Cyclic tetramers of five-membered palladacycle based on head-to-tail-linked isocyanate dimer and their reactivity in cyclotrimerization of isocyanates

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Dalton Transactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID:</td>
<td>DT-ART-02-2015-000534.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>n/a</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Kim, Yong-Joo; Kangnung-Wonju National University, Department of Chemistry Lee, Seon Gye; Kangnung-Wonju National University, Chemistry Choi, Keun-Young; Kangnung-Wonju National University, Chemistry Park, SuJin; Sungkyunkwan University, Chemistry Lee, Soonwon; Sungkyunkwan University, Department of Chemistry;</td>
</tr>
</tbody>
</table>
Cyclic tetramers of five-membered palladacycle based on head-to-tail-linked isocyanate dimer and their reactivity in cyclotrimerization of isocyanates

Seon Gye Lee,‡ Keun-Young Choi,‡ Yong-Joo Kim,‡ SuJin Park§ and Soon W. Lee§

Reactions of [Pd(styrene)(PR₃)]₂, generated from trans-[PdEt₂(PR₃)₂] and styrene, with 2 equiv. of benzyl isocyanate in THF at room-temperature afforded unusual cyclic Pd-tetramers of five-membered rings consisting of organic isocyanate dimers and palladium, [Pd(PR₃){C(O)N(R)C(O)N(R)}]{(PR₃)₄(PR₃) = PMe₃, 1; PR₃ = PMe₃-Ph, 2}. Additionally, a cyclic trimer, (RNCO)₃, 3 (R = benzyl) was produced as a catalytic product. Treatment of the cyclic tetramer (1) with 4 equiv. of chelated phosphine, such as (1,2-bis(diethylphosphino)ethane) (DEPE) or (1,2-bis(dimethylphosphino)ethane) (DMPE), readily caused conversion to a metallacyclic cis-form, [Pd[N(R)C(O)N(R)C(O)]{P~P}] (P~P = DEPE, 4; P~P = DMPE, 5) in quantitative yields. In contrast, reactions of Pd(0)-PR₃ with 2 equiv. of Ar-NCO (Ar = Ph, p-Tolyl, p-CI-C₆H₄) afforded metallacyclic complexes having a dimeric isocyanato moiety, cis-[Pd{C(O)N(AR)C(O)N(AR)}]{PR₃} (PR₃ = PMe₃, Ar = C₆H₅, 6; p-Me-C₆H₄, 7; p-CI-C₆H₄, 8; PR₃ = PMe₃-Ph, Ar = p-CI-C₆H₄, 9). Treatment of the palladacyclic complex (8) with an equimolar amount of chelated phosphine such as DEPE readily caused conversion to a palladacyclic cis-form, [Pd[N(AR)C(O)N(AR)C(O)]{DEPE}], 10 in quantitative yield. The catalytic cyclotrimerization of benzyl isocyanate to [Pd(styrene)(PMe₃)] was achieved by varying the molar ratio of R-NCO (R = benzyl). In addition, catalytic cyclotrimerization was performed from the five-membered palladacyclic complexes or the Pd(0)-PR₃ complex with excess Ar-NCO.

These results strongly indicate that the product formed depends on the attacking isocyanate or supporting ligand. The reactivities of metallacyclic isocyanato complexes of Ni(II) and Pd(II) with olefins and CO, and their thermal behaviors in the presence of other organic isocyanates, have also been reported. Although several transition-metal-catalyzed cyclotrimerization systems for organic isocyanates are known, a few studies of the structural and chemical characterization of the metallacyclic intermediates of alkyl or aryl isocyanates in such reactions have been reported. In particular, studies of the cyclotrimerization of aliphatic isocyanates are scarce compared to those of aryl isocyanates and their intermediates. Among them, Misono and coworkers et. al. reported Ni-catalyzed cyclotrimerization or polymerization of alkyl isocyanates. Paul and coworkers et. al. reported the mechanistic cyclotrimerization of Ar–NCO in the presence of diimine-based Pd(0) catalysts.

We recently observed that certain organic isothiocyanates undergo cyclodaddition to Pd(II) and Pd(0) complexes to afford heterocyclic complexes or organic heterocycles. The aim of this study was to extend the scope of such reactions by investigating the reactivities of the Pd(0) complexes with organic isocyanates. We treated, bis(phosphine)palladium(0) complexes with alkyl or aryl isocyanates. Two significant results were observed: (i) the formation of unexpected cyclic tetramers of a five-membered ring consisting of an alkyl isocyanate dimer and Pd, and (ii) the cyclotrimerization of the isocyanates to isocyanurates.

Introduction

Organic isocyanates have attracted much attention because of their wide range of applications such as the formation of metallacycles or organic heterocycles, coupling with organic unsaturated compounds, and catalytic polymerization. The cyclotrimerization of isocyanates to isocyanurate is important, because these products are organic unsaturated compounds

isocyanate cyclotrimers, or organic heterocycles.

Some catalytic studies using main group zerovalent group 10 metal complexes (sometimes in the presence of research groups have shown that organic isocyanates react with isocyanates have been reported recently. In particular, several studies of the cyclotrimerization of aliphatic isocyanates are scarce compared to those of aryl isocyanates and their intermediates. Among them, Misono and coworkers et. al. reported Ni-catalyzed cyclotrimerization or polymerization of alkyl isocyanates. Paul and coworkers et. al. reported the mechanistic cyclotrimerization of Ar–NCO in the presence of diimine-based Pd(0) catalysts.

We recently observed that certain organic isothiocyanates undergo cyclodaddition to Pd(II) and Pd(0) complexes to afford heterocyclic complexes or organic heterocycles. The aim of this study was to extend the scope of such reactions by investigating the reactivities of the Pd(0) complexes with organic isocyanates. We treated, bis(phosphine)palladium(0) complexes with alkyl or aryl isocyanates. Two significant results were observed: (i) the formation of unexpected cyclic tetramers of a five-membered ring consisting of an alkyl isocyanate dimer and Pd, and (ii) the cyclotrimerization of the isocyanates to isocyanurates.
Results and discussion

The room-temperature reactions of 2 equiv. of benzyl isocyanate with [Pd(styrene)(PR$_3$)$_2$], generated from trans-[PdEt$_2$(PR$_3$)$_2$] and styrene, gave the cyclic tetramers, [Pd(PR$_3$)$_3$(C=O)(R')(C=O)N(R')]$_4$, (PR$_3$ = PMe$_3$, PMe$_2$Ph; R' = benzyl), 1 and 2 in 51 and 40% yields, respectively (Scheme 1). The cyclic isocyanurate 3 was also isolated in 48–56% yield by extracting the reaction products with excess diethyl ether. The yields for compounds 1–3 were all calculated on the basis of R–NCO. Complexes 1 and 2 are white solids and are slightly soluble in common organic solvents. Single crystals of 1 were obtained from dichloromethane/diethyl ether, and its molecular structure was determined by X-ray diffraction. Compound 3 was identified using IR and NMR spectroscopies and GC-MS.

The IR spectra of the complexes display characteristic CO stretching bands at 1653 and 1582 cm$^{-1}$. In the $^1$H NMR spectrum of 1, the four methylene protons (CH$_2$Ph) on the two benzyl groups in the [Pd(PR$_3$)$_3$(C=O)(N(R')(C=O)N(R'))]$_4$ unit are magnetically inequivalent, and appear at 6.72, 4.71, 3.96, and 2.80 ppm with separate geminal couplings. One pair of low-field signals (6.72 and 4.71 ppm; $J_{HH}$ = 16.8 Hz) may arise from the methylene protons in the exo N-benzyl substituents between two ketone groups. Another pair of high-field signals (3.96 and 2.80 ppm; $J_{HH}$ = 15.6 Hz) is assigned to methylene protons in the endo benzyl group near the Pd center. Complex 2 shows a pattern similar to that of complex 1. The $^1$H–$^1$H COSY spectrum of 1 clearly illustrates correlation signals for the low-field (6.72 and 4.71 ppm) and high-field (3.96 and 2.80 ppm) pairs, and this confirms the diastereotopic benzyl proton splittings. It should be mentioned that the signal at 6.72 ppm appears as a doublet ($J$ = 16.8 Hz). At present, it is difficult to assign these doublets because the correlation between the hydrogen in question and the PMe$_3$ ligand is not evident. A singlet in the $^3$P[$^1$H] NMR spectrum clearly demonstrates the magnetic equivalence of all four PMe$_3$ ligands for complex 1, which is consistent with the molecular structure (Fig. 1a). Elemental analysis and MS (ESI-TOF) data for 1 and 2 further support the proposed tetrameric structures.

The molecular structure of complex 1-2(CH$_2$Cl)$_2$ is presented in Fig. 1. It comprises an asymmetric unit, namely a five-membered palladacycle, consisting of a Pd atom and an isocyanate dimer. One of the two ketone oxygen atoms (O2) coordinates with the Pd in the adjacent asymmetric unit, and this type of coordination ultimately creates a cyclic tetrameric structure. The four Pd atoms are not coplanar; two of them lie above and the other two lie below the molecular plane. For simplicity, the structure without the four benzyl groups is shown in Fig. 1b.

We investigated the chemical properties of complex 1 by performing ligand replacement with chelating phosphines. When an equimolar amount of 1,2-bis(diethylphosphino)ethane (DEPE) was added to a dichloromethane suspension of 1, a mixture of a Pd(II) chelate, [Pd(DEPE)−(N(R)(C=O)(N(R')(C=O)−)] (R = benzyl) (4), as the major product, starting material, and an unidentified compound was obtained. However, when excess DEPE (4 equiv.) was added, the reaction mixture rapidly turned to a colorless solution. We finally isolated a pure complex [Pd(DEPE)−{N(R)(C=O)(N(R')(C=O)−)] (R = benzyl) (4) in 94% yield, and it was characterized using spectroscopy and X-ray diffraction (Scheme 2). The corresponding reaction with excess 1,2-bis(dimethylphosphino)ethane (DMPE) also afforded a metallacyclic Pd(II) complex, [Pd(DMPE)−(N(R)(C=O)(N(R')(C=O)−)] (R = benzyl) (5), in 40% yield. The singlet in the $^3$P[$^1$H] NMR spectrum of complex 1 clearly changes to two doublets as a result of the two inequivalent phosphorus atoms in complexes 4 and 5. The molecular structure of 4 is shown in Fig. 2.
and is one of two crystallographically independent molecules. The Pd(II) atom is a member of a pentagonal palladacycle, the same as in the asymmetric unit in complex 1. The structures of complexes 1 and 4 strongly indicate that each of the four units in complex 1 reacts with 4 equiv. of each of the chelating bis(phosphine) ligands to form complex 4.

![Scheme 2](image)

**Scheme 2**

Although we could not isolate the five-membered palladacyclic intermediate cis-[Pd(PR₃)₂{-N(Ar)C(O)N(Ar)C(O)-}]
(Scheme 1), complex 1 could be formed in three steps: (1) the formation of a palladacyclic intermediate, (2) dissociation of one phosphine, and (3) ketone oxygen coordination to the Pd atom in the adjacent asymmetric unit. Several attempts to isolate five-membered palladacyclic complexes using various alkyl isocyanates, e.g., ethyl and isopropyl isocyanate, failed. We then tried to prepare such complexes using aryl isocyanates. The reactions of [Pd(styrene)L₂] with 2 equiv. of ArNCO (Ar = Ph, p-tolyl, p-chlorophenyl) afforded the expected metallacyclic complexes cis-[Pd(PR₃)₂{-N(Ar)C(O)N(Ar)C(O)-}]
(PR₃ = PMe₃, PMe₂Ph; 6–9 in Scheme 3) in moderate to good yields; the complexes were characterized using spectroscopic and elemental analyses. The room-temperature ³¹P{¹H} NMR spectra of the metallacyclic complexes 6–8 exhibit two singlets without P-P coupling. However, the PMe₃ region in the ¹H-NMR spectra of the complexes has two doublets, because of the magnetic inequivalence of the two phosphorus atoms.

When the temperatures of the NMR samples of complexes 6–8 are lowered to −20 °C, the ³¹P-NMR spectra display two doublets as expected, because of the two inequivalent phosphorus atoms. These results indicate that the metallacyclic complexes containing the more basic PMe₃ ligand are more flexible than the metallacyclic complex 9, containing the PMe₂Ph ligand. We also examined phosphine-ligand exchange with a chelating phosphine (eq. 2 in Scheme 3), and the Pd(II) chelate complex 10 was obtained in quantitative yield.

![Fig. 3](image)

**Fig. 3.** ORTEP diagram of complex 10·CH₂Cl₂, with displacement ellipsoids for atoms show a 40% probability level.

<table>
<thead>
<tr>
<th>Table 1.</th>
<th>Selected bond lengths (Å) and bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Dists</td>
<td>4</td>
</tr>
<tr>
<td>Pd1–C4</td>
<td>1.951(3) Pd1–C1 2.042(4) Pd1–C1 2.032(3) Pd1–N2 2.058(2) Pd1–N2 2.060(3) Pd1–N2 2.056(2) Pd1–O2A 2.123(2) Pd1–P2 2.246(1) Pd1–P1 2.246(7) O1–C4 1.219(3) Pd1–P1 2.349(1) Pd1–P2 2.354(7) O2–C12 1.251(3) O1–C1 1.225(5) O1–C1 1.220(3) N2–C12 1.317(3) O2–C2 1.229(5) O2–C2 1.230(3) N1–C12 1.408(3) N1–C1 1.365(5) N1–C1 1.400(3) N1–C2 1.435(5) N1–C2 1.416(3) N2–C2 1.327(5) N2–C2 1.340(3)</td>
</tr>
<tr>
<td>Angles</td>
<td>4</td>
</tr>
<tr>
<td>C4–Pd1–N2 81.67(9) Pd1–C1–C2 120.0(3) Pd1–P2–P1 120.0(3) Pd1–P2–P1 120.0(3)</td>
<td></td>
</tr>
<tr>
<td>C4–Pd1–O2A 177.49(10) Pd1–P1–C2 85.28(5) Pd1–P1–C2 85.28(5) Pd1–P1–C2 85.28(5)</td>
<td></td>
</tr>
<tr>
<td>C12–O2–Pd1B 135.9(2) C1–N1–C3 120.4(2) C1–N1–C3 120.4(2) C1–N1–C3 120.4(2)</td>
<td></td>
</tr>
<tr>
<td>C4–N1–C12 119.6(2) O2–C2–N2 127.7(2) O2–C2–N2 127.7(2) O2–C2–N2 127.7(2)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: A = y + 1, −x + 1, −z + 2; B = −y + 1, x − 1, −z + 2; C = −x + 1, −y, z.
The molecular structure of complex 10 is shown in Fig. 3; the Pd atom is coordinated to a chelating phosphine (DEPE) and an isocyanate dimer. Selected bond lengths and angles are listed in Table 1. The Pd-N bond lengths of the dimeric isocyanate rings for 1, 4, and 10 in Table 1, are slightly longer than the known value (1.996(3) Å) of (α-phenanthrolene)[(C=O)(N(C6H5)(C=O)(N(C6H5))]. The Pd-C bond lengths are longer (for 4 and 10) or shorter (for 1) than that of the complex (1.963(4) Å). These results indicate strong or weak trans influences due to the trans-positions of phosphorous or oxygen atoms coordinated to the Pd center.

We investigated the catalytic cyclotrimerization of the isocyanate in Scheme 1 by systematically varying the molar ratio of R-NCO (R = benzyl) to [Pd(styrene)(PMe$_2$)$_3$]. Fig. 4 shows a plot of the yields for complex 1 and the cyclic trimer (benzyl isocyanurate) as a function of the number of molar equivalents of isocyanate. The yields were determined based on NMR integration of the benzylic protons in the final isolated mixture of complex 1 and the cyclic trimer. As the amount of R-NCO increases from 1 to 3 equiv., the amount of tetramer 1 decreases significantly, whereas the amount of the cyclic trimer increases. However, for more than 3 equiv. of R-NCO, both of the yields increase slightly; i.e., the cyclic trimer is the sole product in this range. The use of 3 equiv. of R-NCO is therefore suitable for the catalytic cyclotrimerization of organic isocyanates. In addition, this result indicates that an increase in the amount of benzyl isocyanate facilitates catalytic cyclotrimerization.

![Fig. 4 Plots of yields of complex 1 and cyclic trimer as a function of R-NCO concentration](image)

Paul and coworkers proposed Pd-catalyzed cyclotrimerization of Ar-NCO and their mechanisms involving metallacyclic or zwitterionic pathways. Our results in this study can be similarly explained by the two pathway. The first is π-coordination of excess R-NCO (R = benzyl or aryl) with Pd(styrene)L$_2$ to give the Pd(0) intermediate, Pd(R-NCO)L$_2$, and then subsequent addition of R-NCO affords a five-membered palladacycle. Finally, the seven-membered palladacycle by cyclodaddition of R-NCO causes the cyclotrimerization of R-NCO including the Pd(0) intermediate via reductive elimination. The second pathway involves the formation of a zwitterionic intermediate, [Pd$^+$](C=O)(N(C6H5)(C=O)(N(C6H5))), followed by the nucleophilic attack of the incoming R-NCO to afford a zwitterionic Pd complex having a linear dimeric isocyanate moiety or a five-membered palladacycle. Then, a nucleophilic attack of R-NCO affords a linearly zwitterionic trimer of R-NCO or a seven-membered palladacycle, and finally causes cyclotrimerization via reductive elimination. As shown in Scheme 4, the higher catalytic yields of the cyclic trimer using the Pd(0) complex rather than the metallacyclic complex suggests a tentative zwitterionic pathway, which is considered one of the active oligomerization processes. During our experiments using Pd(0) compounds, the reactions of Scheme 1 and 4 liberated styrenes, which prohibited further characterization of possible species. Presently, we cannot provide a detailed explanation for the reaction mechanism.

**Conclusions**

In summary, we observed the formation of novel tetrameric Pd(II) complexes linked by five-membered metallacycles based on an organic (alkyl) isocyanate dimer, and the simultaneous cyclotrimerization of the isocyanate. The reactions of aryl isocyanates with the Pd(0)-PR$_3$ complexes, [PdL$_2$-(styrene)], afforded single five-membered palladacycles. In addition, the single palladacycles and Pd(0)-PR$_3$ complexes catalytically cyclotrimerized aryl isocyanates. In particular, it is generally known that the cyclic trimerization of aliphatic isocyanates is more difficult to achieve than that of aromatic isocyanates. The reason may be explained by considering the unstable catalytic intermediate (metallacyclic or zwitterionic complexes) during the catalytic cyclotrimerization of aliphatic isocyanate, compared with that of aryl isocyanate. However, we have demonstrated the cyclic trimerization using alkyl isocyanate with a unique alkyl moiety such as the benzyl group. This is a rare example of cyclic trimerization of alkyl isocyanate mediated by a Pd catalyst.
Experimental

General information. All manipulations of air-sensitive compounds were performed under N₂ or Ar by Schlenk-line techniques. Solvents were distilled from Na-benzophenone. The analytical laboratories at Basic Science Institute of Korea and at Kangnung-Wonju National University carried out elemental analyses. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (1H, 13C) and 31P(1H) spectra were obtained in CDCl₃ on a JEOL Lambda 300, ECA 600 MHz spectrometer. Chemical shifts were referenced to internal Me₃Si and to external 85% H₃PO₄. X-ray reflection data were obtained at either the Korea Basic Science Institute (Seoul Center) and the Cooperative Center for Research Facilities at Sungkyunkwan University.

Complexes trans-[PdEt₂L₂] (L = PMe₃ and PMe₂Ph) were prepared by the literature method.33

Synthesis of 1, 2 and 3.

Styrene (302 µL, 2.63 mmol) and tetrahydrofuran (THF, 4 mL) were added sequentially to a Schlenk flask containing trans-[PdEt₂(PMe₂)] (0.417 g, 1.32 mmol) at 0 °C. The mixture was heated at 55 °C for 30 min to give a pale yellow solution. Benzylic isocyanate (325 µL, 2.63 mmol) was added to the mixture at room temperature, and then the yellow solution turned into a yellow suspension. After stirring for 2 h at room temperature, the volatiles were added sequentially to a Schlenk flask containing CH₂Cl₂ (1 ml x 3) to afford white solids of 1. The extracts were evaporated under vacuum, and then the resulting residues were washed with n-hexane (2 mL × 3) to obtain yellow solids. After stirring for 2 h at room temperature, the volatiles were completely removed under vacuum, and then the resulting residue was washed with hexane (2 mL × 3) to obtain the crude solids. Recrystallization from CH₂Cl₂/n-hexane afforded white crystals of [Pd(PMe₂)(CO)(N(C(Ph))-C(O)N(Ar))], (R = benzy1) (4, 0.199 g, 94%). IR (KBr/cm⁻¹): 1636, 1589 (CO). Anal. Calc. for C₅₃H₆₅N₃O₄Pd 2578.96) C: 53.94; H: 6.61; N: 4.84. Found: C: 53.91; H: 6.69; N: 4.81. ¹H NMR: Δ 0.85-0.96 (m, 6H, P(CH₂CH₃)), 1.08-1.27 (10H, P(CH₂CH₃)), 1.59-1.58 (6H, P(CH₂CH₃)), 2.10-2.26 (2m, 2H, P(CH₂CH₃)), 4.73 (s, 488 (d, J = 2.4 Hz, 2H, CH₂)), 7.10-7.18 (m, 2H, Ar), 7.22-7.32 (m, 6H, Ar), 7.41-7.44 (4m, 2H, Ar). ¹³C[H] NMR: Δ 11.3 (d, Jp-dc = 17 Hz, P(CH₂CH₃)), 12.8 (d, Jp-dc = 30 Hz, P(CH₂CH₃)), 22.5 (d, Jp-dc = 15, 27 Hz, PCH₂)), 23.2 (dd, Jp-dc = 13, 24 Hz, PCH₂), 45.0 (s, 54.4 (s), 125.9, 126.2, 126.4, 128.3, 128.4, 140.6, 143.9, 167.0 (CO), 188.9 (dd, Jp-dc = 13, 148 Hz, CO). ³¹P[H] NMR: 36.5 (d, J = 29 Hz), 58.4 (d, J = 29 Hz).

Synthesis of cis-[Pd(C(O)N(Ph)-C(O)N(Ar)](PR₃)] (Ar = C₆H₅, p-MeC₆H₄, p-ClC₆H₄), 6-9.

Styrene (229 µL, 2.0 mmol) and tetrahydrofuran (THF, 3 mL) were added sequentially to a Schlenk flask containing trans-[PdEt₂(PMe₂)] (0.317 g, 1.0 mmol) at 0 °C. The mixture was heated at 55 °C for 30 min to give a pale yellow solution. Phenyl isocyanate (218 µL, 2.0 mmol) was added to the mixture at room temperature, and then the yellow solution turned into a white suspension. After stirring for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was washed with hexane (2 mL × 3) to obtain the crude solids. Recrystallization from CH₂Cl₂/n-hexane afforded white crystals of cis-[Pd(PMe₂)(C(O)N(Ph)-C(O)N(Ar))].

Synthesis of 4 and 5.

DEPE (24 µL, 0.10 mmol) was added to a CH₂Cl₂ (4 mL) solution containing I (0.090 g, 0.05 mmol) at room temperature. The initial white suspension slowly turned to a homogeneous colorless solution. After stirring for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was washed with hexane (2 mL x 3) to obtain the crude solids. Recrystallization from CH₂Cl₂/n-hexane afforded pure product of cis-[Pd(PMe₂)(CO)[(R)-CO]N(Ar)] (R = benzyl) (5, 61%) was analogously prepared. IR (KBr/cm⁻¹): 1638, 1579 (CO). Anal. Calc. for C₅₃H₆₅N₃O₄Pd 2578.96) C: 50.54; H: 5.78; N: 5.36. Found: C: 50.03; H: 5.65; N: 4.97. ¹H NMR: Δ 0.83 (d, J = 8.1 Hz, P(CH₂CH₃)), 1.49-1.72 (10H, P(CH₂CH₃)), 4.71 (s, 4.91 (s), J = 72-73 Hz, 10H, Ar). ¹³C[H] NMR: Δ 11.3 (d, Jp-dc = 17 Hz, P(CH₂CH₃)), 12.8 (Jp-dc = 30 Hz, P(CH₂CH₃)), 26.5 (dd, Jp-dc = 15, 31 Hz, PCH₂), 23.2 (dd, Jp-dc = 12, 29 Hz, PCH₂), 45.0 (s), 53.8 (s), 66.0, 126.1, 126.7, 128.0, 128.4, 140.5, 143.6, 166.8 (CO), 188.4 (dd, Jp-dc = 13, 155 Hz, CO). ³¹P[H] NMR: 9.05 (d, J = 26 Hz), 29.6 (d, J = 29 Hz).

Synthesis of cis-[Pd(C(O)N(Ph)-C(O)N(Ar))][PR₃] (Ar = C₆H₅, p-MeC₆H₄, p-ClC₆H₄), 6-9.

Styrene (229 µL, 2.0 mmol) and tetrahydrofuran (THF, 3 mL) were added sequentially to a Schlenk flask containing trans-[PdEt₂(PMe₂)] (0.317 g, 1.0 mmol) at 0 °C. The mixture was heated at 55 °C for 30 min to give a pale yellow solution. Phenyl isocyanate (218 µL, 2.0 mmol) was added to the mixture at room temperature, and then the yellow solution turned into a white suspension. After stirring for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was washed with hexane (2 mL x 3) to obtain the crude solids. Recrystallization from CH₂Cl₂/n-hexane afforded white crystals of cis-[Pd(PMe₂)(C(O)N(Ph)-C(O)N(Ar))].

This journal is © The Royal Society of Chemistry 2012

J. Name., 2012, 00, 1-3 | 5
16.7 (d, \( J_{P, C} = 30 \) Hz, \( P(\text{CH}_3) \)), 20.9 (s, \( \text{CH}_3 \)), 21.1 (s, \( \text{CH}_3 \)), 126.9, 127.0, 128.3, 128.9, 132.4, 136.1, 136.4, 149.1, 163.4 (CO), 183.7 (d, \( J_{C, P} = 159 \) Hz, CO). \(^{31}\)P[\(^1\)H] NMR (240 MHz at \(-20^\circ\)C): -27.7 (d, \( J_{P, C} = 26 \) Hz), -6.43 (d, \( J_{P, C} = 23 \) Hz).

\[ \text{Cl}_4\text{Pd}([M(\text{Me})_2], [\text{Cl}(\text{O})([\text{Ar}]-\text{C}(\text{O})([\text{Ar}])]) ([\text{Ar}]=p-\text{ClC}_6\text{H}_4)(8, 97 \%) \]. IR (KBr/cm\(^{-1}\)) 1660, 1613 (CO). Anal. Calc. for \( \text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_4\text{Cl}_4\text{Pd} \), 655.76: C, 42.46; H, 4.63; N, 4.95. Found: C, 42.78; H, 4.73; N, 4.50. \(^1\)H NMR: 0.099 (d, 9H, \( J = 7.8 \) Hz, \( P(\text{CH}_3) \)), 1.58 (d, 9H, \( J = 9.3 \) Hz, \( P(\text{CH}_3) \)), 7.16–7.32 (m, 8H, Ar). \(^{13}\)C[\(^1\)H] NMR: 15.4 (d, \( J_{P, C} = 19 \) Hz, \( P(\text{CH}_3) \)), 16.6 (d, \( J_{P, C} = 31 \) Hz, \( P(\text{CH}_3) \)), 129.7, 129.8, 128.3, 128.4, 123.0, 132.3, 137.1, 150.2, 162.9 (CO), 183.5 (d, \( J_{C, P} = 160 \) Hz, CO). \(^{31}\)P[\(^1\)H] NMR (240 MHz at \(-20^\circ\)C): -27.9 (d, \( J_{P, C} = 26 \) Hz), -6.47 (d, \( J_{P, C} = 23 \) Hz).

**Synthesis of 10**

DEPE (71 \( \mu \)L, 0.30 mmol) was added to a \( \text{Cl}_2\text{H}_4 \) (3 mL) solution containing 8 (0.149 g, 0.30 mmol) at room temperature. After stirring the reaction mixture for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was washed with hexane (2 mL \times 3) to obtain the crude solids. The crude solids were extracted with excess diethyl ether to afford white residues. The collected extracts were evaporated under vacuum to give crude organic products. The remaining residues were recrystallized from THF/hexane to afford the complex 7 (0.092 g, 71 \%). The organic products were purified by chromatography over celite, eluting with ethyl acetate/hexane (1:3).

**Table 2. Crystallographic data for complexes 1, 4, and 10.**

| Compound | Empirical formula | Crystal system | Space group | Formula weight | Cell parameters (Å) | No. of reflns | R (I > 2σ(I)) | 2\( ρ \) (e Å\(^{-3}\)) | \( χ^2 \) | \( ϕ \) (°) | \( δ \) (°) | \( γ \) (°) | \( β \) (°) | \( α \) (°) | No. of reflns independent |
|----------|------------------|----------------|-------------|---------------|---------------------|--------------|---------------|-----------------|----------|------------|-------------|------------|-------------|------------|-----------------|-----------------|
| 1        | \( \text{C}_2\text{H}_8\text{Cl}_4 \) | monoclinic | \( P2_1/\text{c} \) | 1964.91 | C, 46.51; H, 5.20; N, 4.52. Found: C, 46.35; H, 5.22; N, 4.02. | 5978.92 | 15.130(6) | 19.365(8) | 13.1299(9) | 90 | 90 | 90 | 0.902 | 3726 | 13151 |
| 4        | \( \text{C}_2\text{H}_8\text{Cl}_4 \) | tetragonal | \( P2_1/\text{c} \) | 200(2) | C, 46.51; H, 5.20; N, 4.52. Found: C, 46.35; H, 5.22; N, 4.02. | 5978.92 | 15.130(6) | 19.365(8) | 13.1299(9) | 90 | 90 | 90 | 0.902 | 3726 | 13151 |
| 10       | \( \text{C}_2\text{H}_8\text{Cl}_4 \) | monoclinic | \( P2_1/\text{c} \) | 200(2) | C, 46.51; H, 5.20; N, 4.52. Found: C, 46.35; H, 5.22; N, 4.02. | 5978.92 | 15.130(6) | 19.365(8) | 13.1299(9) | 90 | 90 | 90 | 0.902 | 3726 | 13151 |

**Reactions of metallocyclic Pd(II) complexes with excess aryl isocyanate**

\( p \)-Tolyl isocyanate (185 \( \mu \)L, 1.47 mmol) was added to a \( \text{CH}_2\text{Cl}_2 \) (3 mL) solution containing 7 (0.128 g, 0.24 mmol) at room temperature. After stirring the reaction mixture for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue washed with hexane (2 mL \times 3) to obtain the crude solids. The crude solids were extracted with excess diethyl ether to afford white residues. The collected extracts were evaporated under vacuum to give crude organic products. The remaining residues were recrystallized from THF/hexane to afford the complex 7 (0.092 g, 71 \%). The organic products were purified by chromatography over celite, eluting with ethyl acetate/hexane (1:3).
Reactions of Pd⁸−PR₃ with excess aryl isocyanate

Styrene (60 μL, 0.53 mmol) and tetrahydrofuran (THF, 3 mL) were added sequentially to a Schlenk flask containing trans-[PdEt₂(PMe₃)Cl] (0.116 g, 0.263 mmol) at 0 °C. The mixture was heated at 55 °C for 30 min to give a pale yellow solution. p-Chlorophenyl isocyanate (202 μL, 1.58 mmol) was added to the mixture at room temperature. After stirring for 2 h at room temperature, the volatiles were completely removed under vacuum, and then the remaining residue was washed with n-hexane (2 mL × 3) to obtain pale yellow solids. The crude solids were extracted with excess diethyl ether to afford white residues. The collected extracts were evaporated under vacuum to give crude organic products. The remaining residues were recrystallized from THF/n-hexane to afford the complex 9 (0.085 g, 52%). The organic products were purified by chromatography over celite, eluting with ethyl acetate/hexane (1:3). The collected organic products recrystallized from CH₂Cl₂/n-hexane at room temperature to afford white crystals of 12 (0.145 g, 90%).

Analogous reaction of Pd(styrene)(PMe₃)₂ with p-tolyl isocyanate afforded a mixture of compound 11 (75%) and complex 7 (33%).

Crystallography.

Single crystals of 1, 4, and 10 for X-ray crystallography were grown from CH₂Cl₂/ n-hexane at ~35 °C. All X-ray data were collected at 200(2) K with the use of a Bruker Smart diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections. All calculations were carried out with SHELXTL programs. All structures were solved by direct methods. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

Details of crystal data, intensity collection, and refinement details are given in Table 2.

Acknowledgements

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. 2012R1A1B3001569).

Notes and references

34 G. M. Sheldrick, SADABS, Program for Absorption Correction, University of Göttingen.
Table of contents

Cyclic tetramers of five-membered palladacycle based on head-to-tail-linked isocyanate dimer and their reactivity in cyclotrimerization of isocyanates

Seon Gye Lee, Keun-Young Choi, Yong-Joo Kim, SuJin Park and Soon W. Lee

Cyclic tetramers of five-membered palladacycle involving isocyanate dimer were prepared, and the catalytic cyclotrimerization from palladium zero-compound or single palladacycle with organic isocyanates was performed.
February 21, 2015

Associate Editor, Dalton Transactions
Department of Chemistry
University of California
Berkeley, CA 94720-1460
(+1) 510 643 5181

Manuscript ID: DT-ART-02-2015-000534
Title: Cyclic tetramers of five-membered palladacycle based on head-to-tail-linked isocyanate dimer and their reactivity in cyclotrimerization of isocyanates

Dear Prof. Arnold:

Thank you very much for your e-mail on February 17, 2015 with regard to our manuscript, together with the comments from the reviewer. I have revised the manuscript according to the reviewer’s comment and your suggestion. Replies to the comments are found on the following page. I herein also submit our revised manuscript to Dalton Transactions.

I hope the manuscript will be satisfactory.

Sincerely yours,

Yong-Joo Kim
Fax: int +82-33-647-1183
Tel: int +82-33-640-2308

Encl.: reply sheet to reviewer’s
The authors deeply appreciate the suggestions made by the reviewer during the evaluation of our manuscript. We have revised the manuscript according to the reviewer’s comments and submitted a detailed description of the changes.

Reply to Reviewer # 2:

(a) Regarding “page 1, second column, last 3rd sentence in first paragraph: alkyl isocyanates.”: according to the reviewer comment, we corrected the “alkyl isocyanate” to alkyl isocyanates to the revised manuscript.

(b) Regarding the comment “Clarification on the yields of 1 and 3 is still required. In their letter of response, the authors explain that these yields are given with respect to Pd (in the case of 1) and with respect to the RNCO in the case of 3. This explanation is not included in the manuscript. Furthermore, since compounds 1 and 3 are obtained from the same reaction, both yields should be given with respect to the same substrate (RNCO) otherwise they could be misleading”: as described in the previous response letter to Reviewer, the yields in the original manuscript were calculated (i) on the basis of the Pd atom for complexes 1 and 2 and (ii) on the basis of R–NCO for organic trimer 3. These calculations may be misleading for readers, as pointed by Reviewer. Thus, we calculated again the yields for all compounds on the same basis (i.e., the amount of R-NCO). As expected, the new yields for complexes 1 and 2 are the same as those in the original manuscript, but the yield for the organic product (3) decreased. So, we amended the following sentence and added a new sentence to the line 7 page 2 in the first paragraph as well as to the related Experimental Part in the revised manuscript.

The cyclic isocyanurate 3 (based on the R-NCO) was also isolated in 60–62% yield by extracting the reaction products with excess diethyl ether.

⇒ The cyclic isocyanurate 3 was also isolated in 48–56% yield by extracting the reaction products with excess diethyl ether. The yields for compounds 1–3 were all calculated on the basis of R–NCO.