

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



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ABSTRACT

The reactions of [Pt(styrene)(PMe₃)₂] with 2 equiv. of alkyl or aryl isocyanate afforded five-membered platinacycles, *cis*-[Pt{–N(R)C(O)N(R)C(O)–}(PMe₃)₂] (R = CH₂C₆H₅, *p*-ClC₆H₄, *p*-OMeC₆H₄). 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(PR₃){–N(R)C(O)N(R)C(O)–}]₄, were readily obtained. These cyclic tetramers were cleaved using *tert*-butyl isocyanide (CN-^tbutyl, 4 equiv.), affording the corresponding monomeric complexes, [M(PR₃)(CN-^tbutyl){–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.

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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)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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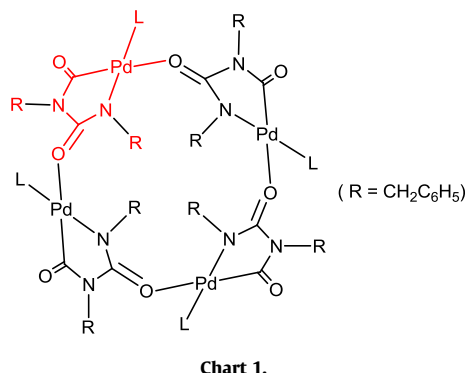


Chart 1.

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)(PMe₃)₂], generated from *cis*-[PtEt₂(PMe₃)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)L₂] were used (Scheme 1).

Two PMe₃ ligands in complex 1 were readily replaced with a chelating phosphine (DMPE), affording a five-membered platinacycle (4) in a good yield. The ¹H-NMR spectra of five-membered platinacycles 1–3 showed two doublets with Pt satellites in the PMe₃ region, and the ³¹P{¹H}-NMR spectra also showed two doublets with the corresponding satellites, indicating that *cis*-Pt(II) complexes contain magnetically inequivalent PMe₃ 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.

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(PMe₃){-N(R)C(O)N(R)C(O)}₄, (R = CH₂C₆H₅) (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.

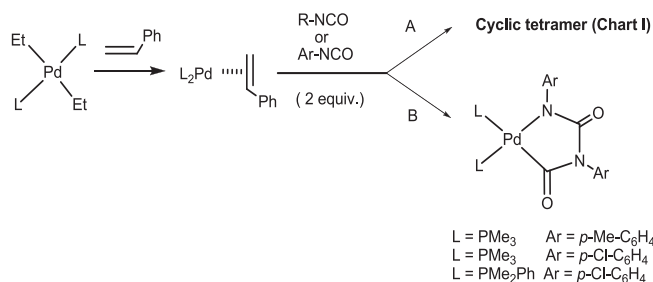
When the same synthetic strategy was applied to several palladacycles, the corresponding Pd cyclic tetramers (6–8) were obtained as white solids in 28–42% yields. Excessive elemental sulfur has been used to make the reaction go to completion, but the relatively low actual yields may be attributed to 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 PMe₃ with satellites at δ 1.25 and 1.67 ppm in the ¹H-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 ³¹P{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 PMe₃ region in the starting *cis*-palladacycles (Ar = *p*-MeOC₆H₄, *p*-MeC₆H₄) became a doublet in the ¹H-NMR spectra of complexes 6 and 7 as expected. Interestingly, in the ¹H-NMR spectrum of complex 8, the methyl group in PMe₂Ph appeared as two doublets at δ 1.38 and 1.42 ppm, which contrast with those in PMe₃ analogs, are also shifted to lower field compared with those in the starting complex, *cis*-[Pd{-N(Ar)C(O)N(Ar)C(O)-}(PMe₂Ph)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(CH₃)₂Ph are chemically inequivalent. The ³¹P{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-^tBu 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 ³¹P{¹H} NMR spectra of 9 and 10 showed a singlet. The monomeric units (metallacycle)

Scheme 1. Reactions of Pd(styrene)₂ with organic isocyanate.

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