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

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Reactions of [Pd(styrene)(PR_3)$_2$], generated from *trans*-[$PdEt_2(PR_3)_2$] 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(PR_3){-C(O)N(R)C(O)N(R)-}]$_4$ (PR_3 = PMe_3, **1**; PR_3 = PMe_2Ph, **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)-PR_3 with 2 equiv. of Ar-NCO (Ar = Ph, *p*-Tolyl, *p*-ClC_6H_4) afforded metallacyclic complexes having a dimeric isocyanato moiety, c*is*-[Pd{C(O)N(Ar)-C(O)N(Ar)}(PR_3)$_2$] (PR_3 = PMe_3 Ar = C_6H_5, **6**; *p*-MeC_6H_4, **7**; *p*-Cl-C_6H_4, **8**; PR_3 = PMe_2Ph, Ar = *p*-Cl-C_6H_4, **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)(PMe_3)$_2$] 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)-PR_3 complex with excess Ar-NCO.

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.[1-19] The cyclotrimerization of isocyanates to isocyanurate is important, because these products are of commercial significance, and are used in industry, *e.g.*, in polymeric processes.[20] Some catalytic studies using main group[21-24] or rare-earth metal complexes[25-28] to produce cyclotrimers of isocyanates have been reported recently. In particular, several research groups have shown that organic isocyanates react with zerovalent group 10 metal complexes (sometimes in the presence of organic unsaturated compounds)[13,14b,17,18] to give metallacycles, isocyanate cyclotrimers, or organic heterocycles. 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.[13,14] 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.[12] reported Ni-catalyzed cyclotrimerization or polymerization of alkyl isocyanates. Paul and coworkers et. al.[14b] reported the mechanistic cyclotrimerization of Ar–NCO in the presence of diimine-based Pd(0) catalysts.

We recently observed that certain organic isothiocyanates undergo cycloaddition to Pd(II) and Pd(0) complexes to afford heterocyclic complexes or organic heterocycles.[29] 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.

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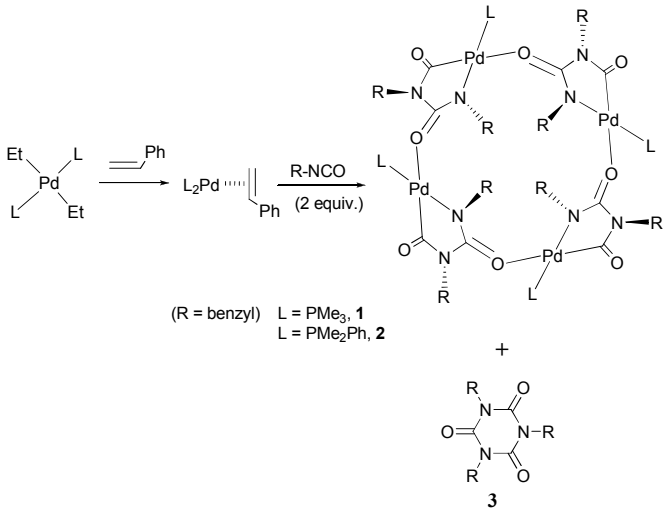
Results and discussion

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){C(O)N(R′)C(O)N(R′)}]$_4$, (PR_3 = PMe_3, PMe_2Ph; 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.



Scheme 1

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_2Ph) on the two benzyl groups in the [Pd(PR_3){C(O)N(R′)C(O)N(R′)}] 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 benzylic proton splittings.[30,31] It should be mentioned that the signal at 6.72 ppm appears as a double 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 ^{31}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_2Cl_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

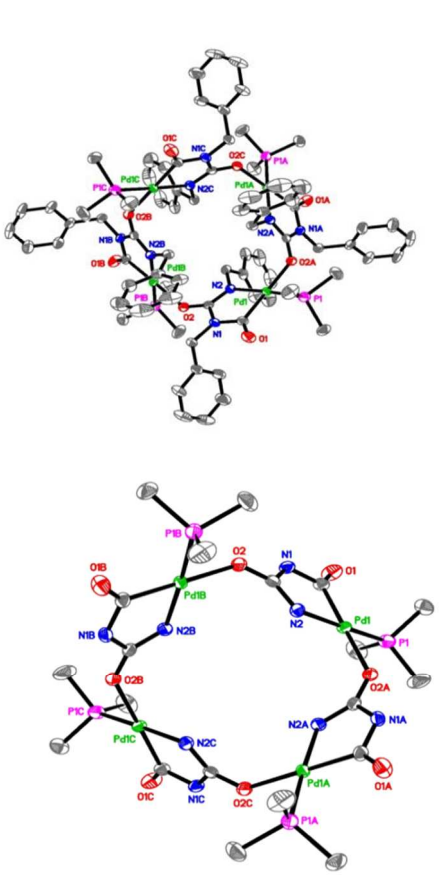
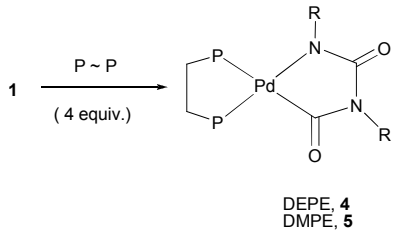


Fig. 1. (a) Molecular structure of complex **1**·2(CH_2Cl_2) (30% probability displacement ellipsoids). The lattice dichloromethane molecules are omitted for clarity. Labeled atoms (A, B, C) are related to unlabeled ones by a crystallographic four-fold rotation–inversion axis. (b) Corresponding molecular structure without benzyl fragments.

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 ^{31}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

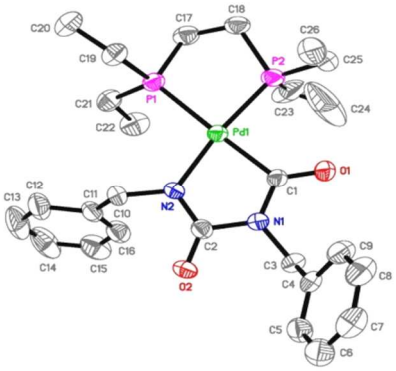
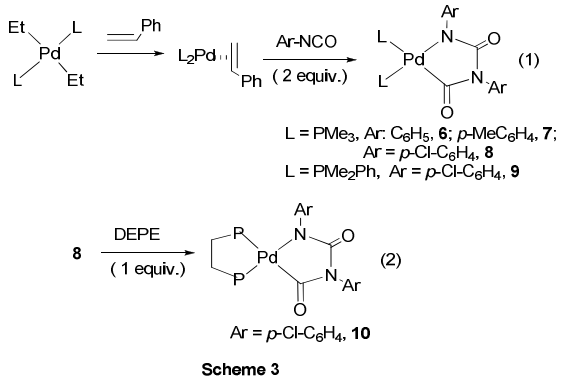


Fig. 2. ORTEP diagram of complex **4**, which is one of two chemically equivalent, crystallographically independent molecules showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Although we could not isolate the five-membered palladacyclic intermediate *cis*-[Pd(PR$_3$)$_2${–N(R)C(O)N(R)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)L$_2$] with 2 equiv. of ArNCO (Ar = Ph, *p*-tolyl, *p*-chlorophenyl) afforded



Scheme 3

the expected metallacyclic complexes *cis*-[Pd(PR$_3$)$_2${–N(Ar)C(O)N(Ar)C(O)–}] (PR$_3$ = PMe$_3$, PMe$_2$Ph; **6–9** in Scheme 3) in moderate to good yields; the complexes were characterized using spectroscopic and elemental analyses. The room-temperature ^{31}P{^{1}H} NMR spectra of the metallacyclic complexes **6–8** exhibit two singlets without P-P coupling. However, the PMe$_3$ region in the ^{1}H-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 ^{31}P-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 PMe$_3$ ligand are more flexible than the metallacyclic complex **9,** containing the PMe$_2$Ph 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.

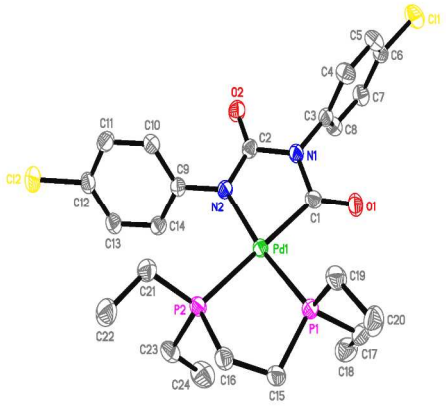


Fig. 3. ORTEP diagram of complex **10**·CH$_2$Cl$_2$, with displacement ellipsoids for atoms show a 40% probability level.

Table 1. Selected bond lengths (Å) and bond angles (°)

1		**4**		**10**	
Distances					
Pd1–C4	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)
Angles					
C4–Pd1–N2	81.67(9)	C1–Pd1–N2	80.2(2)	C1–Pd1–N2	80.55(10)
C4–Pd1–O2A	177.49(10)	N2–Pd1–P2	172.5(1)	C1–Pd1–P1	91.97(8)
N2–Pd1–P1	172.51(6)	C1–Pd1–P1	176.6(1)	N2–Pd1–P1	172.1(6)
O2#1–Pd1–P1	90.44(6)	P2–Pd1–P1	85.28(5)	N2–Pd1–P2	101.65(6)
C12–O2–Pd1B	135.9(2)	C1–N1–C2	120.0(3)	P1–Pd1–P2	85.63(3)
C12–N2–C13	119.6(2)	C1–N1–C3	121.6(4)	C1–N1–C2	120.0(2)
C12–N2–Pd1	113.4(2)	O1–C1–N1	120.7(4)	C1–N1–C3	120.4(2)
C4–N1–C12	119.6(2)	O2–C2–N2	127.9(4)	O2–C2–N2	127.7(2)
O1–C4–Pd1	129.4(2)	O2–C2–N1	118.9(4)	O2–C2–N1	119.2(2)
		N2–C2–N1	113.2(3)	N2–C2–N1	113.1(2)

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)[14a] of (*o*-phenanthrolene)[{C(O)N(Ar)-C(O)N(Ar)}]. 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-positioned 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_3)$_2$]. 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.

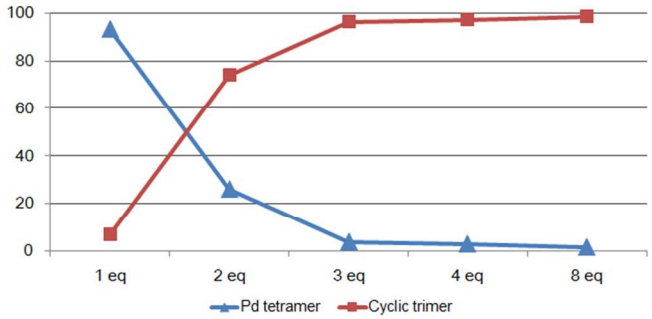
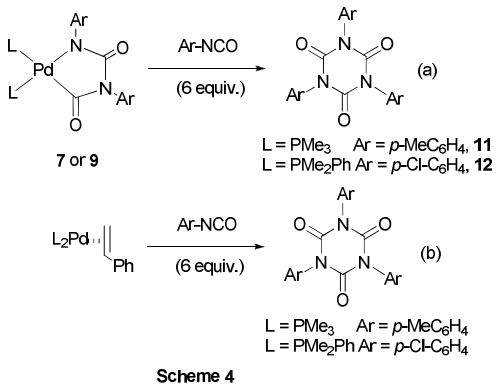


Fig. 4 Plots of yields of complex **1** and cyclic trimer as a function of R–NCO concentration; the *y*-axis shows the relative percentage yields, and the *x*-axis shows molar equivalents of isocyanate.

We examined the possibility that complex **1** is an intermediate in the isocyanate cyclotrimerization. When complex **1** was treated with excess benzyl isocyanate (4 equiv.), no organic product was observed. This result strongly indicates that complex **1** is not a genuine intermediate in the isocyanate cyclotrimerization. We performed the reactions with excess Ar–NCO (Ar = *p*-MeC_6H_4 or *p*-ClC_6H_4; Scheme 4a and 4b) to investigate whether the cyclic trimers of aryl isocyanates are formed from five-membered metallacyclic complexes or Pd(0)-PR_3 complexes.

When a reaction mixture containing compound **7** or **9** was treated with 6 equiv. of Ar–NCO in dichloromethane at room temperature for 2 h, a cyclic trimer (Ar–NCO)$_3$ was formed in 39% or 43% yield, respectively and some starting material was recovered (Scheme 4a). In contrast, the corresponding reactions of the Pd(0)-PR_3 complexes, [PdL_2(styrene)], with excess Ar–NCO afforded cyclic trimers (75% or 90% yield, respectively) and the metallacyclic complexes (Scheme 4b). The above results show that Pd(0)-PR_3 complexes give higher yields than their corresponding metallacyclic complexes.



Scheme 4

Paul and coworkers[14b] proposed Pd-catalyzed cyclotrimerization of Ar–NCO and their mechanisms involving metallacyclic or zwitterionic pathways.[32] 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 cycloaddition 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^+{$C(O)N^-R$}L_2], followed by the nucleophilic attack of the incoming R-NCO to afford a zwitterionic Pd complex having a linearly 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 cyclotrimerzation of aliphatic isocyanate, compared with than 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 N_2 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 (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) spectra were obtained in $CDCl_3$ on a JEOL Lamda 300, ECA 600 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si and to external 85% H_3PO_4. 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*-[$PdEt_2L_2$] (L = PMe_3 and PMe_2Ph) 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*-[$PdEt_2(PMe_3)_2$] (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. Benzyl 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 completely removed under vacuum, and then the remaining residue was washed with n-hexane (2 mL × 3) to obtain yellow solids. The crude solids under ice bath were extracted with excess CH_2Cl_2 (1 ml x 3) to afford white solids of **1.** The extracts were evaporated under vacuum, and then the remaining residues were extracted with THF (2 ml x 3) to afford again white solids of **1.** The collected white solids were recrystallized from CH_2Cl_2/n-hexane to afford pure product of **1**(0.302 g, 51%). The final extracts were evaporated to afford crude organic products which were extracted again with excess diethyl ether to give white solids of **3** (0.170 g, 48%). Complex **1**: IR (KBr/cm^{-1}): 1653, 1589 (CO). *Anal.* Calc. for $C_{76}H_{92}N_8O_8P_4Pd_4$ (1795.17): C, 50.85; H, 5.17; N, 6.24. Found: C, 50.71; H, 5.20; N, 6.16. ^{1}H NMR (300 MHz in $CDCl_3$): □ 0.84 (d, 36H, J = 11 Hz, P(CH_3)$_3$), 2.80 (d, 4H, J = 15.6 Hz, CH_2), 3.96 (d, 4H, J = 15.6 Hz, CH_2), 4.71 (br d, 4H, J = 16.2 Hz, CH_2), 6.72 (dd, 4H, J = 16.8 Hz, CH_2), 6.98–7.48 (m, 40H, Ph). ^{13}C{^{1}H} NMR (75 MHz): □ 13.3 (d, J_{P-C} = 30 Hz, P(CH_3)$_3$), 46.2 (s, CH_2), 125.7, 126.0, 126.1, 126.6, 128.1, 128.3, 140.0, 142.3, 165.0 (C=O). Other CO signal was not detected due to weak intensity. ^{31}P{^{1}H} NMR (120 MHz): –4.36 (s). TOF-MS(ES+): calcd for $[M+H]^+$: 1793.2206; found: 1793.2110.

Complex **2** was analogously prepared. **2** (40 %): IR (KBr/cm^{-1}): 1654, 1589 (CO). *Anal.* Calc. for $C_{96}H_{100}N_8O_8P_4Pd_4$ (2043.45): C, 56.43; H, 4.93; N, 5.48. Found: C, 56.17; H, 5.02; N, 5.68. ^{1}H NMR: □ 0.65 (d, 12H, J = 10 Hz, P(CH_3)$_2$Ph), 1.49 (d, 12H, J = 9.9 Hz, P(CH_3)$_2$Ph), 2.56 (d, 4H, J = 15.9 Hz, CH_2), 3.83 (d, 4H, J = 15.9 Hz, CH_2), 4.76 (br d, 4H, J = 15.9 Hz, CH_2), 6.46 (dd, 4H, J = 8.4, 16.5 Hz, CH_2), 6.91–7.29 (m, 60H, Ph). ^{13}C{^{1}H} NMR: □ 11.6 (s, P(CH_3)$_2$Ph), 11.8 (s, P(CH_3)$_2$Ph), 12.1 (s, P(CH_3)$_2$Ph), 12.4 (s, P(CH_3)$_2$Ph), 43.8 (s, CH_2), 49.2 (s, CH_2), 126.1, 126.2, 126.7, 128.0, 128.3, 128.5, 129.1, 130.7, 135.7, 136.3, 140.2, 142.0, 165.3 (C=O), 172.3 (d, J_{C-P} = 7.4 Hz, CO). ^{31}P{^{1}H} NMR: 1.92 (s). TOF-MS(ES+) : calcd for $[M+H]^+$: 2041.2831; found: 2041.2408.

Compound **3** was isolated in 48-56 % yield. Compound **3:** IR (KBr/cm^{-1}): 1688 (CO). *Anal.* Calc. for $C_{24}H_{21}N_3O_3$ (399.44): C, 72.16; H, 5.3; N, 10.52. Found: C, 72.24; H, 5.39; N, 10.12. ^{1}H NMR: □ 5.03 (s, 6H, CH_2), 7.28–7.34 (m, 6H, Ph), 7.43–7.46 (m, 9H, Ph). ^{13}C{^{1}H} NMR: □ 46.3 (s, CH_2), 128.2, 128.6, 129.1, 135.7, 149.1 (s, CO). MS (*m/e*): 399 (M^+).

Synthesis of 4 and 5.

DEPE (24 μL, 0.10 mmol) was added to a CH_2Cl_2 (4 mL) solution containing **1** (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 washed with hexane (2 mL × 3) to obtain the crude solids. Recrystallization from CH_2Cl_2/*n*-hexane afforded white crystals of [Pd(DEPE){C(O)N(R)-C(O)N(R)}], (R = benzyl) (**4,** 0.109 g, 94%). IR (KBr/cm^{-1}): 1636, 1589 (CO). *Anal.* Calc. for $C_{26}H_{38}N_2O_2P_2Pd$ (578.96): C, 53.94; H, 6.61; N, 4.84. Found: C, 53.91; H, 6.69; N, 4.81. ^{1}H NMR: □ 0.85-0.96 (m, 6H, P(CH_2CH_3)$_2$), 1.08–1.27 (m, 10H, P(CH_2CH_3)$_2$), 1.59–1.58 (m, 6H, P(CH_2CH_3)$_2$), 2.10–2.26 (m, 2H, P(CH_2CH_3)$_2$), 4.73 (s), 4.88 (d, J = 2.4 Hz, 2H, CH_2), 7.10–7.18 (m, 2H, Ar), 7.22–7.32 (m, 6H, Ar), 7.41–7.44 (m, 2H, Ar). ^{13}C{^{1}H} NMR: □ 9.40 (d, J_{P-C} = 24 Hz, P(CH_2CH_3)$_2$), 17.9 (d, J_{P-C} = 16 Hz, P(CH_2CH_3)$_2$), 18.0 (d, J_{P-C} = 30 Hz, P(CH_2CH_3)$_2$), 22.5 (dd, J_{P-C} = 15, 27 Hz, PCH_2), 23.2 (dd, J_{P-C} = 13, 24 Hz, PCH_2), 45.0 (s), 54.4 (s), 125.9, 126.2, 126.4, 128.1, 128.3, 128.4, 140.6, 143.9, 167.0 (CO), 188.9 (dd, J_{P-C} = 13, 148 Hz, CO). ^{31}P{^{1}H} NMR: 36.5 (d, J = 29 Hz), 58.4 (d, J = 29 Hz).

[Pd(DMPE){C(O)N(R)-C(O)N(R)}], (R = benzyl) (**5**, 61%) was analogously prepared. IR (KBr/cm^{-1}): 1638, 1579 (CO). *Anal.* Calc. for $C_{22}H_{30}N_2O_2P_2Pd$ (522.85): C, 50.54; H, 5.78; N, 5.36. Found: C, 50.03; H, 5.65; N, 4.97. ^{1}H NMR: □ 0.83 (d, 6H, J = 8.1 Hz, P(CH_3)$_2$), 1.49–1.72 (m, 10H, P(CH_3)$_2$), 4.71 (s), 4.91 (s), 7.12–7.43 (m, 10H, Ar). ^{13}C{^{1}H} NMR: □ 11.3 (d, J_{P-C} = 17 Hz, P(CH_3)$_2$), 12.8 (d, J_{P-C} = 30 Hz, P(CH_3)$_2$), 26.5 (dd, J_{P-C} = 15, 31 Hz, PCH_2), 23.2 (dd, J_{P-C} = 12, 29 Hz, PCH_2), 45.0 (s), 53.8 (s), 66.0, 126.1, 126.3, 126.7, 128.0, 128.2, 128.4, 140.5, 143.6, 166.8 (CO), 188.4 (dd, J_{P-C} = 13, 155 Hz, CO). ^{31}P{^{1}H} NMR: 9.05 (d, J = 26 Hz), 29.6 (d, J = 29 Hz).

Synthesis of *cis*-[Pd{C(O)N(Ar)-C(O)N(Ar)}(PR_3)$_2$] (Ar = C_6H_5, *p*-MeC_6H_4, *p*-Cl-C_6H_4), 6-9.

Styrene (229 μL, 2.0 mmol) and tetrahydrofuran (THF, 3 mL) were added sequentially to a Schlenk flask containing *trans*-[$PdEt_2(PMe_3)_2$] (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 washed with hexane (2 mL × 3) to obtain the crude solids. Recrystallization from CH_2Cl_2/*n*-hexane afforded white crystals of *cis*-[Pd(PMe_3)$_2$C(O)N(Ph)-C(O)N(Ph)}] (**6,** 0.459 g, 92%). IR (KBr/cm^{-1}): 1655, 1602 (CO). *Anal.* Calc. for $C_{20}H_{28}N_2O_2P_2Pd$ (496.82): C, 48.35; H, 5.68; N, 5.64. Found: C, 48.57; H, 5.72; N, 5.58. ^{1}H NMR: □ 0.93 (d, 9H, J = 7.3 Hz, P(CH_3)$_3$), □ 1.57 (d, 9H, J = 9.9 Hz, P(CH_3)$_3$), 6.96–7.01 (m, 2H, Ar), 7.17–7.38 (m, 8H, Ar). ^{13}C{^{1}H} NMR: □ 15.3 (d, J_{P-C} = 19 Hz, P(CH_3)$_3$), 16.6 (d, J_{P-C} = 30 Hz, P(CH_3)$_3$), 123.0, 126.5, 127.2, 127.8, 128.1, 138.6, 138.9, 151.7, 163.1 (CO), 183.5 (d, J_{C-P} = 159 Hz, CO). ^{31}P{^{1}H} NMR (240 MHz at –20℃): –27.7 (d, J_{P-C} = 26 Hz), –6.10 (d, J_{P-C} = 30 Hz).

Complexes **7-9** were analogously prepared. *C*is-[Pd(PMe_3)$_2$C(O)N(Ar)-C(O)N(Ar)}] (Ar = *p*-MeC_6H_4) (**7,** 92%). IR (KBr/cm^{-1}): 1655, 1618 (CO). *Anal.* Calc. for $C_{22}H_{32}N_2O_2P_2Pd$ (524.87): C, 50.34; H, 6.15; N, 5.33. Found: C, 50.39; H, 6.15; N, 5.36. ^{1}H NMR: □ 0.94 (d, 9H, J = 7.4 Hz, P(CH_3)$_3$), □ 1.56 (d, 9H, J = 9.8 Hz, P(CH_3)$_3$), 2.27 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 6.98–7.26 (m, 8H, Ar). ^{13}C{^{1}H} NMR: □ 15.4 (d, J_{P-C} = 19 Hz, P(CH_3)$_3$),

16.7 (d, J_{P-C} = 30 Hz, P(CH_3)$_3$), 20.9 (s, CH_3), 21.1 (s, 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℃): –27.7 (d, J_{P-C} = 26 Hz), –6.43 (d, J_{P-C} = 23 Hz).

Cis-[Pd(PMe$_3$)$_2${C(O)N(Ar)-C(O)N(Ar)}] (Ar = *p*-ClC$_6$H$_4$) (**8**, 97 %). IR (KBr/cm^{-1}): 1660, 1613 (CO). *Anal.* Calc. for $C_{20}H_{26}N_2O_2P_2Cl_2Pd$ (565.76): C, 42.46; H, 4.63; N, 4.95. Found: C, 42.78; H, 4.73; N, 4.50. ^{1}H NMR: □ 0.99 (d, 9H, *J* = 7.8 Hz, P(CH_3)$_3$), □ 1.58 (d, 9H, *J* = 9.3 Hz, P(CH_3)$_3$), 7.16–7.32 (m, 8H, Ar). ^{13}C{^{1}H} NMR: □ 15.4 (d, J_{P-C} = 19 Hz, P(CH_3)$_3$), 16.6 (d, J_{P-C} = 31 Hz, P(CH_3)$_3$), 127.9, 128.2, 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℃): –27.9 (d, J_{P-C} = 26 Hz), –5.47 (d, J_{P-C} = 26 Hz).

Cis-[Pd(PMe$_2$Ph)$_2${C(O)N(Ar)-C(O)N(Ar)}] (Ar = *p*-ClC$_6$H$_4$) (**9**, 85 %). IR (KBr/cm^{-1}): 1664, 1615 (CO). *Anal.* Calc. for $C_{30}H_{30}N_2O_2P_2Cl_2Pd$ (618.94): C, 52.23; H, 4.38; N, 4.06. Found: C, 52.51; H, 4.57; N, 3.98. ^{1}H NMR: □ 0.68 (d, 2H, *J* = 8 Hz, P(CH_3)$_2$Ph), 1.58 (d, 6H, *J* = 10 Hz, P(CH_3)$_2$Ph), 7.11–7.37 (m, 18H, Ar). ^{13}C{^{1}H} NMR: □ 12.8 (d, J_{P-C} = 18 Hz, P(CH_3)$_2$Ph), 14.4 (d, J_{P-C} = 31 Hz, P(CH_3)$_2$Ph), 128.0, 128.5, 128.6, 128.8, 129.0, 130.1, 130.2, 130.5, 130.6, 130.8, 132.6, 135.6, 135.7, 136.2, 137.5, 150.1, 163.2 (CO), 181.8 (CO). ^{31}P{^{1}H} NMR : -19.04 (d, *J* = 40 Hz), 3.05 (d, *J* = 42 Hz).

Synthesis of 10

DEPE (71 μL, 0.30 mmol) was added to a CH_2Cl_2 (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 washed with hexane (2 mL × 3) to obtain the crude solids. Recrystallization from CH_2Cl_2/diethyl ether afforded white crystals of [Pd(DEPE){C(O)N(Ar)-C(O)N(Ar)}], (Ar = *p*-ClC$_6$H$_4$) (**10,** 0.170 g, 91%). IR (KBr/cm^{-1}): 1654, 1608 (CO). *Anal.* Calc. for $C_{24}H_{32}N_2O_2P_2Cl_2Pd$ (619.80): C, 46.51; H, 5.20; N, 4.52. Found: C, 46.35; H, 5.22; N, 4.02. ^{1}H NMR: □ 0.86-1.3 (m, 15H, P(CH_2CH_3)$_2$), 1.61–1.88 (m, 8H, P(CH_2CH_3)$_2$), 2.16–2.27 (m, 1H, P(CH_2CH_3)$_2$), 2.28 (s), 7.00–7.16 (m, 8H, Ar). ^{13}C{^{1}H} NMR: □ 9.51 (d, J_{P-C} = 14 Hz, P(CH_2CH_3)$_2$), 17.0 (d, J_{P-C} = 17 Hz, P(CH_2CH_3)$_2$), 18.1 (d, J_{P-C} = 29 Hz, P(CH_2CH_3)$_2$), 21.2 (d, J_{P-C} = 14 Hz, PCH_2), 22.7 (s), 25.8 (s), 127.2, 127.3, 128.7, 128.9, 132.7, 135.8, 136.1, 136.3, 164.6, 174.2 (CO). ^{31}P{^{1}H} NMR: 38.8 (d, *J* = 29 Hz), 58.2 (d, *J* = 31 Hz).

Monitoring for tetranuclear Pd(II) complex and cyclotrimerization of the isocyanate

In a typical run, benzyl isocyanate (one equiv.) was added to a THF (3 ml) solution containing Pd(styrene)(PMe$_3$)$_2$ (0.145g, 0.46 mmol) at room temperature and the reaction mixture was stirred for 2 h. The product ratio of cyclic trimer (benzyl isocyanate) and the tetranuclear complexes was confirmed from ^{1}H-NMR intergration of benzylic regions (CH_2Ph) between the complex, **1** and cyclic trimer of the isocyanate, **3**.

Analogous reactions with 2, 3, 4, 6, and 8 equiv. of the isocyanate were carried out.

Reactions of metallacyclic Pd(II) complexes with excess aryl isocyanate

p-Tolyl isocyanate (185 μl, 1.47 mmol) was added to a CH_2Cl_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 × 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/n-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).

Compound **11** was obtained as white solids (39 %). IR (KBr/cm^{-1}): 1706 (CO). *Anal.* Calc. for $C_{24}H_{21}N_3O_3$ (399.44): C, 72.16; H, 5.30; N, 10.52. Found: C, 71.53; H, 5.37; N, 10.41. ^{1}H NMR: □ 2.38 (s, 9H, CH_3), 7.04–7.29 (m, 12H, Ph). ^{13}C{^{1}H} NMR: 21.4 (s, CH_3), 128.2, 131.4,139.5, 149.1 (CO). MS (*m/e*): 399 (M$^+$).

Analogous reaction of complex **9** of with *p*-chlorophenyl isocyanate afforded a mixture of compound **12** (43 %) and complex **9** (87 %). Compound **12:** IR (KBr/cm^{-1}): 1709 (CO). *Anal.* Calc. for $C_{21}H_{12}N_3O_3Cl_3$ (460.71): C, 54.75; H, 2.63; N, 9.12. Found: C, 54.50; H, 2.51; N, 8.98. ^{1}H NMR: □ 7.10–7.61 (m, 12H, Ph). ^{13}C{^{1}H} NMR: □ 129.9, 131.9,135.8, 148.3 (CO). MS (*m/e*): 459 (M$^+$).

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

	1	**4**	**10**
Empirical formula	$C_{78}H_{96}C1_4N_8O_8P_4Pd_4$	$C_{26}H_{38}N_2O_2P_2Pd$	$C_{25}H_{34}Cl_4N_2O_2P_2Pd$
Formula weight	1964.91	578.92	704.68
Temperature, K	200(2)	200(2)	200(2)
Crystal system	tetragonal	monoclinic	monoclinic
Space group	$I\bar{4}$	$P2_1/n$	$P2_1/n$
a, Å	15.1307(6)	19.3654(8)	13.1299(9)
b, Å	15.1307(6)	14.0152(6)	11.2538(8)
c, Å	19.1938(15)	21.2584(9)	20.6433(14)
α, (º)	90	90	90
β, (º)	90	21.2584(9)	99.048(2)
γ, (º)	90	90	90
V, Å^3	4394.2(4)	110.422(1)	3012.3(4)
Z	2	8	4
d_{cal}, g cm^{-3}	1.485	1.422	1.554
μ, mm^{-1}	1.054	0.830	1.103
F(000)	1992	2400	1432
T_{max}	0.8664	0.9676	0.8790
T_{min}	0.6371	0.8132	0.7404
q range (º)	1.90–28.30	2.04–28.29	1.99–28.30
No. of reflns collected	16059	38568	21550
No. of reflns independent	5359	13151	7352
No. of reflns with $I > 2\sigma(I)$	4433	8462	5087
No. of parameters	240	595	325
Max., in $\Delta\rho$ (e Å^{-3})	0.551	1.792	0.794
Min., in $\Delta\rho$ (e Å^{-3})	−0.622	−1.128	−1.142
Absolute structure parameter	-0.03(2)		
GOF on F^2	1.080	1.078	1.002
R^a	0.0213	0.0483	0.0314
$wR2^b$	0.0472	0.1272	0.0647

$^a R = \sum[|F_o| - |F_c|]/\sum|F_o|]$, $^b wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Reactions of Pd^0-PR_3 with excess aryl isocyanate

Styrene (60 μL, 0.53 mmol) and tetrahydrofuran (THF, 3 mL) were added sequentially to a Schlenk flask containing *trans*-[$PdEt_2(PMe_2Ph)_2$] (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 CH_2Cl_2/n-hexane at room temperature to afford white crystals of **12** (0.145 g, 90%).

Analogous reaction of Pd(styrene)$(PMe_3)_2$ of 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 CH_2Cl_2/ *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.[34] All calculations were carried out with SHELXTL programs.[35] 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.

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

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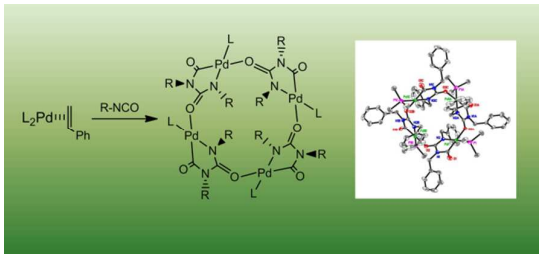

Cyclic tetramers of five-membered palladacycle involving isocyanate dimer were prepared, and the catalytic cyclotrimerization from palladium zero-compound or single palladacycle with organic isocyanates was performed.