Facile Synthesis of New, Stable, Palladium-Ethyl Derivatives Containing Nitrogen-Donor Ligands

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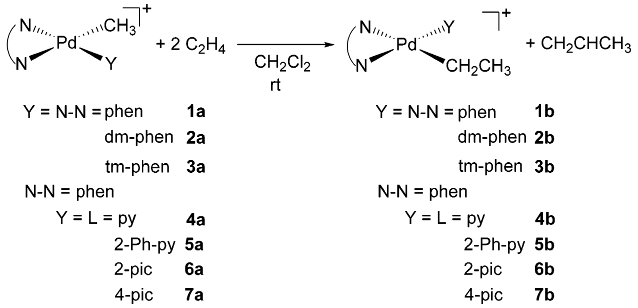
Summary: A study of the insertion reaction of ethylene into the Pd−C bond on complexes of general formula $[Pd(CH_3)(N{-}N)_2][OTf]$ *and* $[Pd(CH_3)(phen)(L)][OTf]$ *led to the development of a facile procedure for the synthesis of new, stable, Pd-ethyl derivatives. The rate of this insertion reaction is affected by the nature of the nitrogen-donor ligand, N−N or L.*

During the last 10 years there has been an increasing interest in the development of catalytic systems, based on late-transition metals, for polymerization of ethylene[1,2] or copolymerization of ethylene, or α-olefins in general, with carbon monoxide.[3] The insertion of ethylene into the metal−carbon bond represents a key step for both polymerization reactions. This insertion has been thoroughly investigated on palladium and nickel complexes with nitrogen-donor chelating ligands, using both theoretical and experimental approaches.[4] In particular, for complexes such as $[Pd(CH_3)(OEt_2)(phen)][B(Ar')_4]$ (phen = 1,10-phenanthroline; $B(Ar')_4 = B[3,5\text{-}(CF_3)_2C_6H_3]_4$) the main product of the insertion reaction was shown to be a mixture of *cis*- and *trans*-2-butene. The Pd-ethyl-ethylene species $[Pd(CH_2CH_3)(CH_2CH_2)(phen)]^+$, which has been detected only at low temperature, is the *resting state* both for the ethylene dimerization and for its polymerization catalyzed by Pd(II)-α-dimine complexes.

Scheme 1. Synthesis of Pd-Ethyl Complexes 1b−7b



For several years we have studied the catalytic behavior of Pd(II) complexes in CO/olefin copolymerization reaction.[5] More recently, we have also investigated the insertion reaction of carbon monoxide into the $Pd{-}CH_3$ bond of complexes of general formula $[Pd(CH_3)(N{-}N)_2][OTf]$ (N−N = phen, **1a**; 4,7-dimethyl-1,10-phenanthroline (dm-phen), **2a**; 3,4,7,8-tetramethyl-1,10-phenanthroline (tm-phen), **3a**) and $[Pd(CH_3)(phen)(L)][OTf]$ (L = pyridine (py), **4a**; 2-phenylpyridine (2-Ph-py), **5a**; 2-picoline (2-pic), **6a**; 4-picoline (4-pic), **7a**; OTf = triflate).[6] The insertion of CO into the palladium−alkyl bond led in all cases to the isolation of the respective Pd-acyl species, $[Pd(COCH_3)(N{-}N)_2][OTf]$ and $[Pd(COCH_3)(phen)(L)][OTf]$. The investigation of this reaction by means of in situ NMR spectroscopy revealed that the reaction is rather fast and the insertion rate is not affected by the nature of N−N or L. Formation of palladium black was not observed in any of these cases.

Here we describe the reactivity of the complexes $[Pd(CH_3)(N{-}N)_2][OTf]$ and $[Pd(CH_3)(phen)(L)][OTf]$ with ethylene. This reaction allowed us to develop a facile procedure for the synthesis of the corresponding Pd-ethyl derivatives, $[Pd(CH_2CH_3)(N{-}N)_2][OTf]$ (N−N = phen, **1b**; dm-phen, **2b**; tm-phen **3b**) and $[Pd(CH_2CH_3)(phen)(L)][OTf]$ (L = py, **4b**; 2-Ph-py, **5b**; 2-pic, **6b**; 4-pic, **7b**), which, notably, are thermally stable at room temperature and can be readily isolated.

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Table 1. Relevant ^{1}H and ^{15}N NMR Data for Complexes [Pd(CH$_2$CH$_3$)(N−N)$_2$][OTf], 1b−3b[a]

N−N	H^{2,9}	CH$_2$	CH$_3$	^{15}N NMR
phen **1b**	8.86 (dd)	1.92 (q)	0.63 (t)	−120.3[b]
dm-phen **2b**	8.68 (dd)	1.86 (q)	0.60 (t)	n.d.
tm-phen **3b**	8.58 (dd)	1.79 (q)	0.56 (t)	n.d.

[a] Spectra recorded in CD$_2$Cl$_2$ at 295 K; dd = double doublet, t = triplet, q = quartet. H^{2,9} for free phen: 9.10 ppm. [b] Average (see text) recorded in CD$_2$Cl$_2$ at 295 K. [Pd(CH$_3$)(phen)$_2$][OTf], **1a**, δ(^{15}N) −123.6.[6a]

When the Pd-methyl complexes **1a**−**7a** were reacted with ethylene, at room temperature, in methylene chloride, the Pd-ethyl derivatives [Pd(CH$_2$CH$_3$)(N−N)$_2$][OTf] **1b**−**3b** and [Pd(CH$_2$CH$_3$)(phen)(L)][OTf] **4b**−**7b** were quantitatively isolated (Scheme 1).[7] Their ^{1}H NMR spectra in CD$_2$Cl$_2$ exhibit the characteristic quartet and triplet pattern in the region of the aliphatic protons, assigned to the Pd-ethyl fragment (Tables 1 and 2). The number of signals observed in the aromatic region of the spectra is different depending on whether the complexes of the type [Pd(CH$_2$CH$_3$)(N−N)$_2$][OTf] **1b**−**3b** or [Pd(CH$_2$CH$_3$)(phen)(L)][OTf] **4b**−**7b** are considered. Indeed, for complexes **1b**−**3b** the number of resonances and their integration confirm the presence of two equivalent molecules of N−N ligand in the coordination sphere of palladium (Table 1). Therefore, we assume the occurrence of a dynamic process by which the two N−N ligands exchange, which is in agreement with the behavior of the Pd-methyl precursors **1a**−**3a** in solution.[6a] This process is fast on the ^{1}H NMR time scale. On the other hand, the resonances observed in the spectra of complexes **4b**−**7b** clearly indicate the coordination of phenanthroline in a nonsymmetrical chemical environment, and no dynamic process is apparent in this case (Table 2). We note that the signal of one of the two "probe-protons" of phen (H^9) has remarkably shifted upfield (by more than 1 ppm) with respect to the free ligand, which is in agreement with the fact that H^9 resides within the shielding cone of the aromatic nitrogen ligand (L) in *cis* position.

For three exponents of the Pd-ethyl complexes, **1b**, **4b**, and **5b**, the ^{15}N NMR spectra were recorded by PFG HMQC ^{1}H{^{15}N} experiments at natural abundance of the ^{15}N isotope.[6a,8] Correlations due to $^4J(^{15}\mathrm{N},^1\mathrm{H})$ in ^{15}N−Pd−C−CH_3 (Figure 1 for **4b**) were observed for all ^{15}N nuclei of each compound, further substantiating the coordination of N atoms. For complex **1b**, one average signal at −120 ppm was observed instead of four, confirming the fast exchange of all N atoms, even on the ^{15}N NMR time scale (Table 1). The observed chemical shift is very close to the estimated value obtained as the average of the expected ^{15}N shifts of the four N atoms belonging to one bidentate and one monodentate coordinated phenanthroline (−152, −117, −152, and −75 ppm). For **4b** and **5b**, three distinct ^{15}N signals were observed (Table 2); the nitrogen atoms in mutual *trans* positions have ^{15}N chemical shifts around −137 (monodentate ligand) and −152 ppm (phen), whereas the resonance of N (phen) in *trans* position relative to the ethyl group is found at approximately −117 ppm. These ^{15}N resonances fall within the expected chemical shift ranges and are 3−5 ppm higher in frequency compared to those of the corresponding methyl complexes **4a** and **5a**.[6a] The values of the coordination chemical shifts are comparable to previously obtained values for, for example, [Pd(CH$_3$)(N−N−N)]$^+$ (N−N−N

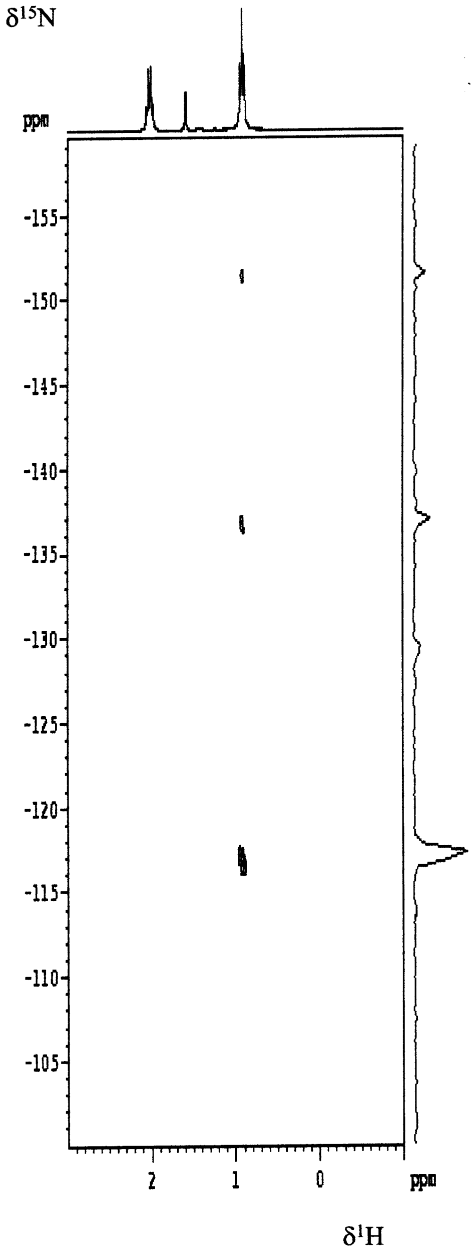

Figure 1. ^{1}H,^{15}N PFG HMQC spectrum of complex **4b**, recorded at natural abundance of ^{15}N in CD$_2$Cl$_2$ at 295 K.

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(7) The complexes **1a**−**7a** were synthesized starting from Pd(CH$_3$COO)$_2$ and accordingly to the procedure previously reported.[6] All manipulations were carried out in argon atmosphere by using standard Schlenk technique. Dichloromethane was previously distilled over CaCl$_2$. Synthesis of complexes [Pd(CH$_2$CH$_3$)(N−N)$_2$][OTf] **1b**−**3b** and [Pd(CH$_2$CH$_3$)(phen)(L)][OTf] **4b**−**7b**: A solution of [Pd(CH$_3$)(N−N)$_2$][OTf] or [Pd(CH$_3$)(phen)(L)][OTf] in dichloromethane (0.05 mmol of complex in 10 mL of CH$_2$Cl$_2$) is kept under ethylene atmosphere for the proper reaction time (see below). The volume of the solution is reduced to half and some diethyl ether is added to complete the precipitation of the product as an orange (**1b**−**3b**) or yellow (**4b**−**7b**) solid. The solid is filtered, washed with diethyl ether, and vacuum-dried. It is stored at 4 °C. Reaction time and yields: **1b** 1 h, 90%; **2b** 2 h, 90%; **3b** overnight, 85%; **4b** 3 h, 74%; **5b** 3 h, 65%; **6b** 4 h, 72%; **7b** 3 h, 72%. The alternative synthetic procedure based on the reaction of [Pd(Cl)$_2$(COD)] with [Sn(C$_2$H$_5$)$_4$] led to the isolation of [Pd(C$_2$H$_5$)(Cl)(COD)] in very low yield (<20%) due to formation of palladium metal.

Table 2. Relevant ^1H and ^{15}N NMR Data for Complexes [Pd(CH_2CH_3)(phen)(L)][OTf], 4b−7b[a]

	phen				^{15}N NMR[b]		
L	H^2	H^9	CH_2	CH_3	N(phen)-*trans*-C	N(phen)-*trans*-N	N(L)
py **4b**	9.05 (dd)	7.97 (dd)	2.04 (q)	0.95 (t)	−117.3	−151.6	−137.0
2-Ph-py **5b**	8.90 (dd)	7.98−8.03 (m)[c]	1.85 (m)	0.70 (t)	−117.6	−151.5	−136.6
2-pic **6b**	9.03 (dd)	7.82−7.78 (m)[d]	2.01 (m)	0.88 (t)	n.d.	n.d.	n.d.
4-pic **7b**	9.05 (dd)	7.98 (dd)	2.01 (q)	0.94 (t)	n.d.	n.d.	n.d.

[a] Spectra recorded in CD_2Cl_2 at 295 K; dd = double doublet, t = triplet, q = quartet, m = multiplet. $H^{2,9}$ for free phen: 9.10 ppm. [b] Spectra recorded in CD_2Cl_2 at 295 K. [c] Overlapped with H^3. [d] Overlapped with H^8.

= 2-(2-((2′-pyridylmethylene)amino)ethyl)pyridine).[10] No agostic Pd−C−*CH* interactions are present, as was apparent from variable-temperature ^1H and ^{13}C NMR and $T_1(^1H)$ studies concerning **1b** and **4b**. The ^{13}C resonances of the ethyl groups are found at normal positions, e.g., δ/ppm **1b**: 17.94 *C*H_2, 17.24 *C*H_3, ^1J(C,H) 124 Hz; **4b**: 20.60 *C*H_2, 16.04 *C*H_3; ^1J(C,H) 125 Hz.

The reaction with ethylene was studied in more detail by in situ ^1H NMR experiments, by bubbling C_2H_4 into a 10 mM solution of the complex in CD_2Cl_2 at room temperature.[11] In the spectrum of a solution of **1a** recorded after 15 min, the signals of the Pd-ethyl species were evident, together with other peaks attributed to propene (multiplets centered at 1.69, 4.95, and 5.75−5.88 ppm), to a mixture of *cis*- and *trans*-2-butene (multiplets at 1.58 and 5.45 ppm, close to the peak of free ethylene), and the unreacted Pd-methyl precursor. The reaction was followed in time without charging the NMR tube with more ethylene. The variations observed in the spectra, recorded after 40 and 60 min from the treatment with C_2H_4, consisted of the decrease and the subsequent disappearance of the signal due to the Pd-methyl moiety and the enhancement of the signals of all other compounds present in solution. In particular, in the spectrum recorded after 60 min, the signals of the unique palladium species **1b** are shown. No signal due to free phenanthroline was present.

Analogous reactivity was observed when complexes **2a** and **3a** were reacted with ethylene, the only difference being the reaction rate, which remarkably decreased on going from phen to dm-phen to tm-phen (Figure 2). For instance, whereas for **1a** 88% of Pd-methyl species was transformed into **1b** in 60 min, only 28% of [Pd(CH_3)(tm-phen)$_2$][OTf] was transformed into the Pd-ethyl derivatives **3b** after the same reaction time. This effect could be related to the Lewis basicity of N−N, which increases in the same order.[12]

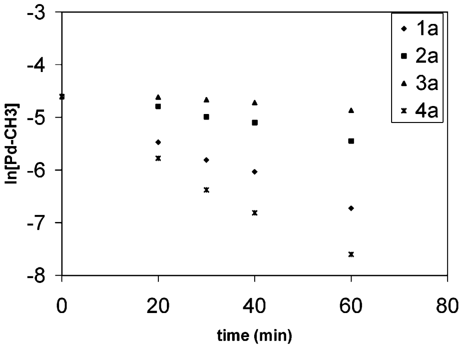

Figure 2. Plot of ln[Pd−CH_3] versus time for complexes **1a**−**4a**. Conditions of pseudo-zero-order in ethylene are assumed.

Even the insertion rate of ethylene into the Pd−CH_3 bond of complexes **4a**−**7a** was affected by the nature of the L ligand. When L was pyridine (complex **4a**), the reaction rate was higher than that of **1a** (Figure 2), and for L = 2-Ph-py (complex **5a**) the palladium-methyl complex was completely transformed in the Pd-ethyl derivative in 20 min. For complexes with picolines, **6a** and **7a**, the reaction was slow, and in particular, for **6a** only 57% of the starting complex was transformed into the Pd-ethyl derivative, **6b**, in 60 min. Therefore, the order of reactivity is 2-Ph-py > py > 4-pic > 2-pic, while the order for the Lewis basicity is 2-Ph-py < py < 2-pic ≈ 4-pic. In agreement with the results obtained for complexes **1a**−**3a**, the insertion rate decreases on increasing the electron-donor power of the ligand and on increasing its steric hindrance, thus indicating that the insertion reaction follows an associative mechanism.

For all complexes the conversion of ethylene into the mixture of *cis*- and *trans*-2-butene proceeded, even after the complete transformation of the Pd-methyl into the Pd-ethyl species, thus indicating that, as expected, these complexes are catalysts for ethylene dimerization. The active species for this reaction is the Pd-hydride derivative, which should form after insertion of the first molecule of ethylene into the Pd−CH_3 bond, followed by the β-hydrogen elimination of propene (detected in the ^1H NMR spectra; Scheme 2). The proposed catalytic cycle is similar to that reported by Brookhart,[4b] the main difference being the *resting state*, which is in this case represented by the Pd-ethyl species, [Pd(CH_2CH_3)(N−N)$_2$][OTf] or [Pd(CH_2CH_3)(N−N)(L)][OTf] (Scheme

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(8) ^{15}N NMR spectra were recorded by a PFG HMQC sequence[9] on a Bruker DRX 300 spectrometer equipped with a 5 mm triple resonance inverse probe with z-gradient, operating at 30.42 MHz ^{15}N frequency and a second 300 W X decoupler giving a ^{15}N 90° pulse of 10 μs. Spectra were recorded without decoupling ^{15}N in f_2, using a spectral width in f_2 (^1H) of 10 ppm, an acquisition time of 0.4 s, giving a digital resolution of 1.2 Hz per point. Two values for $J\{^1H,^{15}N\}$ (2.5 and 6 Hz) were used. The ^{15}N spectral width was 60 ppm with 256 increments and 32−512 scans per increment depending on the concentration of the compound. This provided, after linear prediction to 1024, a digital resolution of 1.8 Hz per point. The relaxation delay was 1 s. For experiments using 256 increments and 16 scans, data collection required 2 h. Chemical shifts were referenced to external nitromethane = 0 ppm, negative chemical shift reported for lower frequencies. Spectra were recorded at 295 K.

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(11) The in situ ^1H NMR experiments were carried out as follows: CD_2Cl_2 (0.7 mL) was added to a 5 mm NMR tube charged with the complex (7 × 10^{-3} mmol). Ethylene was bubbled into the solution for 5 min, via a needle inserted through a rubber cap into the NMR tube. The ^1H NMR spectrum was recorded after 15 min. All manipulations were done at room temperature. The values of chemical shifts reported are referred to the CD_2Cl_2 peak versus TMS at 5.33 ppm.

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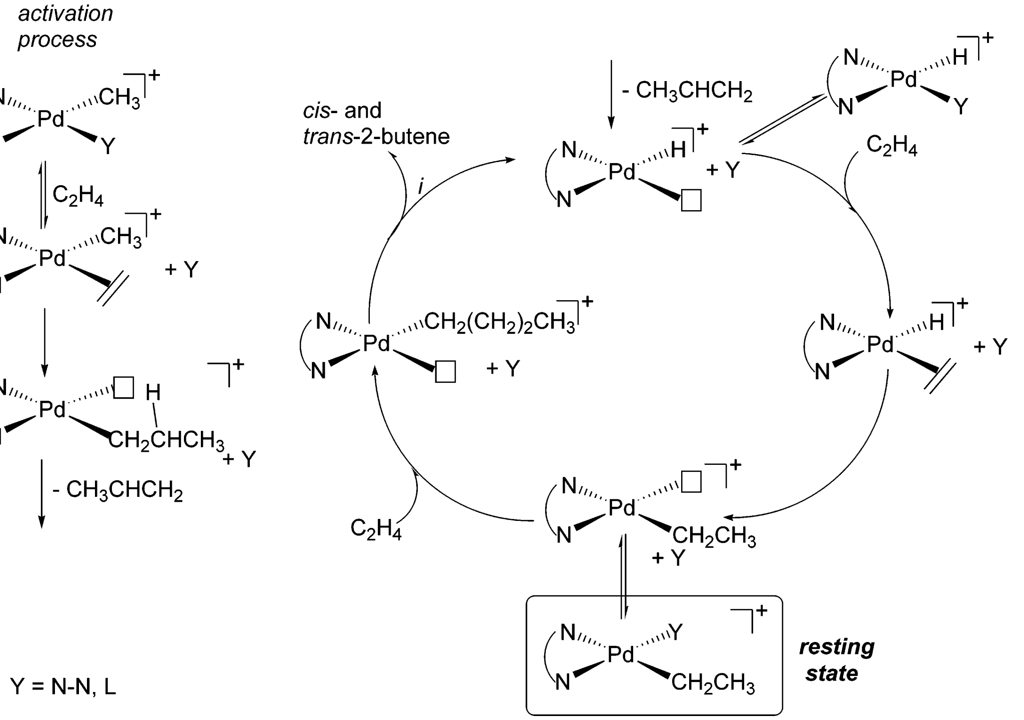
Scheme 2. Proposed Catalytic Cycle for Ethylene Dimerization[a]



[a] Step *i* consists of a series of β-hydrogen elimination and insertion reactions.

2). The reactions were monitored for at least 6 h, and neither decomposition to palladium metal nor any dissociation of N−N or L ligands was observed for the complexes studied.

The reactivity with ethylene was also investigated on the Pd-ethyl complexes **1b** and **4b**, by in situ ^{1}H NMR experiments in CD_2Cl_2, at room temperature. In both cases the catalytic formation of *cis*- and *trans*-2-butene was observed. The reaction was monitored during 2 h, and neither decomposition of the Pd-ethyl species nor dissociation of N ligands occurred. In agreement with the data obtained on the Pd-methyl species, the reaction catalyzed by **4b** is faster than that catalyzed by **1b**.

Summarizing, the reaction of cationic palladium-methyl compounds with ethylene constitutes a facile, general procedure for the quantitative synthesis of stable, monocationic Pd-ethyl compounds without formation of palladium metal. In contrast to the insertion of CO into the Pd−CH_3 bond, the insertion of ethylene is slow (under the applied reaction conditions) and it is affected by the nature of nitrogen-donor ligands bound to palladium.

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Supporting Information Available: The elemental analyses; detailed ^{1}H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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