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Preliminary communication/Communication

Formation de palladacycles à six chaînons à partir de précurseurs bisacétate phénantroline Pd(II) et d'isocyanate de phényle

Formation of six-membered Palladacycles from Phenanthroline Pd(II) Bisacetate Precursors and Phenylisocyanate

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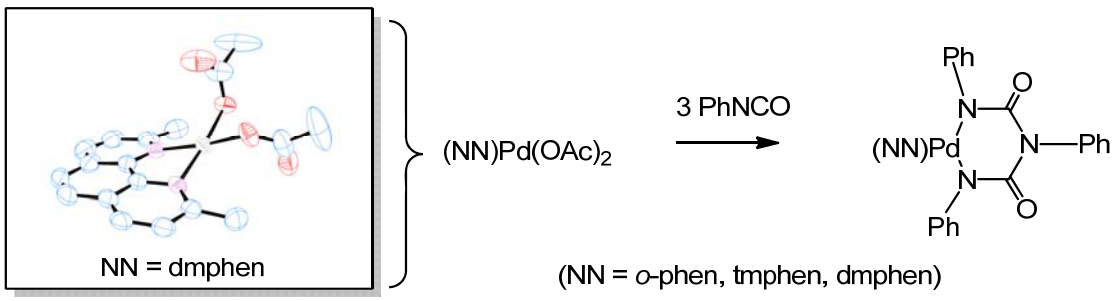
Dedicaced to Professor John A. Osborn.

Résumé

L'isocyanate de phényle réagit avec des complexes phénanthroline de palladium(II) bis-acetate pour former quasi-quantitativement des palladacycles à six chaînons. Dans cette nouvelle réaction, le ligand acétate joue possiblement le rôle d'agent décarbonylant vis-à-vis de l'isocyanate an formant les palladacycles isolés par un réarrangement intramoléculaire.

Abstract

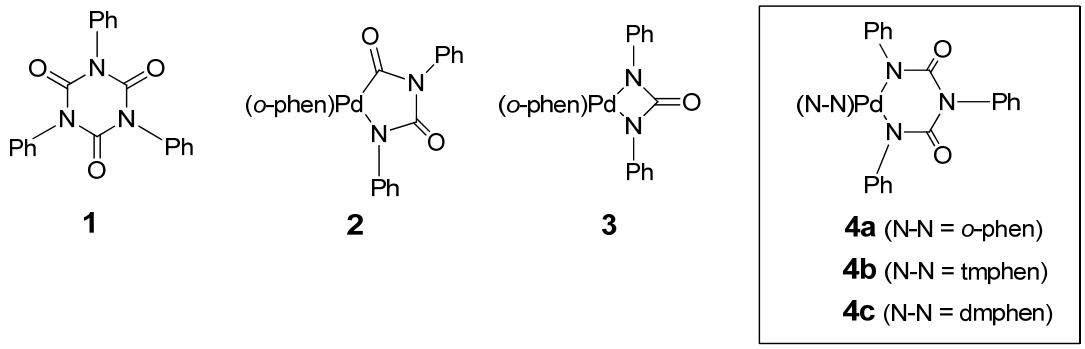
Phenylisocyanate reacts with palladium(II) bis-acetate phenanthroline complexes to give six-membered palladacycles in nearly quantitative yields. In this new reaction, the acetate ligands act as decarbonylating agents toward the isocyanate functionality by possibly forming the isolated palladacycles via an intramolecular rearrangement.



Keywords: Isocyanate, Dimine Pd(II) Complex, Palladacycle, Catlaytic Carbonylation of Nitroaromatics

1. Introduction

To date, the reactivity of isocyanates in the coordination sphere of various group-VIII metal centers is still a field only partially explored.[1-3] Such reactions can provide a very valuable access to various types of heterocycles and are thus especially attractive with respect to atom-economy considerations.[4-7] Moreover, they often bring some information about the possible deactivation pathways of catalytic processes involving isocyanate as reactant or product.[8-10] In this regard, we have previously shown that diimine-Pd(0) precursors catalytically trimerize arylisocyanates to form triarylisocyanurates (**1**, Scheme 1),[11] while some inactive palladacycles like **2**, **3** or **4a**,[9, 12] which possibly result from deactivation of the active species, are eventually also formed.



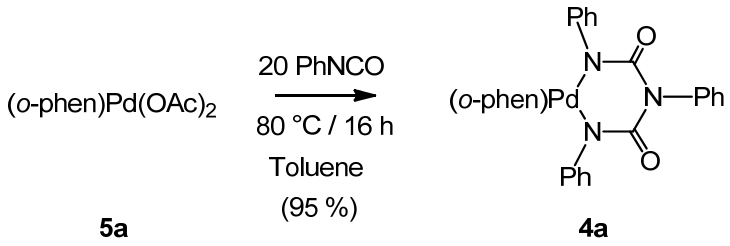
Scheme 1. Cyclotrimer and palladacycles formed from diimine-Pd(0) and Pd(II) complexes.

In the process of exploring the scope of this reaction, we have now investigated the reaction of PhNCO with various Pd(II)-phenanthroline precursors, like $Pd(N\text{-}N)(OAc)_2$ complexes (**5a-c**), where N-N represents 1,10-phenanthroline (*o*-phen), 3,4,7,8-tetra-methylphenanthroline (tmphen) and 2,9-dimethylphenanthroline (dmphen),

respectively. In a manner similar to the reaction with Pd(0) precursors, a reaction yielding the six-membered palladacycles **4a-c** took place, providing thereby an easy access to these interesting compounds.

2. Results and discussion

When reacted with one equivalent phenylisocyanate in dichloromethane at 20 °C, the bis-acetato diimine Pd(II) complex **5a**[13, 14] forms the known 6-membered palladacycle **4a**[9, 12] in *ca.* 30 % yield after two days. In presence of an excess of PhNCO (20 eq.), this reaction becomes nearly quantitative, allowing isolation of *ca.* 95 % of **4a** after the same time. This reaction can also be performed at higher temperature in an aromatic solvent like toluene, **4a** being then quantitatively isolated after 16 h (Scheme 2).

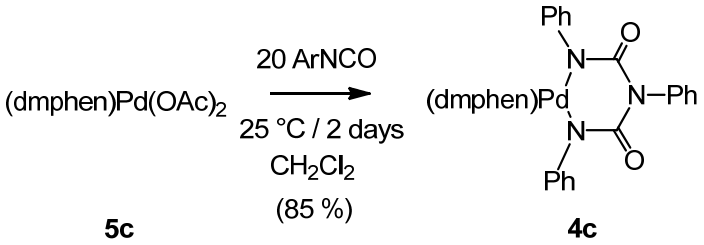


Scheme 2. Reaction between **5a** and PhNCO.

This reaction can also be performed with the analogue of **5a** possessing a tmphen (**5b**) ligand instead of phen to give the corresponding palladacycle **4b** in good yields. This new palladacycle was characterized by high resolution mass spectrometry (HRMS), infrared and ^{1}H NMR. In contrast, this reaction is not observed from other Pd(II) precursors such as Pd(*o*-phen)Cl_2, $Pd(OAc)_2$ or from an equimolar $Pd(acac)_2$/*o*-phen mixture, pointing at the need to have a carboxylate anion and a diimine ligand simultaneously present in the medium for this reaction to proceed. Notably, we have

checked that this reaction takes place with similar yield from a carefully dried complex **5a** in anhydrous toluene, suggesting that traces of water are not involved in its mechanism.[15]

We then turned our attention toward the Pd(II) precursor **5c**, presenting the more bulky dmphen ligand in place of *o*-phen,[14] and with this sterically crowded Pd(II) complex, the reaction takes also place and a nearly complete conversion of **5c** into **4c** is observed in dichloromethane at ambient temperature after 2 days (Scheme 3). The new palladacycle **4c** is the 2,9-dimethylated analogue of **4a**. This complex was fully characterized, allowing notably for the observation of the two strong carbonyl ν_{CO} stretching modes near 1645 and 1625 cm^{-1} diagnostic of the three carbonyl groups of this metallacycle.[9] Attempts to perform this reaction at 80 °C in toluene or other aromatic solvents were, however, not successful with partial decomposition of **5c** taking place.



5c **4c**

Scheme 3. Reaction between **5c** and PhNCO.

The steric pressure exerted by the two methyl groups is revealed by the X-ray structure presently obtained for **5c**•OEt_2•OH_2 (Figure 1).[16] It results in a bending of *ca.* 30° of the phenanthroline core with the mean plane defined by the square planar coordination sphere around the Pd(II) atom. These crystallographic data are in line with those previously obtained for this and the related complex **5a** and clearly indicate that **5a-c** are mononuclear species.[14, 17]

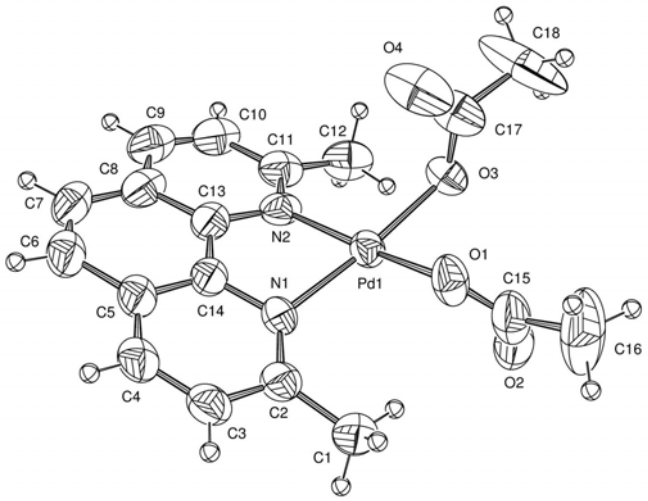
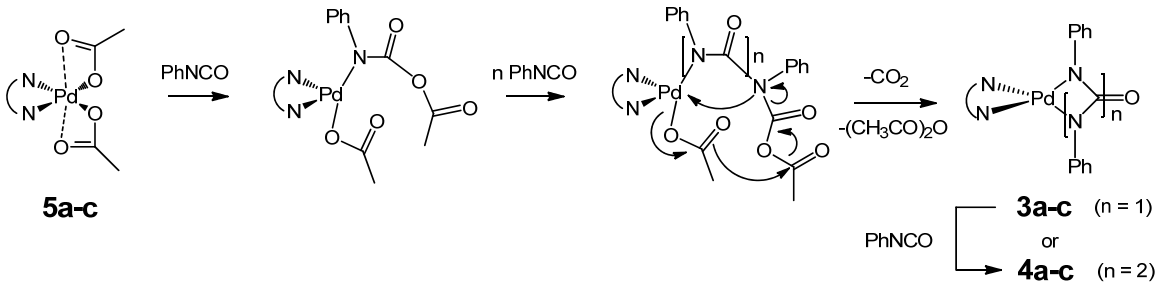


Figure 1. ORTEP plot of the palladacycle of **5c**•OEt_2•OH_2. Thermal ellipsoids are at the 50% probability level (see Supporting Information for details). Selected bond lengths (Å) and angles (deg): Pd1-O1 1.998(3), Pd1-O2 3.015, Pd1-O3 2.008(3), Pd1-O4 2.963, Pd1-N1 2.021(4), Pd1-N2 2.033(4), C15-O1 1.280(8), C15-O2 1.259(9), C17-O3 1.290(7), C17-O4 1.219(7), N1-Pd1-N2 81.64(16), O1-Pd1-O3 85.74(16), O1-Pd1-N1 94.58(16), O3-Pd1-N2 96.89(16).

This reaction presents some analogy with the trimerization reaction of PhNCO catalyzed by "(N-N)Pd^0" species previously studied by some of us.[11] However, the isocyanurate cyclotrimer **1** was never isolated as side-product during any reaction of **5a** with PhNCO, suggesting that "(*o*-phen)Pd^0" is presently not transiently formed in the medium. Furthermore, the catalytic trimerization of PhNCO was previously shown not to take place with the sterically crowded 2,9-dimethylphenanthroline ligand. When this ligand was used, decomposition of the catalyst into metallic palladium was observed.[11] In contrast, the formation of palladacycle **4c** takes readily place at ambient temperatures with the complex **5c**. Thus, it is quite likely that the mechanistic pathway for the formation of **4a-c** *does not* involve an elusive "(N-N)Pd^0" intermediate.

Actually, the reaction is observed *only* from dimine Pd(II) precursors having acetate ligands. A possible reaction mechanism should therefore involve the Pd(II) diimine center and the acetate ligand(s).



Scheme 4. Reaction mechanism proposed for the formation of **4a-c**.

A tentative mechanistic proposal for this transformation is given in Scheme 4. The first step would involve the formal insertion of PhNCO into the Pd-O bond of the carboxylate ligand, possibly on a $[Pd(N\text{-}N)(OAc)]^+$ intermediate, followed by further insertion of PhNCO into the resulting Pd-N bond (n = 2 or 3). These steps would be in line with the well established insertion chemistry for this kind of cationic species.[18] It is indeed well known that on such complexes the carboxylate ligands are labile and can be exchanged for other ligands.[9, 14] Alternatively, this reaction sequence might be seen as a $[Pd(N\text{-}N)(OAc)]^+$-assisted anionic oligomerization of PhNCO by the acetate ion, the latter acting as the nucleophile. This makes sense given the fact that simple acetate salts such as KOAc, in a manner similar to many other inorganic salts,[19] are known to catalyze the cyclotrimerization of arylisocyanates.[20] Moreover, their activity as catalysts in this reaction has been shown to be strongly influenced by the nature of the associated cation.[21] However, this anionic-oligomerization process would not ultimately lead to the cyclotrimer **1**, but to the palladacycle **4a** due to the presence of the second acetate ligand on the nearby Pd(II)

center. Indeed, the final steps would involve an intramolecular rearrangement taking place by elimination of acetic anhydride and carbon dioxide to form the metallacyclic core by ring closure. Such an acetate-based intramolecular rearrangement resemble that which was proposed by Moiseev to rationalize the reduction of Pd(II) acetate clusters in presence of CO,[22] except that the "CO" molecule is presently replaced by PhNCO. Then, depending on the number of inserted isocyanate molecules after ring closure, either **3a-c** (n = 1) or **4a-c** (n = 2) would be generated in the medium. Since we have previously clearly established that strained palladacycles such as **3a** react readily with arylisocyanate to form **4a**,[9] this mechanism rationalizes the selective formation of the 6-membered palladacycles **4a-c** in presence of excess PhNCO.[23] Also, based on literature reports,[14, 25] the acetate ligand should be more labile in **5c** than in **5a**. If the first insertion of isocyanate in the Pd-OAc bond in the former complex is rate determining, the reaction might take place as fast with **5c** than with **5a**, in line with our preliminary observations.

3. Conclusions

In conclusion we report here a novel and efficient reaction toward the six-membered palladacycles **4a-c** from air-stable phenanthroline Pd(II) acetate complexes and phenylisocyanate. While revealing that the particular complexes **5a-c** are reactive toward arylisocyanates, this contribution clearly shows that other synthetic routes than these previously evidenced from [(N-N)Pd^0] intermediates are possible to obtain palladacycles such as **2-4**. Thus, such species might also be directly formed from Pd(II) catalyst precursors when carboxylate ligands are present in the medium. This observation is particularly important in the context of Pd-catalyzed reductive

carbonylations of nitroaromatics, because (Pd(II)/diimine/carboxylic acid) catalytic systems are among the most active ones[10] and because the formation of **2-4** and related palladacycles[26] has been proposed to be at the origin of the rapid deactivation of these catalytic systems, [8, 9] especially when these reactions are performed in absence of alcohol or amine able to trap the isocyanate formed.[27] The scope and reaction mechanism of this new reaction is currently under investigation.

4. Experimental

4.1. General

The solvents were dried and distilled prior to use and the reaction were performed under inert (Ar) atmospheres in deaerated solvents. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Infrared spectra were recorded on a Bruker IFS28 spectrometer (400-4000 cm^{-1}). ^{1}H NMR spectra were obtained on Bruker SY 200 (200 MHz) or SY 400 (400 MHz) Fourier Transform spectrometers. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^{1}H spectra. Mass spectral studies and elemental analyses were submitted to the corresponding services of the Centre Régional de Mesures Physiques de l'Ouest (CRMPO). The complexes **5a-c** were synthesized according to reported procedures (see also Supporting Information).[13, 14]

4.1. Reactions of Pd(N-N)(OAc)$_2$ and PhNCO

Pd(phen){N(C_6H_5)C(O)N(C_6H_5C(O)N(C_6H5)} (4a). To 100 mg of Pd(phen)$(OAc)_2$ (0.24 mmol) were added 600 mg phenyl isocyanate (20 eq.) dissolved in 15 mL toluene. The pale-yellow suspension was subsequently heated at 80 °C under stirring. After 16 h, an abundant orange-yellow suspension has formed in the reaction medium. The medium was cooled and 10 mL of ethanol were added to neutralize the excess isocyanate. The suspension is then decanted and washed with several fractions of diethylether yielding 140 mg of yellow-orange solid after subsequent vacuum-drying. This solid is identified as palladacycle **4a** by comparison with authentic samples (95%).

Pd(tmphen){N(C_6H_5)C(O)N(C_6H_5C(O)N(C_6H_5)} (4b). To 50 mg of Pd(tmphen)$(OAc)_2$ (0.11 mmol) were added 630 mg phenyl isocyanate (50 eq.) dissolved in 15 mL toluene. The pale-yellow suspension was subsequently heated at 80 °C under stirring. After 16 h, the dark red reaction medium was cooled and 1 mL of EtOH followed by excess diethylether were added. The suspension is then decanted and washed with several fractions of diethylether yielding 39 mg of brown-orange solid after vacuum-drying. This solid is identified as palladacycle **4b** (54%). Color: Brown-orange. HRMS (positive ESI, CH_2Cl_2/MeOH, m/Z) *z* 672.1578 $[M+H]^+$, *m/z* calc'd for $[C_{36}H_{32}N_5O_2Pd]$ 672.1591. FT-IR (KBr, ν, cm^{-1}) 1642 (s, C=O), 1623 (s, C=O). ^1H NMR (200 MHz, $CDCl_3$, δ, ppm) 8.53 (d, $^3J_{HH}$ = 8 Hz, 4H, H_{Ph}), 8.05 (s, 24H, H_{phen}), 7.88 (s, 2H, H_{phen}), 7.53 (t, $^3J_{HH}$ = 8 Hz, 4H, H_{Ph}), 7.36 -6.98 (m, 7H, H_{Ph}), 2.68 (s, 6H, $CH_{3/phen}$), 2.20 (s, 6H, $CH_{3/phen}$).

Pd(dmphen){N(C_6H_5)C(O)N(C_6H_5C(O)N(C_6H_5)} ***(4c).*** To 100 mg of Pd(dmphen)$(OAc)_2$ (0.23 mmol) dissolved in 15 mL of CH_2Cl_2 were added 550 mg of phenylisocyanate (*ca.* 20 eq.). The orange solution was stirred 2 days at ambient temperature. The solution is filtrated and diethylether is added to precipitate the title complex as an orange solid. It is collected, washed with several fractions of diethylether and dried *in vacuo*, yielding 130 mg of the title palladacycle (88 %). Color: Orange. Dec. Pt: 180 ± 10 °C. HRMS (positive ESI, CH_2Cl_2, m/Z) 644.1291 $[M+H]^+$, *m/z* calc'd for $[C_{34}H_{28}N_5O_2Pd]$ 644.1278. Anal. Calc'd. for $C_{34}H_{27}N_5O_2Pd \bullet H_2O$: C, 61.68; H, 4.42; N, 10.58; Found: C, 61.67; H, 4.48; N, 10.52. FT-IR (KBr/Nujol, ν, cm^{-1}) 1645 (s, C=O), 1625 (s, C=O). ^1H NMR (200 MHz, CD_2Cl_2, δ, ppm) 8.26 (d, $^3J_{HH}$ = 8 Hz, 2H, H_{phen}), 8.01 (d, $^3J_{HH}$ = 7 Hz, 4H, H_{Ph}), 7.90 (s, 2H, H_{phen}), 7.69 (d, $^3J_{HH}$ = 8 Hz, 2H, H_{phen}), 7.49 (t, $^3J_{HH}$ = 8 Hz, 2H, H_{Ph}), 7.37 (t, $^3J_{HH}$ = 8 Hz, 4H, H_{Ph}), 7.26 (d, $^3J_{HH}$ = 8 Hz, 2H, H_{Ph}), 6.89 (t, $^3J_{HH}$ = 7 Hz, 4H, H_{Ph}), 6.69 (t, $^3J_{HH}$ = 7 Hz, 1 H, H_{Ph}), 2.72 (s, 6H, $CH_{3/phen}$).

X-Ray Crystallography. Diffraction data frames for **5c** were collected on a CCD Saphire 3 Xcalibur apparatus using the graphite monochromatized MoKα radiation (λ = 0.71073 Å). The cell parameters are obtained with Denzo and Scalepack,[28] with 10 frames (psi rotation : 1° per frame). The data collection leads to 4235 independent reflections from which 3338 with $I > 2.0\sigma(I)$.[29] The structures were solved by direct methods using the SIR97 program,[30] and then refined with full-matrix least-square methods based on F^2 (SHELX-97). [31] The contribution of the disordered solvents (*i.e.* one molecule of diethylether and one molecule of water) to the calculated structure factors was removed using the SQUEEZE option in PLATON. Atomic scattering factors were taken from the International Tables for X-ray Crystallography (1992).[32]

Ortep views were realized with PLATON98.[33]

Supplementary material

Synthesis and characterization of **5a-d**. CCDC-221834 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.

Acknowledgements

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[15] We have stated that Pd(II) complexes **5a-c** often give rise to quite stable solvates with water molecules. A water-free sample of **5a** could however be obtained after reacting this complex with acetic anhydride in nitrobenzene (12 h, 80 °C) followed by recrystallization with Et_2O from nitrobenzene.

[16] This solvated complex presents nearly identical crystallographic parameters than two different solvates of **5c** previously reported.[14] Crystallographic data after refinement without solvate(s): $PdC_{18}H_{18}N_2O_4$, M = 524.88, monoclinic, space group *C 2/c*, a = 18.3528(5) Å, b = 18.1223(6) Å, c = 13.4071(4) Å, β = 119.459(1) °, U = 3882.6(2) Å^3, Z = 4, T = 120(2) K, D_c = 1.481 g cm^{-3}. The final *wR*(*F2*) was 0.073 (all data). CCDC deposition N°: CCDC 221834.

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[23] With n = 0, a Pd-imido diimine intermediate would be formed rather than a metallacycle. While such kind of complex has recently been claimed to play a determining role in the catalytic carbonylation of nitroaromatics,[24] we did not consider the possibility of its intermediacy here. However, based on the available data,[1, 9] such a complex should also transform quantitatively into **4a-c** in presence of excess PhNCO.

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Captions

Scheme 1. Cyclotrimer and palladacycles formed from diimine-Pd(0) complexes.

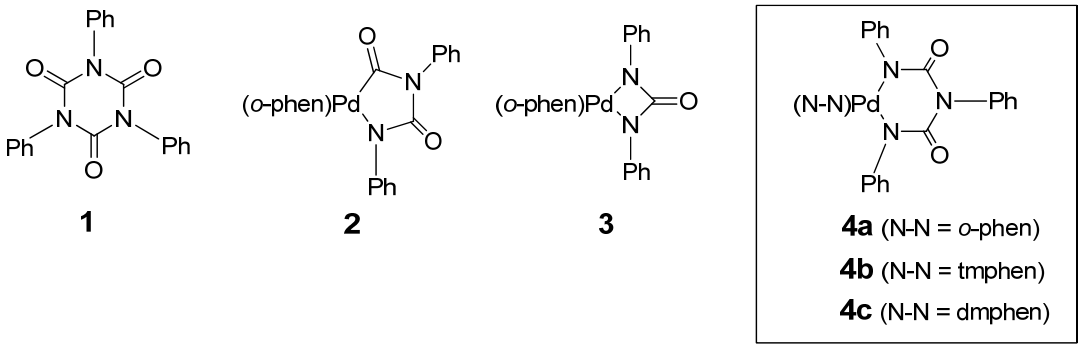
Scheme 2. Reaction between **5a** and PhNCO.

Scheme 3. Reaction between **5c** and PhNCO.

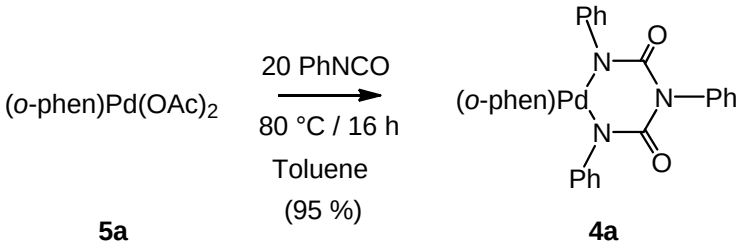
Scheme 4. Reaction mechanism proposed for the formation of **4a-c**.

Figure 1. ORTEP plot of the palladacycle of **5c**•OEt_2•OH_2. Thermal ellipsoids are at the 50% probability level (see Supporting Information for details). Selected bond lengths (Å) and angles (deg): Pd1-O1 1.998(3), Pd1-O2 3.015, Pd1-O3 2.008(3), Pd1-O4 2.963, Pd1-N1 2.021(4), Pd1-N2 2.033(4), C15-O1 1.280(8), C15-O2 1.259(9), C17-O3 1.290(7), C17-O4 1.219(7), N1-Pd1-N2 81.64(16), O1-Pd1-O3 85.74(16), O1-Pd1-N1 94.58(16), O3-Pd1-N2 96.89(16).

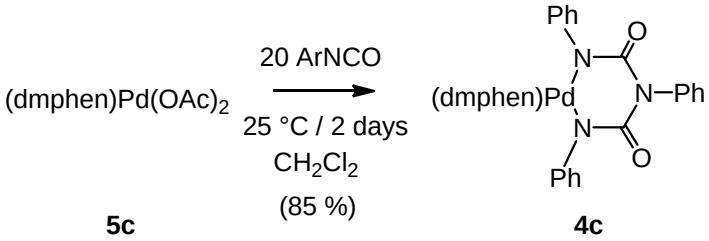
Schemes



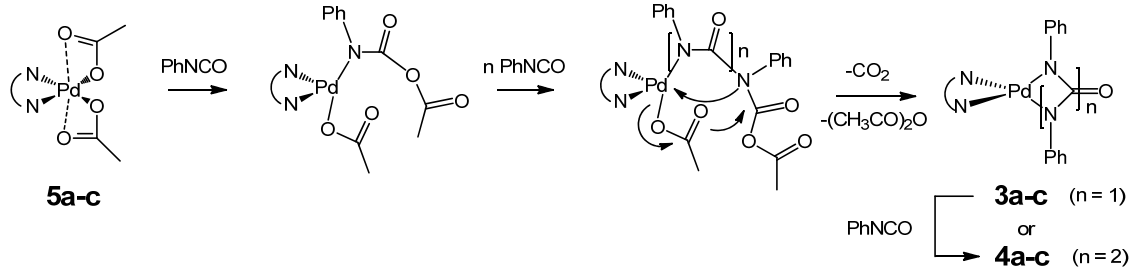
Scheme 1



Scheme 2



Scheme 3



Scheme 4

Figures

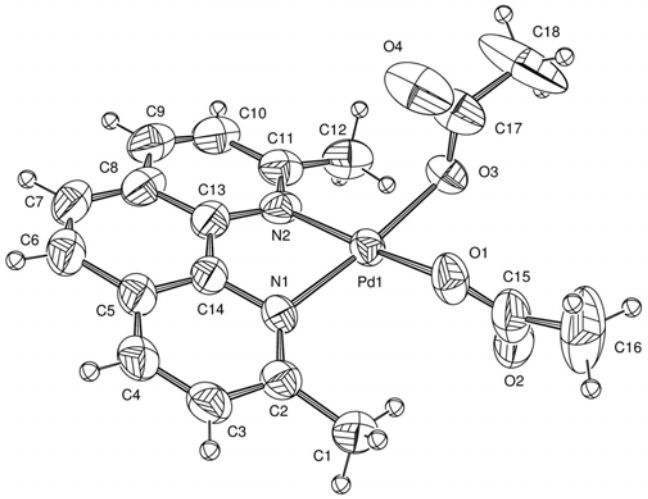


Figure 1

Supplementary Material

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Formation of six-membered Palladacycles from Phenanthroline Pd(II) Bisacetate Precursors and Phenylisocyanate

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Including:

1. Synthesis of Pd(N-N)$(OAc)_2$ complexes 5a-c p. S2

2. Table of crystallographic parameters for Pd(dmphen)$(OAc)_2$ p. S4

Synthesis of Pd(N-N)$(OAc)_2$ complexes 5a-c

The diimine (N-N) in 10 mL of solvent is added to 250 mg palladium acetate (1.1 mmol) in 15 mL of the same solvent. The brown suspension is stirred 48 h at ambient temperature and becomes clearer. A yellow precipitate forms. This air-stable solid is filtered and washed by several fractions of benzene, Et_2O and *n*-pentane, before being died *in vacuo*.

Pd(o-phen)$(OAc)_2$ (5a). Benzene was used as solvent with 1.4 equiv. of phenanthroline. Yield: 91 %. Dec. Pt: 215 ± 5 °C. MS (positive LSI, 3-NBA, m/Z) 345 (M-OAc); 286 (M-2OAc); 181 (phen+1). Elemental analysis, Calc'd for $C_{16}H_{14}N_2O_4Pd$: C 47.48, H 3.49, N 7.00; Fnd: C 47.04, 3.25, N 6.92. FT-IR (KBr/Nujol, ν, cm^{-1}) 1600 (vs, OAc). ^{1}H NMR (200 MHz, CD_2Cl_2, δ, ppm) 8.32 (d, $^3J_{HH}$ = 5 Hz, 2H, H_1+H_9), 8.11 (d, $^3J_{HH}$ = 8 Hz, 2H, H_4+H_7), 7.99 (s, 2H, H_5+H_6), 7.56 (dd, $^3J_{HH}$ = 8 Hz and $^3J_{HH}$ = 5 Hz, 2H, H_3+H_8); 2,04 (s, 6H, CH_3).

Pd(tmphen)$(OAc)_2$ (5b). Benzene was used as solvent with 1.0 equiv. of 3,4,7,8-tetramethylphenanthroline. Yield: 91 %. Dec. Pt: 204 ± 2 °C. Elemental analysis, Calc'd for $C_{20}H_{22}N_2O_4Pd$•1/2 H_2O: C 51.13, H 4.93, N 5.96; Fnd: C 51.26, 4.72, N 5.96. FT-IR (KBr/Nujol, ν, cm^{-1}) 1630 (vs, OAc). ^{1}H NMR (200 MHz, CD_2Cl_2, δ, ppm) 8.24 (s, 2H, H_1+H_4), 8.10 (s, 2H, H_2+H_9), 8.00 (s, 2H, H_5+H_6), 2.74, 2.55 (s, 12 H, C$H_{3/Phen}$), 2.10 (s, 6H, OC(O)CH_3).

Pd(dmphen)$(OAc)_2$ (5c). THF was used as solvent with 6.0 equiv. of 2,9-dimethylphenanthroline. Yield: 95 %. Dec. Pt: 143 ± 5 °C. Elemental analysis, Calc'd

for $C_{18}H_{18}N_2O_4Pd•H_2O$: C 47.96, H 4.44, N 6.21; Fnd: C 47.51, 4.25, N 6.07. MS (positive ESI, CH_2Cl_2, m/Z) 432 (M^+, 3%), 373 (M-OAc, 3%); 286 (M-2OAc, < 1%); 209 (dmphen+1, 10%). HRMS (positive ESI, CH_2Cl_2, m/Z) *z* 432.0301 $[M]^+$, *m/z* calc'd for $[C_{16}H_{15}N_2O_2Pd]$ 373.0173. FT-IR (KBr/Nujol, ν, cm^{-1}) 1620 (vs, OAc). ^1H NMR (200 MHz, CD_2Cl_2, δ, ppm) 8.37 (d, $^3J_{HH}$ = 8 Hz, 2H, H_4+H_7); 7.85 (s, 2H, H_5+H_6), 7.50 (d, $^3J_{HH}$ = 8 Hz, 2H, H_3+H_8), 2.88 (s, 6H, C$H_{3/Phen}$), 1.93 (s, 6H, OC(O)CH_3).

2. Table of crystallographic parameters for Pd(dmphen)(OAc)$_2$

Table S1. Crystal Data, Data Collection, and Refinement Parameters for **5c**•OEt_2•OH_2 without the solvate(s).

Cpnd	**5c**
formula	$C_{36}H_{36}N_4O_8Pd_2$
fw	865.49
temp (K)	120(2)
cryst. syst.	monoclinic
space group	*C2/c*
a (Å)	18.3528(5)
b (Å)	18.1223(6)
c (Å)	13.4071(4)
α (deg)	90.0
β (deg)	119.4590(10)
γ (deg)	90.0
V(Å^3)	3882.6(2)
Z	4
$D_{(calcd)}$ (g cm^{-3})	1.481 (1.796 with solvates)
crystal size (mm)	0.22×0.12×0.08
F(000)	1744
abs. coef. (mm^{-1})	0.978
Θ range	2.85-27.00
h k l range	0/23
	0/23
	-17/14

number total refl.	4235
number unique refl.	4235
number obs. refl.	3338
[$I > 2\sigma(I)$]	
R(int)	0.000
restraints / parameters	0/228
$\omega = 1/[\sigma^2(Fo)^2+(aP)^2+bP]$	a = 0.1
(where $P = [Fo^2+Fc^2]/3$)	b = 0.0
final R	0.0583
R_W	0.1714
R indices (all data)	0.0736
R_W (all data)	0.1935
Goodness of fit/$F^2(S_W)$	1.539
$\Delta\rho_{max}$ (e $Å^{-3}$)	2.396
$\Delta\rho_{min}$ (e $Å^{-3}$)	-2.324