Multinuclear Complexes

DOI: 10.1002/ange.200904745

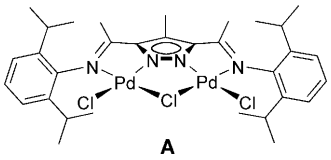
A Unique Pd_4 Platform with CH_3 and μ-CH_2 Groups and Its C–C Coupling Reaction with Simple Olefins**

*Anna Sachse, Michael John, and Franc Meyer**

Bi- and oligonuclear complexes currently attract significant attention in the chemical community, mainly because cooperative effects of adjacent metal ions are expected to lead to unique substrate activation modes and to novel reactivity patterns.[1] While much of the work in this field is inspired by natural enzymes that contain multinuclear active sites,[2] recent years have also seen growing interest and impressive progress in the development of non-biomimetic binuclear complexes for two-center organometallic catalysis,[3,4] including the homogeneous polymerization of olefins.[5,6] An interesting situation arises for multinuclear complexes that contain more than two metal ions, as little is known about the synergetic effects in such systems.

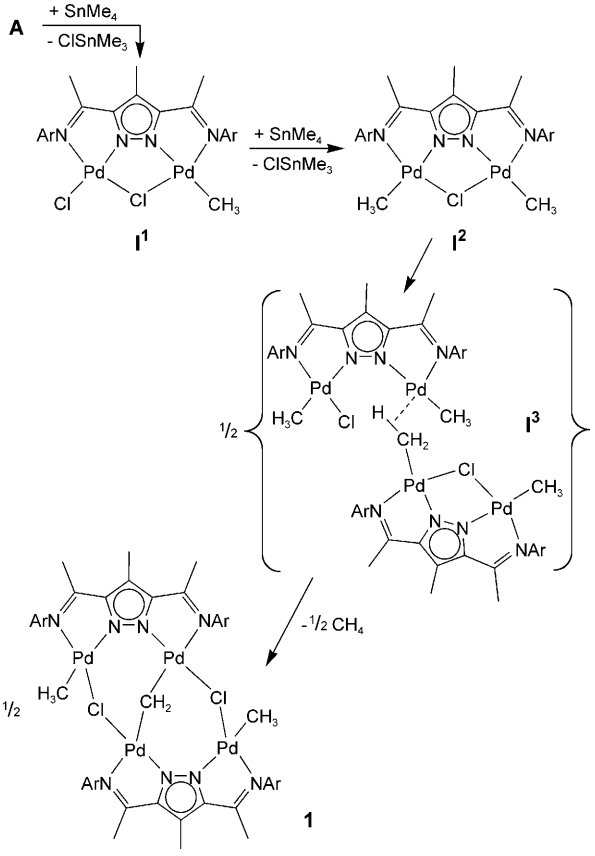
Compartmental ligand systems are of pivotal importance for achieving and controlling metal-ion cooperativity.[7] They allow defined positioning of two or more metal ions and may support controlled aggregation to yield high-nuclearity complexes. In this regard pyrazolate-derived bridging ligands are very useful scaffolds, as their decoration with chelating side arms in the 3- and 5-positions of the central heterocycle provides a means of deliberately tuning various characteristics of the binuclear array.[8] We have recently introduced a series of pyrazole-based ligands that possess appended imine donor functions with bulky aryl substituents.[6,9] These systems can be described as having two adjacent binding compartments akin to the α-diimine type, and their bi- or oligonuclear palladium(II) and nickel(II) complexes, after activation with methylalumoxane (MAO), indeed serve as highly active catalysts for olefin polymerization.[6]

We were interested in elucidating details of the activation process as well as possible internuclear effects in the activated species. Therefore we investigated the methylation of a representative pyrazolate-based dipalladium(II) complex **A** (Scheme 1)[6a] using relatively mild agents such as $SnMe_4$. Unexpectedly, we observed the formation of an unprecedented tetrapalladium complex (**1**, Scheme 2) that features both terminal CH_3 and μ-CH_2 groups, and herein we report insight into its formation, its molecular structure, and its intriguing reactivity with simple olefins such as ethylene.



A

Scheme 1. Pyrazolate-based dipalladium(II) complex **A**.



Scheme 2. Proposed reaction sequence leading to **1**.

The reaction of **A** in dichloromethane with an excess of $SnMe_4$ results in the formation of a yellow solution, from which yellow crystals of complex **1** were obtained in good yields at −20 °C.[10] The molecular structure of **1** was determined by single-crystal X-ray diffraction and is shown in Figure 1. Selected bond lengths and angles are listed in Table S1; crystallographic data are summarized in Table S2;

[*] Dr. A. Sachse, Dr. M. John, Prof. Dr. F. Meyer
Institut für Anorganische Chemie
Georg-August-Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3063
E-mail: franc.meyer@chemie.uni-goettingen.de
Homepage: http://www.meyer.chemie.uni-goettingen.de

[**] Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200904745.

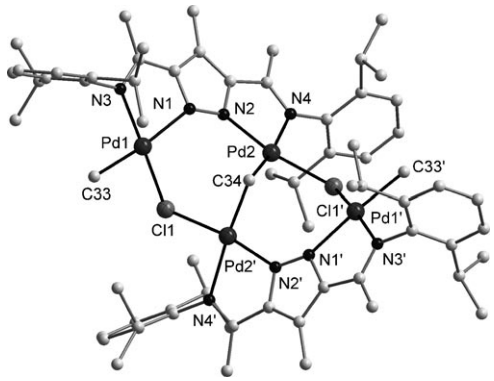


Figure 1. Molecular structure of **1**. For clarity, all hydrogen atoms are omitted.

an ORTEP plot is provided in Figure S1 in the Supporting Information.[11]

Complex **1** contains two {LPd_2} subunits (L = pyrazolate ligand) that have assembled to give a Pd_4 platform with two terminal CH_3 groups (C33/C33′ at the outer Pd1/Pd1′ centers), a bridging CH_2 group (C34 spanning the central metal atoms Pd2···Pd2′), and two bridging chlorides (Cl1/Cl1′ linking the two subunits along the edges Pd1···Pd2′ and Pd1′···Pd2). Metal–metal separations in the pyrazolate-bridged binuclear constituents {LPd_2} are much longer (4.4 Å) than in the starting complex **A** (3.8 Å), which goes along with a severe twisting of the two Pd coordination planes in each {LPd_2} unit against each other by 52° (N1/N3/C33/Cl1/Pd1 and N2/N4/Cl1′/C34/Pd2). The two {LPd_2} subunits are tilted by 69° with respect to each other, and the μ-CH_2 ligand is associated with a Pd2···Pd2′ separation of 3.3 Å and a Pd2-C34-Pd2′ angle of 109°. All palladium atoms have four-coordinate, distorted square-planar coordination spheres.

While mononuclear palladium complexes with Pd–CH_3 bonds are quite abundant and well-studied,[12] there are relatively few examples of binuclear palladium complexes with several Pd–CH_3 bonds.[13] The Pd-(μ-CH_2)-Pd motive is even less common; only two examples are known, namely [Pd_2Cl_2(μ-CH_2)(μ-dppm)$_2$] (dppm = bis(diphenylphosphino)-methane)[14] and [(N^N)Pd(μ-CH_2)(μ-Me)Pd(N^N)]$^+$, (N^N = (C_6H_3-*i*Pr_2-2,6)-N=CMeCMe=N-(C_6H_3-*i*Pr_2-2,6)).[15] The latter contains a Pd–Pd bond that results in a much shorter metal–metal separation (2.7 Å) and a more acute Pd-(μ-CH_2)-Pd angle (85°), while the former exhibits parameters similar to **1** (d(Pd···Pd) = 3.2 Å, ∡(Pd-(μ-CH_2)-Pd) = 103°). However, **1** is the first Pd complex that contains both terminal CH_3 and μ-CH_2 groups.

Complex **1** was fully characterized by NMR spectroscopy using 1D and 2D ^{1}H and ^{13}C techniques. The ^{1}H NMR spectrum of **1** in CD_2Cl_2 shows the expected splitting of the isopropyl methyl group (CH_3^{iPr}) signals into eight doublets and a splitting of the isopropyl methine group (CH^{iPr}) signals into four separate septets ($^3J_{HH}$ = 6.8 Hz; ^{1}H NMR spectra of **1** and **A** are given in the Supporting Information, Figure S2.) An upfield signal at $\delta = -0.06$ ppm can be assigned to the methyl groups on the palladium atoms, while the μ-CH_2 resonance is detected at $\delta = 3.8$ ppm.

In a reaction of **A** with approximately 30 equiv $SnMe_4$, performed at NMR scale, it was possible to detect two sequential intermediates en route to **1**. The first (intermediate $\mathbf{I^1}$) has an asymmetric structure (C_s), while the second (intermediate $\mathbf{I^2}$) is symmetric (C_{2v}). NOESY correlations of the isopropyl methyl groups show the presence of palladium-bound methyl groups in both intermediates (part of the NOESY spectrum is depicted in the Supporting Information, Figure S3). To distinguish the intermediates by their molecular size, diffusion coefficients were measured using DOSY NMR (Figure S4 in the Supporting Information). Diffusion coefficients D of intermediates $\mathbf{I^1}$ and $\mathbf{I^2}$ ($(1.14 \pm 0.03) \times 10^{-9}$ m^{2}s^{-1}) are substantially higher than that of **1** ($(0.85 \pm 0.03) \times 10^{-9}$ m^{2}s^{-1}) but in the same range as that of the starting material **A** ($(1.10 \pm 0.03) \times 10^{-9}$ m^{2}s^{-1}). We thus assume a binuclear {LPd_2} motif for both intermediates.

The buildup and decay of the different intermediates and products was monitored over time by NMR spectroscopy (Figure 2). The concentrations of intermediates $\mathbf{I^1}$ and $\mathbf{I^2}$ reach their maxima after 6 and 10 h, respectively, while **1** becomes detectable after approximately 5 h and predominates after

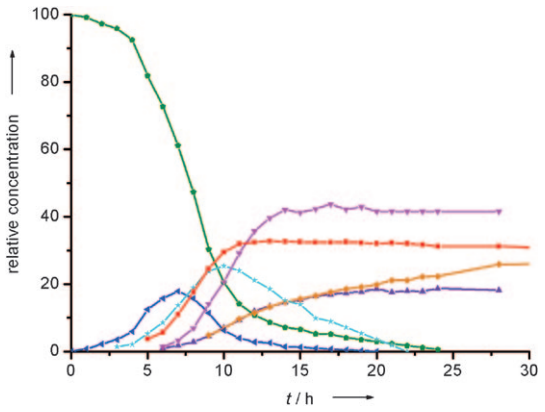


Figure 2. Buildup and decay of selected intermediates and products in the ^{1}H NMR spectrum of the reaction of **1** with approximately 30 equiv of $SnMe_4$. ⬟ complex **A**, ◀ intermediate $\mathbf{I^1}$, ⋆ intermediate $\mathbf{I^2}$, ■ complex **1**, ◆ product **2**, ▼ methane, ▲ ethane.

13 h, when less than 10% of the starting material remains. Formation of $SnMe_3Cl$ is obvious both from ^{119}Sn (δ = 168 ppm) and ^{1}H NMR spectroscopy ($\delta = 0.66$ ppm). Concomitant with the buildup of **1**, the formation of methane could be detected by ^{1}H NMR spectroscopy ($\delta = 0.21$ ppm) and was confirmed by DOSY experiments. At longer reaction times a second (as yet unidentified) product slowly appears, which is accompanied by the formation of ethane. This later product **2** only forms if an excess of $SnMe_4$ is present, and its formation is highly dependent on the $SnMe_4$ concentration.

The wealth of information from NMR spectroscopy allows us to sketch a reaction sequence for the formation of **1** from **A** (Scheme 2). Complex **A** is sequentially methylated by $SnMe_4$ to form intermediates $\mathbf{I^1}$ and $\mathbf{I^2}$, with subsequent dimerization of two molecules $\mathbf{I^2}$ and the elimination of CH_4. Mechanistically, formation of a μ-CH_2 ligand from two Pd–CH_3 fragments has been proposed to proceed by activation of

a methyl C–H bond at a cationic $[MePdL_n]^+$ species, with subsequent hydride transfer to Pd and reductive elimination of methane.[15,16] In the present case, an electrophilic metal site may possibly be generated by a transient shift of the μ-Cl ligand in **I²** to a nonbridging position and intermolecular C–H activation according to the situation in **I³** (Scheme 2).

Besides its unique structure, **1** is of interest since terminal CH_3 and bridging CH_2 groups are considered as essential components for various catalytic transformations on metal clusters and surfaces,[17] and oligonuclear species have been suggested as (often unobserved) resting states in catalytic systems.[18] Since **1** contains both CH_3 and μ-CH_2 groups in close proximity on a tetranuclear platform, we investigated its reactivity towards simple olefins. When ethylene was bubbled through a CD_2Cl_2 solution of **1** at room temperature, propene was detected as the major product (by monitoring with ^{1}H NMR spectroscopy), together with some *trans*-2-butene, *cis*-2-butene, 1-butene, and ethane as well as traces of methane (Figure S5 in the Supporting Information); formation of these compounds was also confirmed by GC-MS. Gradual deposition of Pd^0 and reconstitution of some **A** occurred during the reaction, thus indicating gradual decomposition of the resulting organopalladium complexes. The time course of product accumulation was monitored by ^{1}H NMR spectroscopy, which clearly revealed the emergence of the characteristic olefin resonances and concomitant disappearance of the Pd–Me and μ-CH_2 signals (Figure 3). Given the triple bridging of the two $\{LPd_2\}$ subunits by μ-CH_2 and two μ-Cl ligands, it appears unlikely that **1** initially converts to binuclear fragments upon reaction with ethylene. Furthermore, two lines of evidence suggest that transformation of ethylene is mediated by **1** itself, not by any later decomposition products: 1) propene and butenes are generated right from the beginning without any initiation phase, and 2) their formation ceases when **1** has disappeared (Figure 3). It should also be noted that complex **A** is completely unreactive towards ethylene.

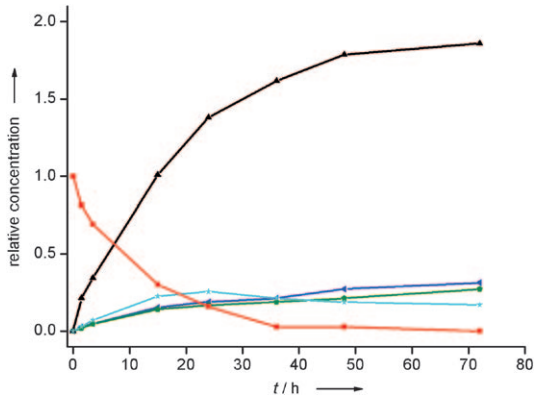
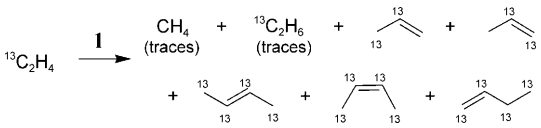


Figure 3. Decay of **1** and buildup of product olefins in the reaction with 22 equiv ethylene. ■ complex **1**, ▲ propene, ● *trans*-2-butene, ◀ *cis*-2-butene, ★ 1-butene.

The simultaneous rise of propene and butenes suggests that the latter do not stem from the primary product propene but are formed independently. When propene was employed as a substrate, *trans*-2-butene, *cis*-2-butene, and 2-methylpropene were detected, although in this case the reaction was at least a factor of five slower. To determine the origin of the C atoms in the C_3 and C_4 products, ^{13}C-labeled ethylene ($^{13}C_2H_4$) was used under the same conditions, and the isotopomers of the different product olefins were identified by ^{13}C NMR spectroscopy (Scheme 3, Figure S6 in the Supporting Information). *trans*-2-Butene, *cis*-2-butene, and 1-butene were found to be fully ^{13}C-labeled, which indicates



Scheme 3. Olefins resulting from the reaction of **1** with $^{13}C_2H_4$; propene isotopomers are the major products.

that all C_4 olefins result from the dimerization of two ethylene molecules. In contrast, the major product propene contained only two ^{13}C labels and is thus assembled from one molecule of ethylene and an unlabeled C_1 unit from complex **1** (either CH_3 or μ-CH_2). The minor byproduct ethane was fully ^{13}C-labeled (suggesting that it results from hydrogenation of the $^{13}C_2H_4$ substrate), while no ^{13}C is found in the trace amounts of methane.

Propene isotopomers $H_3{}^{13}C-{}^{13}CH{=}CH_2$ and $H_3C-{}^{13}CH{=}{}^{13}CH_2$ are formed in a 1:1 ratio right from the beginning, while 1-butene is gradually isomerized to the more stable 2-butenes (Figure 3), thus suggesting that H-scrambling can occur, presumably by Pd-mediated C–H activation. This scrambling is confirmed by experiments using **1** and $[D_4]$ethylene under the same conditions. GC-MS of the gas phase above the reaction mixture using an SPME (solid phase microextraction) probe as well as NMR spectroscopic monitoring of the solution (an example of an $^1H\{^2H\}$ NMR spectrum is depicted in Figure S7 in the Supporting Information) showed that all possible isotopomers of propene and butenes are present. We were also able to detect labeled methane (CH_3D), ethane isotopomers (C_2D_5H, CD_2H–CD_2H), and $[D_2]$ethylene. The ratio of the different propene and butene isotopomers changes over time, gradually accumulating those with higher D content. This accumulation apparently results from continuous $^1H/^2H$ exchanges involving the $[D_4]$ethylene substrate.

In conclusion, a novel Pd_4 complex has been discovered that contains both CH_3 and μ-CH_2 groups in close proximity on the tetranuclear platform, and several intermediates have been spectroscopically identified during its formation from binuclear precursors. This unique Pd_4 system reacts with ethylene to give mainly propene (and some butenes), which has been investigated by isotopic labeling. Besides the interesting structural motif, the present results corroborate that oligonuclear species may well be involved, though often not detected, in reactions with organopalladium catalysts. Once cooperative reactivity patterns are better understood, oligonuclear sites will open new pathways for substrate

transformations. Current work focuses on elucidating initial steps and further details of the interaction of olefins with **1**.

Experimental Section

General considerations: All NMR experiments were performed at 25 °C on a Bruker Avance 500 MHz spectrometer using standard parameters. ^{1}H and ^{13}C chemical shifts were calibrated to the internal solvent signals ($\delta = 5.32$ and 53.8 ppm for CD_2Cl_2) and peaks were assigned using 2D experiments: COSY, NOESY (500 ms mixing), CH-COSY/HSQC, and HMBC (optimized for $J_{CH} = 7$ Hz). DOSY spectra were recorded with 2 ms bipolar z-gradient pulses ramped linearly from 1 to 50 G cm^{-1} and a diffusion delay of 70 ms. $^{1}H\{^{2}H\}$ (2.5 kHz decoupling) and ^{2}H NMR experiments were performed with the lock channel switched off. ^{119}Sn chemical shifts were calibrated with the $SnMe_4$ signal. IR spectra from KBr pellets were recorded on a Digilab Excalibur Series FTS 3000 spectrometer. Elemental analyses were carried out with a Heraeus CHN-O-RAPID instrument. Complex **A** was prepared as reported;[6] all other reagents were purchased from commercial sources and used as supplied.

1: $SnMe_4$ (1.73 mL, 12.4 mol) was added to a solution of **A** (250 mg, 0.31 mol) in CH_2Cl_2 (100 mL). The reaction mixture was stirred at room temperature for 15 h. After evaporation of the solvent and excess $SnMe_4$ under reduced pressure, the crude product was redissolved in CH_2Cl_2 and filtered over Celite. The pure product was obtained after evaporation of the solvent and recrystallization from CH_2Cl_2 at −20 °C. Yellow crystals; yield: 200 mg (86 %). IR (KBr): $\tilde{\nu} = 3441$ (br), 3063 (w), 2960 (vs), 2925 (s), 2868 (m), 1708 (m), 1626 (m), 1564 (vs), 1459 (m), 1435 (vs), 1383 (m), 1363 (m), 1326 (m), 1260 (m), 1225 (m), 1189 (w), 1158 (w), 1098 (m), 1058 (m), 1023 (w), 967 (w), 936 (w), 868 (w), 843 (w), 800 (m), 771 (m), 580 (w), 530 (w) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = -0.06$ (s, 6H, Me^{Pd}), 1.06–1.55 (m, 48H, Me^{iPr}), 2.04 (s, 6H, Me^{imine}), 2.12 (s, 6H, Me^{imine}), 2.49 (s, 6H, Me^{pz4}), 2.71 (sept, $^{3}J_{HH} = 6.8$ Hz, 2H, CH^{iPr}), 2.92 (sept, $^{3}J_{HH} = 6.8$ Hz, 2H, CH^{iPr}), 3.28 (sept, $^{3}J_{HH} = 6.8$ Hz, 2H, CH^{iPr}), 3.52 (sept, $^{3}J_{HH} = 6.8$ Hz, 2H, CH^{iPr}), 3.80 (s, 2H, μ-CH_2), 7.07–7.16 ppm (m, 12H, CH^{Ar}). ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 2.4$ (Me^{Pd}), 11.5 (Me^{pz4}), 20.0, 20.9 (Me^{imine}), 22.9, 23.5, 23.9, 23.9, 24.1, 24.2, 24.2, 25.0 (Me^{iPr}), 28.2, 28.3, 28.5, 28.7 (CH^{iPr}), 50.7 (μ-CH_2), 120.5 (C^{pz4}), 123.4, 123.8, 124.0, 125.9, 127.1 (CH^{Ar}), 140.0, 140.5, 140.8, 141.0, 141.7, 142.5 (C^{Ar}), 150.5, 153.3 ($C^{pz3,5}$), 165.3, 170.3 ppm (C^{imine}). UV/Vis (CH_2Cl_2): λ_{max} (ε/L mol^{-1} cm^{-1}) = 245 (26), 275 (27), 313 nm (26). Elemental analysis (%) calcd for $C_{67}H_{94}N_8Cl_2Pd_4$: C 53.36, H 6.28, N 7.43; found: C 53.74, H 6.24, N 7.39.

Received: August 25, 2009
Revised: October 27, 2009
Published online: February 12, 2010

Keywords: alkene coupling · bridging ligands · C–C coupling · multinuclear complexes · palladium

[1] a) G. Süss-Fink, *Angew. Chem.* **1994**, *106*, 71 – 73; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 67 – 69; b) E. K. van den Beuken, B. Feringa, *Tetrahedron* **1998**, *54*, 12985 – 13011; c) B. Bosnich, *Inorg. Chem.* **1999**, *38*, 2554 – 2562; d) S. Matsunaga, M. Shibasaki, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 60 – 75.

[2] a) H. Steinhagen, G. Helmchen, *Angew. Chem.* **1996**, *108*, 2489 – 2492; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2339 – 2342; b) D. E. Fenton, H. Okawa, *Chem. Ber.* **1997**, *130*, 433 – 442; c) C. Belle, J.-L. Pierre, *Eur. J. Inorg. Chem.* **2003**, 4137 – 4146; d) F. Meyer, *Eur. J. Inorg. Chem.* **2006**, 3789 – 3800; e) M. Jarenmark, H. Carlsson, E. Nordlander, *C. R. Chim.* **2007**, *10*, 433 – 462.

[3] See, for example: a) C. Dubs, T. Yamamoto, A. Inagaki, M. Akita, *Organometallics* **2006**, *25*, 1359 – 1367; b) B. M. Trost, S. Hisaindee, *Org. Lett.* **2006**, *8*, 6003 – 6005; c) D. J. Anderson, R. McDonald, M. Cowie, *Angew. Chem.* **2007**, *119*, 3815 – 3818; *Angew. Chem. Int. Ed.* **2007**, *46*, 3741 – 3744; d) M. F. Pilz, C. Limberg, B. B. Lazarov, K. C. Hultzsch, B. Ziemer, *Organometallics* **2007**, *26*, 3668 – 3676; e) D. C. Powers, T. Ritter, *Nat. Chem.* **2009**, 1, 302 – 309.

[4] *Multimetallic Catalysts in Organic Synthesis* (Eds.: M. Shibasaki, Y. Yamamoto), Wiley-VCH, Weinheim, **2004**.

[5] H. Li, T. J. Marks, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15295 – 15302.

[6] a) G. Noël, J. C. Röder, S. Dechert, H. Pritzkow, L. Bolk, S. Mecking, F. Meyer, *Adv. Synth. Catal.* **2006**, *348*, 887 – 897; b) A. Sachse, V. Daebel, A. Lange, S. Demeshko, S. Dechert, F. Meyer, *Dalton Trans.* **2010**, DOI: 10.1039/b925535d.

[7] L. Gavrilova, B. Bosnich, *Chem. Rev.* **2004**, *104*, 349 – 383.

[8] J. Klingele, S. Dechert, F. Meyer, *Coord. Chem. Rev.* **2009**, *253*, 2698 – 2741.

[9] a) J. C. Röder, F. Meyer, M. Konrad, S. Sandhöfner, E. Kaifer, H. Pritzkow, *Eur. J. Org. Chem.* **2001**, 4479 – 4487; b) J. C. Röder, F. Meyer, H. Pritzkow, *Chem. Commun.* **2001**, 2176 – 2177; c) A. Sachse, G. Noël, S. Dechert, S. Demeshko, A. Honecker, A. Alfonsov, V. Kataev, F. Meyer, *Eur. J. Inorg. Chem.* **2008**, 5390 – 5396; d) A. Sachse, S. Demeshko, F. Meyer, *Dalton Trans.* **2009**, 7756 – 7764.

[10] When only a stoichiometric amount of $SnMe_4$ is used, the reaction is very slow and does not give a single product.

[11] CCDC 743783 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] A search of the CSD for Pd–CH_3 units gave 336 hits with *d*(Pd–C) in the range from 1.946 to 2.309 Å, a mean value of 2.057 Å, and a median value of 2.046 Å; *d*(Pd1–C33) in **1** is 2.036(8) Å.

[13] See, for example: a) S. J. Young, B. Kellenberger, J. H. Reibenspies, S. E. Himmel, M. Manning, O. P. Anderson, J. K. Stille, *J. Am. Chem. Soc.* **1988**, *110*, 5744 – 5753; b) A. Satake, H. Koshino, T. Nakata, *J. Organomet. Chem.* **2000**, *595*, 208 – 214; c) C. R. Baar, M. C. Jennings, R. J. Puddephatt, *Organometallics* **2001**, *20*, 3459 – 3465; d) T. Rüther, M. C. Done, K. J. Cavell, E. J. Peacock, B. W. Skelton, A. H. White, *Organometallics* **2001**, *20*, 5522 – 5531; e) A. D. Burrows, M. F. Mahon, S. P. Nolan, M. Varrone, *Inorg. Chem.* **2003**, *42*, 7227 – 7238; f) A. Scarel, J. Durand, D. Franchi, E. Zangrando, G. Mestroni, C. Carfagna, L. Mosca, R. Seraglia, G. Consiglio, B. Milani, *Chem. Eur. J.* **2005**, *11*, 6014 – 6023; g) N. M. Motsoane, I. A. Guzei, J. Darkwa, *Z. Naturforsch. B* **2007**, *62*, 323 – 330.

[14] S. R. Klopfenstein, C. Kluwe, K. Kirschbaum, J. A. Davies, *Can. J. Chem.* **1996**, *74*, 2331 – 2339.

[15] J. H. Brownie, M. C. Baird, *Organometallics* **2003**, *22*, 33 – 41.

[16] M. Bochmann, T. Cuenca, D. T. Hardy, *J. Organomet. Chem.* **1994**, *484*, c10 – c12.

[17] a) J. R. Torkelson, R. McDonald, M. Cowie, *J. Am. Chem. Soc.* **1998**, *120*, 4047 – 4048; b) P. M. Maitlis, *J. Organomet. Chem.* **2004**, *689*, 4366 – 4374.

[18] See, for example: C. Markert, M. Neuburger, K. Kulicke, M. Meuwly, A. Pfaltz, *Angew. Chem.* **2007**, *119*, 5996 – 5999; *Angew. Chem. Int. Ed.* **2007**, *46*, 5892 – 5895.

