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A new synthesis for thermolabile low-valent palladium complexes by electron transfer reactions from nickel(0) to palladium(II) compounds

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Abstract

The nickel(0) complex [Ni(bpy)(cod)] (bpy: 2,2′-bipyridine, cod: cycloocta-1,5-diene) was used as a mild reducing reagent for the synthesis of the extremely reactive low-valent palladium complexes $[Pd_2X_2(cod)_2]$ (**1**: X = Cl, **2**: X = Br), $Pd(cod)_2$ (**3**) and $Pd(norbornene)_3$ (**4**). The X-ray analysis of **1** showed that the two [Pd(cod)(Cl)] moieties are only connected by a short Pd(I)–Pd(I) bond (bond length: 2.5379(4) Å) with the chloride ions as monodentate ligands. The X-ray structure of **3** which is also known to be an extremely reactive compound could be determined by X-ray diffraction. As expected, the Pd(0) centre is surrounded by the two cod ligands to form a PdC_4 tetrahedron with typical Pd–C bond lengths. The crystal structure of **3** shows it to be very similar to the closely related complexes $M(cod)_2$ (M: Ni, Pt). The X-ray structure of **4** displays that the Pd(0) centre is in a trigonal planar environment of the three olefin groups. According to ^1H NMR measurements the complexes have the same structure in solution as found in the solid state.
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Keywords: 1,5-Cyclooctadiene; Norbornene; Palladium(I) complexes; Palladium(0) complexes; Redox reactions

1. Introduction

Recently we have found that [Ni(bpy)(cod)] reduced $Pt(cod)Cl_2$ to form $Pt(cod)_2$ which could be isolated in good yields [1]. From this finding the question arises whether this type of electron transfer reaction may have a more general preparative value for the formation of low-valent transition metal complexes which often require very sophisticated reaction conditions, particularly if the resulting reduced products are very reactive. Generally, transition metal complexes as reductands offer some advantages compared with other reducing reagents such as the possibility of tuning their redox properties and the controlling of their kinetic behaviour by choosing suitable ligands.

Therefore we continued our investigations in this area and here we report on new procedures for the formation of the thermolabile and extremely reactive low-valent palladium(I) and palladium(0) complexes $[Pd_2X_2(cod)_2]$ (**1**: X = Cl, **2**: X = Br), $Pd(cod)_2$ (**3**) and $Pd(norbornene)_3$ (**4**) by using [Ni(bpy)(cod)] as reducing reagent. Furthermore, we describe the X-ray structures of **1**, **3**, and **4**.

2. Results and discussion

Dimeric Pd(I) complexes have been intensively investigated due to their importance in homogeneous catalytic reactions, as model complexes for clusters and for metallic surfaces [2–18]. Dimeric Pd(I) complexes, however, consisting only of the Pd_2Cl_2 core and olefins (e.g. cod) as additional ligands are hitherto unknown, although they would be of great interest as starting material for the synthesis of other Pd(I) compounds with variable stabilizing ligands and as potential homogeneous catalysts, also in combination with additional controlling ligands.

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Our attempts for preparing the cod complexes were carried out below −20 °C, since the cod complexes of Pd(I) were expected to be thermically instable. For reducing Pd(II) a suspension of Pd(cod)Cl_2 in THF containing a small amount of anthracene or 1,3-butadiene which prevented fast decomposition of the reaction products was slowly treated with a THF solution of [Ni(bpy)(cod)]. Upon addition of 0.5 equiv of the nickel(0) complex to the reaction mixture, an immediate colour change from yellow to red-violet was observed and upon workup complex **1** was isolated as a red compound. Single crystals of **1** were grown by layering a toluene solution of **1**with heptane. Its mass spectrum (FAB-MS) showed one major peak at $m/z = 498$ corresponding to the composition $[Pd_2Cl_2(cod)_2]$. This suggests that a redox reaction has occurred in which two electrons were transferred from Ni(0) to two Pd(II) centres accompanied by the exchange of cod and two chloride ligands (Eq. (1)):

$$\begin{aligned}&[\mathrm{Ni(bpy)(cod)}] + 2\mathrm{Pd(cod)Cl_2}\\ &\quad\rightarrow [\mathrm{Pd_2Cl_2(cod)_2}] + \mathrm{Ni(bpy)Cl_2} + \mathrm{cod}\end{aligned} \tag{1}$$

Fig. 1 shows the solid state structure of **1** determined by a low-temperature X-ray analysis and contains relevant bond lengths and angles in the caption. Complex **1** is a bimetallic Pd(I) complex with a Pd–Pd bond of 2.5379(4) Å. Each Pd ion is in a planar environment created by cod acting as bidentate chelate ligand, one monodentate chloride ligand and the other Pd(I). The Pd–C bond lengths are unsymmetrical due to the strong *trans* influence of the Pd(I)–Pd(I) bridge [19]. The two Cl–Pd–Pd angles are 83.72(3)° and 81.11(3)°. Furthermore, the two planar coordination polyeders form an angle of 82.4°.

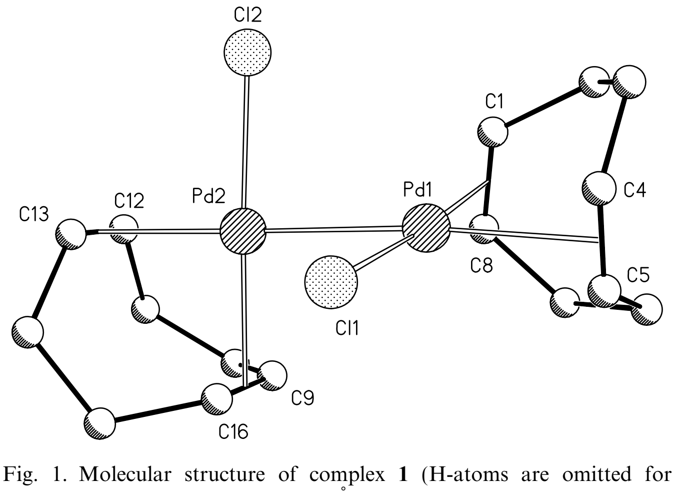


Fig. 1. Molecular structure of complex **1** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°): Pd1–Pd2 2.5379(4), Pd1–Cl1 2.3293(9), Pd1–C4 2.327(4), Pd1–C5 2.338(4), Pd1–C1 2.209(4), Pd1–C8 2.194(4), Pd2–Cl2 2.3218(9), Pd2–C9 2.206(3), Pd2–C16 2.205(4), Pd2–C12 2.311(4), Pd2–C13 2.307(4), Pd1–X1 2.090(1), Pd1–X2 2.232(1), Pd2–X3 2.095(1), Pd2–X4 2.208(1) Cl1–Pd1–Pd2 81.11(3), Cl1–Pd1–X1 175,5(1), Cl1–Pd1–X2 98.2(1), X1–Pd1–Pd2 94.9(1), X1–Pd1–X2 85.9(1), X2–Pd1–Pd2 175.2(1), Cl2–Pd2–Pd1 83.72(3), Cl2–Pd2–X3 177.8(1), Cl2–Pd2–X4 95.8(1), X3–Pd2–Pd1 94.4(1), X3–Pd2–X4 86.1(1), X4–Pd2–Pd1 178.4(1) (centroids: X1 (C1–C8), X2 (C4–C5), X3 (C9–C16), X4 (C12–C13)).

It is interesting to note that the known dimeric Pd(I) complexes usually contain strong ligands with P- or N-donor atoms or mixed N–P chelate ligands [2–18]. In many of them the Pd centres are connected by bridging ligands.

The ^{1}H NMR spectrum of **1** in THF-d_8 at −20 °C showed the typical singlet for the CH protons at 6.15 ppm (integrated to four protons) and two resonances for the CH_2 protons at 2.86 and 2.57 ppm (each integrated to four protons). This splitting into two signals indicated that the solid state structure of **1** is stable as well in solution.

The compound **2** containing bromide in place of chloride was prepared in analogy to the synthesis of **1** starting with Pd(cod)Br_2. Mass spectroscopic and NMR measurements display that **2** has the same composition and structure as observed for **1**. The FAB-MS showed an envelope of peaks at $m/z = 588$ corresponding to the dimeric complex $[Pd_2Br_2(cod)_2]$ and in the ^{1}H NMR spectrum the CH protons were observed at 6.27 ppm and the CH_2 protons resonated at 2.74 and 2.46 ppm; each of these signals corresponded to four protons.

Compounds **1** and **2** are extremely air and moisture sensitive compounds which decomposed above −15 °C as well in solution as in the solid state resulting in the formation of elementary palladium. It is noteworthy that attempts to isolate **1** and **2** using sodium/naphthalene as reducing agent failed so far. Under these conditions palladium black was formed as main product together with a very small amount of the Pd(I) complexes. Furthermore, the conproportionation reaction between $Pd(dba)_2$ and Pd(cod)Cl_2 in the presence of an excess of cod was unsuccessful as well. This demonstrates that [Ni(bpy)(cod)] is indeed a valuable mild agent for reducing organometallic compounds which may offer numerous other applications.

To prove this potential we investigated the electron transfer reaction between the Ni(0) centre and Pd(II) complexes in order to form Pd(0) complexes and succeeded in preparing $Pd(cod)_2$ (complex **3**) by careful tuning the reaction conditions. Compound **3** is known to be an extremely sensitive compound which decomposes very easily. It was obtained by metal atom synthesis [20], by reducing Pd(II) with Mg(anthracene) [21] in relatively low yields and by reacting Pd(cod)Cl_2 with cyclooctatetraendiyl lithium [22,23] in good yields; however in the latter reaction the use of liquid propene was required. To the best of our knowledge neither the solid state structure of **3** nor its NMR data are known.

The reaction to form **3** was carried out as follows: In the presence of an excess of 1,3-butadiene [Ni(bpy)(cod)] and Pd(cod)Cl_2 were reacted at −20 °C and **3** could be obtained as light yellow crystals according to Eq. (2). For the success of the synthesis the presence of 1,3-butadiene was essential. In the absence of added butadiene [Ni(bpy)(cod)] failed to afford **3**, and **1** together with palladium black was obtained.

$$[\mathrm{Ni(bpy)(cod)}] + \mathrm{Pd(cod)Cl_2} \rightarrow \mathrm{Pd(cod)_2} + \mathrm{Ni(bpy)Cl_2} \tag{2}$$

The EI mass spectrum showed an envelope of peaks at $m/z = 322$ that match well with the isotopic distribution calculated for the ion $[Pd(cod)_2]^+$. In addition, the ^1H NMR spectrum in THF-d_8 at −20 °C showed the expected simple pattern for two symmetrically bonded cod ligands at 5.50 ppm for the CH protons and at 2.33 ppm for the signals of the CH_2 groups.

Single crystals were grown from toluene at −25 °C and the crystal structure of **3** has been solved by X-ray diffraction analysis. Its molecule structure is displayed in Fig. 2 containing relevant bond lengths and angles in the caption.

The crystal structure of **3** shows it to be very similar to the closely related $M(cod)_2$ complexes of Ni(0) and Pt(0) [1,24] with the Pd(0) centre in a tetrahedral environment of the centroids of the olefin groups of the two chelating cod ligands. The Pd–C bond distances lie in the range usually observed for this type of bonding and need therefore no further discussion.

The use of [Ni(bpy)(cod)] for reducing Pd(II) complexes is not restricted to the synthesis of cod containing complexes. For example, the reaction of [Ni(bpy)(cod)] with $Pd(cod)Cl_2$ in the presence of norbornene afforded the complex $Pd(norbornene)_3$ (**4**) (Eq. (3)):

$$[Ni(bpy)(cod)] + Pd(cod)Cl_2 + 3\,norbornene \rightarrow Pd(nbn)_3 + Ni(bpy)Cl_2 + 2cod \qquad (3)$$

Compound **4** has been prepared earlier by Stone by using cyclooctatetraendiyl lithium as reducing agent and the compound was found to be isomorphous with the structurally elucidated $Pt(nbn)_3$ [23]. We succeeded in obtaining single crystals of **4** by slow crystallization of the complex from hexane/diethyl ether. Fig. 3 displays the molecular structure determined by X-ray diffraction and relevant bond lengths and angles are listed in the figure caption. The Pd(0) centre is in a trigonal planar environment of three olefin groups and its structure is very similar to the related platinum complex [23].

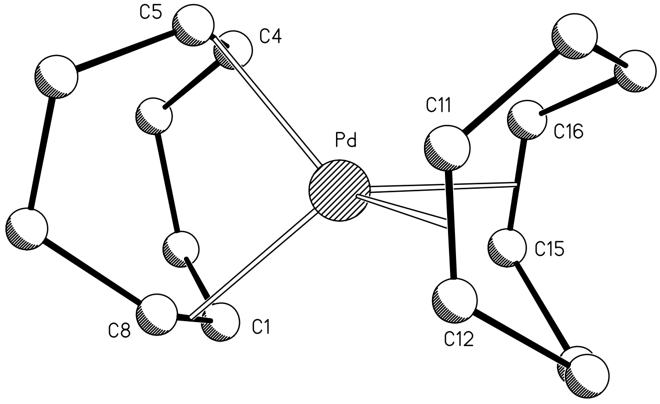


Fig. 2. Molecular structure of complex **3** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°) : Pd–C1 2.148(6), Pd–C8 2.160(6), Pd–C4 2.151(6), Pd–C5 2.158(6), Pd–C11 2.146(6), Pd–C12 2.144(6), Pd–C15 2.163(6), Pd–C16 2.188(5), Pd–X1 2.040(6), Pd–X2 2.040(6), Pd–X3 2.037(6), Pd–X4 2.063(6), X1–Pd–X2 88.4(2), X1–Pd–X3 117.0(2), X1–Pd–X4 125.4(2), X2–Pd–X3 126.6(2), X2–Pd–X4 115.8(2), X3–Pd–X4 87.7(2) (centroids: X1 (C1–C8), X2 (C4–C5), X3 (C11–C12), X4 (C15–C16)).

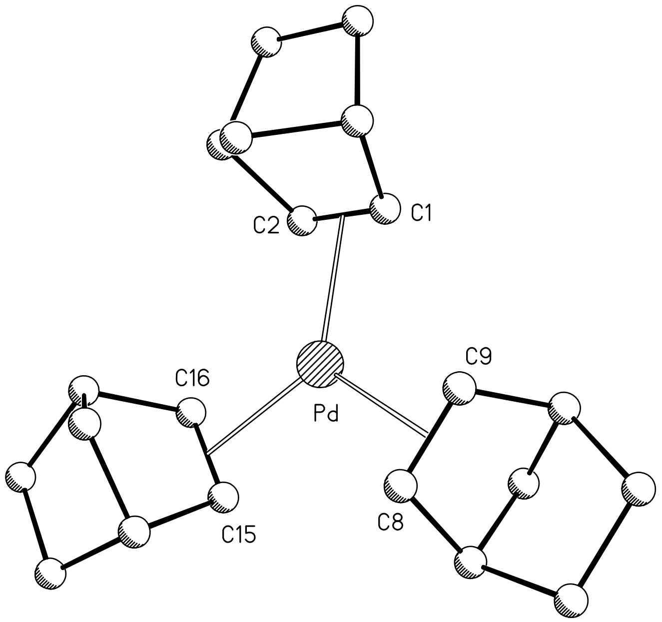
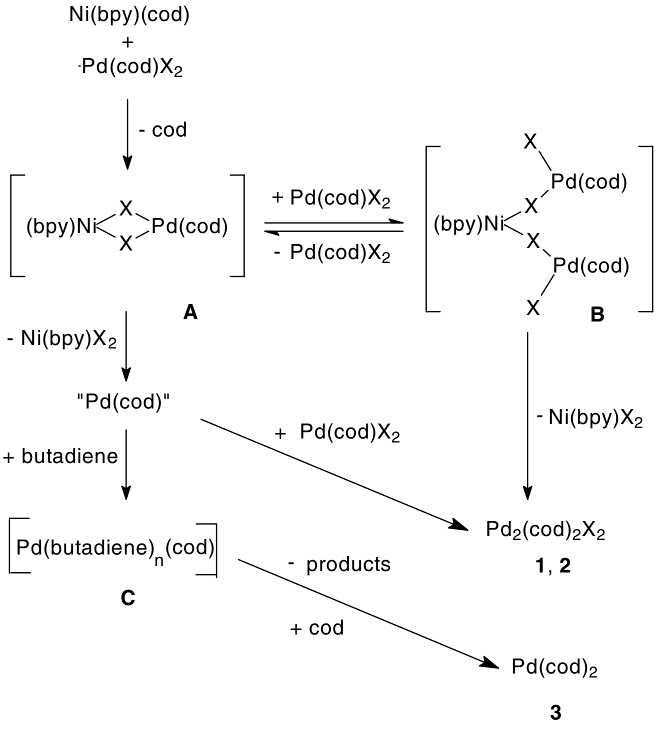


Fig. 3. Molecular structure of complex **4** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°): Pd–C1 2.207(2), Pd–C2 2.210(3), Pd–C8 2.214(3), Pd–C9 2.224(2), Pd–C15 2.212(3), Pd–C16 2.207(3), Pd–X1 2.098(3), Pd–X2 2.108(3), Pd–X3 2.098(3), X1–Pd–X2 119.7(1), X1–Pd–X3 121.9(1), X2–Pd–X3 118.2(1) (centroids: X1 (C1–C2), X3 (C8–C9), X3 (C15–C16)).

For the electron transfer reaction between the Ni(0) complex and the Pd(II) compounds, two competitive pathways may be envisioned (Scheme 1): the first one would start with the formation of a 1:1 complex **A** as an intermediate in



Scheme 1. Possible pathways for generating **1**, **2** and **3**.

which the (bpy)Ni fragment and Pd(cod)X_2 are bridged by two halogenide ligands. Subsequent two-electron transfer could then result in the formation of the instable "Pd(cod)" fragment followed by a fast conproportionation reaction of this intermediate with a Pd(cod)X_2 molecule to generate **1** or **2**.

Alternatively, **A** may react with a further molecule Pd(cod)X_2 to form **B** in equilibrium with **A**. Subsequent electron transfer from the Ni(0) centre in **B** to two Pd centres and elimination of Ni(bpy)X_2 may result in **1** or **2** as well.

In the presence of an excess of 1,3-butadiene, however, complex **3** was obtained. We assume therefore that the fragment "Pd(cod)(0)" may react under these conditions with the diene to form a butadiene Pd(0) complex **C** which is transformed into **3** in the last step. When the reaction was carried out in the presence of deuterium-labelled butadiene the deuterated product of the composition $C_{16}D_{24}Pd$ was detected. This suggests that in the course of the reaction an oxidative coupling of two butadienes to form allyl-Pd species as intermediates could play a role [25,26] which may undergo reductive elimination to form **3**. However, this assumption needs further support by mechanistic investigations.

3. Conclusions

In this work we have demonstrated that [Ni(bpy)(cod)] could be used for the reduction of Pd(II) centres resulting in the extremely sensitive low-valent Pd complexes [$Pd_2Cl_2(cod)_2$], [$Pd_2Br_2(cod)_2$], Pd$(cod)_2$ or Pd(norbornene)$_3$, depending on the reaction conditions. We suggest that three factors contribute to the ability of the Ni(0) complex to act as a mild reagent for such reactions: First, bpy increases the reducing power of the Ni(0) centre compared with other neutral ligands due to its relatively strong σ-donor-behaviour. Second, Ni forms stable (bpy)Ni fragments in both oxidation states 0 and +2. Third, the final product Ni(bpy)X_2 is sparingly soluble in most organic solvents which allow easy separation of this reaction product by filtration. Since Ni$(cod)_2$ and bpy are commercially available and a combination of both substances in situ can also be used as reducing agent this method may find a number of other applications for preparing very sensitive low-valent metal complexes.

4. Experimental

4.1. General procedures

^{1}H NMR spectra were recorded at low temperature on a Bruker AC 200 MHz spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard. Mass spectra were recorded using a Finnigan MAT SSQ 710. FAB-Measurements were made using *dmba* as a matrix. All manipulations were carried out by using Schlenk techniques under an atmosphere of argon. Prior to use, tetrahydrofurane, toluene, *n*-alkanes and diethyl ether were dried over potassium hydroxide and distilled over Na/benzophenone. Dichloromethane was distilled over CaH_2. Pd(cod)$Cl_2$and Pd(cod)Br_2 were prepared according to literature procedures [27,28]. Compounds **1**–**4** are extremely reactive and decompose above −20 °C.

4.1.1. [Ni(bpy)(cod)]

The starting complex [Ni(bpy)(cod)] was synthesized in a procedure similar to that described in Refs. [29,30]: Ni$(cod)_2$ (2.75 g, 10 mmol) and 2,2′-bipyridine (1.64 g, 10.5 mmol) were dissolved in 120 ml THF at 20 °C. The mixture was stirred for 3 h to give a deep blue solution. After filtration the solvent of the filtrate was evaporated under vacuum and the remaining residue was treated with 80 ml diethyl ether. The deep blue precipitate of [Ni(bpy)-(cod)] was filtered off and washed with diethyl ether and with *n*-pentane. Yield: 2.94 g (91%). After drying under vacuum this product was used for the reduction of the Pd(II) complexes to form **1**–**4**. Alternatively, a 1:1 mixture of Ni$(cod)_2$ and 2,2′-bipyridine can be used giving the same reduction products.

4.1.2. [$Pd_2Cl_2(cod)_2$] (**1**)

A solution of [Ni(bpy)(cod)] (0.16 g, 0.5 mmol) or a freshly prepared mixture of Ni$(cod)_2$ and 2,2′-bipyridine (1:1) in 10 ml of THF was added drop wise into a suspension of Pd(cod)Cl_2 (0.29 g, 1.0 mmol) and anthracene (18 mg, 0.1 mmol) in a mixture of 10 ml of THF and 1 ml of cod at −25 °C. It was crucial that the temperature was kept below −20 °C during the reaction time and work up to avoid fast decomposition of the product. The blue violet colour of the [Ni(bpy)(cod)] should always disappear before adding the next portion to the reaction mixture. When the addition was completed the deep red violet suspension was stirred for further 2 h. All insoluble parts were then filtered off over Celite and washed with 10 ml of THF. The formed red solution was concentrated under reduced pressure whereupon a solid appeared which was washed with hexane. The red solid obtained was dried i.V. Yield: 0.075 g (30%); $C_{16}H_{24}Cl_2Pd_2$ (500.1). Due to the extreme thermolability of **1** only its chloride content was be determined by volumetric titration. Calc.: Cl, 14.18. Found: Cl, 14.05%; MS-FAB (in dmba) *m/z*: 498 $[M]^+$, 463 $[M-Cl]^+$; ^{1}H NMR (200 MHz, THF-d_8, −20 °C): $\delta = 2.57$ (m, 4H, CH_2), 2.86 (m, 4H, CH_2), 6.15 (s, 4H, CH) ppm. Crystals, suitable for the X-ray diffraction, were obtained from a diffusion of heptane into a solution of toluene.

4.1.3. [$Pd_2Br_2(cod)_2$] (**2**)

The compound was prepared analogously to **1**. Higher yields of the product were obtained by using dichloromethane instead of THF for the reaction suspension and work up. Yield: 0.20 g (70%) – using dichloromethane; $C_{16}H_{24}Br_2Pd_2$; (589.0); Calc.: C, 32.63; H, 4.11. Found: C, 32.82; H, 4.21%; MS-FAB (in dmba) *m/z*: 588 $[M]^+$, 508 $[M-Br]^+$; ^{1}H NMR (200 MHz, THF-d_8, −20 °C):

$\delta = 2.46$ (m, 4H, CH_2), 2.74 (m, 4H, CH_2), 6.27 (s, 4H, CH) ppm.

4.1.4. *[Pd(cod)$_2$] (**3**)*

A solution of [Ni(bpy)(cod)] (0.24 g, 0.75 mmol) or a freshly prepared mixture of Ni(cod)$_2$ and 2,2′-bipyridine (1:1) in 10 ml of THF was added drop wise into a suspension of Pd(cod)Br$_2$ (0.37 g, 1.0 mmol) or Pd(cod)Cl$_2$, respectively, in a mixture of 15 ml of THF, 1 ml of cod and 3 ml of 1,3-butadiene at −25 °C. It was important to keep the temperature below −20 °C during the synthesis to avoid fast decomposition of the product. The blue violet colour of the [Ni(bpy)(cod)] should always disappear before adding the next portion to the reaction mixture. When the addition was completed the deep red-violet suspension was further allowed to stir for 2 h. All insoluble parts were filtered off over Celite and washed with 10 ml of THF. Then the remaining yellow solution was concentrated under reduced pressure. For further preparative use it is recommended to use the Pd(cod)$_2$ as its THF solution. For isolation all liquids were removed under reduced pressure and the yellowish white solid was recrystallized from toluene or hexane to give a white solid. Yield: 0.05 g (20%); $C_{16}H_{24}Pd$ (322.8); Calc.: C, 59.53; H, 7.50. Found: C, 59.44; H, 7.74%; MS-EI *m/z*: 322 $[M]^+$, 268 $[M-C_4H_6]^+$, 214 $[M-C_8H_{12}]^+$; ^1H NMR (200 MHz, THF-d_8, −20 °C): $\delta = 2.33$ (m, 8H, CH_2), 5.50 (m, 4H, CH) ppm. Crystals, suitable for the X-ray diffraction, were obtained from a solution of toluene at −25 °C.

4.1.5. *[Pd(norbornene)$_3$] (**4**)*

A solution of [Ni(bpy)(cod)] (0.097 g, 0.30 mmol) or a freshly prepared mixture of Ni(cod)$_2$ and 2,2′-bipyridine (1:1) in 5 ml of THF was added drop wise into a suspension of Pd(cod)Cl$_2$ (0.094 g, 0.33 mmol) and norbornene (0.42 g, 4.5 mmol) in a mixture of 5 ml THF, 1 ml 1,3-butadiene at −30 °C. When the addition was completed the orange suspension was allowed to stir for further 2 h. All insoluble parts were filtered off over Celite and washed with 5 ml of THF. Then the remaining yellow solution was concentrated under reduced pressure. The yellowish white solid was washed with a small portion of hexane and dried in vacuum. Recrystallization can be made using hexane to give a white solid. Yield: 0.064 g (50%); $C_{21}H_{30}Pd$ (388.87); the spectroscopic properties of the compound were identical with those of an authentic sample [23]. ^1H NMR (200 MHz, toluene-d_8, −40 °C): $\delta = 3.80$ (s, 2H, =CH), 2.81 (s, 2H, CH), 1.38 (m, 4H, CH_2), 0.27 (m, 2H, CH_2*bridge*) ppm. Crystals, suitable for the X-ray diffraction, were obtained from a solution of pentane/diethyl ether at −40 °C.

4.1.6. *Reaction of [Ni(bpy)(cod)] and Pd(cod)Cl$_2$ in the presence of 1,3-butadiene-d_6*

The reaction was carried out as stated above for the preparation of Pd(cod)$_2$ in the presence of 1,3-butadiene-d_6 instead of 1,3-butadiene. The crude white product was extracted with heptane and analysed by mass spectroscopy. $C_{16}D_{24}Pd$; MS-EI *m/z*: 346 $[M]^+$, 286 $[M-C_4D_6]^+$, 226 $[M-C_8D_{12}]^+$. It decomposes very rapidly above −20 °C.

5. Crystal structure determination

The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects [31,32].

The structures were solved by direct methods (SHELXS [33]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [34]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [34]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

5.1. *Crystal data for **1***

$C_{16}H_{24}Cl_2Pd_2 * C_7H_8$, $M_r = 592.19\ g\ mol^{-1}$ orange prism, size $0.02 \times 0.02 \times 0.02\ mm^3$, monoclinic, space group $P2/n$, $a = 15.7960(3)$, $b = 6.9767(1)$, $c = 20.9746(5)$ Å, $\beta = 103.965(1)°$, $V = 2243.16(8)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calc} = 1.754\ g\ cm^{-3}$, $\mu(Mo\text{-}K\alpha) = 18.47\ cm^{-1}$, $F(000) = 1184$, 15187 reflections in $h(-19/20)$, $k(-8/9)$, $l(-27/25)$, measured in the range $2.66° \leqslant \Theta \leqslant 27.48°$, completeness $\Theta_{max} = 99.2\%$, 5101 independent reflections, $R_{int} = 0.042$, 4153 reflections with $F_o > 4\sigma(F_o)$, 244 parameters, 0 restraints, $R_{1\,obs} = 0.034$, $wR_{2\,obs} = 0.076$, $R_{1\,all} = 0.050$, $wR_{2\,all} = 0.082$, GOOF = 1.027, largest difference peak and hole: 0.793/−0.790 e Å^{-3}.

5.2. *Crystal data for **3***

$C_{16}H_{24}Pd$, $M_r = 322.75\ g\ mol^{-1}$, colourless prism, size $0.03 \times 0.03 \times 0.02\ mm^3$, triclinic, space group $P\bar{1}$, $a = 7.3858(2)$, $b = 9.2342(2)$, $c = 10.7138(4)$ Å, $\alpha = 72.015(1)$, $\beta = 84.375(1)$, $\gamma = 69.717(1)°$, $V = 651.87(3)$ Å^3, $T = -90$ °C, $Z = 2$, $\rho_{calc} = 1.644\ g\ cm^{-3}$, $\mu(Mo\text{-}K\alpha) = 13.99\ cm^{-1}$, $F(000) = 332$, 4591 reflections in $h(-9/9)$, $k(-11/11)$, $l(-11/13)$, measured in the range $2.46° \leqslant \Theta \leqslant 27.46°$, completeness $\Theta_{max} = 98.9\%$, 2953 independent reflections, $R_{int} = 0.038$, 2767 reflections with $F_o > 4\sigma(F_o)$, 155 parameters, 0 restraints, $R_{1\,obs} = 0.051$, $wR_{2\,obs} = 0.130$, $R_{1\,all} = 0.054$, $wR_{2\,all} = 0.133$, GOOF = 1.075, largest difference peak and hole: 2.207/−2.177 e Å^{-3}.

5.3. *Crystal data for **4***

$C_{21}H_{30}Pd$, $M_r = 388.85\ g\ mol^{-1}$, colourless prism, size $0.03 \times 0.03 \times 0.03\ mm^3$, orthorhombic, space group $P2_12_12_1$, $a = 5.5943(1)$, $b = 10.7699(2)$, $c = 28.5210(4)$ Å, $V = 1718.39(5)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calc} = 1.503\ g\ cm^{-3}$, $\mu(Mo\text{-}K\alpha) = 10.75\ cm^{-1}$, $F(000) = 808$, 12,292 reflections in $h(-7/7)$, $k(-13/12)$, $l(-36/37)$, measured in the range

$2.86° \leqslant \Theta \leqslant 27.47°$, completeness $\Theta_{max} = 99.8\%$, 3925 independent reflections, $R_{int} = 0.034$, 3582 reflections with $F_o > 4\sigma(F_o)$, 199 parameters, 0 restraints, $R1_{obs} = 0.026$, $wR2_{obs} = 0.053$, $R1_{all} = 0.032$, $wR2_{all} = 0.056$, GOOF = 1.022, Flack-parameter −0.07(3), largest difference peak and hole: 0.415/−0.590 e Å^{-3}.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 601441 (**1**), 601442 (**3**), and 601443 (**4**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.015.

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