

Synthesis and reactions of heterodinuclear organopalladium–cobalt complexes acting as copolymerization catalyst for aziridine and carbon monoxide

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Abstract

A series of heterodinuclear acylpalladium–cobalt complexes having a bidentate nitrogen ligand, $L_2(RCO)Pd-Co(CO)_4$ ($L_2 = bpy$, $R = Me$ (**5**), Ph (**6**); $L_2 = tmeda$, $R = Me$ (**7**), Ph (**8**); $L_2 = phen$, $R = Me$ (**9**), Ph (**10**)) are prepared by metathetical reactions of $PdRIL_2$ with $Na^+[Co(CO)_4]^-$ followed by treatment with CO. These complexes are characterized by NMR and IR spectroscopies and elemental analyses, and the molecular structures of **6**, **8**, and **9** are determined by X-ray structure analysis. Geometry at Pd is essentially square planar and the Co atom is considered to have d^{10} tetrahedral structure, where cobalt(-I) anion coordinates to palladium(II) cation. Heterodinuclear organopalladium–cobalt complexes are shown to catalyze copolymerization of aziridines and CO under mild conditions. Reaction of $(dppe)MePd-Co(CO)_4$ (**1**) with aziridine gives a cationic (aziridine)palladium(II) complex with $[Co(CO)_4]^-$ anion, $[PdMe(aziridine)(dppe)]^+[Co(CO)_4]^-$ (**13**).

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1. Introduction

Heterodinuclear complexes and heterometallic clusters have attracted much attention due to cooperative effect of different metal centers [1]. We have reported the synthesis and reactions of heterodinuclear organometallic complexes having both M–M' and M–C bonds, $L_2RM-M'L_n$ ($M = Pt, Pd$; $M'L_n = MoCp(CO)_3, WCp(CO)_3, Mn(CO)_5, Re(CO)_5, FeCp(CO)_2, Co(CO)_4$; $R = alkyl, aryl, acyl, H$; $L_2 = cod, dppe, tmeda, bpy, phen$) [2], some of which show remarkable reactions based on cooperative effect of two metals such as organic group migration along different metals [2a,2c,2d,2i], enhanced CO insertion into M–C bond [2f,2j], and selective ring-opening reactions of thiranes

[2h]. Catalytic carbonylation of thietanes giving thiobutyrolactones [3a] and copolymerization of aziridines and CO promoted by heterodinuclear organopalladium–cobalt complexes [3b] are notable applications to catalysis. We wish to report details of the synthesis and reactions of heterodinuclear organopalladium–cobalt complexes as well as copolymerization of aziridines and carbon monoxide catalyzed by these complexes.

2. Results and discussion

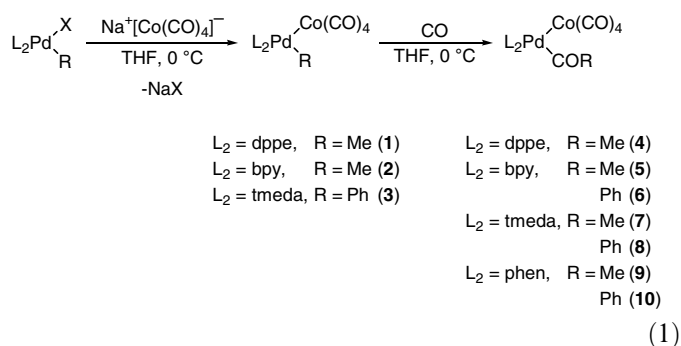
2.1. Synthesis and structure of heterodinuclear organopalladium–cobalt complexes

Methylpalladium–cobalt complexes with 1,2-bis(diphenylphosphino)ethane (dppe) ligand, $(dppe)MePd-Co(CO)_4$ (**1**) was prepared by the metathesis reaction

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of PdMe(NO₃)(dppe) with corresponding metalate anions Na⁺[Co(CO)₄]⁻ as reported previously [2f,2j]. Acetyl complex (dppe)(MeCO)Pd–Co(CO)₄ (**4**) was prepared by the reaction of **1** with CO. However, analogous preparations of organopalladium–cobalt derivatives with nitrogen ligands such as 2,2'-bipyridine (bpy), *N,N,N',N'*-tetramethylethylenediamine (tmeda) and 1,10-phenanthroline (phen) ligand always gave mixtures of alkyl (or aryl) and acyl complexes or acyl complexes contaminated with unseparable materials, resigning isolation of the pure compounds. Probably CO, which was produced by partial decomposition of tetracarbonylcobalt anion, is considered to insert into the Pd–C bond. In fact, under carbon monoxide atmosphere, pure acylpalladium–cobalt complex, L₂(RCO)Pd–Co(CO)₄ (L₂ = bpy, R = Me (**5**), Ph (**6**); L₂ = tmeda, R = Me (**7**), Ph (**8**); L₂ = phen, R = Me (**9**), Ph (**10**)) was obtained by the reactions of PdRIL₂ with anionic cobalt complex Na⁺[Co(CO)₄]⁻ in THF (Eq. (1)). These acetyl derivative can also be prepared by oxidative addition of Co(CO)Me(CO)₄ to Pd(dba)₂ in the presence of the corresponding ligands [2i].



These dinuclear acylpalladium–cobalt complexes (**5–10**) were characterized by ¹H NMR and IR spectroscopies and elemental analysis as well as by X-ray structure analysis. Selected IR and ¹H NMR data of newly prepared compounds **6**, **8**, and **10** are summarized in Table 1. IR spectra of these acyl complexes display strong ν(C=O) bands due to the PdCOR group at 1650 cm⁻¹ and a few strong ν(C≡O) bands at 1880–2000 cm⁻¹ whose frequencies are close to the broad peak due to anionic metal carbonyls Na⁺[Co(CO)₄]⁻, suggesting valency of the Co center close to Co(-I).

Molecular structures of the acylpalladium–cobalt complexes having bidentate nitrogen ligand, L₂(RCO)Pd–Co(CO)₄ (L₂ = bpy, R = Ph (**6**); L₂ = tmeda, R = Ph (**8**); L₂ = phen, R = Me (**9**)) were determined by X-ray structure analysis. The crystallographic data and selected bond distances and angles are summarized in Tables 2 and 3, respectively, and ORTEP drawings are depicted in Fig. 1. All Pd–Co bond distances (ca. 2.6 Å) are in a typical range of the Pd–Co single bond and similar to that for (py)(PhHNHN=CMeC₆H₄)Pd–Co(CO)₄ (py = pyridine, 2.604(1) Å) [4a], but shorter than that for (Me₃P)₂(PhCO)Pd–Co(CO)₄ (2.7856(7) Å) [4b] and (dppe)MePd–Co(CO)₄ (2.682(7) Å) [2f,2j]. The geometry at Pd is essentially square planar, where Co and the acyl groups are bonded to Pd in a cis fashion. The Co atom is considered to have *d*¹⁰ tetrahedral structure, where cobalt(-I) anion coordinates to palladium(II) cation. Though two carbonyl ligands in these complexes lie close to Pd atom, they are not considered to be bridging carbonyls, since the Co–C–O angles are more than 170°. However one of the C–Co–C angles (ca. 130°) is significantly larger than the ideal tetrahedral angle of 109° (Table 3), suggesting strong steric repulsion between ligands at Pd and Co moieties. On the other hand,

Table 1
Selected IR and ¹H NMR data of heterodinuclear acylpalladium–cobalt complexes

Complex	IR (νCO, cm ⁻¹) ^a	¹ H NMR (ppm)	
		R	L ₂
6 ^b	2026 (m)	8.15 (d, <i>J</i> _{HH} = 7.5 Hz, 2H, <i>o</i> -C ₆ H ₅)	8.7 (br, 1H, bpy H6)
	1961 (s)	7.45 (t, <i>J</i> _{HH} = 7.5 Hz, 2H, <i>m</i> -C ₆ H ₅)	8.1–8.3 (br, 2H, bpy H4, H4')
	1923 (s)	7.40 (t, <i>J</i> _{HH} = 7.5 Hz, 1H, <i>p</i> -C ₆ H ₅)	8.1 (br, 2H, bpy H3, H3')
	1899 (s)		7.6 (br, 1H, bpy H5)
	1645 (m)		7.4–7.6 (br, 2H, bpy H5', H6')
8 ^c	2019 (m)	8.26 (d, <i>J</i> _{HH} = 8.1 Hz, 2H, <i>o</i> -C ₆ H ₅)	1.85 (br, 12H, tmeda CH ₃)
	1948 (s)	7.0–7.2 (br, 3H, <i>m</i> , <i>p</i> -C ₆ H ₅)	1.4–1.5 (br, 4H, tmeda CH ₂)
	1897 (s)		
	1650 (m)		
10 ^d	2027 (m)	8.17 (d, <i>J</i> _{HH} = 7.2 Hz, 2H, <i>o</i> -C ₆ H ₅)	9.0 (brs, 1H, H2)
	1952 (s)	7.53 (t, <i>J</i> _{HH} = 7.2 Hz, 2H, <i>m</i> -C ₆ H ₅)	8.9 (br, 2H, H4, H7)
	1932 (s)	7.44 (t, <i>J</i> _{HH} = 7.2 Hz, 1H, <i>p</i> -C ₆ H ₅)	8.4 (br, 1H, H9)
	1890 (s)		8.0–8.2 (brs, 2H, H3, H8)
	1645 (m)		

^a IR spectra were measured by KBr pellet method.

^b ¹H NMR spectrum was measured in CDCl₃ at room temperature.

^c ¹H NMR spectrum was measured in C₆D₆ at room temperature.

^d ¹H NMR spectrum was measured in acetone-*d*₆ at room temperature.

Table 2
Crystallographic data for (bpy)(PhCO)Pd–Co(CO)₄ (**6**), (tmeda)(PhCO)Pd–Co(CO)₄ (**8**), and (phen)(MeCO)Pd–Co(CO)₄ (**9**)

	6 · C ₆ H ₆	8	9
Empirical formula	C ₂₇ H ₁₉ CoN ₂ O ₅ Pd	C ₁₇ H ₁₉ CoN ₂ O ₅ Pd	C ₁₈ H ₁₁ CoN ₂ O ₅ Pd
Formula weight	616.79	496.68	500.63
Crystal color, habit	Orange, cubic	Dark red, cubic	Red, prismatic
Crystal dimension (mm × mm × mm)	0.22 × 0.14 × 0.14	0.63 × 0.40 × 0.32	0.67 × 0.33 × 0.20
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.41(1)	8.69(1)	9.990(4)
<i>b</i> (Å)	12.38(1)	16.30(1)	12.460(4)
<i>c</i> (Å)	16.328(7)	14.078(7)	7.541(4)
α (°)			105.72(3)
β (°)	95.84(5)	92.97(6)	104.01(4)
γ (°)			86.30(3)
<i>V</i> (Å ³)	2493(2)	1990(2)	876.6(7)
<i>Z</i>	4	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.643	1.657	1.896
<i>F</i> ₀₀₀	1232.00	992.00	492.00
μ (Mo K α) (cm ⁻¹)	14.27	17.65	20.06
Diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
Radiation (Å)	0.71069	0.71069	0.71069
Temperature (°C)	-160.0	-160.0	20.0
Scan type	ω -2 θ	ω -2 θ	ω -2 θ
2 θ _{max} (°)	55.0	55.0	55.0
No. of reflection measured			
Total	5822	4847	4254
Unique	5563	4537	4021
No. of observation (<i>I</i> > 3.00 σ (<i>I</i>))	1557	3698	3719
Structure solution	Patterson methods (SAPI)	Patterson methods (SAPI)	Direct methods
<i>R</i> ^a	0.113	0.035	0.028
<i>R</i> _w ^b	0.171	0.056	0.041
Goodness of fit indicator	1.50	1.30	1.20

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|.$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^{2+0.5}].$$

the Co atom is deviated from the least square plane consisted of Pd, C1, N1 and N2 atoms by 0.12–0.58 Å for the acyl and related complexes **1** [2j], **5** [2i], **6**, **8** and **9**, and the coordination plane at Pd is slightly twisted, displaying dihedral angles of 3–13° between N–N–Pd and Co–C–Pd planes (Table 4). These deviations may also be due to steric congestion of the Pd metal, causing some twisting from square planar structure. These structural features around both metals are consistent with the electronic configurations of *d*⁸-Pd(II) and *d*¹⁰-Co(-I) electronic configurations, which are also supported by the IR data.

2.2. Copolymerization of aziridine and carbon monoxide catalyzed by heterodinuclear organopalladium–cobalt complexes

When aziridine was heated to 100 °C under 5 MPa of CO in THF for 6 h in the presence of 1 mol% of dinuclear organopalladium–cobalt complexes having a bidentate nitrogen or phosphorus ligand, smooth alternative copolymerization of aziridine and CO proceeded to give water-soluble copolymer in good yield. Results of copolymerization are summarized in Table 5. 2-Methylaziridine and *N*-ethylaziridine were also copolymerized under similar conditions. These polymers

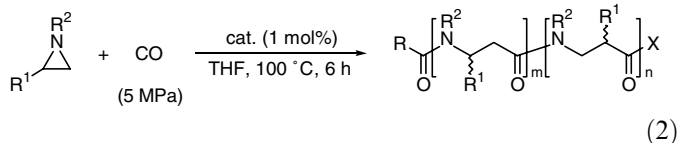
were characterized by comparing the reported NMR and IR data [5]. The yield was estimated on the basis of aziridine used and also by assuming that aziridine was consumed as alternative copolymer [6]. Resultant copolymer from 2-methylaziridine and CO was consisted of regio- and stereo-isomeric mixtures which were originated from regioselectivity of the C–N bond cleavage (Table 5, entries 4–10). Ratio of these two units in the copolymer (*m/n* as defined in Eq. (2)) were estimated by ¹H NMR. In all cases, less hindered C–N bond of 2-methylaziridine was preferentially cleaved as shown in Table 5. Heterodinuclear complexes having a dppe ligand showed slightly higher catalytic activity than those having a bpy, phen, or tmeda ligand. In contrast, heterodinuclear methylpalladium–molybdenum complex (dppe)MePd–MoCp(CO)₃ (**11**) and methylplatinum–cobalt complex (dppe)MePt–Co(CO)₄ (**12**) [2f,2j] showed no or low catalytic activity for copolymerization (Table 5, entries 11 and 12). It is interesting to note that catalytic activity of these Pd–Co complexes were higher than that of mononuclear Jia's catalysts Co(COME)(CO)₃(PPh₃) [5a] and Co(COCH₂Ph)(CO)₄ [5b] (Table 5, entries 13 and 14), and corresponding mononuclear cationic palladium(II) complexes [PdMe(NCMe)(bpy)]⁺[BF₄]⁻ and anionic cobalt complex [PPN]⁺[Co(CO)₄]⁻ showed no catalytic activity

Table 3

Selected bond lengths and angles for (bpy)(PhCO)Pd–Co(CO)₄ (**6**), (tmeda)(PhCO)Pd–Co(CO)₄ (**8**), and (phen)(MeCO)Pd–Co(CO)₄ (**9**)

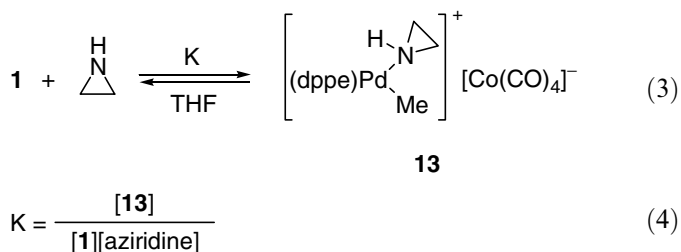
<i>Bond lengths (Å) for (bpy)(PhCO)Pd–Co(CO)₄ (6)</i>			
Pd(1)–Co(1)	2.569(5)	Pd(1)–C(1)	1.99(3)
Pd(1)–N(1)	2.11(3)	Pd(1)–N(2)	2.07(3)
Pd(1)–C(14)	2.48(3)	Pd(1)–C(17)	2.53(3)
Co(1)–C(18)	1.79(4)	Co(1)–C(19)	1.78(4)
Co(1)–C(20)	1.81(3)	Co(1)–C(21)	1.70(4)
C(18)–O(2)	1.15(4)	C(19)–O(3)	1.13(5)
C(20)–O(4)	1.18(4)	C(21)–O(5)	1.16(4)
<i>Bond angles (°) for (bpy)(PhCO)Pd–Co(CO)₄ (6)</i>			
Co(1)–Pd(1)–C(1)	84.9(10)	Co(1)–Pd(1)–N(1)	104.3(9)
C(1)–Pd(1)–N(1)	104.3(9)	N(1)–Pd(1)–N(2)	73(1)
Co(1)–C(18)–O(2)	165(3)	Co(1)–C(19)–O(3)	172(3)
Co(1)–C(20)–O(4)	173(3)	Co(1)–C(21)–O(5)	174(3)
C(18)–Co(1)–C(19)	100(1)	C(18)–Co(1)–C(20)	103(1)
C(18)–Co(1)–C(21)	132(1)	C(19)–Co(1)–C(20)	110(1)
C(19)–Co(1)–C(21)	101(1)	C(20)–Co(1)–C(21)	107(1)
<i>Bond lengths (Å) for (tmeda)(PhCO)Pd–Co(CO)₄ (8)</i>			
Pd(1)–Co(1)	2.594(2)	Pd(1)–C(1)	1.967(4)
Pd(1)–N(1)	2.283(3)	Pd(1)–N(2)	2.190(3)
Pd(1)–C(14)	2.452(4)	Pd(1)–C(17)	2.521(5)
Co(1)–C(14)	1.758(5)	Co(1)–C(15)	1.781(6)
Co(1)–C(16)	1.770(5)	Co(1)–C(17)	1.754(4)
C(14)–O(2)	1.153(5)	C(15)–O(3)	1.147(6)
C(16)–O(4)	1.150(6)	C(17)–O(5)	1.162(5)
<i>Bond angles (°) for (tmeda)(PhCO)Pd–Co(CO)₄ (8)</i>			
Co(1)–Pd(1)–C(1)	88.1(1)	Co(1)–Pd(1)–N(1)	99.5(1)
C(1)–Pd(1)–N(1)	90.1(1)	N(1)–Pd(1)–N(2)	82.0(1)
Co(1)–C(15)–O(2)	171.7(3)	Co(1)–C(16)–O(3)	177.5(3)
Co(1)–C(17)–O(4)	177.4(4)	Co(1)–C(18)–O(5)	173.3(3)
C(14)–Co(1)–C(16)	101.6(2)	C(14)–Co(1)–C(15)	103.5(2)
C(14)–Co(1)–C(17)	131.7(2)	C(15)–Co(1)–C(16)	111.0(2)
C(15)–Co(1)–C(17)	107.7(2)	C(16)–Co(1)–C(17)	100.5(2)
<i>Bond lengths (Å) for (phen)(MeCO)Pd–Co(CO)₄ (9)</i>			
Pd(1)–Co(1)	2.5729(4)	Pd(1)–C(1)	1.972(3)
Pd(1)–N(1)	2.208(2)	Pd(1)–N(2)	2.152(2)
Pd(1)–C(15)	2.442(4)	Pd(1)–C(18)	2.555(4)
Co(1)–C(15)	1.776(4)	Co(1)–C(16)	1.772(3)
Co(1)–C(17)	1.792(3)	Co(1)–C(18)	1.784(4)
C(15)–O(2)	1.144(5)	C(16)–O(3)	1.138(4)
C(17)–O(4)	1.128(4)	C(18)–O(5)	1.145(4)
<i>Bond angles (°) for (phen)(MeCO)Pd–Co(CO)₄ (9)</i>			
Co(1)–Pd(1)–C(1)	87.17(8)	Co(1)–Pd(1)–N(1)	99.24(6)
C(1)–Pd(1)–N(1)	96.4(1)	N(1)–Pd(1)–N(2)	76.99(8)
Co(1)–C(15)–O(2)	171.7(3)	Co(1)–C(16)–O(3)	177.5(3)
Co(1)–C(17)–O(4)	177.4(4)	Co(1)–C(18)–O(5)	173.3(3)
C(15)–Co(1)–C(16)	100.6(2)	C(15)–Co(1)–C(17)	111.9(2)
C(15)–Co(1)–C(18)	129.3(2)	C(16)–Co(1)–C(17)	103.8(2)
C(16)–Co(1)–C(18)	104.2(2)	C(17)–Co(1)–C(18)	104.1(2)

(entries 15,16). Ligands such as bpy and dppe themselves had also no catalytic activity toward polymerization. These results suggest that the presence of Pd–Co bond plays an important synergistic role in this catalytic copolymerization.



2.3. Reaction of organopalladium–cobalt complex with aziridines

In order to obtain further insight concerning the reaction mechanism, reaction of (dppe)MePd–Co(CO)₄ (**1**) with a stoichiometric amount of aziridine was followed by ³¹P{¹H} NMR. Upon mixing in THF-*d*₈ at 20 °C, new two doublets at 60.5 and 40.3 ppm were appeared (Fig. 2). These signals were assigned to the signal of cationic (aziridine) palladium complex, [PdMe(aziridine)(dppe)]⁺[Co(CO)₄][−] (**13**) by comparing with [PdMe(aziridine)(dppe)]⁺[SO₃CF₃][−] which was independently prepared by the reaction of [PdMe(NCMe)(dppe)]⁺[SO₃CF₃][−] with aziridine (see Section 4). The reaction is considered to be in equilibrium as shown in Eq. (3). Thus, on lowering the temperature, the equilibrium shifts to the side of aziridine complex **13** as shown in Fig. 2.



In ¹H NMR at −40 °C, the methylene protons of aziridine coordinated to palladium were observed as two broad signals at 1.7 and 2.1 ppm, whose coordination shift is ca. 0.5 ppm downfield from free aziridine resonance (Fig. 3). On raising temperature, the signals due to coordinated aziridine gradually coalesced. On the other hand, addition of one equivalent of free aziridine at −40 °C caused extensive mixing of these signals giving one broad signal at the averaged chemical shift. These facts suggest facile exchange between the coordinated and free aziridine.

In contrast, the acetyl derivative (dppe)(MeCO)Pd–Co(CO)₄ (**4**) showed no apparent reaction with aziridine. However in the presence of large excess aziridine, extensive line broadening of the ³¹P{¹H} signals of **4** was observed, suggesting presence of similar coordination equilibrium of aziridine accompanied by heterolytic cleavage of Pd–Co bond for **4**. Apparent low reactivity may be due to strong electron withdrawing property by the acyl ligand discouraging ionization of the Pd–Co bond. These facts indicate that coordination of aziridine is in facile equilibrium in solution.

The equilibrium constants of the reaction of (dppe)MePd–Co(CO)₄ (**1**) with various aziridines, such as aziridine, 2-methylaziridine and *N*-ethylaziridine were estimated by ³¹P{¹H} NMR in THF (see Section 4). Thermodynamic parameters of these processes were obtained from van't Hoff analysis (Table 6). Coordination ability of *N*-ethylaziridine was significantly small in comparison with aziridine and 2-methylaziridine. This may be mainly due to steric congestion by the *N*-ethyl substituent on coordination. Large negative values of the entropy change probably suggest strong solvation in the ionic products.

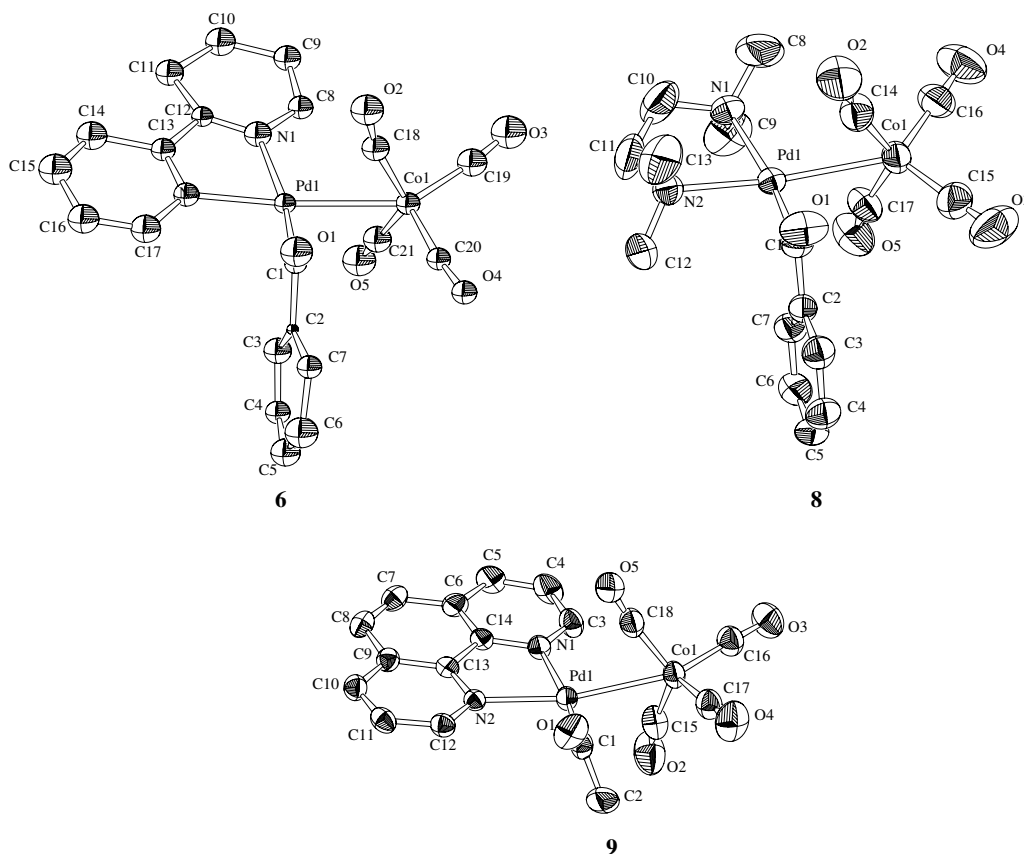


Fig. 1. ORTEP drawings of (bpy)(PhCO)Pd–Co(CO)₄ (**6**), (tmeda)(PhCO)Pd–Co(CO)₄ (**8**), and (phen)(MeCO)Pd–Co(CO)₄ (**9**) and all hydrogen atoms and solvent are omitted for clarity. Ellipsoids represent 50% probability.

Table 4

Dihedral angles between PdL₂ and PdRCo planes and deviations of cobalt atom from PdRL₂ plane of L₂RPd–Co(CO)₄

	Dihedral angles (°) between PdL ₂ and PdRCo	Deviation (Å) of cobalt atom from PdRL ₂
1	8.1	0.38
5	3.0	0.12
6	8.2	0.29
8	10.9	0.49
9	12.9	0.58

Unfortunately no relation between the polymer yield after 3 h catalyzed by complex **1** and the free energy difference ΔG for aziridine coordination to **1** was observed. This suggests the importance of the successive following process such as C–N bond cleavage and CO insertion in the catalytic copolymerization. Analogous coordination equilibrium was also observed for (dppe)MePd–MoCp(CO)₃ (**11**) ($\Delta H = -19 \text{ kJ mol}^{-1}$, $\Delta S = -53 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G (25 \text{ }^\circ\text{C}) = -3.4 \text{ kJ mol}^{-1}$), though it showed no catalytic activity for polymerization.

2.4. Mechanism of catalytic copolymerization

A possible mechanism for the alternative copolymerization of aziridine and carbon monoxide catalyzed by

heterodinuclear organopalladium–cobalt complexes is shown in Scheme 1. First of all, reversible coordination of aziridine to palladium takes place to give cationic (aziridine)palladium(II) complex with tetracarbonylcobalt anion. Then, cobalt anion attacks the methylene carbon of the coordinated aziridine to open the ring forming a Pd–NCH₂CH₂Co unit, where facile CO insertion takes place to give the acylcobalt moiety [2f,2j]. An analogous S_N2 mechanism has been proposed for ring-opening reactions of the coordinated thiirane and thietane by the heterodinuclear organoplatinum–cobalt (or manganese, rhenium) complexes [2h,3a]. In these cases, less hindered side of 2-methylaziridine was selectively cleaved, being consistent with this mechanism. Since coordination equilibrium is not related to their catalytic activity, the following C–N bond cleavage or CO insertion processes may be rate-determining step, in which the substituent at N atom does not play an important role. Reductive elimination of amido moiety associated with interaction of Pd atom with the acylcobalt moiety may give a new heterodinuclear acylpalladium–cobalt complex [7]. Repeated coordination of aziridine followed by insertion of CO at Co gives copolymer, though further study is required to clarify the detail mechanism.

Table 5
Copolymerization of aziridines and CO^a

Entry	R ¹	R ²	Catalyst	Yield (%)	m/n ^g
1	H	H	(dppe)MePd–Co(CO) ₄ (1)	68	–
2 ^b			(dppe)(MeCO)Pd–Co(CO) ₄ (4)	51	–
3			(bpy)(MeCO)Pd–Co(CO) ₄ (5)	25	–
4	Me	H	(dppe)MePd–Co(CO) ₄ (1)	68	3.0
5			(dppe)(MeCO)Pd–Co(CO) ₄ (4)	69	1.5
6			(bpy)(MeCO)Pd–Co(CO) ₄ (5)	38	2.7
7			(bpy)(PhCO)Pd–Co(CO) ₄ (6)	38	1.5
8			(tmeda)(MeCO)Pd–Co(CO) ₄ (7)	50	1.9
9			(tmeda)(PhCO)Pd–Co(CO) ₄ (8)	32	2.2
10			(phen)(MeCO)Pd–Co(CO) ₄ (9)	27	3.4
11			(dppe)MePd–MoCp(CO) ₃ (11)	0	–
12			(dppe)MePt–Co(CO) ₄ (12)	25	3.9
13			Co(COMe)(CO) ₃ (PPh ₃)	11 ^f	–
14			Co(COCH ₂ Ph)(CO) ₄	21	2.0
15			[PdMe(NCMe)(bpy)] ⁺ BF ₄ [–]	0	–
16			[PPN] ⁺ [Co(CO) ₄] [–]	0	–
17 ^c			dppe	0	–
18 ^c			bpy	0	–
19 ^d	H	Et	(dppe)MePd–Co(CO) ₄ (1)	27	–
20 ^d			(dppe)(MeCO)Pd–Co(CO) ₄ (4)	34	–
21 ^d			(bpy)(MeCO)Pd–Co(CO) ₄ (5)	69	–
22 ^d			(bpy)(PhCO)Pd–Co(CO) ₄ (6)	63	–
23 ^d			(tmeda)(MeCO)Pd–Co(CO) ₄ (7)	39	–
24 ^d			(tmeda)(PhCO)Pd–Co(CO) ₄ (8)	63	–
25 ^d			Co(COCH ₂ Ph)(CO) ₄	62	–
26 ^d			[PdMe(NCMe)(bpy)] ⁺ BF ₄ [–]	12 ^e	–
27 ^d			[PPN] ⁺ [Co(CO) ₄] [–]	0	–
28 ^e			bpy	0	–

^a Reaction conditions: catalyst (0.01 mmol), aziridine (1 mmol), CO (5 MPa), THF = 8.0 mL, 100 °C, 6 h.

^b CO (3 MPa).

^c catalyst (0.05 mmol).

^d CO (3 MPa), 60 °C.

^e Catalyst (0.05 mmol), CO (3 MPa), 60 °C.

^f Yield and ratio were not obtained, since the polymer contained a significant amount of aziridine homopolymer.

^g See Eq. (2).

3. Conclusions

In the present study, synthesis of novel heterodinuclear acylpalladium–cobalt complexes having a bidentate nitrogen ligand, L₂(RCO)Pd–Co(CO)₄ (L₂ = bpy, R = Me (**5**), Ph (**6**); L₂ = tmeda, R = Me (**7**), Ph (**8**); L₂ = phen, R = Me (**9**), Ph (**10**)) is described. Heterodinuclear organopalladium–cobalt complexes are shown to catalyze copolymerization of aziridines and CO under mild conditions. The reaction of (dppe)MePd–Co(CO)₄ (**1**) with aziridine gave a cationic (aziridine)palladium(II) complex with [Co(CO)₄][–] anion, [PdMe(aziridine)(dppe)]⁺[Co(CO)₄][–] (**13**). The present results suggest the importance of the initial cationic aziridine complex formation, to which the [Co(CO)₄][–] anion attacks the less-substituted carbon of the coordinated aziridine.

4. Experimental

4.1. General

All manipulations were carried out under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were dried over and distilled from appropriate drying agents under N₂: hexane, benzene, toluene, diethyl ether and THF from Na/benzophenone ketyl; CH₂Cl₂ from P₂O₅; acetone from Drierite. NMR solvents were commercially obtained and dried with appropriate drying agents before use (C₆D₆ and THF-*d*₈ from Na; CD₂Cl₂ and CDCl₃ from P₂O₅; acetone-*d*₆ from Drierite). PdPhI(bpy) [8], PdPhI(tmeda) [9], Na⁺[Co(CO)₄][–] [10], Co(COMe)(CO)₃(PPh₃) [11], Co(COCH₂Ph)(CO)₄ [4b], [PdMe(NCMe)(bpy)]⁺[BF₄][–] [12], [PPN]⁺[Co(CO)₄][–] [13], [PdMe(NCMe)(dppe)]⁺[SO₃CF₃][–] [14], aziridine [15], and

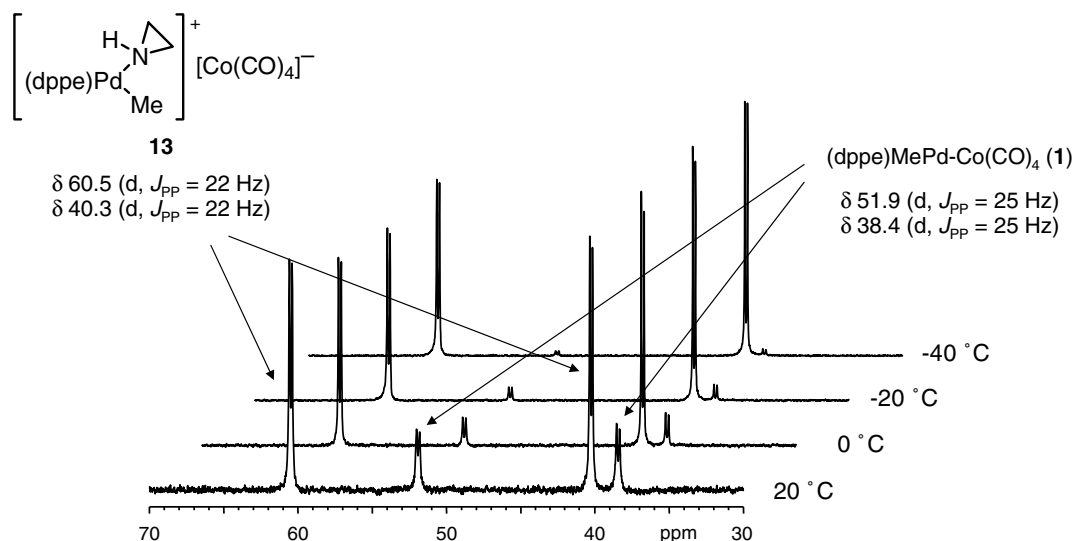


Fig. 2. Variable temperature ³¹P{¹H} NMR spectra for the reaction of (dppe)MePd–Co(CO)₄ (**1**) with aziridine in THF-*d*₈.

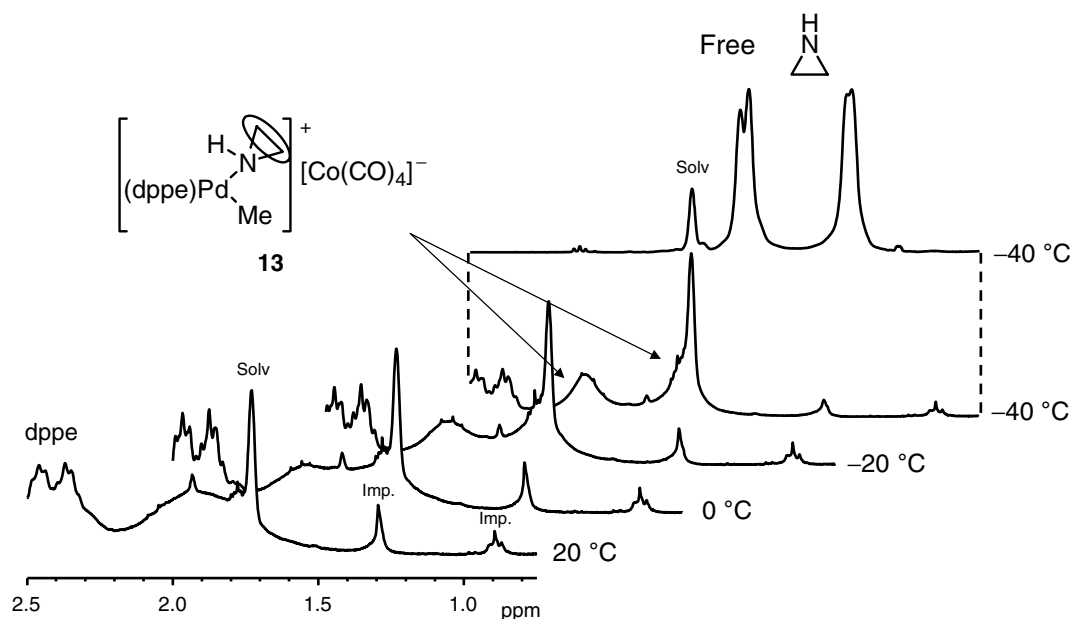


Fig. 3. Variable temperature ^1H NMR spectra for the reaction mixture of $(\text{dppe})\text{MePd-Co}(\text{CO})_4$ (**1**) with aziridine in $\text{THF-}d_8$.

Table 6
Thermodynamic parameters for the equilibrium of aziridine coordination to **1**

R^1	R^2	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G (25^\circ\text{C})/\text{kJ mol}^{-1}$
H	H	-44	-110	-12
H	Me	-43	-110	-12
Et	H	-38	-120	-0.87

N-ethylaziridine [15] were prepared by the literature methods with minor modifications. 2-Methylaziridine was purchased from Aldrich. NMR spectra were recorded on a JEOL LA-300 spectrometer (300.4 MHz for ^1H , 121.6 MHz for ^{31}P). Chemical shifts were reported in ppm downfield from TMS for ^1H and from 85% H_3PO_4 in D_2O for ^{31}P . IR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr disks. Elemental analyses were carried out with a Perkin-Elmer 2400 series II CHN analyzer. Molar electric conductivity was measured on a TOA Conduct Meter CM 7B.

4.2. Synthesis of heterodinuclear organopalladium complexes having a bidentate nitrogen ligand

A typical procedure for $(\text{tmeda})(\text{PhCO})\text{Pd-Co}(\text{CO})_4$ (**8**) is given. $\text{PdPhI}(\text{tmeda})$ (142 mg, 0.333 mmol) and $\text{Na}^+[\text{Co}(\text{CO})_4]^-$ (74.8 mg, 0.386 mmol) were dissolved in THF, and they were stirred for 2 h at 0°C under CO atmosphere to give a red solution. The solution was evaporated, and the resultant solid was extracted with benzene. After removal of all volatile matters in a vacuum, the residual solid was recrystallized from $\text{CHCl}_3/\text{ether}$ to give deep red cubes of $(\text{tmeda})(\text{PhCO})\text{Pd-Co}(\text{CO})_4$ (**8**). Yield: 40% (66.3 mg, 0.133 mmol). M.p. 100°C (dec.). Anal. Calc. for $\text{C}_{17}\text{H}_{21}\text{CoN}_2\text{O}_5\text{Pd}$: C, 40.94; H, 4.24; N, 5.62. Found:

C, 40.47; H, 4.01; N, 5.43%. Molar electric conductivity Λ (THF, r.t.): $0.0189 \text{ S cm}^2 \text{ mol}^{-1}$.

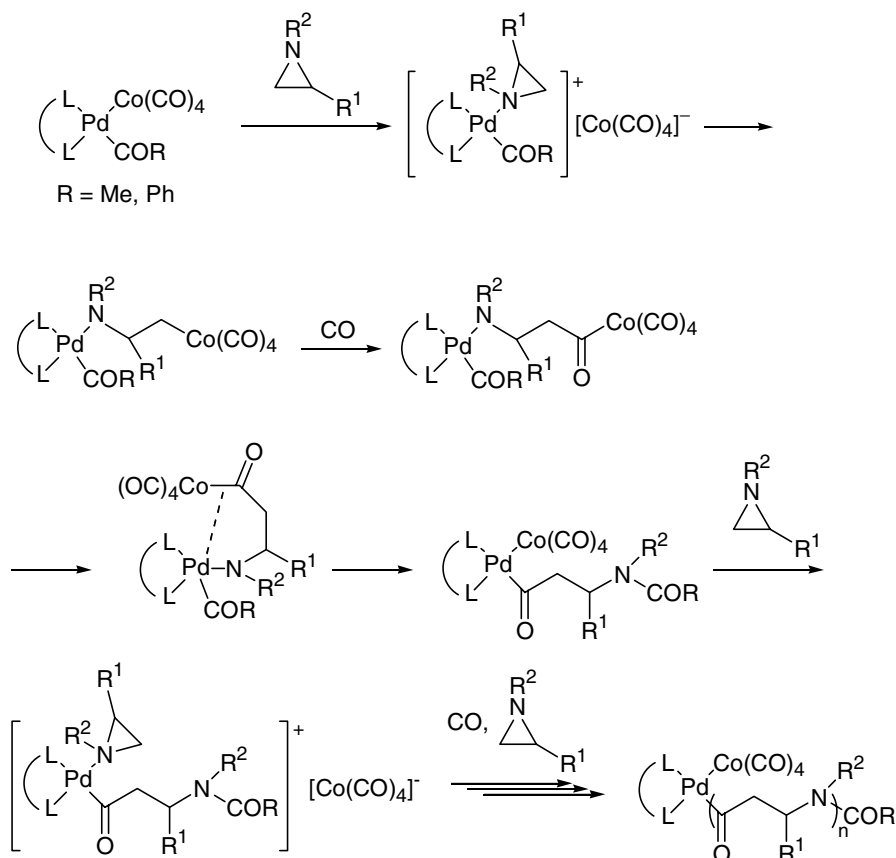
^1H NMR and IR data of the new heterodinuclear acylpalladium-cobalt complexes **6**, **8**, and **10** are summarized in Table 1. Complexes **6** and **10** were synthesized by a similar method to that for **8** and the yields, melting point, elemental analytical data and molar electric conductivity in THF were described below.

$(\text{bpy})(\text{PhCO})\text{Pd-Co}(\text{CO})_4$ (**6**). $\text{PdPhI}(\text{bpy})$ was used instead of $\text{PdPhI}(\text{tmeda})$. Yield: 82%. M.p. 107°C (dec.). Anal. Calc. for $\text{C}_{25}\text{H}_{21}\text{CoN}_2\text{O}_6\text{Pd}$: C, 49.16; H, 3.47; N, 4.59. Found: C, 49.42; H, 3.64; N, 4.17%. Molar electric conductivity Λ (THF, r.t.): $0.0199 \text{ S cm}^2 \text{ mol}^{-1}$.

$(\text{phen})(\text{PhCO})\text{Pd-Co}(\text{CO})_4$ (**10**). $\text{PdPhI}(\text{phen})$ was used instead of $\text{PdPhI}(\text{tmeda})$. Yield: 8%. M.p. 127°C (dec.). Molar electric conductivity Λ (THF, r.t.): $0.018 \text{ S cm}^2 \text{ mol}^{-1}$.

4.3. Synthesis of $[\text{PdMe}(\text{aziridine})(\text{dppe})]^+[\text{SO}_3\text{CF}_3]^-$ (**13**)

To a suspension of $[\text{PdMe}(\text{NCMe})(\text{dppe})]^+[\text{SO}_3\text{CF}_3]^-$ (181.3 mg, 0.2557 mmol) in THF (12 ml) was added aziridine (15.0 μl , 0.290 mmol). Stirring at room temperature for ca. 5 min gave a colorless solution. The reaction mixture was evaporated to dryness in vacuo giving white solid. Recrystallization from THF with hexane gave white powder of **13**. Yield: 70% (128.0 mg, 0.1798 mmol). Anal. Calc. for $\text{C}_{30}\text{H}_{32}\text{F}_3\text{NO}_3\text{P}_2\text{PdS}$: C, 50.61; H, 4.53; N, 1.97. Found: C, 50.45; H, 4.70; N, 1.96%. ^1H NMR (CD_2Cl_2 , r.t.): δ 0.53 (dd, $J_{\text{HH}} = 7.1, 2.3 \text{ Hz}$, 3H, PdCH_3), 1.61 (brs, 2H, $\text{NH}(\text{CH}_2)_2$), 2.1–2.6 (m, 6H, dppe CH_2), 2.2 (brs, 2H, $\text{NH}(\text{CH}_2)_2$), 2.8 (brs, 1H, NH), 7.3–7.9 (m, 12H, *Ph* of dppe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , r.t.): δ 38.8 (d, $J_{\text{PP}} = 23 \text{ Hz}$), 59.6 (d, $J_{\text{PP}} = 23 \text{ Hz}$).



Scheme 1. A possible mechanism for copolymerization.

4.4. Copolymerization procedure

A typical procedure for the copolymerization reactions is given. A THF (8.0 ml) solution of catalyst (0.01 mmol) and aziridine was transferred into a stainless steel autoclave under N_2 or Ar flow. The autoclave was immediately closed and pressurized with CO. Then it was heated to desired temperature using oil bath and the solution was stirred by magnetic stirrer for an appropriate time. After the reaction, the autoclave was cooled by ice water and CO pressure was removed. Water (10 ml) was added to the reaction mixture and the resulted heterogeneous solution was filtered to remove the catalyst. The aqueous solution was evaporated to dryness to give copolymer which was purified by reprecipitation from water/acetone if necessary for aziridine and 2-methylaziridine. For *N*-ethylaziridine, the product was extracted with CH_2Cl_2 and reprecipitated by THF/hexane. Copolymer of aziridine and carbon monoxide [5a,5c]. IR (KBr, cm^{-1}): 1648, 1560 (ν_{CO}). 1H NMR (D_2O , r.t.): δ 2.2 (br, CH_2CO), 3.2 (br, $NHCH_2$). Copolymer of *N*-ethylaziridine and carbon monoxide [5b]: IR (KBr, cm^{-1}): 1636, 1459 (ν_{CO}). 1H NMR ($CDCl_2/CDCl_2$, 120 $^\circ C$): δ 1.0 (br, CH_3CH_2N), 2.4 (br, $NHCH_2CH_2CO$), 3.2 (br, CH_3CH_2N), 3.5 (br, $NHCH_2CH_2CO$). Copolymer of 2-methylaziridine and carbon monoxide: IR (KBr, cm^{-1}): 1649, 1553 (ν_{CO}). Major unit: 1H NMR (D_2O , r.t.): δ

1.0 (br, CH_3), 2.2 (br, CH_2), 4.0 (br, CH). Minor unit: 1H NMR (D_2O , r.t.): 1.0 (brs, CH_3), 2.3 (CH), 3.1 (br, CH_2).

4.5. Measurement of equilibrium constants and thermodynamic parameters

(dppe)MePd– $Co(CO)_4$ (**1**) (18.5 mg, 0.0268 mmol) was placed in a NMR tube, and THF (600 μl) was added. Glass capillary containing settled amount of PPh_3 in C_6D_6 was added as an external standard. Then a THF solution of aziridine (1.10 M, 17.0 μl , 0.0187 mmol) was added. The amount of the products and starting compounds in solution was estimated by $^{31}P\{^1H\}$ and 1H NMR with calibration. Equilibrium constants were given by an expression of $[[PdMe(aziridine)(dppe)]^+[Co(CO)_4]^-$ (**13**)]/[**1**][aziridine]. [**13**] and [**1**] were measured by the relative intensities of the dppe signals to external standard. Concentration of aziridine was calculated by subtracting the concentration of **13** from the initial aziridine concentration, since no side reaction was observed. Thermodynamic parameters ΔH and ΔS were obtained according to van't Hoff plot. Estimated equilibrium constants K/M^{-1} (temperature/ $^\circ C$) for **1** are shown below. Aziridine: 140(19), 86(30), 47(40), 31(50), 14(60). 2-Methylaziridine: 150(20), 89(30), 50(40), 29(50), 17(60). *N*-Ethylaziridine: 1.9(19), 1.1(30), 0.71(40), 0.42(50), 0.28(60).

4.6. X-ray structure analyses

Diffraction experiments were performed on a Rigaku four-circle diffractometer RASA-7R diffractometer with graphite-monochromatized Mo K α radiation (0.71069 Å). A single crystal was selected by use of a polarized microscope and mounted in a capillary tube (GLASS, 0.7 mm ϕ), which was sealed by small flame torch. The unit cells were determined by the automatic indexing of the 20 centered reflections. The structures were solved and refined by a full matrix least-square procedure using the TEXSAN crystal solution package (Rigaku) operating on a SGI O2 workstation [16]. An absorption correction was applied with the program PSI-scan. The structure of **6** and **8** were solved by Patterson methods (SAPI), and the structure of **9** was solved by direct methods. For complexes **8** and **9**, all non-hydrogen atoms were found on difference Fourier maps, and refined anisotropically, and all hydrogen atoms were located in the calculated positions, which were not refined. Complex **6** was refined isotropically due to low quality of the crystal and the hydrogen atoms were not included for the least-square calculations. The crystallographic data and details associated with data collection are given in Table 2. ORTEP drawings of complexes **6**, **8** and **9** were illustrated in Fig. 1 and the bond lengths and angles are listed in Table 3.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis of **6**, **8**, and **9** have been deposited with the Cambridge Crystallographic Data Centre, as CCDC Nos. 299822, 299821 and 299820. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax_{int.} +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.044.

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- [6] Degree of polymerization of the copolymers was calculated as 30–70 by comparing ¹H NMR signals due to the terminal acetyl group methylene signal of the copolymer, though accurate values were difficult to obtain due to signal overlapping. These estimated values are approximately the same order to the obtained yields, suggesting that one catalyst molecule produces one alternative copolymer molecule.
- [7] Introduction of carbon monoxide to a THF solution of complex **13**, which was prepared from **1** and aziridine (1:2), at room temperature gave a complex having high catalytic activity for copolymerization on interaction with CO (1 atm) at room temperature in low yield (~20 w%/1). This complex had low solubility in non polar solvents such as benzene and toluene, and could also be formed from the acyl complex, but it gradually decomposed to give uncharacterizable material in solution. IR spectrum of this compound shows strong $\nu(\text{CO})$ bands at 1884 cm⁻¹ assignable to [Co(CO)]⁻ and 1676 cm⁻¹ due to the acyl unit. ³¹P{¹H} NMR in CD₂Cl₂ shows an AB quartet at δ 49.0 and 30.5 ppm with a coupling constant of 38 Hz, suggesting square planar cis configuration at Pd. Three resonances at δ 2.74 (t, $J = 6.8$ Hz), 3.0 (br), and 4.4 (br) in 1:1:1 ratio in CD₂Cl₂ are assignable to the two methylene and NH₂ protons. The compound is tentatively characterized as a cationic acylpalladium complex [(dppe){NH₂CH₂CH₂C(O)- κ^2 C,N}Pd]⁺[Co(CO)₄]⁻, which could be

- formed by hydrolysis of a putative intermediate [(dppe){NH(CO-Me)CH₂CH₂C(O)- κ^2 C,N}Pd]⁺[Co(CO)₄]⁻ under the reaction conditions, though further detail studies are still required to clarify the structure and formation mechanism. The copolymer, which was obtained by this complex, contained a negligible amount of terminal acyl unit.
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