ketone were detected by GC/MS.

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Table 6. $^{31}P\{^1H\}$ **NMR Chemical Shifts (ppm), (Multiplicity), and [PP Coupling Constants] (Hz) for the Palladium Complexes** $[Pd(X)(Y)(P-P)]^{0/+}$ **in** CD_2Cl_2 **Solutions at {*T*} (°C)**

P−P	X = Me Y = NCMe	X =Me Y = CO	X = COMe Y = CO	X = COMe Y = NCMe	X = Me Y = Cl	X = COMe Y = Cl	X, Y = CH_2CH_2-C(O)Me	X = $CO(CH_2)_2$-COMe Y = CO
dppe	61.2 (d) [27.0]	61.5 (d) [27.1]	40.0 (d) [50.2]	38.4 (d) [44.2]	59.9 (d) [27.2]	40.0 (d) [45.1]	57.4 (d) [29.6]	40.6 (d) [50.8]
	39.5 (d) {rt}	46.5 (d) {−80}	36.2 (d) {rt}	23.7 (d) {rt}	31.9 (d) {rt}	22.2 (d) {rt}	36.8 (d) {rt}	35.9 (d) {rt}
meso-2,3-dppb	64.8 (d) [34.0]	63.0 (d) [32.9]	44.0 (d) [57.4]	45.1 (d) [53.6]	62.8 (d) [32.0]	42.8 (d) [48.7]	61.2 (d) [35.7]	44.1 (d) [60.7]
	42.7 (d) {rt}	49.2 (d) {−80}	40.3 (d) {rt}	36.1 (d) {rt}	36.8 (d) {rt}	58.3 (d) {rt}	41.0 (d) {rt}	41.5 (d) {−40}
rac-2,3-dppb	63.5 (d) [40.7]	60.0 (d) [44.1]	47.2 (d) [66.8]	49.0 (d) [64.7]	63.8 (d) [38.0]	49.4 (d) [54.8]	61.7 (d) [36.8]	47.4 (d) [64.8]
	42.8 (d) {rt}	44.5 (d) {−80}	38.3 (d) {rt}	36.8 (d) {rt}	38.8 (d) {rt}	32.4 (d) {rt}	40.7 (d) {rt}	38.8 (d) {−40}

Table 7. ^1H **NMR Chemical Shifts (ppm), (Multiplicity), and [Coupling Constants] (Hz) for Selected Resonances of the Palladium Complexes** $[Pd(X)(Y)(P-P)]^{0/+}$ **in** CD_2Cl_2 **Solutions at {*T*} (°C)**

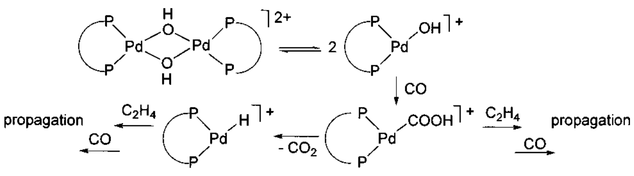
P−P	X =Me Y = NCMe	X =Me Y = CO	X = COMe Y = CO	X = COMe Y = NCMe	X = Me Y = Cl	X = COMe Y = Cl	X, Y = CH_2CH_2COMe	X = $(CO)(CH_2)_2COMe$ Y = CO
dppe	0.62 (dd) Me [*J*(HP) 2.0, 7.3] {rt}	0.78 (brs) Me {−80}	2.05 (s) COMe {rt}	2.08 (s) COMe {rt}	0.78 (dd) Me [*J*(HP) 3.0, 8.0] {rt}	2.05 (s) COMe {rt}	1.74 (ddd) $PdCH_2$ [*J*(HP) 8.2, 2.1; *J*(HH) 6.5] 2.53 (s) COMe 3.31 (dd) CH_2CO [*J*(HP) 9.0; *J*(HH) 7.0] {rt}	not detected
meso-2,3-dppb	0.39 (dd) Me [*J*(HP) 2.1, 7.5] {rt}	055 (brs) Me {−80}	2.10 (s) COMe {rt}	2.10 (s) COMe {rt}	0.55 (dd) Me [*J*(HP) 3.0, 8.1] {rt}	1.90 (s) COMe {rt}	1.85 (ddd) $PdCH_2$ [*J*(HP) 8.0, 2.0; *J*(HH) 6.8] 2.53 (s) COMe 3.30 (dd) CH_2CO [*J*(HP) 8.5; *J*(HH) 6.8] {rt}	1.80 (s) COMe 2.40 (m) CH_2CO 2.75 (m) $Pd(CO)CH_2$ {−40}
rac-2,3-dppb	0.57 (dd) Me [*J*(HP) 2.0, 7.3] {rt}	0.75 (brs) Me {−80}	2.04 (s) COMe {rt}	2.08 (s) COMe {rt}	0.55 (dd) Me [*J*(HP) 3.1, 8.2] {rt}	2.03 (s) COMe {rt}	1.60 (m) $PdCH_2$ 2.50 (s) COMe 3.20 (m) CH_2CO {rt}	1.50 (s) COMe 2.10 (m) CH_2CO 2.35 (m) $Pd(CO)CH_2$ {−40}

In comparison to **18**, the β-chelates **19** and **20** showed a slightly decreased stability in CD_2Cl_2, where they decomposed within 10 h, yielding more methyl vinyl ketone than methyl ethyl ketone (ca. 4:1). In the presence of added water, only traces of methyl vinyl ketone were detected by GC/MS, while methyl ethyl ketone was produced in almost quantitative yield together with the μ-OH complexes *cis*-**17** and *trans*-**17** in a ca. 1:5 ratio.

The thermal behavior of the β-chelates in CD_2Cl_2 was also studied at 50 and 70 °C; identical results were obtained except for faster decomposition rates. The isolated β-chelates were also employed to catalyze the CO/ethene copolymerization in either dry or wet CD_2Cl_2 in HPNMR tubes. The NMR picture was identical to those reported in Figures 7, 8, and 9. In particular, the $^{31}P\{^1H\}$ NMR resonances of the β-chelates became broader as the NMR tube was pressurized to 40 bar with CO/C_2H_4. Such a broadening was attributed to the formation of different β-chelates of the general formula $[Pd(dppe)(CH_2CH_2C(O)\text{-chain})]^+$, where chain is a propagating co-oligomeric chain.[2,17]

The Role of the μ-OH Complexes in Catalysis. Interestingly, the μ-OH complexes do not represent a dead end for the alternating copolymerization in CH_2Cl_2. Under the experimental conditions reported in Table 5, isolated **16** and *cis*/*trans*-**17** were effective catalysts for the CO/ethene copolymerization. The μ-OH complexes were not as efficient as their mononuclear precursors **10** and **11** however (Table 5), which we ascribe to the occurrence of an induction period. Independent reactions of **16** and **17** in CH_2Cl_2 with either C_2H_4 or CO showed that only the latter substrate was able to degrade the μ-OH complexes at 70 °C, yielding the bis-chelate complexes **7**·PF_6 and *cis*/*trans*-**15**, respectively.

Scheme 10



By analogy with CO/ethene copolymerization reactions in water, the binuclear structure of the μ-OH complexes is apparently destroyed by CO to give mononuclear Pd−OH initiators that may start the propagation step with either Pd−COOH or Pd−H species (Scheme 10).[21−23]

Generation and Migratory Insertion Barriers of $[Pd(Me)(CO)(P-P)]PF_6$**.** In an attempt to rationalize the different catalytic performance of the dppe, *meso*-2,3-dppb, and *rac*-2,3-dppb precursors in CH_2Cl_2 distilled over CaH_2, the migratory insertion barriers relative to reactions occurring during the propagation of the alternating CO/ethene copolymerization have been determined by NMR spectroscopy for various model intermediates.

The methyl carbonyl precursors $[Pd(Me)(CO)(P-P)]PF_6$ (P−P = dppe, **30**; *meso*-2,3-dppb, **31**; *rac*-2,3-dppb, **32**) were generated in HPNMR tubes by pressurizing CD_2Cl_2 solutions of the corresponding methyl acetonitrile compounds with CO (15 bar) at −117 °C. $^{31}P\{^1H\}$ and ^1H NMR spectra showed the only presence of the methyl carbonyl complexes **30**−**32** also at −80 °C. Upon

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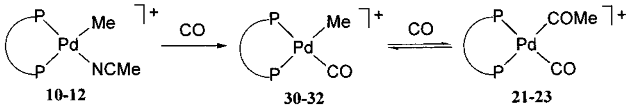
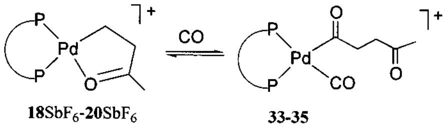
Table 8. Experimental Activation Barriers and Temperatures for Migratory Insertions

	$[Pd(Me)(CO)(P-P)]^+$			$[Pd(CH_2CH_2C(O)Me)(P-P)]^+$		
P−P	$\Delta G^{\ddagger}$ (kcal/mol)	$t_{1/2}$ (min)	T (°C)	T (°C)	$t_{1/2}$ (min)	p(CO) (bar)
dppe	16.9(1)	12	−40	20	15	20
meso-2,3-dppb	16.1(1)	3	−40	−40	97	20
rac-2,3-dppb	17.5(1)	62	−40	−40	480	20

Scheme 11



Scheme 12



slow heating of the NMR probe-head, the latter complexes transformed selectively into the corresponding carbonyl acyl derivatives $[Pd(COMe)(CO)(P-P)]PF_6$ (**21**−**23**) (Scheme 11).

The *meso*-2,3-dppb and *rac*-2,3-dppb acyl carbonyl complexes started to form at −50 °C. The highest temperature required for CO insertion was observed for the dppe derivative (−40 °C).

Kinetics of transformation of the methyl carbonyl complexes with dppe, *meso*-2,3-dppb, and *rac*-2,3-dppb ligands into the corresponding acyl carbonyl products were studied by $^{31}P\{^1H\}$ NMR spectroscopy at −40 °C, where the reactions were sufficiently fast to allow for a reliable determination of the half-life times ($t_{1/2}$).

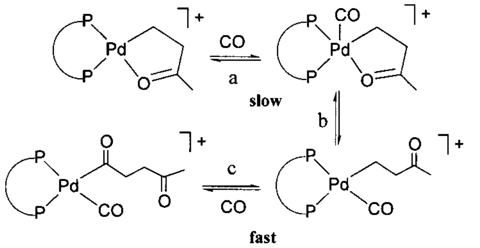
As previously observed by Brookhart and co-workers for $[Pd(Me)(CO)(dppp)]BAr'_4$,[19] the rate of conversion of the methyl carbonyl complexes was independent of the CO pressure (5−25 bar) and followed first-order kinetics. The observed rate constants are therefore the true rate constants, and the $\Delta G^{\ddagger}$ values associated with the migratory insertion of the methyl carbonyl complexes could be straightforwardly calculated from the $t_{1/2}$ values. The data obtained show the energy barrier to increase in the ligand order *meso*-2,3-dppb < dppe < *rac*-2,3-dppb (Table 8). The activation barriers for insertion reported for the dppe derivative nicely fit previous data for $[Pd(Me)(CO)(dppe)]SO_3CF_3$ (16.6 kcal mol^{-1} at −38 °C).[15]

Generation and Carbonylation of *β*-Chelates $[Pd(CH_2CH_2C(O)Me)(P-P)]SbF_6$. The *β*-chelate complexes $[Pd(CH_2CH_2C(O)Me)(P-P)]SbF_6$ (P−P = dppe, **18**SbF_6; *meso*-2,3-dppb, **19**SbF_6; *rac*-2,3-dppb, **20**SbF_6) were prepared as outlined in Scheme 9.[19]

After each *β*-chelate was identified by NMR spectroscopy, the HPNMR tube was removed from the spectrometer and was purged with Ar to remove free ethene. The tube was cooled to ca. −117 °C, pressurized with 20 bar CO, and then inserted into the probe-head precooled at −90 °C. The conversion of the *β*-chelates to the carbonyl acyl complexes $[Pd(CO)(COCH_2CH_2C(O)Me)(P-P)]SbF_6$ (**33**−**35**) was followed by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 12).

The formation of the *meso*-2,3-dppb and *rac*-2,3-dppb carbonyl acyl complexes started to occur at −40 °C, while the dppe derivative was much more stable, as only at 20 °C was the *β*-chelate ring opened by CO. At this temperature, the reaction went further on and the formation of the carbonyl acyl was accompanied by that of several products, including Pd metal.

Scheme 13

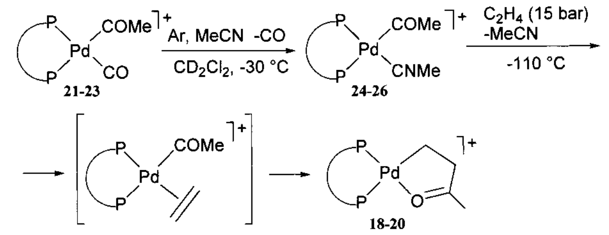


The rates of conversion of the *β*-chelates to the carbonyl acyl complexes **33**−**35** were evaluated as half-life times obtained from the decay (and increase) of the phosphorus resonances at appropriate temperatures: −40 °C for the *meso*-2,3-dppb and *rac*-2,3-dppb complexes **34** and **35**; 20 °C for the dppe complex **33**. The activation barriers for the process could not be calculated straightforwardly from the $t_{1/2}$ values as the reaction rates proved to be dependent on the CO pressure in the range investigated (15−25 bar). The observed CO dependence suggests that the rate-limiting step is related to the opening of the metallacycle by CO (steps a, b in Scheme 13) rather than to the following migratory insertion of the alkyl carbonyl complex that should be independent of the CO pressure (step c). Remarkably, the highest energy barrier required to disrupt the metallacycle structure was shown by complex **33**, which contains dppe, namely, the ligand that originates the least efficient catalysts in both MeOH and CH_2Cl_2.

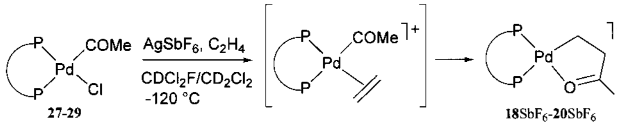
Attempted Determination of the Migratory Insertion Barriers of $[Pd(COMe)(C_2H_4)(P-P)]PF_6$. The acyl acetonitrile derivatives **24**−**26** were prepared in situ following the procedure illustrated in Scheme 8. To CD_2Cl_2 solutions of the acyl carbonyl complexes **21**−**23** was added 30 *μ*L of CD_3CN at −30 °C. The reaction mixtures were purged with Ar at −30 °C to remove excess and coordinated CO. As a result, the acyl acetonitrile complexes were formed quantitatively.

In an attempt to generate acyl ethene complexes of the general formula $[Pd(COMe)(C_2H_4)(P-P)]^+$, the acyl acetonitrile complexes were reacted with C_2H_4 (15 bar) at −110 °C. In no case, however, was an acyl ethene intermediate intercepted, the *β*-chelate complexes being rapidly and quantitatively formed (Scheme 14), which is consistent with a slower replacement of MeCN by C_2H_4 as compared to the migratory insertion of the acyl ethene intermediate. Alternatively, one may suggest that this ethylene intermediate is in rapid equilibrium with the acetonitrile complex and that the equilibrium lies to the left. A quite similar reactivity pattern has been reported by Brookhart and co-workers for the reaction of isolated $[Pd(Me)(CO)(dppp)]^+$ with C_2H_4.[19]

Scheme 14



Scheme 15



Following a procedure reported by these authors, we have also tried to determine the activation barriers to the migratory insertion of $[Pd(COMe)(C_2H_4)(P-P)]^+$ by scavenging the chloride ligand from the acyl chloride derivatives **27**, **28**, and **29** with $AgSbF_6$ in the presence of ethene (15 bar) at −120 °C (Scheme 15). All our attempts were unsuccessful, as only the β-chelates were seen by NMR spectroscopy at −120 °C, which is consistent with an activation barrier lower than 12 kcal mol^{-1}. A $\Delta G^{\ddagger}$ value of 12.3(1) kcal mol^{-1} has been reported by Brookhart for $[Pd(COMe)(C_2H_4)(dppp)]SbF_6$.[19]

It is noteworthy that the trend of the activation barriers of migratory insertion reactions at the metal center in the Pd^{II}(dppp) system is in nice agreement with ours, in particular as regards the barriers for alkyl carbonyl complexes that, irrespective of the diphosphine, are higher than those for acyl ethene compounds.[19]

Discussion

Alternating Copolymerization in MeOH by $Pd(OAc)_2(P-P)$ Precursors. The HPNMR experiments (Figures 4 and 5) show that the much lower productivity in MeOH of the dppe precursor **4** as compared to both **5** and **6** (Table 4) is substantially determined by the solvent. Already at room temperature, MeOH rapidly transforms **4** into the catalytically inactive bis-chelate **7** and palladium acetate, which gives palladium metal on long standing in solution under copolymerization reaction conditions. The fact that no apparent degradation of the *meso*-2,3-dppb and *rac*-2,3-dppb catalysts occurs within 1 h of copolymerization indicates that the methyl substituents on the ligand backbone inhibit somehow the formation of bis-chelates species and unstable palladium acetate.

In the absence of added diphosphine, the formation of bis-chelates from $Pd(OAc)_2(P-P)$ should proceed via acetate decoordination (assisted by solvation), followed by a complex rearrangement involving monodentate diphosphine ligands. Consistent with this mechanism, the autoionization of $M(OAc)_2$(dppe) complexes (M = Ni,[7] Pd) has been found to be favored by a high dielectric constant of the solvent as well as a small P−Pd−P bite angle; that is, the $M(OAc)_2$(dppp) complexes do not undergo ionization even in MeOH.[7] Within this context, we suggest that the propensity to autoionization of **4** is related to the higher skeletal flexibility of dppe as compared to *meso*-2,3-dppb and *rac*-2,3-dppb, which may ultimately facilitate Pd−P unfastening.[2f,3,16a,24,25] Indeed, in the series of the palladium(II) complexes **4**, **5**, and **6**, which, by the way, exhibit comparable electron density at palladium (Table 3) as well as Pd−P distances (Table 2), the P−Pd−P bite angles cannot play any role, as they are practically identical within the three complexes (Table 2).

Indirect support for an inverse correlation between ligand rigidity and autoionization in diphosphine palladium(II) complexes is provided by the previous observation that $Pd(OAc)_2$(*o*-dppbe) and $Pd(OAc)_2$(*cis*-dppen) containing the rigid *o*-bis(diphenylphosphino)benzene and *cis*-bis(diphenylphosphino)ethylene ligands, respectively, do not undergo autoionization in MeOH, where, unlike dppe, they give rise to quite efficient CO/ethene copolymerization catalysts.[6] Moreover, it is worth mentioning that Vrieze and co-workers have demonstrated that backbone rigidity of dinitrogen ligands disables dissociation of one ligating nitrogen.[24]

Alternating Copolymerization in CH_2Cl_2 by $[Pd(Me)(MeCN)(P-P)]^+$ Precursors. The copolymerization reactions catalyzed by the $Pd(OAc)_2(P-P)$ precursors in MeOH are clearly biased by the solvent that selectively damages the dppe catalyst, thus preventing one from making reliable comparisons of the intrinsic activities. In MeOH, therefore, there is no way to either confirm or discard the existence of a ligand effect, in particular of a *meso* effect, in the alternating copolymerization of CO/olefin by palladium catalysts stabilized by diphosphine ligands containing two carbon spacers.

Unlike MeOH, dry CH_2Cl_2 behaves as an innocent solvent in the CO/ethene copolymerization. Accordingly, the results obtained in CH_2Cl_2 (batch reactions, in situ HPNMR experiments, and kinetic studies) can be used to rationalize both the intrinsic activity and the productivity that decrease in the order $[Pd(Me)(MeCN)($*meso*-2,3-dppb$)]^+ > [Pd(Me)(MeCN)($*rac*-2,3-dppb$)]^+ > [Pd(Me)(MeCN)(dppe)]^+$ (Table 5). Since the barriers to migratory insertion of the methyl carbonyl complexes follow a different order ($[Pd(Me)(CO)($*rac*-2,3-dppb$)]^+ > [Pd(Me)(CO)(dppe)]^+ > [Pd(Me)(CO)($*meso*-2,3-dppb$)]^+$), they should not control the propagation rate, which is consistent with previous experimental studies.[2,15] In contrast, it is very likely that the opening/CO migratory insertion of the β-chelates constitutes the rate-limiting step or a step close to it in the catalytic cycle. Indeed, the HPNMR experiments in catalytic conditions show the β-chelates to be resting states of the catalysis (Figures 7 and 8), which is again in agreement with previous studies.[2,13b,26] Although the activation barriers relative to the opening/carbonylation of the β-chelates could not be calculated due to the complex dependence on CO pressure (Scheme 13), there is little doubt that dppe forms the most stable β-chelate (catalyst resting state), while *meso*-2,3-dppb forms the least stable β-chelate, which accounts for the observed intrinsic activity trend. Within this context, it is worth mentioning that an inverse relationship between catalytic activity and

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(25) Xu, F. Y.; Zhao, A. X.; Chien, J. C. W. *Macromol. Chem.* **1993**, *194*, 2579.

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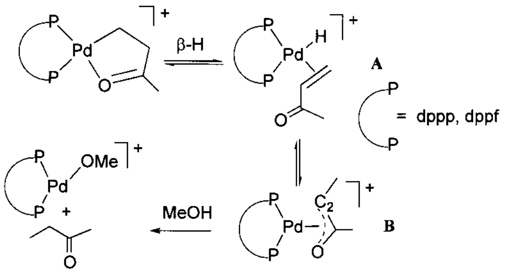
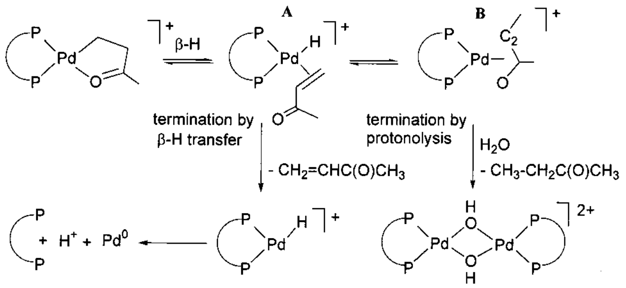
Scheme 16



Scheme 17



β-chelate stability has been previously proposed by Barron to account for the higher catalytic activity of [PdCl(COBu^t)(dppp)] vs [PdCl(COBu^t)(dppe)] in the alternating copolymerization of CO/ethene in CH_2Cl_2.[16a]

Why the rigid diphosphines *meso*- and *rac*-2,3-dppb form β-chelate complexes that are less kinetically stable than that with dppe is hard to state in the absence of a detailed kinetic study as well as a theoretical analysis of the energy profile associated with the rupture of the β-ketoalkyl ring by CO in the dppe, *meso*-2,3-dppb, and *rac*-2,3-dppb complexes. We are inclined to ascribe the easier opening of the β-chelates with *meso*- and *rac*-2,3-dppb to their greater backbone rigidity that would destabilize the five-coordinate transition state for the turnover-limiting step.[27]

Besides Consiglio[5] and ourselves,[4,6] a relation between productivity in CO/ethene polyketone and backbone rigidity of the chelating diphosphine has also been observed by Doherty for reactions catalyzed in MeOH by palladium(II) complexes containing bis(phospholyl) ligands.[28]

A directly proportional correlation between chelate ligand rigidity and polymer productivity has been also reported by Keim and Schultz for the homogeneous polymerization of ethene by nickel(II)−(P−O) catalysts.[29]

Chain-Transfer by Protonolysis. Termination by protonolysis in Pd-diphosphine-catalyzed CO/ethene copolymerizations has been demonstrated by Van Leeuwen to occur via a mechanism involving the conversion of β-chelates $[Pd(CH_2CH_2C(O)Me)(P-P)]^+$ to palladium enolates **B** via PdH(η^2-vinyl ketone) complexes (**A**) (Scheme 16).[18c]

For P−P = dppp or 1,1′-diphenylphosphino ferrocene, the enolate **B** is a long-living species that undergoes chain transfer by protonolysis with MeOH by regioselective proton delivery at the C_2 carbon atom to give Pd−OMe and methyl ethyl ketone.

In light of the HPNMR experiments in dry and wet CD_2Cl_2, it is apparent that also the β-chelates with dppe, *meso*-2,3-dppb, and *rac*-2,3-dppb undergo chain transfer by the van Leeuwen mechanism (Scheme 17).

The production of both methyl ethyl ketone and μ-OH complexes in wet CH_2Cl_2 does imply the formation of enolates of type **B**. In turn, the production of methyl vinyl ketone in dry CH_2Cl_2 implies the intermediacy of hydride η^2-olefin complexes of type **A**. Since we have observed that the rate of production of methyl ethyl ketone increases with the water concentration in CH_2Cl_2, compounds **A** and **B** are presumably in equilibrium with each other; in contrast, we can neither verify nor exclude that the β-chelate is in equilibrium with **A**. Indeed, neither **A** nor **B** was seen by NMR spectroscopy in experiments performed in dry and wet CD_2Cl_2 in the temperature range from −60 to 30 °C.

Conclusion

The productivity of a catalyst and its intrinsic activity are terms frequently misused or confused for each other, although they signify different concepts. The catalytic productivity is related to the amount of product obtained, and as such, it is determined by a complex web of factors, the most important of which is the catalyst durability in the chosen experimental conditions. In contrast, the intrinsic activity is related to the rate of catalyst formation (initiation step) and to the rate of a single catalytic cycle. The intrinsic activity is therefore an indirect measure of the activation barrier involved in the rate-limiting step.

We have shown here that the productivity of $Pd(OAc)_2(P-P)$ precursors (P−P = dppe, *meso*-2,3-dppb, *rac*-2,3-dppb) in the alternating CO/ethene copolymerization in MeOH is dramatically affected by the solvent which selectively damages the dppe-based catalyst. This does not happen in CH_2Cl_2, which behaves as an innocent solvent and therefore allows for the evaluation of the intrinsic activity of the palladium catalysts investigated. Batch catalytic reactions, high-pressure NMR experiments in catalytic conditions, and the determination of activation barriers of migratory insertions agree to indicate the relative kinetic stability of the β-chelate ring in $[Pd(CH_2CH_2C(O)Me)(P-P)]^+$ as the factor that controls the copolymerization rate in CH_2Cl_2 by alkyl palladium(II) precursors. A study in progress in this laboratory confirms the existence of a similar intrinsic activity/β-chelate stability relationship also for palladium catalysts containing the diphosphine ligands dppp, *rac*-2,4-bdpp, and *meso*-2,4-bdpp.[30]

The β-chelate complexes $[Pd(CH_2CH_2C(O)Me)(P-P)]PF_6$ with diphosphine ligands containing two carbon atoms between the phosphorus donors have been isolated for the first time[18a] and employed to study the chain transfer by protonolysis, which proceeds via the enolate mechanism reported by van Leeuwen for the dppp-based catalysts.[18c] It has been shown that μ-OH complexes of the formula $[Pd(OH)(P-P)]_2^{2+}$ are active

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catalyst precursors for the alternating CO/ethene copolymerization.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen by using Schlenk-type techniques. Diethyl ether and tetrahydrofuran (THF) were distilled from $LiAlH_4$. Reagent grade methanol or CH_2Cl_2, freshly distilled from CaH_2, was used in the copolymerization reactions. All the other reagents and solvents were used as purchased from Aldrich, Fluka, or Strem. The palladium complexes PdCl(Me)(COD) (COD = cycloocta-1,5-diene),[31] $PdCl_2$(dppe),[15] [PdCl(Me)(dppe)],[15] and $[Pd(Me)(MeCN)(dppe)]PF_6$[15] were prepared following literature methods. All of the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerization reactions were performed with a 250 mL stainless steel autoclave, constructed at the ISSECC−CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over all the catalytic reactions. Deuterated solvents for NMR measurements, except as stated otherwise, were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively) or a Bruker DPX 300 spectrometer (300.13, 75.49, and 121.51 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ISSECC−CNR (Firenze, Italy).[32] *Caution*: Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Molecular weights of selected polyketone materials were measured on a Waters gel permeation chromatograph equipped with a differential refractometer. Either pure HFIP or a mixture of trichlorobenzene/phenol was used as the solvent, and polystyrene standards were used to calibrate the instrument. Viscosity measurements (LVN) were carried out in *m*-cresol at 60 °C in a standard capillary viscosity-measuring device. Melting points were determined in glass capillaries under air.

***meso*-$(CH_3CH(OMs))_2$.** Methanesulfonyl chloride (18 mL, 0.23 mol) was added dropwise to a CH_2Cl_2 solution (50 mL) of *meso*-2,3-butanediol (10.0 g, 0.11 mol) and NEt_3 (33.5 mL, 0.24 mol). The solution was allowed to stir overnight. The organic layer was washed with water (2 × 100 mL), separated, and concentrated to dryness under reduced pressure. The crude solid residue was recrystallized with CH_2Cl_2 and petroleum ether to give a white solid. Yield: 71%. ^1H NMR ($CDCl_3$): δ 1.4 (d, *J*(HH) = 6.5 Hz, 6 H, CHC*H*$_3$), 3.1 (s, 6 H, SO_2CH_3), 4.9 (m, 2 H, CH).

***rac*-$(CH_3CH(OMs))_2$.** A pure sample of *rac*-$(CH_3CH(OMs))_2$ was obtained by fractional recrystallization of an isomeric mixture of $(CH_3CH(OMs))_2$ from CH_2Cl_2 and ethanol. Large crystals of *rac*-$(CH_3CH(OMs))_2$ separated first. Yield: 10%. ^1H NMR ($CDCl_3$): δ 1.5 (d, *J*(HH) = 5.5 Hz, 6 H, CHC*H*$_3$), 3.1 (s, 6 H, SO_2CH_3), 4.8 (m, 2 H, CH). The preparation of the isomeric mixture of $(CH_3CH(OMs))_2$ was similar to that of *meso*-$(CH_3CH(OMs))_2$ and started with 40.0 g of a isomeric mixture of 2,3-butanediol (0.444 mol). Yield: 83%.

***meso*-$(CH_3CHPPh_2)_2$ (*meso*-2,3-dppb).** A 60 mL sample of a THF solution of 5.7 g of *meso*-$(CH_3CH(OMs))_2$ (23.23 mmol) was slowly added to 100 mL of a THF solution of $KPPh_2$ dioxane adduct (22 g, 55.00 mmol) at 0 °C. The mixture was allowed to stir overnight at room temperature. The solvent was removed completely under vacuum. Then 100 mL of water was added to give a white solid. The solid was filtered, washed with petroleum ether, and dried under vacuum overnight. Yield: 85%. Anal. Calcd for $C_{28}H_{28}P_2$: C, 78.86; H, 6.62. Found: C, 78.15; H, 6.51. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −7.2 (s).^1H NMR (CD_2Cl_2): δ 1.1, (pseudo quartet, *J*(HP) = *J*(HH) = 7.0 Hz, 6H, CHC*H*$_3$), 2.6 (m, 2H, C*H*CH$_3$), 7.2−7.5 (m, 20H, Ph).

***rac*-$(CH_3CHPPh_2)_2$ (*rac*-2,3-dppb).** The compound was prepared in a similar manner as *meso*-2,3-dppb. Anal. Calcd for $C_{28}H_{28}P_2$: C, 78.86; H, 6.62. Found: C, 78.42; H, 6.58. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −9.4 (s). ^1H NMR (CD_2Cl_2): δ 1.2 (dd, *J*(HP) = 14.0 Hz, *J*(HH) = 7.0 Hz, 6 H, CHC*H*$_3$), 2.4 (m, 2 H, C*H*CH$_3$), 7.2−7.4 (m, 20H, Ph).

$PdCl_2$(*meso*-2,3-dppb). A mixture of 400 mg of *meso*-2,3-dppb (0.939 mmol) and 167 mg of $PdCl_2$ (0.939 mmol) in 20 mL of *N*,*N*-dimethylformamide (DMF) solution was stirred for 12 h. During this time, a yellow solid precipitated. The solution was first concentrated to ca. 4 mL under reduced pressure, and then 30 mL of petroleum ether was slowly added. The formed solid was filtered off, washed with petroleum ether, and dried in a stream of nitrogen. Yield: 85%. Anal. Calcd for $C_{28}H_{28}Cl_2P_2Pd$: C, 55.70; H, 4.67. Found: C, 55.23; H, 4.57. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 69.5 (s). ^1H NMR (CD_2Cl_2): δ 0.98 (dd, *J*(HP) = 15.2 Hz, *J*(HH) = 7.1 Hz, 6H, CHC*H*$_3$), 3.00 (m, 2H, C*H*CH$_3$), 7.45−7.63 and 7.78−8.02 (m, 20H, Ph).

$PdCl_2$(*rac*-2,3-dppb). A mixture of 300 mg of *rac*-2,3-dppb (0.704 mmol) and 125 mg of Pd(II) chloride (0.704 mmol) in 20 mL of DMF was stirred for 12 h. During the reaction, a pink solid precipitated. The solution was concentrated to ca. 4 mL under reduced pressure, and then 30 mL of petroleum ether was slowly added. The precipitate was filtered off. Recrystallization from CH_2Cl_2 gave a white solid. Yield: 63%. Anal. Calcd for $C_{28}H_{28}Cl_2P_2Pd$: C, 55.70; H, 4.67. Found: C, 55.52; H, 4.71. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 66.2 (s). ^1H NMR (CD_2Cl_2): δ 1.05 (dd, *J*(HP) = 13.1 Hz, *J*(HH) = 6.3 Hz, 6H, CHC*H*$_3$), 2.43 (m, 2H, C*H*CH$_3$), 7.52−7.83 and 7.90−8.01 (m, 20H, Ph).

$Pd(OAc)_2$(dppe) (4). To 10 mL of a methanol solution of 169 mg of Pd(II) acetate (0.753 mmol) was added a CH_2Cl_2 solution of 300 mg of dppe (0.753 mmol). The orange-red mixture was allowed to stir for 20 min. Then the volume was reduced to ca. 1 mL under reduced pressure. Petroleum ether (30 mL) was slowly added to give an orange-red solid of **4**, which was filtered, washed with petroleum ether, and dried in a stream of nitrogen. Yield: 35%. Anal. Calcd for $C_{30}H_{30}O_4P_2Pd$: C, 57.84; H, 4.85. Found: C, 57.62; H, 4.78. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.9 (s). ^1H NMR (CD_2Cl_2): δ 1.66 (s, 6H, CO_2CH_3), 2.23 (m, 4H, CH_2), 7.52−7.83 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.5 (s, CO$_2$*C*H$_3$), 27.5 (AXX′ system, m, CH_2), aromatic carbons [129.6 (s), 131.4 (s), 132.8 (s), 134.1 (s)], 176.6 (s, *C*O$_2$CH$_3$). Crystals of **4·CH_2Cl_2** suitable for an X-ray structure analysis were obtained by slow crystallization of **4** from CH_2Cl_2/petroleum ether under nitrogen at room temperature.

$Pd(OAc)_2$(*meso*-2,3-dppb) (5). To a 20 mL CH_2Cl_2 solution of 280 mg of $PdCl_2$(*meso*-2,3-dppb) (0.464 mmol) was added 194 mg of silver acetate (1.16 mmol). After 5 h stirring, the mixture was passed through a column of Celite to remove AgCl formed. The solution was concentrated to ca. 2 mL under vacuum. Then 30 mL of diethyl ether was added at 0 °C to give **5** as a pale yellow solid. Yield: 70%. Anal. Calcd for $C_{32}H_{34}O_4P_2Pd$: C, 59.04; H, 5.26. Found: C, 58.95; H, 5.31. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 20 °C, δ 61.8 (s); −80 °C, δ 65.6 (br s), 60.4 (br s); coalescence temperature at −70 °C. ^1H NMR (CD_2Cl_2): δ 1.55 (s, 6H, CO_2CH_3), 1.05 (dd, ^3J(HH) = 7.0 Hz, ^3J(HP) = 15.0 Hz, 6H, CHC*H*$_3$), 2.83 (m, 2H, C*H*CH$_3$), 7.4−

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8.1 (m, 20H, aromatic protons). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 24.0 (s, CO_2CH_3), 12.0 (s, $CHCH_3$), 39.5 (AXX′ system, m, $CHCH_3$), aromatic carbons [129.5 (s), 132.6 (s), 133.9 (s), 135.8 (s)], 177.0 (s, CO_2CH_3). Crystals suitable for an X-ray structure analysis were obtained by slow crystallization of **5** from CH_2Cl_2/diethyl ether solutions under nitrogen at room temperature.

Pd(OAc)$_2$(*rac*-2,3-dppb) (6). This complex was obtained as a white solid in 70% yield following a procedure analogous to that used for **5** starting from $PdCl_2$(*rac*-2,3-dppb). Anal. Calcd for $C_{32}H_{34}O_4P_2Pd$: C, 59.04; H, 5.26. Found: C, 58.79; H, 5.21. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20/−80 °C): δ 60.5 (s). ^1H NMR (CD_2Cl_2): δ 1.48 (s, 6H, CO_2CH_3), 1.04 (m, 6H, $CHCH_3$), 2.31 (br s, 2H, $CHCH_3$), 7.57−8.15 (m, 20H, aromatic protons). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 24.0 (s, CO_2CH_3), 14.0 (AXX′ system, m, $^2J(CP) + {}^1J(CP) = 14.7$ Hz, $CHCH_3$), 36.4 (AXX′ system, m, $CHCH_3$), aromatic carbons [129.6 (s), 132.0 (s), 133.5 (s), 137.4 (s)], 176.0 (s, CO_2CH_3). Crystals of **6**·H_2O suitable for an X-ray structure analysis were obtained by slow crystallization of **6** from CH_2Cl_2/diethyl ether under nitrogen at room temperature.

[Pd(dppe)$_2$](OAc)$_2$ (7). To a stirred CH_2Cl_2 solution (5 mL) of dppe (0.60 g, 1.5 mmol) was added a solution of Pd(II) acetate (0.17 g, 0.75 mmol) in MeOH (20 mL) at room temperature. After 20 min, the volume was reduced to ca. 5 mL under reduced pressure. Petroleum ether (10 mL) was slowly added to give **7** as a red solid that was filtered off, washed with petroleum ether, and dried in a stream of nitrogen. Yield: 75%. Anal. Calcd for $C_{56}H_{54}O_4P_4Pd$: C, 65.86; H, 5.33. Found: C, 66.14; H, 5.25.

[Pd(dppe)$_2$](PF$_6$)$_2$ (7·PF$_6$). To a stirred solution of $PdCl_2$(dppe) (0.29 g, 0.5 mmol) and dppe (0.20 g, 0.5 mmol) in 20 mL of CH_2Cl_2 was added 2 equiv of $AgPF_6$ (1 mmol). After 30 min, the mixture was passed through a column of Celite to remove the formed AgCl. The solution was concentrated to ca. 5 mL under vacuum. Addition of diethyl ether led to the precipitation of **7**·PF_6 in 85% yield. Anal. Calcd for $C_{52}H_{48}F_{12}P_6Pd$: C, 52.34; H, 4.05. Found: C, 52.13; H, 4.02.

Autoionization Equilibrium between 4 and 7. NMR Experiment. A 5 mm NMR tube was charged with a solution of **4** (12 mg, 1.8 × 10^{-2} mmol) in MeOH-d_4 (1 mL) at room temperature under nitrogen. $^{31}P\{^1H\}$ and ^1H NMR spectra showed the large (80%) conversion of **4** into **7**. Subsequently, the solvent was evaporated under vacuum, and the remaining residue was dissolved in 1 mL of CD_2Cl_2. $^{31}P\{^1H\}$ and ^1H NMR spectra showed that **4** had re-formed quantitatively.

Pd(CN)$_2$(P−P) (P−P = dppe, *meso*-2,3-dppb, *rac*-2,3-dppb). To 0.126 mmol of diphosphine in 5 mL of DMF was added 0.126 mmol of $Pd(CN)_2$. The resulting clear yellow solution was allowed to stir overnight. Slow addition of 30 mL of diethyl ether gave a colorless solid that was filtered off, washed with diethyl ether, and dried under vacuum overnight. $^{31}P\{^1H\}$ NMR and selected IR data for the cyanide complexes are reported in Table 3.

PdCl(Me)(P−P) (P−P = *meso*-2,3-dppb, *rac*-2,3-dppb). To a stirred solution of PdCl(Me)(COD) (0.13 g, 0.50 mmol) in THF (20 mL) was added 1 equiv of diphosphine (0.50 mmol) at room temperature. Almost immediately an off-white product began to precipitate. After 20 min, diethyl ether was added to the reaction mixture to complete the precipitation of the product, which was filtered off, washed with petroleum ether, and dried in a nitrogen stream. Yield: 85−95%. **PdCl(Me)(*meso*-2,3-dppb)**. Anal. Calcd for $C_{29}H_{31}ClP_2Pd$: C, 59.71; H, 5.36. Found: C, 59.43; H, 5.31. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 62.8 (d, $J(PP) = 32.0$ Hz), 36.8 (d). ^1H NMR (CD_2Cl_2): δ 0.55 (dd, $^3J(HP) = 3.1$ Hz, $^3J(HP) = 8.2$ Hz, 3H, $PdCH_3$), 0.70 (dd, $^3J(HH) = 7.3$ Hz, $^3J(HP) = 14.4$ Hz, 3H, $CHCH_3$), 1.21 (dd, $^3J(HH) = 6.9$ Hz, $^3J(HP) = 13.0$ Hz, 3H, $CHCH_3$), 2.71 (m, 2H, $CHCH_3$), 7.3−8.1 (m, 20H, aromatic protons). **PdCl(Me)(*rac*-2,3-dppb)**. Anal. Calcd for $C_{29}H_{31}ClP_2Pd$: C, 59.71; H, 5.36. Found: C, 59.54; H, 5.30. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.8 (d, $J(PP) = 38.0$ Hz), 38.8 (d). ^1H NMR (CD_2Cl_2): δ 0.55 (dd, $^3J(HP) = 3.0$ Hz, $^3J(HP) = 8.1$ Hz, 3H, $PdCH_3$), 1.05 (dd, $^3J(HH) = 7.3$ Hz, $^3J(HP) = 12.4$ Hz, 3H, $CHCH_3$), 1.10 (dd, $^3J(HH) = 7.0$ Hz, $^3J(HP) = 13.2$ Hz, 3H, $CHCH_3$), 2.05 (m, 1H, $CHCH_3$), 2.51 (m, 1H, $CHCH_3$), 7.3−8.1 (m, 20H, aromatic protons).

[Pd(Me)(MeCN)(P−P)]PF$_6$ (P−P = *meso*-2,3-dppb, 11; *rac*-2,3-dppb, 12). A solid sample of $AgPF_6$ (0.13 g, 0.50 mmol) was added to a magnetically stirred solution of the appropriate PdCl(Me)(P−P) complex (0.45 mmol) in a 10:1, v/v mixture of CH_2Cl_2/MeCN. After 30 min stirring at room temperature, AgCl was removed by filtration on Celite. The resultant colorless solution was concentrated to ca. 2 mL under reduced pressure. Addition of a 1:10 v/v mixture of diethyl ether/*n*-hexane (20 mL) led to the precipitation of a brownish solid, which was filtered off, washed with petroleum ether, and dried in a nitrogen stream. Yield: 50−55%. **11**. Anal. Calcd for $C_{31}H_{34}F_6NP_3Pd$: C, 50.73; H, 4.67; N, 1.91. Found: C, 50.54; H, 4.59; N, 1.82. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 64.8 (d, $J(PP) = 34.0$ Hz), 42.7 (d). ^1H NMR (CD_2Cl_2): δ 0.57 (dd, $^3J(HP) = 1.9$ Hz, $^3J(HP) = 7.3$ Hz, 3H, $PdCH_3$), 0.85 (dd, $^3J(HH) = 7.3$ Hz, $^3J(HP) = 14.6$ Hz, 3H, $CHCH_3$), 1.14 (dd, $^3J(HH) = 7.1$ Hz, $^3J(HP) = 14.3$ Hz, 3H, $CHCH_3$), 2.21 (s, 3H, MeCN), 2.80 (m, 1H, $CHCH_3$), 2.90 (m, 1H, $CHCH_3$), 7.3−7.9 (m, 20H, aromatic protons). IR (Nujol mull, KBr plates): (MeCN) 2319, 2287 cm^{-1}. **12**. Anal. Calcd for $C_{31}H_{34}F_6NP_3Pd$: C, 50.73; H, 4.67; N, 1.91. Found: C, 50.81; H, 4.71; N, 1.83. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.5 (d, $J(PP) = 40.7$ Hz), 42.8 (d). ^1H NMR (CD_2Cl_2): δ 0.39 (dd, $^3J(HP) = 2.1$ Hz, $^3J(HP) = 7.5$ Hz, 3H, $PdCH_3$), 1.09 (dd, $^3J(HH) = 6.3$ Hz, $^3J(HP) = 13.2$ Hz, 6H, $CHCH_3$), 2.15 (s, 3H, MeCN), 2.50 (m, 2H, $CHCH_3$), 7.4−78.0 (m, 20H, aromatic protons). IR (Nujol mull, KBr plates): (MeCN) 2319, 2287 cm^{-1}.

[Pd(OH)(P−P)]$_2$(PF$_6$)$_2$ (P−P = dppe, 16; *meso*-2,3-dppb, *cis*-/*trans*-17). Solid $AgPF_6$ (0.18 g, 0.72 mmol) was added to a CH_2Cl_2 (30 mL) solution of the appropriate $PdCl_2$(P−P) complex (0.33 mmol) at room temperature. After AgCl was removed by filtration, $KOBu^t$ (41 mg, 0.33 mmol) dissolved in 1 mL of water was added under vigorous stirring. After 30 min, the solvent was removed under reduced pressure and the solid residue was treated with 20 mL of CH_2Cl_2. The CH_2Cl_2 phase was passed through Celite, and the resulting clear yellow solution was concentrated to 5 mL under reduced pressure. Addition of a 1:1 mixture of diethyl ether and *n*-hexane led to the precipitation of a yellow microcrystalline solid, which was filtered off, washed with diethyl ether, and dried in a stream of nitrogen. Yield: 40−60%. **16**. Anal. Calcd for $C_{52}H_{50}F_{12}O_2P_6Pd_2$: C, 46.83; H, 3.78. Found: C, 46.95; H, 3.68. IR (Nujol mull, KBr plates): (ν_{OH}) 3591 cm^{-1}. $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 64.2 (s). ^1H NMR (CD_2Cl_2): δ −1.69 (s, OH). ***cis*-/*trans*-17**. Anal. Calcd for $C_{56}H_{58}F_{12}O_2P_6Pd_2$: C, 48.40; H, 4.21. Found: C, 48.00; H, 4.11. IR (Nujol mull, KBr plates): (ν_{OH}) 3595 cm^{-1}. $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ_1 67.7 (s), δ_2 68.2 (s) in a ratio of 85:15. ^1H NMR (CD_2Cl_2): $\delta_1 + \delta_2$ −1.71 (s, OH).

[Pd(CH$_2$CH$_2$C(O)Me)(P−P)]PF$_6$ (P−P = dppe, 18; *meso*-2,3-dppb, 19; *rac*-2,3-dppb, 20). In a typical experiment, a solution of 0.035 mmol of the methyl acetonitrile complex **10** (**11** or **12**) in 2 mL of CD_2Cl_2 was transferred into a 10 mm sapphire HPNMR tube and pressurized to 15 bar with CO at room temperature. $^{31}P\{^1H\}$ and ^1H NMR spectra recorded at room temperature showed the quantitative conversion of **10** into the corresponding acyl carbonyl derivative **21** (**22** or **23**) (selected $^{31}P\{^1H\}$ and ^1H NMR data are reported in Tables 6 and 7, respectively). After the tube was immersed into a cooling bath at −40 °C and depressurized to ambient pressure 20 μL of MeCN was added by a syringe under nitrogen. $^{31}P\{^1H\}$ and ^1H NMR spectra recorded at −40 °C showed the quantitative conversion of the acyl carbonyl derivatives into the corresponding acyl acetonitrile derivatives [Pd(COMe)(MeCN)(P−P)]PF_6 (**24**−**26**) (selected $^{31}P\{^1H\}$ and ^1H NMR data for these complexes are reported in Tables 6 and 7, respectively). Bubbling ethene for 2 min into the solutions of the latter complexes maintained at −40 °C led to the quantitative formation of the β-chelate complexes. The final solution was transferred from the HPNMR tube into a flask immersed in a bath at −20 °C. Evaporation of the solvent under reduced pressure gave a solid product, which was washed with *n*-pentane and dried (selected $^{31}P\{^1H\}$ and ^1H NMR data for **18**−**20** are reported in Tables 6 and 7, respectively). **18**. Anal. Calcd for $C_{30}H_{31}F_6OP_3Pd$: C, 49.98; H, 4.33. Found: C, 49.55; H, 4.25. IR (Nujol mull, KBr plates): (νC═O) 1624 cm^{-1}. **19**. Anal. Calcd for $C_{32}H_{35}F_6OP_3Pd$: C, 51.32; H, 4.71. Found: C, 50.99; H, 4.65. IR (Nujol mull, KBr plates): (νC═O) 1621 cm^{-1}. **20**. Anal. Calcd for $C_{32}H_{35}F_6OP_3Pd$: C, 51.32; H, 4.71. Found: C, 51.11; H, 4.61. IR (Nujol mull, KBr plates): (νC═O) 1622 cm^{-1}.

Copolymerization of Ethene and Carbon Monoxide Catalyzed by $Pd(OTs)_2$(P−P) in MeOH. A. Autoclave Experiments. MeOH (100 mL) was introduced by suction into a 250 mL autoclave containing 86.5 mg of BQ (0.8 mmol), 38.0 mg of TsOH (0.2 mmol), and 0.01 mmol of catalyst precursor previously evacuated by a vacuum pump. The autoclave was charged with a 1:1 CO/C_2H_4 mixture to 40 bar at room temperature. After the contents of the autoclave had been brought to 85 °C, the pressure was then maintained at ca. 45 bar by continuous feeding of an equimolar mixture of CO and C_2H_4 from a gas reservoir. The reaction mixture was then stirred (1400 rpm) for the required reaction time. The reaction was stopped by cooling the autoclave to room temperature by means of an ice−water bath. After the unreacted gases were released, the formed insoluble ethene−carbon monoxide copolymer was filtered off, washed with methanol, and dried in a vacuum oven at 70 °C overnight. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.3; H, 7.2. Found: C, 64.1; H, 7.1. IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m) cm^{-1}. ^1H NMR (HFIP-d_2): δ 3.73 (s, $CH_2CO_2CH_3$), 2.83 (s, CH_2COCH_2), 2.55 (q, J(HH) = 7.4 Hz, $COCH_2CH_3$), 1.09 (t, J(HH) = 7.4 Hz, $COCH_2CH_3$). $^{13}C\{^1H\}$ NMR (HFIP/$CDCl_3$, 9:1, v/v): δ 217.2 ($COCH_2CH_3$), 213.0 (CH_2COCH_2), 176.6 ($CH_2CO_2CH_3$), 52.6 ($CH_2CO_2CH_3$), 36.1 (CH_2COCH_2), 27.9 ($CH_2CO_2CH_3$), 7.1 ($COCH_2CH_3$).

B. HPNMR Experiments. The reactions were followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Details of the procedure are exemplified for **5**. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 5. A 10 mm sapphire HPNMR tube was charged with a solution of **5** (12 mg, 1.8×10^{-2} mmol) in MeOH-d_4 (2 mL) under nitrogen and then placed into the NMR probe at room temperature ($^{31}P\{^1H\}$ NMR singlet at δ 66.9, trace a). Addition of TsOH (0.09 mmol) and BQ (0.18 mmol) led to the conversion of **5** into $Pd(OTs)_2$(*meso*-2,3-dppb) (**9**) (downfield shift of the $^{31}P\{^1H\}$ NMR resonance to δ 78.1, trace b). Pressurizing with a 1:1 mixture of carbon monoxide/ethene to 40 bar at room temperature caused no change in both the ^1H and $^{31}P\{^1H\}$ NMR spectra (trace c). Complex **9** was the only phosphorus-containing species visible by NMR also during the copolymerization reaction (1 h at 85 °C). The tube was then allowed to cool to room temperature. A comparison between the $^{31}P\{^1H\}$ NMR spectrum of this sample (trace d) and the spectrum acquired at room temperature before the catalytic reaction (trace c) showed no decrease in the intensity of the signal of **9**. Once the tube was removed from the probe-head, the copolymer appeared as an off-white solid. Appreciable degradation of the *meso*-2,3-dppb-derived catalyst to palladium metal was observed only in parallel experiments lasting 3 h at 85 °C.

Terpolymerization of Ethene/Propene and Carbon Monoxide Catalyzed by $Pd(OTs)_2$(P−P) in MeOH. Autoclave Experiments. The procedure was similar to that employed in the above-reported CO/C_2H_4 copolymerization. Propene (20 g) was introduced into the autoclave after the catalyst solution with the autoclave cooled at 4 °C. The autoclave was charged with 20 bar of CO and 20 bar of C_2H_4. After the contents of the autoclave had been brought to 85 °C, the pressure was then maintained at ca. 55 bar by introducing under pressure a 1:1 CO/C_2H_4 mixture. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.3; H, 7.2. Found: C, 64.1; H, 7.1. IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m) cm^{-1}. ^1H NMR (HFIP-d_2): δ 3.73 (s, $CH_2CO_2CH_3$), 3.05 (m, CH_2CHCH_3), 2.81 (s, CH_2COCH_2), 2.55 (q, J(HH) = 7.4 Hz, $COCH_2CH_3$), 1.15 (d, J(HH) = 6.5 Hz, CH_2CHCH_3), 1.09 (t, J(HH) = 7.4 Hz, $COCH_2CH_3$). $^{13}C\{^1H\}$ NMR (HFIP/C_6H_6, 9:1, v/v): δ 217.1 ($COCH_2CH_3$), 214.1 ($CH_2COCHCH_3$), 212.8 (CH_2COCH_2), 176.6 ($CH_2CO_2CH_3$), 52.6 ($CH_2CO_2CH_3$), 45.0 ($COCH_2CHCH_3$), 41.3 ($COCH_2CHCH_3$), 35.7 (CH_2COCH_2), 34.5 ($CH_2COCHCH_3$), 27.9 ($CH_2CO_2CH_3$), 15.7 ($CH_2COCHCH_3$), 6.5 ($COCH_2CH_3$).

Copolymerization of Ethene and Carbon Monoxide Catalyzed by the Methyl Acetonitrile Complexes 10−**12 in CH_2Cl_2. A. Autoclave Experiments.** Under a nitrogen atmosphere, a 100 mL solution of CH_2Cl_2 (freshly distilled under nitrogen from CaH_2) containing the catalyst precursor (0.01 mmol) was introduced into a 250 mL autoclave equipped with a magnetic drive stirrer and a temperature and pressure controller. The autoclave was charged with 20 bar of CO and 20 bar of C_2H_4. After the contents of the autoclave had been brought to 70 °C, the pressure was maintained at ca. 40 bar by continuous feeding of an equimolecular mixture of C_2H_4 and CO from a high-pressure gas reservoir connected to the autoclave. A pressure gauge connected to the gas reservoir was employed to determine the gas consumption during the reactions. The reaction mixture was then stirred (1400 rpm) for the desired time. The reaction was stopped by cooling the autoclave to room temperature using an ice−water bath. After the unreacted gases were released, the insoluble copolymer was filtered off, washed with CH_2Cl_2, and dried in a vacuum oven at 70 °C overnight. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.3; H, 7.2. Found: C, 64.1; H, 7.1. IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m) cm^{-1}. ^1H NMR (HFIP-d_2): δ 2.85 (s, $CH_2C(O)CH_2$). $^{13}C\{^1H\}$ NMR (HFIP-d_2): δ 213.6 ($CH_2C(O)CH_2$), 36.0 ($CH_2C(O)CH_2$).

A series of reactions were carried in the presence of BQ (0.87 g, 0.8 mmol). The composition and molecular weight of the polyketone products were analogous to those obtained in the absence of oxidant.

B. HPNMR Experiments. Details of the procedure are exemplified for **11**. A 10 mm sapphire HPNMR tube was charged with a solution of the methyl acetonitrile complex (12 mg, 1.8×10^{-2} mmol) in 2 mL of CD_2Cl_2 (freshly distilled from CaH_2) under nitrogen and then placed into the NMR probe at room temperature. After $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired, the tube was pressurized with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature. The reactions were followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy for 30 min at 50 °C and 1 h at 70 °C. Afterward, the tube was cooled to room temperature, and the internal pressure was released. Palladium metal was found in the NMR tube together with the copolymer.

A series of analogous experiments were carried out in the presence of 10 μL of water.

Copolymerization of Ethene and Carbon Monoxide Catalyzed by the μ-OH Complexes 16 and *cis-/trans*-17 in CH_2Cl_2. Autoclave Experiments. The catalytic activity of the μ-OH binuclear complexes was tested in 30 min experiments following a procedure analogous to that employed for the methyl acetonitrile complexes.

Thermal Stability of the β-Chelates 18 and 19 in Dry and Wet CD_2Cl_2. Details of the procedure are exemplified for

18. A 5 mm NMR tube was charged with a solution of **18** (0.01 mmol) in 1 mL of either dry or wet CD_2Cl_2 (10 μL of H_2O) under nitrogen at room temperature. The reactions were followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy by acquiring NMR spectra every hour. Sequences of selected $^{31}P\{^1H\}$ NMR spectra are reported in Figures 11 (dry CD_2Cl_2) and 12 (wet CD_2Cl_2). The organic products formed during the reactions were detected by GC and GC/MS analysis of the final reaction solutions.

Experiments carried out at 50 and 70 °C gave identical results except for faster chemical transformations.

In Situ Carbonylation of the Methyl Acetonitrile Complexes 10−12. HPNMR Experiments. In a typical experiment, the methyl acetonitrile complex (0.035 mmol) was dissolved in 2 mL of CD_2Cl_2 (distilled over CaH_2 under nitrogen), and the resulting solution was then transferred into a 10 mm sapphire tube. After $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample were acquired at room temperature, the NMR probe-head was cooled to −80 °C. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at this temperature. The sapphire tube was removed from the spectrometer, immersed into an ethanol/liquid nitrogen thermostat bath (−117 °C), and charged with 15 bar of CO. The tube was then placed into the probe-head precooled to −80 °C. Irrespective of the diphosphine ligand, the $^{31}P\{^1H\}$ and ^1H NMR spectra showed the quantitative conversion of the starting methyl acetonitrile complex into the corresponding methyl carbonyl derivative $[Pd(Me)(CO)(P-P)]PF_6$ (selected $^{31}P\{^1H\}$ and ^1H NMR data of the methyl carbonyl complexes **30**−**32** are reported in Tables 6 and 7, respectively). The probe temperature was gradually increased, and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at each intermediate temperature. Increasing the temperature converted each methyl carbonyl complex into the corresponding carbonyl acyl derivative $[Pd(COMe)(CO)(P-P)]PF_6$ (**21**−**23**). At the conversion temperature, the decrease in concentration of the methyl carbonyl complex was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra were taken at intervals of 5−10 min, depending on conditions. Each reaction was followed for 2−3 half-lives. Experiments were repeated with varying pressures of CO (5−25) to determine the dependence of the reaction rate on the CO concentration. The results indicated that the rate of the reaction is independent of CO. According to first-order kinetics, the free energy of activation was calculated as follows: $\Delta G^{\ddagger} = RT(\ln k_r - \ln kT/h)$ with $k_r = \ln 2/t_{1/2}$.

Generation and Carbonylation of the *β*-Chelate Complexes 18SbF$_6$-20SbF$_6$. HPNMR Experiments. In a typical experiment, the chloride methyl complex PdCl(Me)(P−P) (0.035 mmol) was dissolved in 2 mL of deoxygenated CD_2Cl_2, and the resulting solution was transferred into a 10 mm sapphire tube and then pressurized to 20 bar of CO at room temperature. The formation of the chloride acyl complexes containing dppe, *meso*-2,3-dppb, or *rac*-2,3-dppb required heating to 40 °C for 2 h (selected $^{31}P\{^1H\}$ and ^1H NMR data of the chloride acyl complexes **27**−**29** are reported in Tables 6 and 7, respectively). Once the chloride acyl complex was obtained, the tube was removed from the spectrometer and the excess CO was released. The tube was then immersed into a thermostat bath at −20 °C, and nitrogen was bubbled throughout the solution for 15 min to eliminate any trace of CO. Ethene was bubbled into the solution maintained at −20 °C for 5 min, and then a solid sample of $AgSbF_6$ (0.08 mmol) was added to the solution. The immediately formed AgCl settled on the bottom of the tube. Irrespective of the diphosphine ligand, the $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the quantitative conversion of the chloride acyl complex into the corresponding *β*-chelate complex $[Pd(CH_2CH_2C(O)Me)(P-P)]SbF_6$. Afterward, the NMR probe-head was cooled to −90 °C, and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at this temperature. The sapphire tube was removed from the probe, and nitrogen was bubbled throughout the solution at room temperature to eliminate any trace of ethene. The sapphire tube was immersed into an ethanol/liquid nitrogen thermostat bath (−117 °C) and charged with 20 bar of CO. After this procedure, the tube was placed into the probe-head precooled to −90 °C. $^{31}P\{^1H\}$ and ^1H NMR spectra showed that the *β*-chelate complexes were still present. The probe temperature was gradually increased, and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at each intermediate temperature. Increasing the temperature converted the *β*-chelate complex into the carbonyl acyl derivative $[Pd(COCH_2CH_2C(O)Me)(CO)(P-P)]SbF_6$ (selected $^{31}P\{^1H\}$ and ^1H NMR data of the carbonyl acyl complexes **33**−**35** are reported in Tables 6 and 7, respectively). At the conversion temperature, the decrease in concentration of the methyl carbonyl complex was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra were taken at intervals of 5−10 min, depending on conditions. The reaction was followed for 2−3 half-lives.

Analogous experiments in the pressure range from 15 to 25 bar showed that the $t_{1/2}$ values decrease with increasing pressure.

$[Pd(CH_2CH_2C(O)Me)(P-P)]SbF_6$/$[Pd(COCH_2CH_2C(O)Me)(CO)(P-P)]SbF_6$ Equilibria. Solutions of the carbonyl acyl complexes **33**−**35**, prepared as reported above in HPNMR tubes, were immersed in a thermostat bath at −20 °C. CO was released, and then couples of vacuum−nitrogen cycles were applied. $^{31}P\{^1H\}$ and ^1H NMR spectra of these samples acquired at −20 °C let us follow the transformation of the carbonyl acyl complexes into the corresponding *β*-chelates **18**SbF$_6$−**20**SbF$_6$.

Attempted Determination of the Migratory Insertion Barriers of $[Pd(COMe)(C_2H_4)(P-P)]BF_4$. CD_2Cl_2 solutions of the carbonyl acyl complexes **21**−**23**, prepared as reported above in HPNMR tubes, were immersed in a thermostat bath at −30 °C. CO was released, and then 30 μL of CD_3CN was added. The reaction mixtures were purged with Ar to remove excess and coordinated CO. $^{31}P\{^1H\}$ and ^1H NMR spectra of these samples showed the quantitative formation of the acyl acetonitrile derivatives $[Pd(COMe)(MeCN)(P-P)]PF_6$ (**24**−**26**) (selected $^{31}P\{^1H\}$ and ^1H NMR data are reported in Tables 6 and 7, respectively). The tubes were pressurized with C_2H_4 (15 bar) at −110 °C. In no case were acyl ethene intermediates of the general formula $[Pd(COMe)(C_2H_4)(P-P)]^+$ intercepted, the *β*-chelate complexes **18**−**20** being rapidly and quantitatively formed.

X-ray Data Collection and Structure Determination of 4·CH$_2$Cl$_2$, 5, and 6·H$_2$O. Suitable crystals were sealed in a glass capillary and transferred to a Enraf-Nonius CAD4 diffractometer. Data were collected at room temperature. A set of 25 carefully centered reflections having $6.5° \leq \theta \leq 10.0°$ were used to determine the lattice constants. The intensities of three standard reflections were measured every 2 h for orientation and intensity control. This procedure revealed no decay of intensity. The data were corrected for Lorentz and polarization effects. Atomic scattering factors with anomalous dispersion correction were taken from X-ray crystallography tables.[33] Absorption correction was applied via ψ scan. The computational work was performed with a DIGITAL DEC 5000/200 workstation using the program SHELX-93.[34] The structures were solved by direct methods using the SIR92 program,[35] and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and finally with anisotropic thermal parameters for all the atoms but the hydrogens. The phenyl

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rings were treated as rigid bodies with D_{6h} symmetry, and hydrogen atoms were introduced at calculated positions.

Acknowledgment. Thanks are due to the European Commission for contract no. HPRN CT 2000-00010 and to COST Action D17 for sponsoring the Working Group 0007/2000.

Supporting Information Available: Tables of bond lengths and angles and positional and thermal parameters for compounds **4**·CH_2Cl_2, **5**, and **6**·H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010727B