Copolymerization of Aziridines and Carbon Monoxide Catalyzed by a Heterodinuclear Organopalladinum–Cobalt Complex

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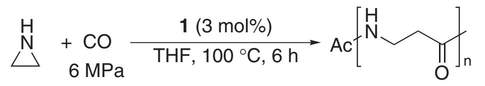
Heterodinuclear organopalladium–cobalt complex having a 2,2′-bipyridine ligand (bpy)AcPd–Co(CO)$_4$ catalyzes copolymerization of unsubstituted and both *C*- and *N*-monosubstituted aziridines, such as aziridine, 2-methylaziridine, and *N*-ethylaziridiene, and CO (3–6 MPa) in THF at 100 °C for 6 h.

Cooperative effect of different transition metals is one of the most intriguing unsolved subjects both in homo- and heterogeneous catalyses and needs to be understood at a molecular level.[1] We previously reported the synthesis and reactions of heterodinuclear organometallic complexes having both M–M′ and M–C bonds, $L_nRM–M'L_m$ (M = Pt, Pd; M′ = Mo, W, Co, Fe, Mn, Re; R = Me, Et, Ph, H, Ac; L = cod, dppe, bpy; L′ = Cp, CO).[2] Remarkable results are organic group migration along different metals, enhanced CO insertion into Pd (or Pt)–C bond, selective and controlled ring-opening reactions of thiiranes and thietanes, etc., which are probably arisen from the cooperative effect of different metals. An application of these heterodinuclear complexes to efficient catalyst for carbonylation of thietanes giving thiobutyrolactones is also notable one.[3] Extension of these substrates to *N*-containing three-membered heterocycles led us to find copolymerization of aziridine and CO giving poly-β-peptides. Though cobalt complex-catalyzed copolymerization of aziridines and CO has recently been developed by Jia et al.,[4] only unsubstituted and *N*-alkyl aziridines were reported to be copolymerized. As regards polypeptide synthesis, polymerization of *C*-substituted aziridines such as alkenylimines promises to expand this field extensively giving fruitful chemical and biological applications. We now report copolymerization of aziridines and CO catalyzed by organopalladium–cobalt heterodinuclear complexes with 2,2′-bipyridine ligand.

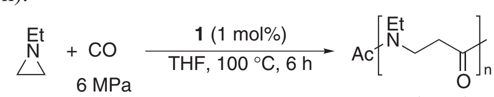
When aziridine was heated to 100 °C under 6 MPa of CO in THF for 6 h in the presence of 3 mol % of (bpy)AcPd–Co(CO)$_4$ (**1**),[2i] copolymerization of aziridine and CO proceeded to give water-soluble orange powder in good yield. IR and NMR spectra of the resulted copolymer are consistent with those of poly-β-alanine reported by Jia[4a,4c] (Eq 1).



89% (n=16)

(1)

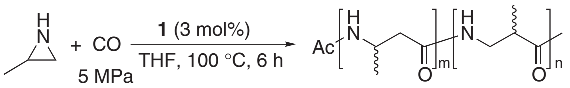
IR spectrum of the copolymer shows two prominent amide bands at 1649 and 1551 cm^{-1}. In the ^{1}H NMR, the two methylene protons appear as two broad signals at δ 3.27 and 2.74.[4] A resonance at δ 1.80 is assigned to the acetyl end group of the copolymer, which originates from the acetyl group of (bpy)AcPd–Co(CO)$_4$ (**1**). The degree of polymerization was estimated to be ca. 16.[5] **1** also catalyzed the copolymerization of *N*-ethylaziridine and CO[4b] as shown in Eq 2. The catalytic activity of **1** was found to be comparable to that of Jia's catalyst CoAc(CO)$_3$(PPh$_3$) (**2**) (Yield of copolymer of aziridine and CO: 100%, Cat.: **2** (3 mol %), CO: 5 MPa, THF, 100 °C, 6 h) and Co(COBn)(CO)$_4$ (**3**) (Yield of copolymer of *N*-ethylaziridine and CO: 88%, Cat.: **3** (3 mol %), CO: 7 MPa, dioxane, 60 °C, 6 h).[4b]



69% (n=75)

(2)

When 2-methylaziridine was used as a reactant, the copolymer was also obtained in 81% yield, though the resultant copolymer was consisted of regio- and stereo-isomeric mixtures (Eq 3).[6] 3-Methyl-β-alanine units were dominantly incorporated than 2-methyl-β-alanine (3-methyl : 2-methyl = 2.4:1.0) in the copolymer, indicating the preferential ring-opening at the less hindered C-N bond. The result is consistent with S$_N$2 type ring-opening reaction of coordinated aziridine. Analogous trend has also been observed in the ring-opening reactions of thiirane promoted by heterodinuclear organoplatinum complexes.[3]

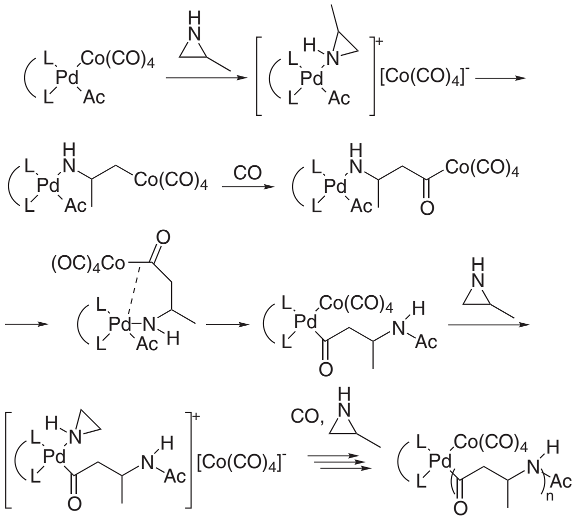


81% (m+n =15)

(3)

Approximate degree of polymerization was 15.[5] Catalytic activity of **1** (Yield: 71%, Cat.: **1** (1 mol %), CO: 5 MPa, THF, 100 °C, 6 h) was much higher than that of CoAc(CO)$_3$(PPh$_3$) (yield: <11%, Cat.: **2** (1 mol %), CO: 5 MPa, THF, 100 °C, 6 h) or Co(COBn)(CO)$_4$ (yield: 21%, Cat.: **3** (1 mol %), CO: 5 MPa, THF, 100 °C, 6 h) for this copolymerization propyleneimine and CO. When corresponding mononuclear palladium(II) complexes such as [PdMe(MeCN)(bpy)]$^+$[BF$_4$]$^-$ (**4**) and the anionic cobalt complex [PPN]$^+$[Co(CO)$_4$]$^-$ (**5**), were used as catalysts, the homopolymer of propyleneimine was exclusively obtained. It is interesting to note that the heterodinulcear Pd-Mo complexes (bpy)PhPd-MoCp(CO)$_3$ (**6**) did not catalyze this copolymerization. These results suggest that the presence of Pd-Co bond plays an important synergistic role in this catalytic copolymerization.

A plausible mechanism of this catalytic reaction is proposed as shown in Scheme 1. The first step of the catalytic cycle is considered to be coordination of aziridine to palladium, which is formed by heterolytic cleavage of the Pd–Co bond, giving [PdAc(aziridine-κN)(bpy)]$^+$[Co(CO)$_4$]$^-$. Then the [Co(CO)$_4$]$^-$ anion attacks the less-substituted carbon of the coordinated aziridine to cause C-N bond cleavage giving the dinuclear complex (bpy)AcPd–NCHMeCH$_2$–Co(CO)$_4$, followed by facile insertion of CO into the cobalt-carbon bond. Analogous heterolytic cleavage of Pd–Co bond and coordination of the substrate followed by S_N2 type ring-opening reaction has been shown in the reactions of these heterodinuclar organoplatinum complexes with thiiranes, supporting these processes.[2h] Then facile CO insertion into Co–C bond takes place to give (acyl)(amido)palladium-cobalt complex. Failure of copolymerization by **6** may be due to very slow CO insertion process into Mo-C bond.[3] Similar trend is also observed in the carbonylation of thietane catalyzed by (dppe)-RPt–Co(CO)$_4$.[3] Reductive elimination of the amido and acyl ligands at Pd may be promoted by interaction of Co–C bond with Pd, leading to oxidative addition giving (acyl)Pd–Co dinuclear complex. Repetition of this process gives the alternating copolymer. Another possible mechanism involving monometallic cationic intermediates as proposed by Jia is not excluded at present, though the role of Pd is difficult to be interpreted.



Scheme 1. A possible mechanism for copolymerization.

In conclusion, organopalladium–cobalt heterodinucler complexes are shown to catalyze copolymerization of unsubstituted and both *C*- and *N*-substituted aziridines under mild conditions. Elucidation of the origin of this cooperative effect in this reaction and the scope and limitation including application toward regio- and stereo-selective synthesis of poly-β-peptides are the future important applications.

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5 Numbers of repeating units of the polymers were determined using the integral ratio of the methyl peaks of the acetyl end group and the methylene and/or methine peaks of the repeating units.

6 The structure of copolymer of 2-methylaziridine with CO was characterized spectroscopically, by use of ^{1}H-^{1}H COSY. The NMR spectra of the resulted copolymer are consistent with regio- and stereo-isomeric mixtures containing of the two kinds of 3-methy-β-alanine units and 2-methy-β-alanine unit (ratio: ca 1.0:0.2:0.5). ^{1}H NMR (300 Hz, D_2O): δ 0.931 (brs, NHCH$_2$CHMeCO), 1.00 (brs, NHCHMeCH$_2$CO), 1.14 (brs, NHCHMeCH$_2$CO), 1.80 (brs, COCH$_3$), 2.20 (brs, NHCHMeCH$_2$CO), 2.39 (brs, NHCHMeCH$_2$CO and NHCH$_2$CHMeCO), 3.10 (brs, NHCH$_2$CHMeCO), 3.49 (brs, NHCHMeCH$_2$CO), 4.02 (brs, NHCHMeCH$_2$CO).

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