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Taking Too Many Precautions in Making a Catalyst Is Never a Loss of Time: A Lesson We Learned at Our Own Expense

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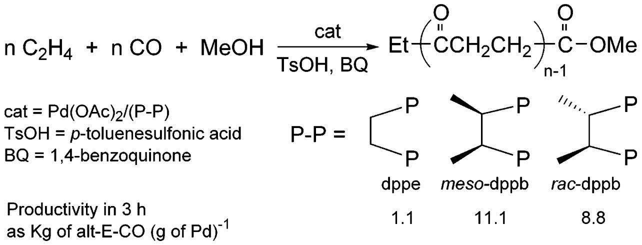
The reaction in MeOH between the bis-chelate complex $[Pd(dppe)_2](OAc)_2$ and $Pd(OAc)_2$ to give the monochelate product $Pd(OAc)_2(dppe)$ is assisted by free acetate ion, and its rate is proportional to the concentrations of both reagents (dppe = 1,2-bis(diphenylphosphino)ethane). The aggregation of $Pd(OAc)_2$ in CH_2Cl_2 and the low dielectric constant of this solvent are proposed to be important factors in accelerating the formation of $Pd(OAc)_2(dppe)$ in CH_2Cl_2.

Introduction

The alternating copolymerization[1] of carbon monoxide and ethene in MeOH has been recently investigated by us using as catalyst precursor $Pd(OAc)_2$ modified with the chelating diphosphines 1,2-bis(diphenylphosphino)ethane (dppe), *meso*-2,3-bis(diphenylphosphino)butane (*meso*-2,3-dppb), and *rac*-2,3-bis(diphenylphosphino)butane (*rac*-2,3-dppb).[2] Under comparable experimental conditions, the productivity in polyketone obtained with the dppe catalyst was found to be lower than those with either *meso*-2,3-dppb or *rac*-2,3-dppb by a factor of 10 (Scheme 1). Such a remarkable decrease in activity for a catalyst precursor, differing from the other two only for the methyl substituents in the ligand backbone, was surprising and chemically intriguing. Therefore, a detailed study of the chemical−physical properties of all Pd^{II} precursors was undertaken in our laboratories.

The dppe catalyst used in the CO/C_2H_4 copolymerization reactions (denoted as **1***) was prepared by reacting a MeOH solution of $Pd(OAc)_2$ with an equivalent amount of dppe dissolved in CH_2Cl_2. The addition of petroleum ether gave a yellow-orange crystalline product that multinuclear NMR spectroscopy in CD_2Cl_2 and a single-crystal X-ray analysis showed to be the known complex $Pd(OAc)_2(dppe)$ (**1**).[2] Every sample of **1*** was regularly checked by NMR spectroscopy in CD_2Cl_2 prior to use in the copolymerization reactions. The complexes $Pd(OAc)_2$(*meso*-2,3-dppb) (**2**) and $Pd(OAc)_2$(*rac*-2,3-dppb) (**3**) were synthesized by a different procedure, involving metathetical reactions of the corresponding bis-chloride derivatives $Pd(Cl)_2(P{-}P)$ with silver acetate in CH_2Cl_2. Multinuclear NMR spectroscopy and X-ray analyses showed **2** and **3** to have the same primary structure of **1**.

Scheme 1



The following step was to study the kinetics of the catalytic reactions, measuring the gas uptake with time: None of the precursors showed an induction period; in accord with the batch catalytic reactions, the dppe-modified catalyst consumed less CO/C_2H_4 than the other two, steadily since the early stages of the reaction. Next, a high-pressure NMR study of the copolymerization reactions was carried out under experimental conditions comparable to those in the batch reactions. A remarkable difference was immediately noticed in the behavior of the three Pd^{II} precursors **1***, **2**, and **3**. The latter two complexes dissolved in MeOH-d_4 maintained the monochelate structure, yet undergoing the exchange of one or two acetate groups for solvent molecules.[3] In contrast, the $^{31}P\{^1H\}$ NMR spectrum of **1*** in MeOH-d_4 showed the presence of both **1** and the bis-chelate complex $[Pd(dppe)_2](OAc)_2$ (**4**). Remarkably, the **1**:**4** ratio remained constant for 1 h (longer times were not investigated), while the addition of TsOH, alone or in conjunction with BQ, had the only effect of converting the acetate precursors into the tosylate derivatives $Pd(OTs)_2(P{-}P)$ ($P{-}P$ = dppe, **5**; *meso*-2,3-dppb, **6**) and $[Pd(dppe)_2](OTs)_2$ (**4OTs**). The **5**:**4OTs** ratio remained constant for 24 h at room temperature, and the addition

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* Corresponding author.

[1] (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.* **2002**, *225*, 35. (g) Bianchini, C.; Meli, A.; Oberhauser, W. *J. Chem. Soc., Dalton Trans.* **2003**, 2627. (h) Freisa, Z.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **2003**, 1890.

[2] Bianchini, C.; Lee, H. M.; Meli, A.; Oberhauser, W.; Peruzzini, M.; Vizza, F. *Organometallics* **2002**, *21*, 16.

[3] (a) Pignat, K.; Vallotto, J.; Pinna, F.; Strukul, G. *Organometallics* **2000**, *19*, 5160. (b) Brown, J. M.; Hii (Mimi) K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 657. (c) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, *14*, 1110.

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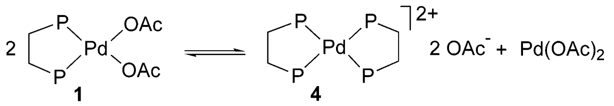
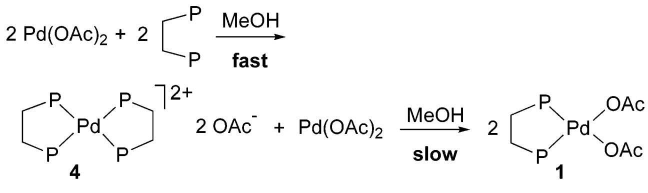
Scheme 2



Scheme 3



of 40 bar of CO/C_2H_4 did not appreciably affect the ^{31}P NMR picture of either system.

Our interpretation of this experimental evidence was that **1** undergoes in MeOH ($\epsilon = 32.6$) the autoionization process illustrated in Scheme 2, whereas it remains intact in a solvent with a lower dielectric constant such as CH_2Cl_2 ($\epsilon = 9.1$).

Any other residual doubt of this interpretation was seemingly dispelled by a paper published almost contemporaneously to the writing of our article. In this paper,[4] Mul, Bouwman, and co-workers reported that $Ni(OAc)_2(dppe)$ undergoes autoionization in MeOH to give equilibrium concentrations of $[Ni(dppe)_2]^{2+}$ and $[Ni(OAc)_4]^{2-}$. A previous work by Sadler et al. was in line with the occurrence of $NiCl_2(dppe)$ autoionization in MeOH.[5]

In late 2002, Mul and co-workers published a paper in which it was unambiguously shown that the bis-chelate complex **4** is the kinetic product of the stoichiometric reaction between $Pd(OAc)_2$ and dppe in MeOH (Scheme 3).[6] On standing in MeOH at room temperature, **4** slowly converted into the thermodynamic product **1**. This means that the autoionization of **1** in MeOH does not occur. Therefore, the question is, what misled us and what really was **1***?

Results and Discussion

As reported by Mul and co-workers,[6] the stoichiometric reaction of $Pd(OAc)_2$ with dppe in CD_2Cl_2 at room temperature gave **1** immediately and quantitatively ($^{31}P\{^1H\}$ and ^1H NMR analysis). When a solid sample of **1** prepared in CH_2Cl_2 was dissolved in MeOH-d_4 under nitrogen, no trace of **4** was formed over 24 h at room temperature. Next, the reaction between $Pd(OAc)_2$ and dppe was investigated in CD_2Cl_2 at low temperature by $^{31}P\{^1H\}$ NMR spectroscopy. The two reagents were dissolved in a 5 mm NMR tube containing degassed CD_2Cl_2 at −70 °C. Immediately, a solid product precipitated,[7] which was filtered off and identified as pure **4** by NMR spectroscopy in CD_2Cl_2. In a second experiment, the solid precipitate of **4** was not removed from the NMR tube which was placed into a probe-head precooled at −70 °C. As shown in Figure 1 (trace a), the solution contained **4** together with a minor amount of **1**. Increasing the temperature led to the dissolution of precipitated **4** with concomitant formation of **1** (trace b). The first spectrum at room temperature showed the exclusive presence of **1** (trace c). In comparable concentrations of $Pd(OAc)_2$ and dppe, but in MeOH-d_4, the conversion of the kinetic product **4** into the thermodynamic product **1** was much slower, occurring with a $t_{1/2}$ value of ca. 4 h at room temperature (see below).[6]

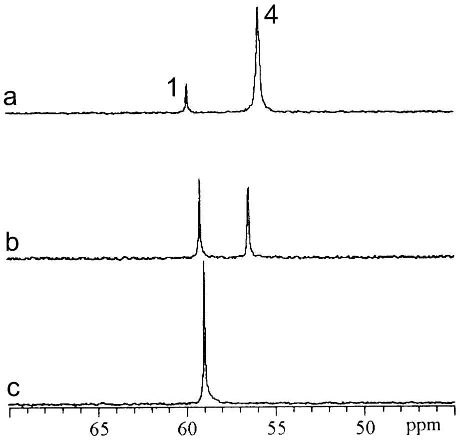


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR study (CD_2Cl_2, 81.01 MHz) of the reaction of $Pd(OAc)_2$ with dppe: (a) at −70 °C after dissolving $Pd(OAc)_2$ and dppe in CD_2Cl_2 at −70 °C; (b) at −20 °C after 50 min; (c) at room temperature after 10 min.

The NMR study described above proves that the reaction of $Pd(OAc)_2$ in MeOH with a stoichiometric amount of dppe in CH_2Cl_2 at room temperature, followed by precipitation with petroleum ether, yields a solid mixture, namely, **1***, comprising **4**, $Pd(OAc)_2$, and **1**. The relative ratio between **4** and **1** in this mixture decreases with the reaction time, yet the dissolution of any sample of **1*** in CH_2Cl_2 at room temperature leads to the immediate formation of **1**, which explains why we were confident to use pure **1** in the catalytic experiments.[2] As shown by Mul and co-workers,[6] the transformation of **4** into **1** in MeOH is too slow to be appreciated in 1 h (as we tried to do)[2] and is also immediately stopped by the addition of TsOH, which is an essential component of the $Pd(OAc)_2$/(diphosphine) catalytic systems under investigation.[2]

In an attempt to understand the role of TsOH in inhibiting the formation of the thermodynamic monochelate complex **1**, the bis-chelate **4OTs** was prepared by metathetical reaction of $[Pd(dppe)_2]Cl_2$[8] with AgOTs in CH_2Cl_2. Remarkably, **4OTs** was found to be fully stable in MeOH and CH_2Cl_2 at room temperature for 24 h *even in the presence of* $Pd(OAc)_2$ (Scheme 4a). In contrast, **4** reacted with $Pd(OAc)_2$ in either MeOH or CH_2Cl_2, yielding **1** (Scheme 4b). Interestingly, **4** was unstable in CH_2Cl_2, where it underwent slow and irreversible reduction to the Pd^0 derivative $Pd(dppe)_2$ (**7**) with concomitant formation of **1**, dppe=O, and acetic anhydride (Scheme 4b).[7,8a,b,9] This redox transformation is

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[4] Angulo, I. M.; Bouwman, E.; Lutz, M.; Mul, W. P.; Spek, A. L. *Inorg. Chem.* **2001**, *40*, 2073.

[5] Jarrett, P. S.; Sadler, P. J. *Inorg. Chem.* **1991**, *30*, 2098.

[6] Marson, A.; van Oort, A. B.; Mul, W. P. *Eur. J. Inorg. Chem.* **2002**, 3028.

[7] Grushin, V. V. *Organometallics* **2001**, *20*, 3950.

[8] (a) Mason, M. R.; Verkade, J. G. *Organometallics* **1990**, *9*, 864. (b) Lindsay, C. H.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1980**, *19*, 3503. (c) Engelhardt, L. M.; Patrick, J. M.; Raston, C. L.; Twiss, P.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 2193.

[9] (a) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A. *Organometalllics* **1995**, *14*, 1818. (b) Amatore, C.; Jutand, A.; Thuilliez, A. *Organometalllics* **2001**, *20*, 3241.

Scheme 4

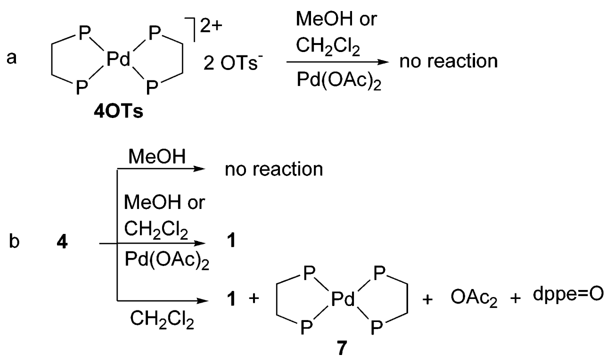

Table 1. Alternating Copolymerization of Carbon Monoxide with Ethene Catalyzed by Pd/dppe Precursors in MeOH[a]

entry	precursor	alt-E-CO g	alt-E-CO prod.[b]
1	**1**[c]	3.20	3.01
2	[**4** + $Pd(OAc)_2$ + **1**][d]	1.20	n.c.
3	[**4** + $Pd(OAc)_2$ + **1**][e]	0.14	n.c.
4	**4**[c]	0.06	0.06

[a] Initial $p(C_2H_4)$ (20 bar), initial p(CO) (20 bar), temperature (85 °C), time (3 h), stirring rate (1400 rpm). [b] Productivity expressed as kg of polymer (g of Pd)$^{-1}$. [c] Precursor (0.01 mmol), MeOH (100 mL), BQ (0.8 mmol), TsOH (0.2 mmol). [d] See ref 2; the precursor (6.2 mg) employed in the catalytic run was part of a solid sample precipitated with petroleum ether from a reaction mixture obtained by mixing $Pd(OAc)_2$ in MeOH and dppe in CH_2Cl_2. [e] The precursor was prepared in situ by reacting $Pd(OAc)_2$ (0.01 mmol) and dppe (0.01 mmol) in MeOH (50 mL) for 10 min before the addition of BQ (0.8 mmol) and TsOH (0.2 mmol) in MeOH (50 mL).

known by the name of Amatore reaction and is typical for $Pd(OAc)_2(phosphine)_2$ complexes (see below).[9]

The results reported in Scheme 4 prove that the presence of *free* acetate ions is required to promote the conversion of **4** into **1**. This explains why the addition of TsOH to MeOH solutions of **1***, converting OAc^- into HOAc, stops immediately the formation of the catalytic precursor **1**. Table 1 illustrates clearly the influence of the preparation procedure of some dppe-based catalysts on the productivity in alternating polyketone under standard copolymerization conditions.

The highest activity was shown by isolated **1**, prepared by mixing equivalent amounts of $Pd(OAc)_2$ and dppe in CH_2Cl_2 (entry 1), while the precursors obtained in either $MeOH/CH_2Cl_2$ or MeOH, being kinetic mixtures of **4**, $Pd(OAc)_2$, and **1**, enriched in catalytically inactive **4**, were much less active (entries 2 and 3). In particular, the activity of the kinetic mixtures decreased by decreasing the reaction time before quenching by either precipitation[2] (entry 2) or TsOH addition (entry 3).[6]

As anticipated in Scheme 4, both free OAc^- and $Pd(OAc)_2$ are required to accomplish the transformation of the kinetic bis-chelate product into **1**. In an attempt to understand the mechanism by which **4** converts into **1**, a kinetic study was undertaken for the reaction between **4** and $Pd(OAc)_2$ in MeOH-d_4 at 23 °C, using $^{31}P\{^1H\}$ NMR spectroscopy to monitor the variation of the concentrations of **4** and **1** with time (Table 2).

A plot of ln [**4**] versus time showed the formation of **1** to proceed with first-order kinetics in **4** (Table 2, entry 1; Figure 2, trace a). This rate dependence was also noticed by Mul.[6] We have now found that the rate of the reaction depends also on the concentration of $Pd(OAc)_2$. Indeed, increasing the initial concentration of $Pd(OAc)_2$, at constant concentration of **4**, was found to accelerate the formation of **1** (Table 2, entries 2−4; Figure 2, traces b−d).

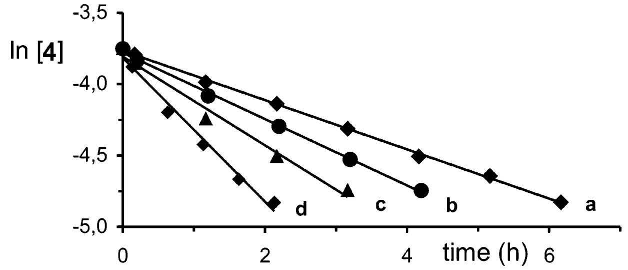

Figure 2. Plot of ln [**4**] versus reaction time for the reaction of **4** with $Pd(OAc)_2$ in MeOH at 23 °C; traces a−d refer to the experiments 1−4 of Table 2, respectively.

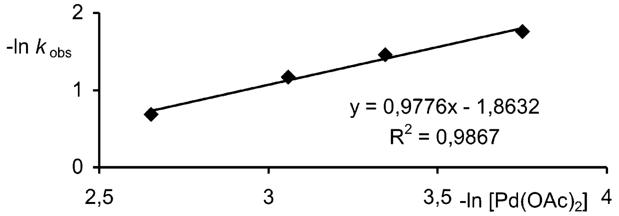

Figure 3. Plot of −ln k_{obs} versus −ln $[Pd(OAc)_2]$ for different initial concentrations of $Pd(OAc)_2$ (Table 2, experiments 1−4).

Table 2. Kinetic Data for the Conversion 4 + $Pd(OAc)_2$ into 1 in MeOH

entry	**4**:$Pd(OAc)_2$ ratio	$10^2[\mathbf{4}]$ M	$10^2[Pd(OAc)_2]$ M	$10k_{obs}$ h^{-1}
1	1:1	2.35	2.35	1.72
2	1:1.5	2.35	3.52	2.33
3	1:2	2.35	4.70	3.11
4	1:3	2.35	7.05	5.04
5	1:1	1.17	1.17	1.22
6	1:1	3.52	3.52	1.79
7	1:1	4.70	4.70	2.00

For a rate law of the type $-d[\mathbf{4}]/dt = k[\mathbf{4}][Pd(OAc)_2]^p = k_{obs}[\mathbf{4}]$ with $k_{obs} = k[Pd(OAc)_2]^p$, a plot of −ln k_{obs} versus −ln $[Pd(OAc)_2]$ gave a straight line, indicating a first-order dependence of the reaction rate also on $Pd(OAc)_2$ (Figure 3). However, the complex nature of $Pd(OAc)_2$ in MeOH (see below) biases this plot, at least to draw out the true kinetic constant, because the initial concentrations of $Pd(OAc)_2$ given in the x-axis cannot correspond to the actual concentrations of monomeric $Pd(OAc)_2$.

Indeed, palladium acetate is a trimer in the solid state and may exist in solution in various forms, from monomers to aggregates, depending on solvent, temperature, and concentration.[10,11] In particular, various species, $[Pd(OAc)_2]_n$ with $n = 1, 2, 3, 4$, etc., have been reported to form in MeOH at room temperature.[6] The ^1H NMR spectrum in MeOH-d_4 of the palladium acetate employed in this study showed several signals around δ 2 for the acetate methyl group. Therefore, the concentration of $Pd(OAc)_2$ available for the interaction with

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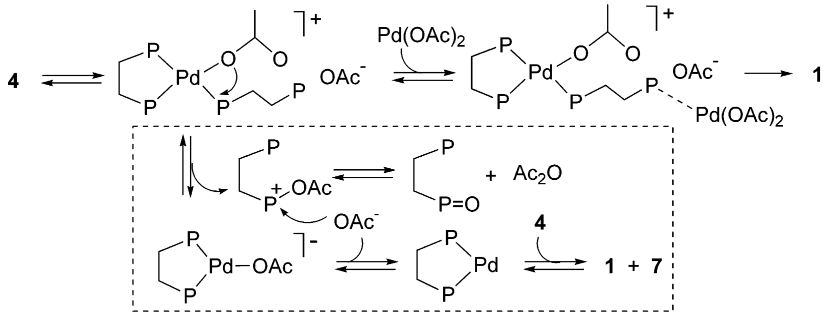
(10) (a) Skapsky, C.; Smart, M. L. *Chem. Commun.* **1970**, 658. (b) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. J. *Chem. Soc.* **1965**, 3632.

(11) Stoyanov, E. S. *J. Struct. Chem. (Engl. Transl.)* **2000**, *41*, 440.

Scheme 5



4, depending on the nature of the clusters, cannot be the theoretical one at any stage of the reaction. As a matter of fact, when some reactions were carried out varying the initial equimolecular concentration of both **4** and $Pd(OAc)_2$ (from 1.17×10^{-2} to 4.70×10^{-2} M, Table 2, entries 1 and 5−7) and the kinetic data were treated with the fractional-life method, the seeming second-order of the reaction was not confirmed (a value of 1.4 was obtained, in fact). In conclusion, the rate of formation of **1** is first-order in **4** and depends also on the concentration of $Pd(OAc)_2$, yet the order in the latter reagent cannot be determined reliably.

Incorporation of all of the experimental data obtained for the reaction of **4** with $Pd(OAc)_2$ in MeOH leads to a mechanism involving a fast and reversible opening of one of the chelating dppe ligands in **4** by acetate, followed by slow and rate-determining interaction between the free phosphine arm and $Pd(OAc)_2$ (Scheme 5, upper). The formation of a four-coordinate transient species containing coordinated OAc^- and monodentate dppe is indirectly confirmed by the occurrence of the Amatore reaction[9] in CH_2Cl_2 leading to phosphine oxidation and metal reduction (Scheme 5, dashed box).

The mechanism of formation of **1** as proposed in Scheme 5 is presumably valid also in CH_2Cl_2, where the rate is too fast to allow for kinetic studies. The faster kinetics in CH_2Cl_2 may be due to the fact that $Pd(OAc)_2$ exists mainly as a linear dimer in dilute solutions of halogenated solvents such as those employed in this study.[11] A higher concentration of active $Pd(OAc)_2$ would therefore accelerate the formation of **1**. Another factor that might contribute to speed up the transformation of **4** in CH_2Cl_2 is the low dielectric constant of this solvent, which should favor the coordination of the acetate counteranion to favor the four-coordinate intermediate $[Pd(OAc)(\eta^2\text{-dppe})(\eta^1\text{-dppe})]OAc$ (Scheme 5). This may explain why the Amatore reaction of **4** is rather fast in CH_2Cl_2 and does not appreciably occur in MeOH over 24 h.

A perusal of the relevant literature shows that the (kinetic) bis-chelate to (thermodynamic) monochelate transformation is not limited to either $Pd(OAc)_2$ or dppe. Precedents have been reported for the reactions of various chelating diphosphines (dppm, dppe, dppp, dppb, and DIOP) with $Pd(dba)_2$[12] that, like $Pd(OAc)_2$, may form polynuclear species in solution.[13]

Conclusions

This study has confirmed[6] that the reaction of $Pd(OAc)_2$ with dppe in MeOH yields the bis-chelate complex $[Pd(dppe)_2](OAc)_2$ as kinetic product, which slowly converts to the thermodynamic monochelate $Pd(OAc)_2(dppe)$. The formation of the kinetic bis-chelate product is due to the instantaneous shortage of active $Pd(OAc)_2$ released by the $[Pd(OAc)_2]_n$ clusters. It has been found that the rate of the reaction of $[Pd(dppe)_2](OAc)_2$ with $Pd(OAc)_2$ in MeOH ($t_{1/2} = 4$ h at 23 °C) is first-order in the bis-chelate and also depends on the $Pd(OAc)_2$ concentration. The formation of the monochelate complex $Pd(OAc)_2(dppe)$ from either $\{dppe + Pd(OAc)_2\}$ or $\{[Pd(dppe)_2](OAc)_2 + Pd(OAc)_2\}$ is much faster in CH_2Cl_2 than in MeOH, which has been ascribed to the lower nuclearity of $Pd(OAc)_2$ in the former solvent, whose small dielectric constant would favor the formation of the rate-determining species $[Pd(OAc)(\eta^2\text{-dppe})(\eta^1\text{-dppe})]OAc$.

The results reported in this paper may be considered as a warning to all the chemists who intend to study a catalytic reaction whereby the catalyst is prepared in situ: such a procedure is correct and may provide reliable results only when the *quantitative* formation of the catalytically active precursor is unambiguously proved to occur within the residence time preceding the addition of the other reagents involved in the process.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry nitrogen by using Schlenk-type techniques. All the reagents and solvents were used as purchased from Aldrich. The palladium complexes $Pd(OAc)_2(dppe)$[6] and $[Pd(dppe)_2](OAc)_2$[2,6] 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 the catalytic reactions. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker ACP 200 (200.13 and 81.01 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H) or 85% H_3PO_4 (^{31}P). Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer.

NMR Study of the Reaction of $Pd(OAc)_2$ with dppe in CD_2Cl_2. A. Room Temperature. Solid dppe (10.9 mg, 2.8 ×

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(12) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

(13) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. (b) Mosely, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 982.

10^{-2} mmol) was added to a 5 mm NMR tube containing a solution of Pd(OAc)$_2$ (6.2 mg, 2.8×10^{-2} mmol) in CD_2Cl_2 (0.8 mL) at room temperature. $^{31}P\{^1H\}$ and ^1H NMR spectra, acquired at room temperature after ca. 10 min of mixing, showed the quantitative formation of **1**.

B. Low Temperature. Solid dppe (10.9 mg, 2.8×10^{-2} mmol) was added to a 5 mm NMR tube containing a solution of Pd(OAc)$_2$ (6.2 mg, 2.8×10^{-2} mmol) in CD_2Cl_2 (0.8 mL) at −70 °C. There was the immediate precipitation of an off-white solid that was separated by filtration. The solid, dissolved in CD_2Cl_2 at room temperature, was identified as **4** by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.

In a parallel experiment, the NMR tube was placed into a probe-head precooled at −70 °C without removing the formed solid. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 1. The first spectrum at −70 °C showed the solution to contain **4** together with a minor amount of **1** in a molar ratio of 6 to 1 (trace a). Increasing the temperature led to the progressive dissolution of precipitated **4** with concomitant formation of **1**. The exclusive presence of **1** was observed when the solution reached room temperature. The spectra acquired at −20 °C after 50 min (trace b) and at room temperature after 10 min (trace c) are reported as examples.

NMR Study of the Stability of 1 in MeOH-*d*$_4$. A solid sample of **1** (11.8 mg, 1.9×10^{-2} mmol), prepared from Pd(OAc)$_2$ and dppe in CH_2Cl_2, was dissolved in MeOH-d_4 (0.8 mL) under nitrogen at room temperature and then transferred into a 5 mm NMR tube. The reaction was monitored by recording $^{31}P\{^1H\}$ and ^1H NMR spectra every hour. No trace of **4** formed in 24 h.

NMR Study of the Reaction of Pd(OAc)$_2$ with dppe in MeOH-*d*$_4$ at Room Temperature. Solid dppe (15.1 mg, 3.8×10^{-2} mmol) was added to a 5 mm NMR tube containing a solution of Pd(OAc)$_2$ (8.5 mg, 3.8×10^{-2} mmol) in MeOH-d_4 (0.8 mL) at room temperature. $^{31}P\{^1H\}$ and ^1H NMR spectra, acquired at room temperature after ca. 5 min of mixing, showed the almost quantitative formation of **4**.[6] The reaction was monitored at room temperature by recording $^{31}P\{^1H\}$ and ^1H NMR spectra every 30 min. Compound **4** slowly converted into **1** with a $t_{1/2}$ of ca. 4 h.

Identical kinetic data were obtained by using 1.9×10^{-2} mmol of both **4** (19.4 mg) and Pd(OAc)$_2$ (4.2 mg) in place of 3.8×10^{-2} mmol of both dppe and Pd(OAc)$_2$.

Synthesis of 4OTs. To a stirred solution of $PdCl_2$(dppe) (287.9 mg, 0.5 mmol) and dppe (199.2 mg, 0.5 mmol) in 20 mL of CH_2Cl_2 was added 2 equiv of AgOTs (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 **4OTs** in 80% yield. Anal. Calcd for $C_{66}H_{62}P_4PdS_2O_6$: C, 63.64; H, 5.02. Found: C, 63.53; H, 4.99.

Attempted Reactions of 4OTs with Pd(OAc)$_2$. A 5 mm NMR tube was charged with a solution of **4OTs** (16.2 mg, 1.3×10^{-2} mmol) in either MeOH-d_4 or CD_2Cl_2 (0.8 mL) under nitrogen. After $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired ($^{31}P\{^1H\}$ NMR singlet of **4OTs** at δ 58.8 and 56.9 in MeOH-d_4 and CD_2Cl_2, respectively), a solid sample of Pd(OAc)$_2$ (3.0 mg, 1.3×10^{-2} mmol) was added into the tube. The reactions were followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy at room temperature. No reaction involving the bis-chelate **4OTs** occurred in 24 h, as shown by the NMR spectra acquired at intervals of 1 h.

Kinetic Study of the Reaction of 4 with Pd(OAc)$_2$ in MeOH-*d*$_4$. A 5 mm NMR tube was charged with a solution prepared by mixing **4** and Pd(OAc)$_2$ in appropriate ratios (see Table 2) in MeOH-d_4 (0.8 mL) at room temperature and placed into the probe of a NMR spectrometer at 23 °C. The reaction was followed with the use of $^{31}P\{^1H\}$ NMR spectroscopy by determining the concentrations of both **4** and **1** as a function of time. The first spectrum was acquired after ca. 5 min of mixing, while the following spectra were recorded every 30 min. Table 2 summarizes the kinetic data.

NMR Study of the Stability of 4 in CD_2Cl_2. A 5 mm NMR tube was charged with a solution of **4** (13.3 mg, 1.3×10^{-2} mmol) in CD_2Cl_2 (0.8 mL) under nitrogen. The $^{31}P\{^1H\}$ NMR spectrum acquired 10 min after the dissolution showed ca. 5% decomposition of **4** into an almost equimolecular mixture **1**, the known bis-chelate Pd^0 complex **7** ($^{31}P\{^1H\}$ NMR singlet at δ 30.7), and dppe=O ($^{31}P\{^1H\}$ NMR doublets at δ 31.8 and −12.1, $J(PP) = 48.1$ Hz).[7,8a,b,9] The corresponding ^1H NMR spectrum showed a signal at δ 2.21, which was indicative of acetic anhydride production. The disappearance of **4** occurred slowly at room temperature (ca. 30% in 1 h). In contrast, when **4** was dissolved in CD_2Cl_2 containing Pd(OAc)$_2$ (2.9 mg, 1.3×10^{-2} mmol), the immediate and quantitative formation of **1** occurred.

Copolymerization of Ethene and Carbon Monoxide Catalyzed by Pd/dppe Precursors in MeOH. 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 an 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. The results of the catalytic experiments are reported in Table 1.

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