Polyhedron 117 (2016) 283–292

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Macrocyclic complexes containing a platinacycle or palladacycle composed of an isocyanate dimer unit: Reactivity towards isocyanides and cyclotrimerization of isocyanates

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ARTICLE INFO

Article history:
Received 28 April 2016
Accepted 29 May 2016
Available online 3 June 2016

Keywords:
Macrocycle
Platinacycle
Palladacycle
Organic isocyanate
Isocyanurate

ABSTRACT

The reactions of [Pt(styrene)(PMe_3)$_2$] with 2 equiv. of alkyl or aryl isocyanate afforded five-membered platinacycles, *cis*-[Pt{–N(R)C(O)N(R)C(O)–}(PMe_3)$_2$] (R = $CH_2C_6H_5$, p-ClC_6H_4, p-$OMeC_6H_4$). These complexes are the first examples of platinacycles containing an isocyanate dimer unit. When the five-membered bis(phosphine) platinacycles or palladacycles were treated with 2 equiv. of elemental sulfur, 16-membered cyclic products as an assembly of four platinacycles or palladacycles, [M(PR_3){–N(R)C(O)N(R)C(O)–}]$_4$, were readily obtained. These cyclic tetramers were cleaved using *tert*-butyl isocyanide (CN–^{t}butyl, 4 equiv.), affording the corresponding monomeric complexes, [M(PR_3)(CN–^{t}butyl){–N(R)C(O)N(R)C(O)–}] (M = Pt, Pd). An unusual cyclotrimerization of organic isocyanates catalyzed by zerovalent Pt complexes or five-membered platinacycles was observed. In addition, the direct cyclotrimerization of alkyl or aryl isocyanates using dialkyl Pt(II) or Pd(II) complexes was investigated. The cross cyclotrimerization of an aryl isocyanate and its derivative using a zerovalent Pd complex was also investigated.

1. Introduction

The formation of metallacycles containing organic isocyanate units (R–N=C=O) is one of the important steps in the cyclodimerization or trimerization of isocyanates and the catalytic coupling of isocyanates, in the presence of an olefin or CO by transition (or main group)-metal-catalyzed reactions [1–24]. In particular, five-membered Ni or Pd metallacycles containing organic isocyanate units have been considered as key intermediates in the catalytic cyclotrimerization of organic isocyanates or a precursor to afford various heterocycles [8,10]. Although several studies on the main-group- or transition-metal-catalyzed cyclotrimerization of organic isocyanates have been reported, group 10 metal complexes showing such reactivity are currently rare. Furthermore, the catalytic cyclotrimerization of aliphatic isocyanates and their metallacyclic intermediates have been rarely investigated. Some transition-metal or rare-earth metal complexes previously exhibited catalytic activity for the cyclotrimerization of aliphatic isocyanates [14–23]. Notably, Misono and co-workers [7] reported the Ni-catalyzed cyclotrimerization of alkyl isocyanates, whereas Paul and co-workers [10b] reported theoretical studies on the mechanism for the Pd(0)-catalyzed cyclotrimerization of such species. Recently, we observed that unique cyclic tetramers of a five-membered metallacycle containing a dimeric isocyanate unit and a Pd atom were produced from zerovalent Pd complexes and alkyl isocyanate (Chart 1) [24]. These interesting results led us to investigate the formation of other cyclic tetramers of a Pt or Pd atom and study their reactivity towards nucleophiles.

In this study, using metallacyclic complexes and elemental sulfur, we prepared a series of macrocyclic complexes of these metallacycles, 16-membered cyclic compounds, in which each metallacycle contains an organic (alkyl or aryl) isocyanate dimer unit and a group 10 metal (Pt or Pd). Their reactivity towards organic nucleophiles and catalytic activity for the cyclotrimerization of organic isocyanates were investigated.

2. Results and discussion

2.1. Syntheses of five-membered platinacycles

We recently demonstrated that the reactions of [Pd(styrene)L_2] with R–NCO afforded cyclic tetramers (Path A: R = alkyl) or five-membered palladacycles (Path B: aryl), depending on the type of

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http://dx.doi.org/10.1016/j.poly.2016.05.061
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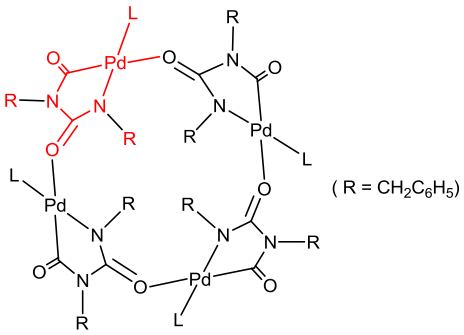


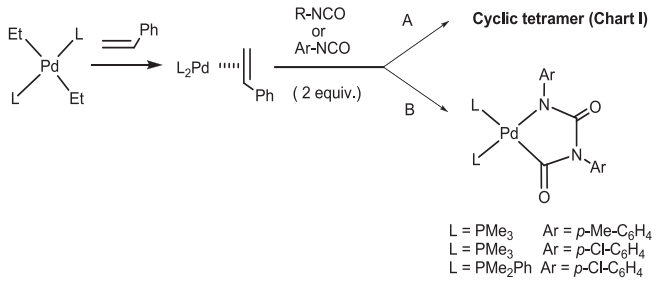
Chart 1.

isocyanate (Scheme 1) [24]. These reactions also suggest that aryl isocyanates cannot afford cyclic tetramers composed of five-membered palladacycles involving dimeric aryl isocyanate ring, because the four aryl substituents involving the palladacycle do not fit inside the tetrameric cavity, probably due to the sterically rigid ring.

In this study, attempts were made to extend the aforementioned reactivity to Pt metal and other isocyanates. Based on Scheme 1, we first tried to generate platinacycles containing a dimeric alkyl isocyanate. More vigorous reaction conditions are required for the preparation of zerovalent complexes, Pt(II) dialkyl starting complexes, than the Pd analogs. When *cis*-[Pt(styrene)$(PMe_3)_2$], generated from *cis*-[$PtEt_2(PMe_3)_2$] and styrene at 80 °C, was treated with 2 equiv. of alkyl or aryl isocyanate at room temperature, only five-membered platinacycles were obtained in moderate-to-good yields (Scheme 2). Even benzyl (alkyl) isocyanate produced the corresponding five-membered platinacycle. These results contrast with those obtained previously when zerovalent Pd complexes [Pd(olefin)L_2] were used (Scheme 1).

Two PMe_3 ligands in complex **1** were readily replaced with a chelating phosphine (DMPE), affording a five-membered platinacycle (**4**) in a good yield. The ^{1}H-NMR spectra of five-membered platinacycles **1**–**3** showed two doublets with Pt satellites in the PMe_3 region, and the $^{31}P\{^1H\}$-NMR spectra also showed two doublets with the corresponding satellites, indicating that *cis*-Pt(II) complexes contain magnetically inequivalent PMe_3 ligands. Notably, the platinacycles (**1**–**4**) obtained in this study are the first examples of five-membered platinacycles containing an alkyl (or aryl) isocyanate dimer unit.

The crystal and refinement data for complex **4** are summarized in Table 1. The molecular structure of **4** is shown in Fig. 1; the Pt metal has a square-planar coordination sphere containing a benzyl isocyanate dimer unit. The geometry of the five-membered ring, defined by Pt1, C7, N1, C8, and N2, clearly shows the N–C coupling of the two isocyanates.



Scheme 1. Reactions of Pd(styrene)L_2 with organic isocyanate.

2.2. Syntheses of macrocyclic complexes containing a platinacycle or palladacycle

The bis(phosphine) Pd(II) metallacycle shown in Scheme 1 acts as a precursor of cyclic tetramers; and the abstraction of one phosphine from the metallacycle is the key step for the formation of tetramers. Thus, we first attempted to prepare cyclic tetramers by ligand (phosphine) exchange with *N*-heterocyclic carbene (NHC) or elemental sulfur. The treatments of platinacycle, **1** with elemental sulfur produced the expected cyclic tetramer, $[Pt(PMe_3)\{-N(R)C(O)N(R)C(O)\}]_4$, ($R = CH_2C_6H_5$) (**5**) by one phosphine abstraction (Scheme 3). The product was isolated in 37% yield as white solids after repeated recrystallization. The spectral, elemental and MS (TOF-MS) data confirmed the formation of the cyclic tetramer.

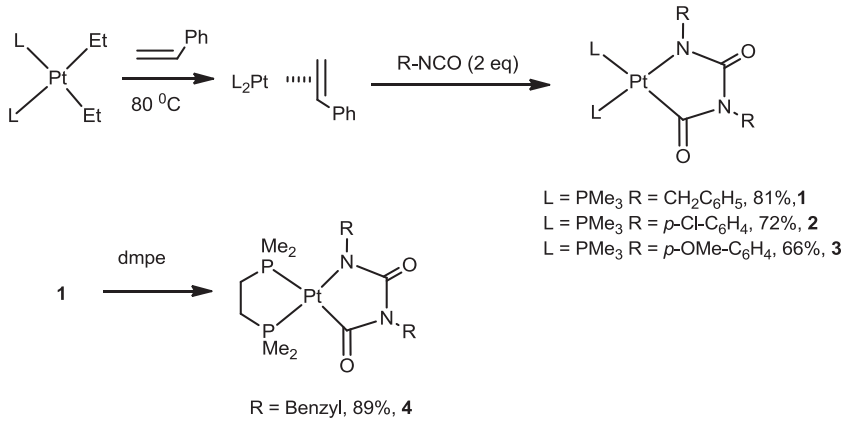
When the same synthetic strategy was applied to several palladacycles, the corresponding Pd cyclic tetramers (**6**–**8**) were obtained as white solids in 28–42% yields. Excessive elemental sulfur has been used to make the reaction go to completion, but the relatively low actual yields may be attributed to the formation of a by-product.

IR spectra of the cyclic tetramers **5**–**8** display two CO stretching bands at 1647–1655 and 1560–1563 cm^{-1}, whose intensities are somewhat weaker than those (1645–1661 and 1589–1614 cm^{-1}) of the starting metallacycles. Particularly, the second carbonyl bands are shifted to lower wavenumbers, supporting the coordination of one of the carbonyl groups to the metal. The two doublets of PMe_3 with satellites at δ 1.25 and 1.67 ppm in the ^{1}H-NMR spectrum of complex **1** became a doublet at 0.92 ppm in complex **5**. The two doublets at −25.0 ppm (J = 13.2 Hz, J_{Pt-P} = 1709 Hz) and −23.9 ppm (J = 15.4 Hz, J_{Pt-P} = 3376 Hz) in the $^{31}P\{^1H\}$-NMR spectrum of **1** are also became a singlet at −14.8 ppm with a satellite (J_{Pt-P} = 3990 Hz), confirming the loss of one phosphine ligand to afford the cyclic tetramer of Pt(II).

The two doublets in the PMe_3 region in the starting *cis*-palladacycles (Ar = *p*-$MeOC_6H_4$, *p*-MeC_6H_4) became a doublet in the ^{1}H-NMR spectra of complexes **6** and **7** as expected. Interestingly, in the ^{1}H-NMR spectrum of complex **8**, the methyl group in PMe_2Ph appeared as two doublets at δ 1.38 and 1.42 ppm, which contrast with those in PMe_3 analogs, are also shifted to lower field compared with those in the starting complex, *cis*-[Pd{–N(Ar)C(O)N(Ar)C(O)–}$(PMe_2Ph)_2$ (two doublets at δ 0.68 and 1.58 ppm). The integration ratio of alkyl to aryl signals for complex **8** agrees well with the proposed structure. These results indicate that the two methyl groups in $P(CH_3)_2Ph$ are chemically inequivalent. The $^{31}P\{^1H\}$ NMR spectra of **6**–**8** showed a singlet, indicating the magnetic equivalence of all the phosphorus nuclei. Thus, the phosphine abstraction by elemental sulfur [25] is an effective synthetic route to macrocyclic tetramers of Pt(II) or Pd(II).

2.3. Cleavage reactions of macrocyclic tetramers with tert-butyl isocyanide

Suitable crystals of the cyclic tetramers of Pt or Pd (Scheme 3) for X-ray diffraction analysis could not be obtained. Therefore, the following cleavage reactions of these species were carried out using 4 equiv. of CN–*tert*-butyl to confirm the formation of cyclic tetramers in an indirect manner (Scheme 4). CN–^{t}Bu cleaved complexes **5** and **6** at room temperature, affording the corresponding monomeric complexes **9** (platinacycle) and **10** (palladacycle), respectively, in quantitative yields. These products were hygroscopic solids and exhibited a characteristic strong absorption at 2194 or 2198 cm^{-1} assignable to the N≡C bond of the isocyanide, consistent with those obtained for late transition-metal complexes of *tert*-butyl isocyanide [26–32]. As expected, the $^{31}P\{^1H\}$ NMR spectra of **9** and **10** showed a singlet. The monomeric units (metallacycle)



Scheme 2. Reactions of Pt(olefin)L_2 with organic isocyanates.

Table 1
Crystallographic data for complexes **4**, **9**, and **10**.

	4	9	10
Empirical formula	$C_{22}H_{32}N_2O_3P_2Pt$	$C_{24}H_{32}N_3O_2PPt$	$C_{24}H_{36}N_3O_6PPd$
Formula weight	629.53	620.58	599.93
Temperature, K	193(2)	223(2)	223(2)
Crystal system	tetragonal	monoclinic	triclinic
Space group	$PI\bar{4}2_1c$	$P2_1/c$	$P\bar{1}$
a (Å)	16.1709(5)	9.975(2)	9.8999(3)
b (Å)	16.1709(5)	13.270(2)	10.1587(4)
c (Å)	19.0459(7)	19.128(3)	15.6864(5)
α (°)	90	90	71.764(1)
β (°)	90	92.518(7)	84.200(1)
γ (°)	90	90	84.395(2)
V (Å^3)	4980.5(3)	2529.5(7)	1487.04(9)
Z	8	4	2
D_{cald} (g cm^{-3})	1.679	1.630	1.340
μ (mm^{-1})	5.787	5.634	0.716
F(000)	2480	1224	620
T_{max}	0.5435	0.844	0.9450
T_{min}	0.3907	0.588	0.8701
θ range (°)	2.48–28.32	1.87–28.49	2.14–28.32
No. of reflns collected	71319	74080	39888
No. of reflns independent	6138	6410	7116
No. of reflns with $I > 2\sigma(I)$	5180	4788	6283
No. of parameters	271	280	316
Maximum, in $\Delta\rho$ (e Å^{-3})	1.526	1.519	1.947
Minimum, in $\Delta\rho$ (e Å^{-3})	−0.956	−0.831	−0.475
Absolute structure parameter *GOF* on F^2	1.092	1.067	1.072
R^a	0.0292	0.0306	0.0398
$wR_2{}^b$	0.0577	0.0478	0.1016

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|]$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

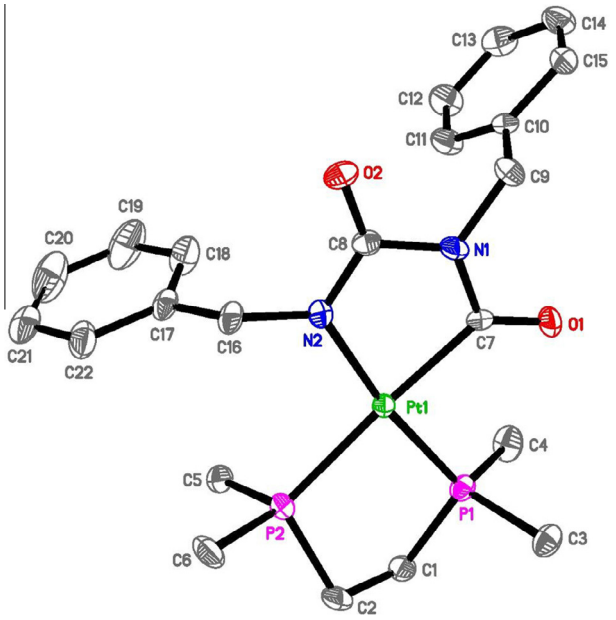
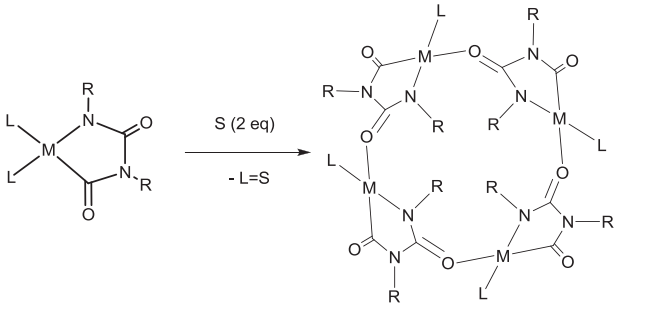


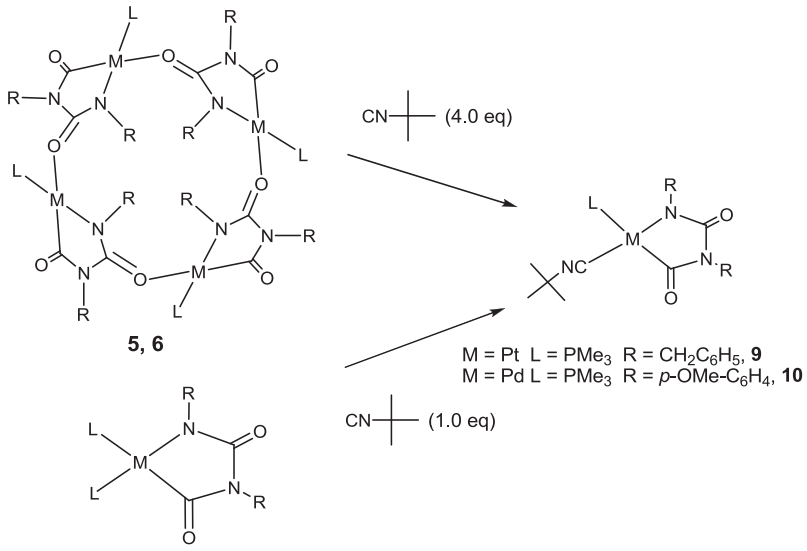
Fig. 1. ORTEP drawing of complex **4**. Displacement ellipsoids for atoms exhibit 40% probability level.

of the tetramers (**5** and **6**) were treated with an equimolar amount of CN–^{t}Bu to check whether the same products would be formed by ligand replacement. As expected, the same products were obtained in quantitative yields (**9**: 98–99% and **10**: 93–96%).

The molecular structures of complex **9** and **10** are shown in Figs. 2 and 3, respectively. Both the crystal structures show a square-planar coordination sphere of the metal, a *tert*-butyl isocyanide, and a five-membered metallacycle containing an isocyanide dimer unit. The Pt–C bond length (1.990(4) Å, Table 2) in complex **9** falls in the typical range (1.902(10)–1.998(6) Å) [26–29] for other known (CN–^{t}Bu)–Pt complexes. The Pd-C (*tert*-butyl isocyanide) bond length, Pd–C(20) (2.046(3) Å), in complex **10** was slightly longer than those observed for other Pd–(*tert*-butyl isocyanide) complexes, (1.921(15)–2.038 Å) Å) [30–32].



Scheme 3. Reactions of metallacycles with elemental sulfur.



Scheme 4. Treatments of cyclic tetramers or metallacycles with *tert*-butyl isocyanide.

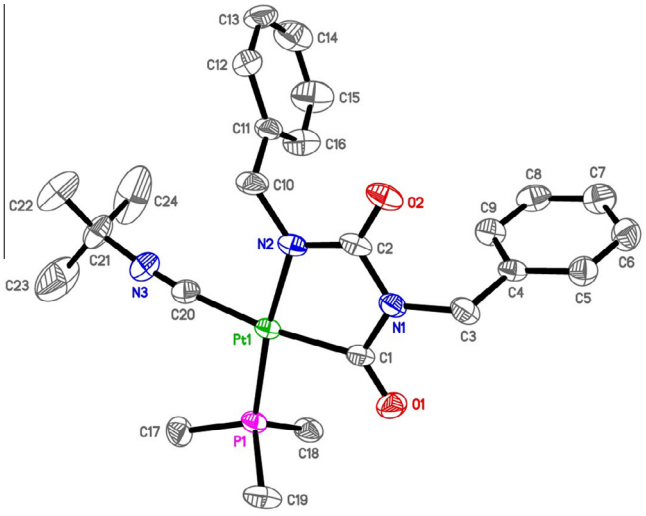


Fig. 2. ORTEP drawing of complex **9**. Displacement ellipsoids for nonhydrogen atoms exhibit 40% probability level.

2.4. Reactions of bis(phosphine) Pt(II) or Pd(II) dialkyl complexes with organic isocyanates

The reactivity of *cis*-[$PtEt_2(PMe_2Ph)_2$], a PMe_2Ph analog of *cis*-[$PtEt_2(PMe_3)_2$], towards aromatic isocyanates has been investigated (Eq. (1) in Scheme 5). Interestingly, these reactions afforded aryl (*p*-chloro or *p*-CH_3) isocyanurates as a major product; they were isolated by chromatography. The $^{31}P\{^1H\}$ NMR spectrum of the remaining solid showed two doublets at −11.7 ppm (J = 19.4 Hz, J_{Pt-P} = 3504 Hz) and −14.3 ppm (J = 13.0 Hz, J_{Pt-P} = 1794 Hz). These two doublets can be arrtibuted to the magnetic inequivalence of the two PMe_2Ph, and therefore the solid can be assigned to *cis*-[Pt{–N(Ar)C(O)N(Ar)C(O)–}$(PMe_2Ph)_2$] (Ar = *p*-ClC_6H_4,**11**), as in platinacycles in Scheme 2).

To further confirm the cyclotrimerization and the identity of the solid, complexes **2** and **3** were treated with excess (6 equiv.) Ar–NCO at 55 °C in THF for 18 h (Eq. (2) in Scheme 5). The isocyanurates were obtained in high yields. In contrast, the same reaction of **2** at room temperature produced a *p*-chlorophenyl isocyanurate in 31% yield.

The above results strongly indicate that the zerovalent Pt complex and platinacycle act as the catalyst or precursor in the

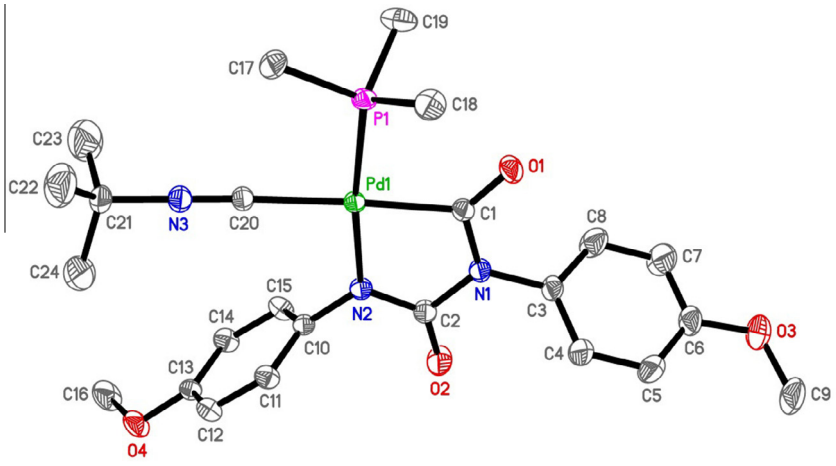


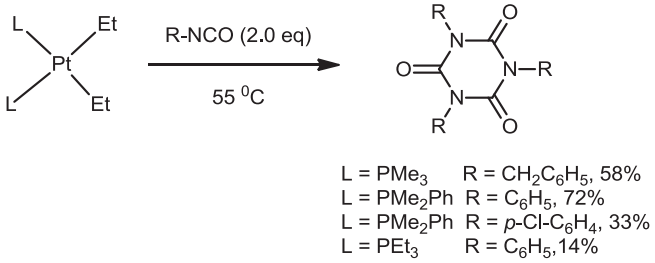
Fig. 3. ORTEP drawing of complex **10**·$2H_2O$. Displacement ellipsoids for nonhydrogen atoms exhibit 40% probability level. The lattice water molecules are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°).

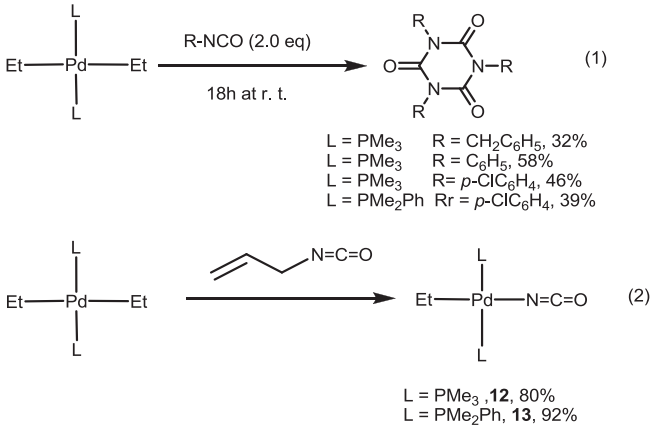
4		9		10	
Distances					
Pt1–N2	2.049(5)	Pt1–C1	2.018(4)	Pd1–C1	2.010(3)
Pt1–C7	2.053(6)	Pt1–N2	2.040(3)	Pd1–N2	2.041(2)
Pt1–P1	2.233(2)	Pt1–C20	1.990(4)	Pd1–C20	2.046(3)
Pt1–P2	2.326(2)	Pt1–P1	2.255(1)	Pd1–P1	2.282(7)
O1–C7	1.201(7)	O1–C1	1.225(4)	O1–C1	1.207(3)
O2–C8	1.232(6)	O2–C2	1.235(4)	O2–C2	1.225(3)
N1–C7	1.390(7)	N1–C1	1.391(5)	N1–C1	1.402(3)
N1–C8	1.427(7)	N1–C2	1.411(5)	N1–C2	1.427(4)
N2–C8	1.330(7)	N2–C2	1.331(5)	N2–C2	1.332(4)
		N3–C20	1.144(5)	N3–C20	1.150(4)
Angles					
N2–Pt1–C7	80.4(2)	C1–Pt1–N2	80.6(14)	C1–Pd1–N2	80.9(1)
C2–Pt1–C7	91.9(2)	C1–Pt1–C20	171.6(2)	C1–Pd1–C20	174.7(1)
N2–Pt1–P2	103.1(1)	N2–Pt1–C20	94.9(1)	N2–Pd1–C20	94.4(1)
P1–Pt1–P2	84.63(6)	N2–Pt1–P1	171.6(9)	N2–Pd1–P1	172.3(7)
C7–N1–C8	120.4(5)	C1–N1–C2	118.9(3)	C1–N1–C2	119.5(2)
C8–N2–Pt1	116.4(4)	C2–N2–Pt1	115.5(3)	C2–N2–Pd1	116.2(2)
O1–C7–Pt1	130.6(4)	C20–N3–C21	174.7(4)	C20–N3–C21	179.7(4)
N2–C8–N1	112.9(5)	O1–C1–Pt1	129.8(3)	O1–C1–Pd1	129.1(2)
		N1–C1–Pt1	111.1(3)	N1–C1–Pd1	110.7(2)
		N3–C20–Pt1	172.5(4)	N3–C20–Pd1	176.6(2)

formation of isocyanurates. Particularly, the platinacycle may be one of the intermediates during the reactions. To the best of our knowledge, this is the first example of the cyclotrimerization of organic isocyanates using Pt complexes. Notably, dialkyl bis(phosphine) Pt(II) complexes without the styrene ligand directly reacted with aryl isocyanates, producing the corresponding isocyanurates in 14–72% yields, depending on the phosphine ligands (Scheme 6). As shown in Eq. (1) of Schemes 5 and 6, the reactions via the zerovalent Pt complex, [Pt(styrene)L_2] resulted in higher yields for the isocyanurates than the corresponding dialkyl Pt(II) complexes.

For comparison, direct cyclotrimerization with [$PdEt_2L_2$] complexes was also performed; the reactions also produced (benzyl, phenyl, and *p*-chlorophenyl) isocyanurates (Eq. (1) in Scheme 7). The Pd(II) complexes exhibited slightly lower yields than the corresponding Pt(II) complexes. This phenomenon may arise from



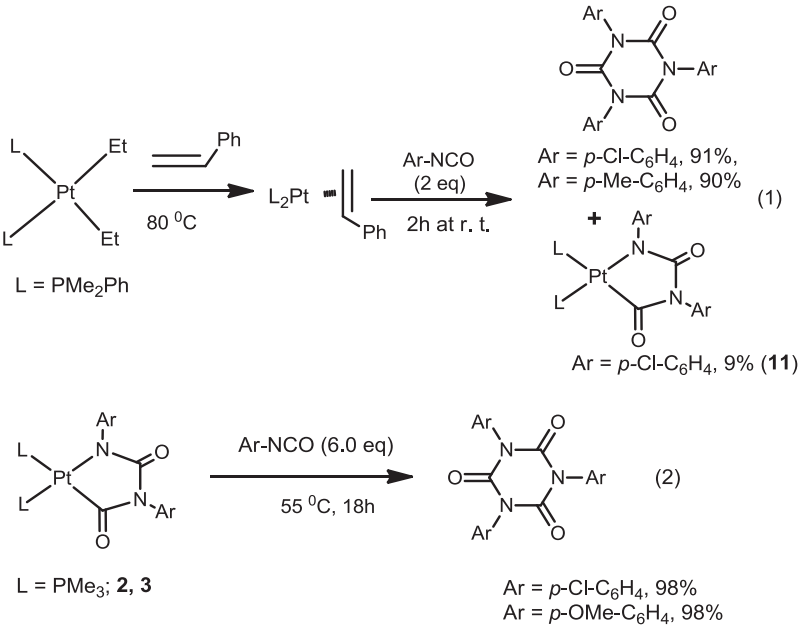
Scheme 6. Reactions of dialkyl Pt(II) complexes with R-NCO.



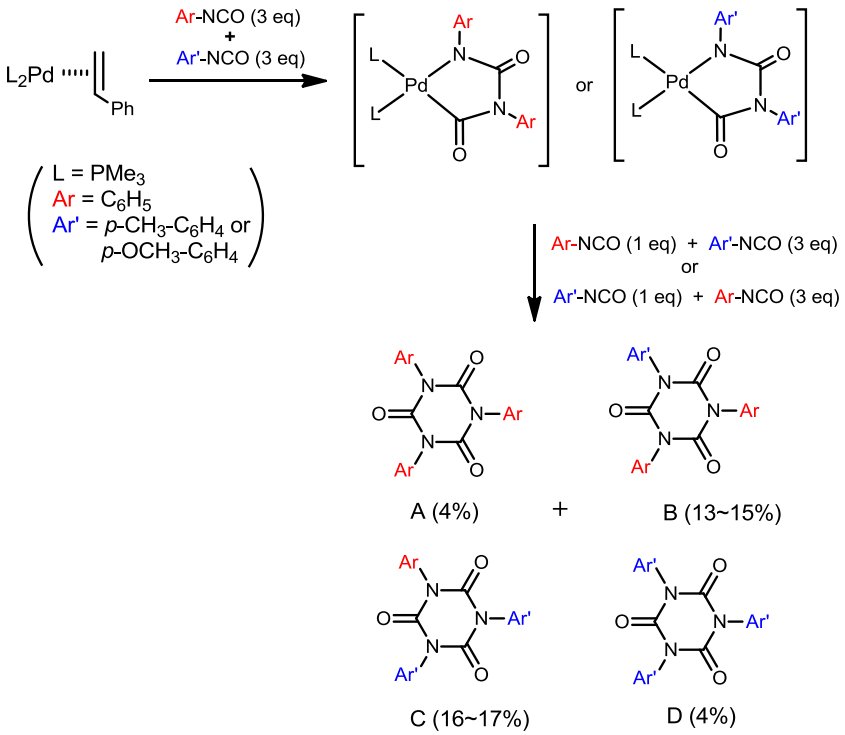
Scheme 7. Reactions of dialkyl Pd(II) complexes with organic isocyanates.

the difficulty of the formation of the [Pd(olefin)L_2] intermediate due to the thermal instability of the dialkyl Pd(II) complexes. As shown in Scheme 6 and Eq. (1) in Scheme 7, even alkyl isocyanates readily underwent cyclotrimerization, despite the general difficulty in forming the π-coordinated intermediate of an alkyl isocyanate because of their poor electron-accepting properties [10b].

Paul and co-workers [10b] reported the Pd-catalyzed cyclotrimerization of Ar–NCO in the presence of diimines and



Scheme 5. Reactions of Pt(olefin)L_2 or platinacycle with Ar-NCO.



Scheme 8. Reactions of Pd(olefin)L_2 with Ar–NCO and Ar′–NCO.

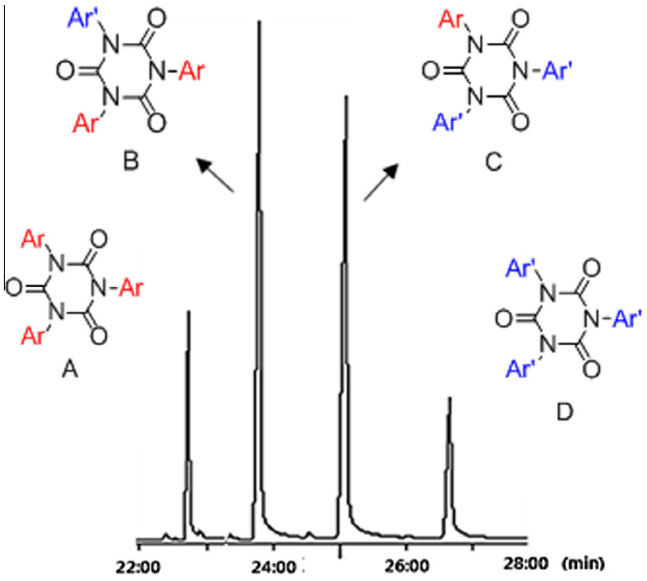


Fig. 4. GC–MS spectrum of cyclic trimers (A–D; Ar = phenyl, Ar′ = tolyl): injection temperature, 250 °C; oven temperature, 50–250 °C; helium (1.5 mL/min).

their theoretical calculations on mechanisms involving the metallacyclic or zwitterion [33]. Our results can be similarly explained by the following pathways. The isocyanurate formation may proceed in four steps: (i) the initial formation of a π-coordinated intermediate, [Pd(olefin)L_2], followed by the conversion to [Pd(R–NCO)L_2] or the formation of a zwitterionic intermediate, [Pd^+{$C(O)N^-R$}L_2], (ii) the subsequent cycloaddition of R–NCO to the five-membered metallacyclic intermediate, or the formation of a linear zwitterionic intermediate having a dimeric R–NCO unit, [Pd^+{$C(O)N^-R$}$_2L_2$], by the nucleophilic attack of the incoming R–NCO at [Pd^+{$C(O)N^-R$}L_2], (iii) the cycloaddition of R–NCO into the five-membered metallacycle to afford seven-membered palladacycle or the nucleophilic attack of R–NCO to give a linear zwitterionic Pd trimer of R–NCO, and (iv) the formation of a final isocyanurate by reductive elimination.

Interestingly, *trans*-[$PdEt_2(PR_3)_2$] complexes reacted with an allyl isocyanate to afford the corresponding isocyanato Pd(II) complexes, *trans*-[Pd(Et)(NCO)$(PR_3)_2$] in high yields (Eq. (2) in Scheme 7). The product formation seems to involve the π-coordination of the allylic double bond to the metal and β-H elimination of one of ethyl ligands, followed by the N–C bond cleavage of the coordinated allyl ligand. The isolated complexes, **12** and **13**, showed a strong absorption band at 2200 cm^{-1} because of the presence of NCO group. These ethyl Pd(II) isocyanato complexes were rather stable at room temperature, despite the presence of the ethyl ligand susceptible to β-H elimination.

To investigate the formation of various isocyanurate, the cross cyclotrimerization reactions were carried out at room temperature with a 1:1 mixture of Ar–NCO and Ar′–NCO (Scheme 8). The isolated product yields clearly indicate that the heteroaryl isocyanurates, B (composed of phenyl and *p*-tolyl isocyanates in 2:1 ratio) and C (phenyl and *p*-tolyl isocyanates in 1:2 ratio), formed in higher yields than the homoaryl (composed of all three phenyl or *p*-tolyl isocyanates) counterparts (A and D). When the cyclotrimerization is carried out with a mixture of phenyl and 4-methoxyphenyl isocyanates, a similar yield distribution is obtained.

One possible route (metallacyclic pathway) to a mixture of these products (A–D) shown in Scheme 8 has two steps: (i) the formation of a palladacyclic intermediate and (ii) the subsequent reductive elimination with an external aryl isocyanate forming an iaocyanurate. Therefore, the ratio of homo to heteroaryl isocyanurates depends on the ratio of amounts of the two palladacyclic intermediates and the external aryl isocyanate. Unfortunately, we could not isolate the heteroaryl isocyanurates (B and C). Several attempts to separate the heteroaryl isocyanurates failed even when column chromatography or HPLC was used, because of their

very similar solubility (one spot on the TLC). However, the product mixture could be analyzed by GC–MS. Fig. 4 clearly shows four distinct peaks assignable to the homo or heteroaryl isocyanurates.

3. Conclusion

In summary, new five-membered platinacycles containing an organic isocyanate dimer unit were obtained from bis(phosphine) Pt(0) complexes and alkyl or aryl isocyanate. When five-membered bis(phosphine) Pt(II) or Pd(II) metallacyclic complexes were treated with elemental sulfur, macrocyclic complexes (16-membered cyclic products) of palladacycle or platinacycle, $[M(PR_3)\{-N(R)C(O)N(R)C(O)-\}]_4$, containing a dimeric organic isocyanate unit were produced. These sulfur treatments are an effective synthetic route to such cyclic tetramers. An unexpected catalytic cyclotrimerization of aryl isocyanate was observed when the bis(phosphine) Pt(0) complexes or five-membered platinacycles were used. Furthermore, the direct cyclotrimerization of alkyl or aryl isocyanate with dialkyl Pt(II) or Pd(II) complexes occurred in moderate yields, probably depending on the phosphine ligands. In particular, the cross cyclotrimerization reactions with a 1:1 mixture of Ar–NCO and Ar′–NCO, catalyzed by $[Pd(styrene)(PMe_3)_2]$, showed that the heteroaryl isocyanurate is more favorable than the homoaryl isocyanurate.

4. Experimental

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 (Seoul) of Korea and at Kangnung-Wonju National University carried out elemental analyses. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained in $CDCl_3$ on a JEOL Lamda 300, ECA 600 MHz spectrometer. Chemical shifts were referenced to internal $SiMe_4$ 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. GC–MS spectra were analyzed by Agilent Technologies, 7890N/5975C-MSD and column HP-5MS ((5%)-diphenyl-(95%)-dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm). Complexes *trans*-$[PdEt_2L_2]$ (L = PMe_3 and PMe_2Ph) and *trans*-$[PtEt_2L_2]$ (L = PMe_3 and PMe_2Ph) were prepared by the literature method [34,35]. Complexes *cis*-$[Pd\{-N(Ar)C(O)N(Ar)C(O)-\}(PR_3)_2]$ (PR_3 = PMe_3, PMe_2Ph; Ar = *p*-methoxyphenyl, *p*-tolyl, *p*-chlorophenyl) were prepared by the literature method [24].

Cis-$[Pd\{-N(Ar)C(O)N(Ar)C(O)-\}(PMe_3)_2]$ (Ar = *p*-methoxyphenyl): *Anal.* Calc. for $C_{22}H_{32}N_2O_4P_2Pd$ (556.87): C, 47.45; H, 5.79; N, 5.03. Found: C, 47.55; H, 5.91; N, 5.13. IR (KBr/cm^{-1}): 1654, 1591 (CO). ^1H NMR ($CDCl_3$): δ 0.96 (d, 9H, J = 7.8 Hz, P(CH_3)$_3$), 1.56 (d, 9H, P(CH_3)$_3$), 3.75 (s, 6H, OMe), 6.65–6.99 (m, 4H, Ar), 7.08–7.30 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.6 (d, J = 19.1 Hz, P(CH_3)$_3$), 16.9 (d, J = 30.2 Hz, P(CH_3)$_3$), 55.6 (s, OMe), 55.8 (s, OMe), 113.4, 113.8, 128.2 (d, J = 1.8 Hz), 129.8, 132.2 (d, J = 3.8 Hz), 145.2 (d, J = 3.3 Hz), 156.0, 158.2 (Ar), 163.9 (CO), 184.3 (d, J = 157.9 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, at r.t.): δ −7.9 (s), −29.2 (s).

4.1. Synthesis of platinacycles (**1**–**3**)

Styrene (120 mg, 1.02 mmol) and toluene (3 cm^3) were added sequentially to a Schlenk flask containing *cis*-$[PtEt_2(PMe_3)_2]$ (207 mg, 0.51 mmol). The mixture was heated at 80 °C for 18 h to give a colorless solution. Benzyl Isocyanate (137 mg, 1.02 mmol) was added to the mixture at room temperature. After stirring for 3 h at room temperature, the volatiles were completely removed under vacuum, and then the remaining residue was solidified with CH_2Cl_2/diethyl ether to obtain a white solid. The crude solid was recrystallized from CH_2Cl_2/*n*-hexane to afford pure product of *cis*-$[Pt\{-N(R)C(O)N(R)C(O)-\}(PMe_3)_2]$ (R = $CH_2C_6H_5$) (**1**, 253 mg, 81%). *Anal.* Calc. for $C_{22}H_{32}N_2O_2P_2Pt$ (613.53): C, 43.07; H, 5.26; N, 4.57. Found: C, 43.35; H, 5.38; N, 4.09. IR (KBr/cm^{-1}): 1643, 1589 (CO). ^1H NMR ($CDCl_3$): δ 1.25 (d, 9H, J = 8.3 Hz, J_{Pt-H} = 17 Hz, P(CH_3)$_3$), 1.67 (d, 9H, J = 10.5 Hz, J_{Pt-H} = 33 Hz, P(CH_3)$_3$), 4.68 (s, 2H, CH_2), 5.06 (d, J = 3.6 Hz, J_{Pt-H} = 27 Hz, 2H, CH_2), 7.12–7.44 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.3 (d, J = 3.8 Hz, P(CH_3)$_3$), 17.8 (d, J = 16.7 Hz, P(CH_3)$_3$), 44.6 (s, CH_2), 53.5 (s, CH_2), 126.1, 126.3, 126.6, 128.2, 128.3, 128.4, 140.2, 143.6 (Ar), 168.0 (CO), 183.3 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −25.0 (d, J = 13.2 Hz, J_{Pt-P} = 1707 Hz), −23.9 (d, J = 15.4 Hz, J_{Pt-P} = 3375 Hz).

Complexes **2** and **3** were analogously prepared. Complex **2** (72%): *Anal.* Calc. for $C_{20}H_{26}N_2O_2Cl_2P_2Pt$ (653.36): C, 36.71; H, 4.00; N, 4.28. Found: C, 36.27; H, 4.00; N, 4.14. IR (KBr/cm^{-1}): 1720, 1663 (CO). ^1H NMR ($CDCl_3$): δ 1.12 (d, 9H, J = 8.4 Hz, J_{Pt-H} = 17 Hz, P(CH_3)$_3$), 1.74 (d, 9H, J = 10.5 Hz, J_{Pt-H} = 34 Hz, P(CH_3)$_3$), 7.18–7.36 (m, 8H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.5 (d, J = 28.4 Hz, P(CH_3)$_3$), 17.1 (dd, J = 39.3 Hz, J = 2.3 Hz, 2.9 Hz, P(CH_3)$_3$), 128.0, 128.6, 129.1, 129.2, 130.2, 132.4, 137.3, 150.5 (Ar), 164.3 (CO), 183.3 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −24.5 (d, J = 17.5 Hz, J_{Pt-P} = 1744 Hz), −23.3 (d, J = 17.6 Hz, J_{Pt-P} = 3410 Hz).

Complex **3** (66%): *Anal.* Calc. for $C_{22}H_{32}N_2O_4P_2Pt$ (645.53): C, 40.93; H, 5.00; N, 4.34. Found: C, 41.24; H, 5.11; N, 4.45. IR (KBr/cm^{-1}): 1654, 1588 (CO). ^1H NMR ($CDCl_3$): δ 1.09 (d, 9H, J = 8.4 Hz, J_{Pt-H} = 17 Hz, P(CH_3)$_3$), 1.73 (d, 9H, J = 10.2 Hz, J_{Pt-H} = 42 Hz, P(CH_3)$_3$), 3.76 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.67–7.31 (m, 8H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.5 (d, J = 27.2 Hz, P(CH_3)$_3$), 17.3 (dd, J = 37.6 Hz, J = 4.6 Hz, 4.3 Hz, P(CH_3)$_3$), 55.6 (s, OCH_3), 55.8 (s, OCH_3), 113.3, 113.9, 128.8, 129.8, 145.2, 156.4, 158.3, 163.4 (Ar), 175.6 (CO), 182.9 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.9 (d, J = 15.4 Hz, J_{Pt-P} = 1733 Hz), −23.5 (d, J = 15.4 Hz, J_{Pt-P} = 3386 Hz).

4.2. Synthesis of cis-[Pt{C(O)N(R)–C(O)N(R)}(DMPE)] (R = benzyl), **4**

DMPE (17 mg, 0.11 mmol) was added to a CH_2Cl_2 (2 cm^3) solution containing **1** (35 mg, 0.06 mmol) at room temperature. After stirring for 1 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue washed with hexane (2 cm^3 × 2) to obtain the crude solids. Recrystallization from diethyl ether afforded white crystals of *cis*-[Pt(DMPE){C(O)N(R)–C(O)N(R)}], (R = benzyl) (**4**, 31 mg, 89%). *Anal.* Calc. for $C_{22}H_{30}N_2O_2P_2Pt$ (611.51): C, 43.21; H, 4.94; N, 4.58. Found: C, 43.62; H, 4.65; N, 4.97. IR (KBr/cm^{-1}): 1639, 1589 (CO). ^1H NMR ($CDCl_3$): δ 0.968 (d, 6H, J = 8.7 Hz, J_{Pt-H} = 16.8 Hz, –P(CH_3)$_2$), 1.73 (d, 6H, J = 11.1 Hz, J_{Pt-H} = 35.7 Hz, –P(CH_3)$_2$), 1.806–1.524 (m, 4H, (CH_2)$_2$) 4.71 (s, 2H, CH_2), 5.28 (d, J = 3.9 Hz, J_{Pt-H} = 31.8 Hz, 2H, CH_2), 7.13–7.44 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.2 (d, J = 45.0 Hz, P(CH_3)$_2$), 12.2 (d, J = 37.5 Hz, P(CH_3)$_2$), 47.7 (s, CH_2), 52.2 (s, CH_2), 126.2, 126.3, 126.6, 128.2, 128.3, 128.5, 141.2, 143.1 (Ar), 165.4 (CO), 182.8 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.1 (d, J = 6.6 Hz, J_{Pt-P} = 1648 Hz), 18.5 (d, J = 6.6 Hz, J_{Pt-P} = 3188 Hz).

4.3. Reactions of **1** with elemental sulfur

Dichloromethane (3 cm^3) was added to a Schlenk flask containing **1** (57 mg, 0.09 mmol) and elemental sulfur (7 mg, 0.21 mmol). The initial colorless solution slowly turned to a dark red solution. After stirring for 3 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3 times) to yield crude solids. Recrystallization from CH_2Cl_2/diethyl ether gave white crystals of **5** (17 mg, 37%). *Anal.* Calc. for $C_{76}H_{92}N_8O_8P_4Pt_4$ (2149.80): C, 42.46; H, 4.31; N, 5.21.

Found: C, 42.51; H, 4.38; N, 5.23. IR (KBr/cm^{-1}): 1647, 1566 (CO). ^{1}H NMR ($CDCl_3$): 0.92 (d, 36H, J = 11.1 Hz, P(CH_3)$_3$), 2.54 (d, 4H, J = 15.6 Hz, CH_2), 4.05 (d, 4H, J = 15.6 Hz, CH_2), 4.74 (d, 4H, J = 17.1 Hz, CH_2), 6.98 (d, 4H, J = 6.9 Hz CH_2), 7.13–7.41 (m, 40H, Ar). ^{31}P{^{1}H} NMR ($CDCl_3$): −14.8 (s, J_{Pt-P} = 3990 Hz). TOF-MS(ES +): calcd for [M+H]$^+$: 2149.4658; found: 2149.0176. ^{13}C{^{1}H} NMR spectrum could not be measured because of its poor solubility.

4.4. Reactions of palladacyclic complexes with elemental sulfur

Dichloromethane (5 cm^3) was added to a Schlenk flask containing *cis*-[Pd{–N(Ar)C(O)N(Ar)C(O)–}(PMe_3)$_2$] (Ar = *p*-MeOC_6H_4) (284 mg, 0.51 mmol) and elemental sulfur (36 mg, 1.12 mmol). The initial orange solution slowly turned to a homogeneous dark red solution. After stirring for 3 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3 times) to yield crude solids. Recrystallization from CH_2Cl_2/diethyl ether gave white crystals of **6** (74 mg, 42%). *Anal.* Calc. for $C_{76}H_{92}N_8O_{16}P_4Pd_4$ (1923.16): C, 47.46; H, 4.82; N, 5.83. Found: C, 47.29; H, 4.89; N, 5.82. IR (KBr/cm^{-1}): 1654, 1563 (CO). ^{1}H NMR ($CDCl_3$): δ 1.02 (d, 36H, J = 10.2 Hz, P(CH_3)$_3$), 3.81 (s, 12H, OMe), 3.85 (s, 12H, OMe), 6.39 (br, 4H, Ar), 6.73–6.93 (m, 24H, Ar), 7.26 (br, 4H, Ar). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.3(d, J = 29.0 Hz, P(CH_3)$_3$), 55.7 (s, OMe), 56.0 (s, OMe), 113.5, 121.3, 130.5, 131.9, 133.6, 137.5, 156.7, 158.3 (Ar), 161.7 (CO), 173.8 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −5.5. TOF-MS (ES$^+$): calcd for [M +H]$^+$: 1921.1799; found: 1921.1095.

Analogous reactions of *cis*-[Pd{–N(Ar)C(O)N(Ar)C(O)–}(PR_3)$_2$] (Ar = *p*-tolyl or *p*-chlorophenyl) by elemental sulfur gave corresponding cyclic tetramers **7** and **8**, respectively. Complex **7** (28%): *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, 50.82; H, 5.26; N, 6.28. IR (KBr/cm^{-1}): 1655, 1560 (CO). ^{1}H NMR ($CDCl_3$): δ 1.01 (d, 36H, J = 5.1 Hz, P(CH_3)$_3$), 2.40 (s, 12H, CH_3), 2.42 (s, 12H, CH_3), 6.55 (d, 4H, J = 3.6 Hz, Ar), 6.75 (d, 4H, J = 3.6 Hz, Ar), 6.79 (d, 8H, J = 4.2 Hz, Ar), 7.17 (d, 4H, J = 3.9 Hz, Ar), 7.21 (d, 8H, J = 3.9 Hz, Ar), 7.35 (d, 4H, J = 3.6 Hz, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.3 (d, J = 14.6 Hz, P(CH_3)$_3$), 21.6, (s, CH_3), 21.9, (s, CH_3), 127.1, 129.0, 129.4, 129.8, 132.8, 136.3, 136.6, 142.2 (Ar), 162.0 (CO), 173.6 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.7. TOF-MS(ES$^+$): calcd for [M+H]$^+$: 1793.2206; found: 1793.1477.

Complex **8** (34%): *Anal.* Calc. for $C_{88}H_{76}N_8O_8Cl_8P_4Pd_4$ (2206.79): C, 47.89; H, 3.47; N, 5.08. Found: C, 47.74; H, 3.42; N, 5.09. IR (KBr/cm^{-1}): 1655, 1560 (CO). ^{1}H NMR ($CDCl_3$): δ 1.29 (d, 12H, J = 10.2 Hz, P(CH_3)$_2$Ph), 1.42 (d, 12H, J = 10.2 Hz, P(CH_3)$_2$Ph), 6.57–7.44(m, 52H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.9 (d, J = 32.9 Hz, P(CH_3)$_2$Ph), 14.2 (d, J = 27.6 Hz, P(CH_3)$_2$Ph), 128.5, 128.6, 128.7, 130.2, 130.9, 130.9, 131.0, 133.1, 135.0, 135.0, 137.0, 142.3 (Ar), 161.4 (CO), 170.6 (d, J = 10.4 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 2.3(s). TOF-MS(ES$^+$): calcd for [M+Na]$^+$: 2222.8281; found: 2223.0322.

4.5. Reactions of cyclic tetramers (**5** and **6**) with tert-butyl isocyanide

tert-Butyl isocyanide (9 mg, 0.11 mmol) was added to a CH_2Cl_2 (2 cm^3) solution containing **5** (59 mg, 0.027 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 cm^3 × 3) to obtain the crude solids. Recrystallization from THF/(diethyl ether) afforded white crystals of [Pt(PMe_3)(CN–^{t}butyl){C(O)N(R)–C(O)N(R)}], (R = $CH_2C_6H_5$) (**9**, 67 mg, 98%). *Anal.* Calc. for $C_{24}H_{32}N_3O_2P_1Pt$ (620.58): C, 46.45; H, 5.20; N, 6.77. Found: C, 46.56; H, 5.34; N, 6.60. IR (KBr/cm^{-1}): 1646, 1595 (CO), 2194 (NC). ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H, C(CH_3)$_3$), 1.67 (d, 9H, J = 10.8 Hz, J_{Pt-H} = 35 Hz P (CH_3)$_3$), 4.65 (s, 2H, CH_2), 5.17 (d, J = 5.4 Hz, J_{Pt-H} = 37 Hz, 2H, CH_2), 7.11–7.40 (m, 10H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.0 (d, J = 40.1 Hz, P(CH_3)$_3$), 29.7 (s, C(CH_3) $_3$), 44.4 (s, CH_2), 54.4 (s, CH_2) 68.1 (s, C(CH_3) $_3$), 125.9, 126.2, 126.4, 128.1, 128.1, 128.2, 140.2, 143.3 (Ar), 155.1 (NC), 167.1 (CO), 180.7 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −23.8(s, J_{Pt-P} = 3212 Hz).

Complex [Pd(PMe_3)(CN–^{t}butyl){C(O)N(Ar)–C(O)N(Ar)}], (Ar = *p*-OMeC_6H_4), **10** was analogously prepared. Complex **10** (96%): *Anal.* Calc. for $C_{24}H_{36}N_3O_6P_1Pd$ (599.95): C, 48.05; H, 6.05; N, 7.00. Found: C, 48.47; H, 5.59; N, 6.79. IR (KBr/cm^{-1}): 1659, 1604 (CO), 2198 (NC). ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 9H, C(CH_3)$_3$), 1.53 (d, 9H, J = 10.2 Hz, P(CH_3)$_3$), 3.75 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.78–6.86 (m, 4H, Ar), 7.13–7.24 (m, 4H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.9 (d, J = 30.8 Hz, P(CH_3)$_3$), 29.7 (s, C(CH_3) $_3$), 55.6 (s, OCH_3), 55.9 (s, OCH_3), 68.2 (s, C(CH_3) $_3$), 113.5, 113.8, 128.3, 129.8, 132.0, 145.5, 155.7, 158.1 (Ar), 163.8 (NC), 183.0 (CO), 207.3 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −7.6.

4.6. Reactions of bis(phosphine) metallacycles with with tert-butyl isocyanide

tert-Butyl isocyanide (21 mg, 0.25 mmol) was added to a CH_2Cl_2 (2 cm^3) solution containing **1** (139 mg, 0.23 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 cm^3 × 3) to obtain the crude solids. Recrystallization from CH_2Cl_2/diethyl ether afforded white crystals of **9** (142 mg, 99%). Complex **10** (93%) was similarly obtained. Spectroscopic data of the above products coincided with those in the cleavage reactions.

4.7. Reactions of Pt(olefin)(PR_3)$_2$ or platinacycles with aryl isocyanate

Styrene (65 mg, 0.62 mmol) and tetrahydrofuran (toluene, 3 cm^3) were added sequentially to a Schlenk flask containing *cis*-[$PtEt_2$(PMe_2Ph)$_2$] (164 mg, 0.31 mmol) at room temperature. The mixture was heated at 80 °C for 18 h to give a pale yellow solution. *p*-Chlorophenyl isocyanate (95 mg, 0.62 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 extracted with excess diethyl ether. The collected extracts were evaporated under vacuum to give crude organic products. The organic products were purified by chromatography over silica gel, eluting with ethyl acetate/hexane (1:3). The collected organic products recrystallized from excess diethyl ether at room temperature to afford white solids of *p*-chlorophenyl isocyanurate, (Ar–NCO)$_3$ (Ar = *p*-ClC_6H_4) (87 mg, 91%). The remaining solid, **11**, was characterized by IR and NMR spectroscopy. Complex **11**: IR (KBr/cm^{-1}): 1719, 1690 (CO). ^{1}H NMR ($CDCl_3$): δ 0.83 (d, 6H, J = 8.4 Hz, P(CH_3)$_2$Ph), 1.76 (d, 6H, J = 11.1 Hz, P(CH_3)$_2$Ph), 7.02–7.48 (m, 18H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.5 (d, J = 26.6 Hz, P(CH_3)$_2$Ph), 15.3 (d, J = 18.5 Hz, P(CH_3)$_2$Ph), 128.0, 128.5, 128.6, 128.7, 128.8, 129.1, 129.3, 129.4, 130.2, 130.3, 130.4, 130.5, 130.7, 130.8, 131.9, 148.3 (Ar), 166.5 (CO), 183.8 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −14.3 (d, J = 13.0 Hz, J_{Pt-P} = 1794 Hz), −11.7 (d, J = 19.4 Hz, J_{Pt-P} = 3504 Hz). We could not obtain pure analytical data due to the presence of isocyanurate.

Analogous reaction with *p*-tolyl isocyanate was performed. *p*-Tolyl isocyanurate (Ar–NCO)$_3$ (Ar = *p*-MeC_6H_4) was obtained in 90% yield.

p-Chlorophenyl isocyanate (0.074 g, 0.48 mmol) was added to a THF (3 cm^3) solution containing **2** (0.055 g, 0.08 mmol) at room temperature. After stirring the reaction mixture for 18 h at 55 °C temperature, the solvent was completely removed under vacuum, and then the resulting residue extracted with excess diethyl ether to afford white solids. The collected extracts were evaporated

under vacuum to give crude organic products. The organic products were purified by chromatography over silica gel, eluting with ethyl acetate/hexane (1:3). The final product, p-chlorophenyl isocyanurate (Ar–NCO)$_3$ (Ar = *p*-ClC$_6$H$_4$) was obtained in 98% yield.

Analogous reaction of **3** with *p*-methoxyphenyl isocyanate was performed. *p*-Methoxyphenyl isocyanurate (Ar–NCO)$_3$ (Ar = *p*-OMeC$_6$H$_4$) was obtained in 98% yield.

4.8. Reactions of dialkyl Pt(II) complexes with organic isocyanate

Phenyl isocyanate (71 mg, 0.60 mmol) was added to a THF (5 cm^3) solution containing *cis*-[PtEt$_2$(PMe$_2$Ph)$_2$] (158 mg, 0.30 mmol) at room temperature. The mixture was heated at 55 °C for 18 h to give a pale yellow solution. The solvent was completely removed under vacuum, and then the resulting residue extracted with excess diethyl ether to afford white solids. The collected extracts were evaporated under vacuum to give crude organic products. The organic products were purified by chromatography over silica gel, eluting with ethyl acetate/hexane (1:3). The final product, (Ar–NCO)$_3$ (Ar = C$_6$H$_5$), was obtained in 72% yield. The remaining solid was analyzed by ^{1}H and ^{31}P{^{1}H} NMR spectra.

Similar reactions of *p*-chlorophenyl or benzyl isocyanate with *cis*-[PtEt$_2$(PMe$_3$)$_2$] or *cis*-[PtEt$_2$(PEt$_3$)$_2$] were performed. Organic isocyanurates, (R–NCO)$_3$ (R = *p*-ClC$_6$H$_4$, 33%; C$_6$H$_5$, 14%; R = benzyl, 58%), were obtained, respectively.

4.9. Reactions of dialkyl Pd(II) complexes with organic isocyanate

Tetrahydrofuran (4 cm^3) was added to a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (73 mg, 0.23 mmol) and benzyl isocyanate (61 mg, 0.46 mmol) at 0 °C. After stirring for 18 h at room temperature, the volatiles were completely removed under vacuum, and then the remaining residue was extracted with excess diethyl ether. The collected extracts were evaporated under vacuum to give crude organic products.

The organic products were purified by chromatography over silica gel, eluting with ethyl acetate/hexane (1:3). The final product, (R–NCO)$_3$ (R = benzyl), was obtained in 32% yield.

Analogous reactions with phenyl or *p*-chlorophenyl isocyanate with *trans*-[PtEt$_2$(PMe$_3$)$_2$] or *trans*-[PtEt$_2$(PMe$_2$Ph)$_2$] were performed. Organic isocyanurates, (Ar–NCO)$_3$ (Ar = *p*-ClC$_6$H$_4$, C$_6$H$_5$), were obtained in 39–58% yields.

4.10. Reactions of dialkyl Pd(II) complexes with allyl isocyanate

THF (5 cm^3) was added to a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (410 mg, 1.29 mmol) and allyl isocyanate (215 mg, 2.59 mmol) at 0 °C. The initial colorless solution slowly turned to yellow solution. After stirring for 18 h at room temperature, the volatiles were completely removed under vacuum, then the remaining residue was solidified with a diethyl ether (2 cm^3), washed with *n*-hexane (2 cm^3 × 2) to afford white solids. Complex **12** (410 mg, 80%): *Anal.* Calc. for C$_9$H$_{23}$NOP$_2$Pd (329.65): C, 32.79; H, 7.03; N, 4.24. Found: C, 32.44; H, 6.97; N, 4.19. IR (KBr/cm^{-1}): 2211 (NCO). ^{1}H NMR (CDCl$_3$): δ 0.98–1.06 (m, 5H, C*H*$_2$C*H*$_3$), 1.40 (t, 18H, J = 3.2 Hz, P(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 4.9 (br, *C*H$_2$), 13.5 (t, J = 13.9 Hz, P(*C*H$_3$)$_3$), 16.1 (s, *C*H$_3$), 100.6 (s, NCO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −14.9.

Complex **13** (92%) was analogously prepared. Complex **13**: *Anal.* Calc. for C$_{19}$H$_{27}$NOP$_2$Pd (453.79): C, 50.28; H, 5.99; N, 3.08. Found: C, 50.17; H, 5.98; N, 3.19. IR (KBr/cm^{-1}): 2202 (NCO). ^{1}H NMR (CDCl$_3$): δ 0.62 (m, 3H, C*H*$_3$), 0.92 (m, 2H, *CH*$_2$), 1.71 (s, 12H, P(C*H*$_3$)$_2$), 7.26–7.66 (m, 10H, Ar). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 6.9 (br, *C*H$_2$), 12.5 (t, J = 13.9 Hz, P(*C*H$_3$)$_2$Ph), 15.6 (s, *C*H$_3$), 128.4 (s, Ar), 128.6 (t, J = 4.6 Hz, Ar), 129.9 (s, Ar), 131.1 (t, J = 6.2 Hz, Ar) 134.6 (s, NCO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −3.5.

4.11. The cross cyclotrimerization of aryl isocyanate

Styrene (79 mg, 0.76 mmol) and THF (3 cm^3) were added sequentially to a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (120 mg, 0.38 mmol) at 0 °C. The mixture was heated at 55 °C for 30 min to give a pale yellow solution. *p*-Tolyl isocyanate (151 mg, 1.13 mmol) and phenyl isocyanate (135 mg, 1.13 mmol) were dissolved in THF (2 cm^3) and then transferred to the solution at room temperature. After stirring for 3 h at room temperature, the volatiles were completely removed under vacuum, and then the remaining residues were extracted with excess ethyl acetate. The collected extracts were evaporated under vacuum to give crude organic products. The remaining residues were analyzed by NMR spectroscopy. The organic products were purified by chromatography over silica gel, eluting with ethyl acetate/hexane (1:1 to 1:3). The isolated organic product was analyzed by GC–MS.

The cross cyclotrimerization with *p*-methoxyphenyl isocyanate and phenyl isocyanate carried out analogously.

4.12. Crystallography

Single crystals of **4**, **9**, and **10** for X-ray crystallography were grown from CH$_2$Cl$_2$/*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 [36]. All calculations were carried out with SHELXTL programs [37]. All structures were solved by direct methods. Unless otherwise stated, all nonhydrogen 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.

Acknowledgments

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). K.-Y. Jung also thanks the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology for financial support (Grant No.: 2011-0010745).

Appendix A

CCDC 1455962–1455964 contain the supplementary crystallographic data for compounds **4**, **9**, and **10**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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