

Reaction of carbon monoxide with strained alkenes catalyzed by a cationic palladium(II) complex

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Received 19 May 1998; accepted 10 July 1998

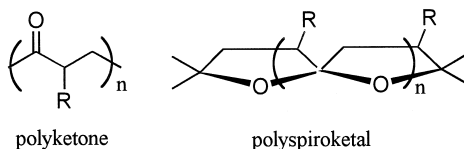
Abstract

The reaction of carbon monoxide with strained alkenes such as norbornene, dicyclopentadiene and bicyclo[2.2.2]oct-2-ene catalyzed by a cationic palladium complex $[\text{Pd}(\text{MeCN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$ has been studied. Normally, 2:2 cooligomers having enol lactone structure and 3:3 cooligomers having ketal lactone structure were obtained. A mechanism involving alternate insertion of alkene and carbon monoxide into an initial Pd–H bond followed by enolization–cyclization is proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbon monoxide; Strained alkene; Palladium; Lactone

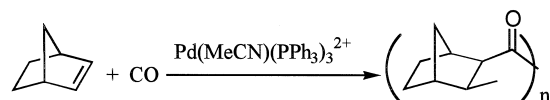
1. Introduction

The alternating copolymerization of carbon monoxide and α -olefins such as ethene, propene and styrene has been the subject of many investigations. For ethene and propene, the excellent catalysts are proved to be cationic palladium complexes coordinated with tertiary (especially bidentate) phosphine ligands [1–4]. For styrene, somewhat different catalytic system has been employed. For example, palladium complexes of bidentate nitrogen ligands and weakly coordinated anions have been used in the presence of an oxidizing cocatalyst in an alcoholic media [5–7]. A palladium complex coordinated with a phosphine–phosphite ligand is demonstrated to be useful as well [8]. Usually, the copolymerization product is ‘polyketone’ (poly-3-oxotrimethylene). In certain cases, polymers with polyspiroketal repeating units in the backbone are observed [9–12].

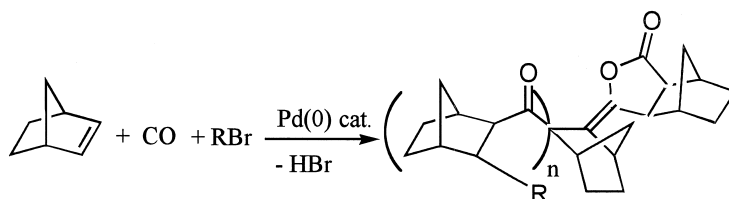


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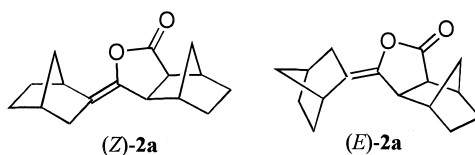
For strained olefins like norbornene and norbornadiene, palladium(II) complexes are also active catalysts to afford polyketone. Early works dealt with the copolymerization of carbon monoxide and norbornadiene catalyzed by PdCl_2 [13,14]. In 1982, Sen et al. reported the reaction of carbon monoxide with norbornadiene and norbornene under mild conditions using $[\text{Pd}(\text{MeCN})(\text{PPh}_3)_3](\text{BF}_4)_2$ as catalyst in noncoordinating solvents such as chloroform where norbornadiene afforded the copolymers of molecular weight 3380 and norbornene yielded the cooligomers of molecular weight 350. The overall reaction of norbornene with carbon monoxide has been depicted as follows [15].



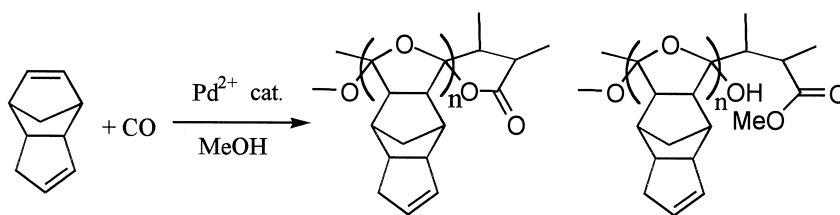
Carbon monoxide–norbornene copolymers of molecular weight 1350 terminated by a γ -lactone with exocyclic double bond have been prepared under the catalytic action of a palladium(0) complex and alkyl bromide [16].



Addition of trifluoroacetic acid instead of the alkyl bromide changed the reaction course to afford 2:2 cooligomers **2a** of *cis*, *exo* stereochemistry.



Drent et al. reported the alternating copolymerization of carbon monoxide and dicyclopentadiene catalyzed by cationic palladium complexes of 2,2'-bipyridine in methanol in the presence of an oxidant. The reaction produced spiroketal repeating units having lactone and ester end groups of the polymer chains instead of the expected ketone repeating units [11,12].



We have found that the reaction of carbon monoxide with strained alkenes **1** such as norbornene and bicyclo[2.2.2]oct-2-ene in acetonitrile catalyzed by cationic palladium–triphenylphosphine complex affords 2:2 and 3:3 cooligomers having lactone structures predominantly.

2. Results and discussion

2.1. Reaction of carbon monoxide with norbornene (**1a**)

Reaction of carbon monoxide (10 atm) with **1a** at 100°C for 5 h in acetonitrile in the presence of a catalytic amount of [Pd(MeCN)₂(PPh₃)₂](BF₄)₂ afforded white solids (81% on **1a**) after isolation by column filtration and evaporation of the solvent. This product was soluble in common organic solvents and melted over a range of 86–130°C. Mass (CI) analysis indicated that the product was composed mainly of 2:2 and 3:3 cooligomers. The peaks attributed to more than 4-unit cooligomers could also be detected but the intensities were quite weak. The IR spectrum showed a strong absorption around 1780 cm⁻¹ indicating the presence of γ -lactone structure. The absorption at 1700 cm⁻¹ which would indicate the presence of ketonic groups was very weak. Purification of the product by silica gel column chromatography gave 2:2 and 3:3 cooligomers in 9 and 66% yield, respectively. GLC analysis revealed that the 2:2 cooligomers were composed of two isomers. Both the strong IR absorptions at 1781 and 1721 cm⁻¹ and the ¹³C NMR characteristic peaks at 177.4, 142.3, 141.8, 120.6 and 120.4 ppm are consistent with the known enol lactone structure **2a**. The 3:3 cooligomers were composed of more than eight isomers (by GLC). The IR spectrum showed strong bands at 1775 and 1727 cm⁻¹ attributed to γ -lactone and vinyl ether structures, respectively. The lack of peaks around 1700 cm⁻¹ suggested the absence of ketonic carbonyl groups. The ¹³C NMR spectrum of the 3:3 cooligomers showed characteristic signals at 177, 146, 117 and 116 ppm. The peaks at 146 and 116 (or 117) ppm are assigned to vinyl ether carbons (Fig. 1). The most remarkable characteristic of the spectrum is the resonance at 117 (or 116) ppm, which can be assigned to a ketal carbon

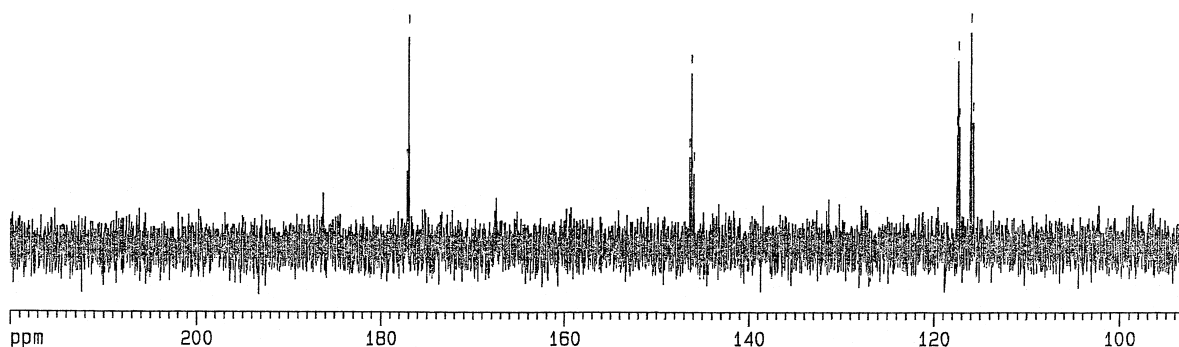
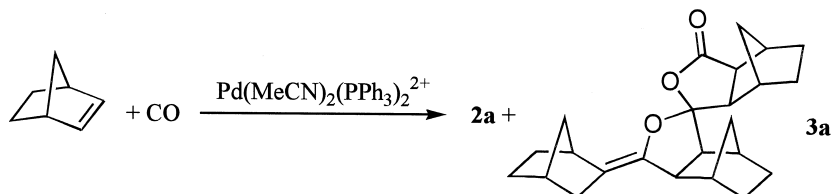


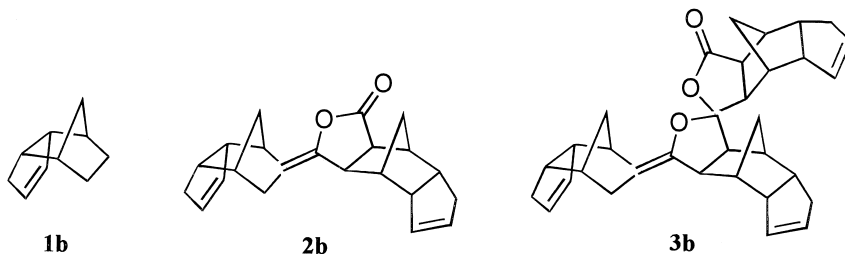
Fig. 1. ¹³C NMR spectrum of **3a**.

[11,12,17]. The complete absence of carbonyl resonance expected at 200–220 ppm indicates the absence of a ketonic group. These spectroscopic data are consistent with the ketal lactone structure **3a** and its possible isomers.



2.2. Reaction of carbon monoxide with dicyclopentadiene (**1b**)

The reaction of carbon monoxide with **1b** gave white solids in 96% yield (on **1b**) after the column filtration and evaporation of the solvent. GPC and Mass (CI) spectrum indicated the solids were mainly composed of 2:2 and 3:3 cooligomers, which were isolated in 44 and 18% yield, respectively, by column chromatography on silica gel. The 2-unit product was a mixture of eight isomers (by GLC). They showed strong absorptions at 1790 and 1721 cm⁻¹ in the IR spectrum and characteristic peaks at 178, 144 and 117 ppm in ¹³C NMR spectrum indicating the presence of enol lactone structure. The olefinic carbons of the cyclopentene ring appeared at 131 ppm. The paraffinic protons appeared at 1.36–3.23 (20H) and the olefinic ones at 5.32–5.75 (4H) in the ¹H NMR spectrum. These spectroscopic data are compatible with the structures **2b** and the possible isomers. The 3-unit oligomers showed strong absorptions at 1775 and 1710–1735 cm⁻¹ in the IR spectrum indicating the presence of γ -lactone and vinyl ether groups. The paraffinic protons appeared at 1.2–3.2 ppm and the olefinic ones at 5.3–5.8 ppm in the ¹H NMR spectrum, the ratio being 5:1. In the ¹³C NMR spectrum the peaks of lactone carbonyl carbons appeared at 178–179 ppm. The peaks at 147–149 and 109–112 ppm can be attributed to vinyl ether groups. The resonances at 116–120 can be assigned to the spiroketal carbon atoms [9–12]. Olefinic carbons in the cyclopentene ring appeared at 130–136 ppm. Ketonic groups, which would be expected in the range of 200–220 ppm, were not observed. The structure **3b** and the possible isomers are responsible for the spectroscopic data.



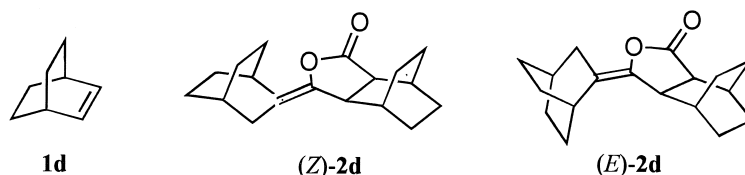
2.3. Reaction of carbon monoxide with norbornadiene (**1c**)

The reaction of carbon monoxide with **1c** gave yellow solids in 24% yield (assuming a 1:1 reaction) after the usual work-up. The molecular weight ranged from 800–1200 (by GPC). The IR

spectrum exhibited characteristic peaks at 1778 (s), 1722 (m) and 1702 (m) cm^{-1} indicating the presence of γ -lactone, vinyl ether, ketone groups. The ^{13}C NMR spectrum exhibited many poorly resolved absorptions. The absorption attributable to a lactone carbonyl appeared around 175 ppm. The peaks based on the ketonic carbons were not observed distinctly. The higher ratio of paraffinic protons vs. olefinic ones in the ^1H NMR spectrum indicates that another double bond is partially taking part in the reaction. Further studies on the elucidation of the cooligomer structure were not performed.

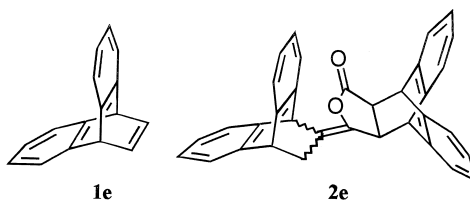
2.4. Reaction of carbon monoxide with bicyclo[2.2.2]oct-2-ene (**1d**)

The reaction of carbon monoxide with **1d** gave white solids in 69% yield after the usual work-up. (The increase in the carbon monoxide pressure to 40 atm gave the product in 77% yield.) GLC analysis revealed that they were composed of two 2:2 cooligomers in the ratio of 43:57. They were isolated by preparative HPLC and characterized spectroscopically to be enol lactone (*Z*)-**2d** (minor component) and (*E*)-**2d** (major component). 3-Unit cooligomers were not detected by GLC.



2.5. Reaction of carbon monoxide with dibenzobicyclo[2.2.2]octatriene (**1e**)

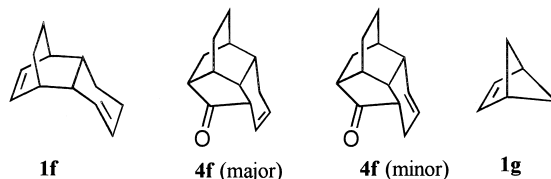
The reaction of carbon monoxide with **1e** at 100°C for 10 h gave yellow solids in 41% yield after silica gel column chromatography, which were composed of two 2:2 cooligomers in a ratio of 39:61. Characteristic ^{13}C NMR peak at 173.7 ppm and IR absorptions at 1791–1793 and 1707–1708 cm^{-1} indicate that they have enol lactone structures **2e**.



2.6. Reaction of carbon monoxide with *endo* tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (**1f**)

The reaction of carbon monoxide with **1f** gave a yellow oil after the preliminary work-up. Treatment of the oil on silica gel column chromatography gave a mixture of 2:2 cooligomers in 18% yield and two 1:1 codimers of 58:42 ratio in 32% yield. Characteristic IR absorptions at 1790 and 1710 cm^{-1} indicate that the 2:2 cooligomers have enol lactone structure **2f**. The 1:1 codimers showed

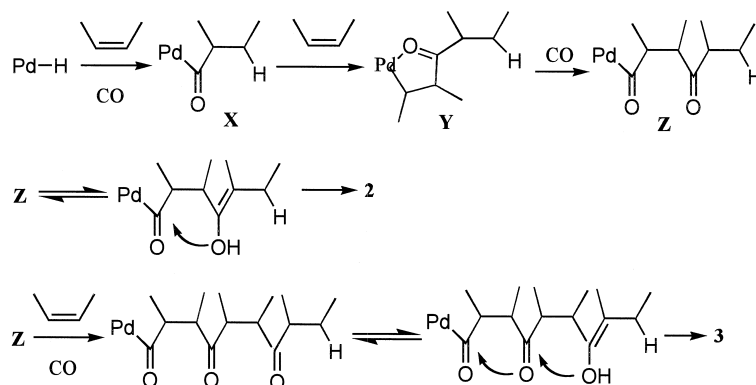
ketonic carbonyl absorptions at 1740 cm^{-1} in the IR spectrum and at 220 and 224 ppm in the ^{13}C NMR spectrum. Analytical samples were obtained by preparative HPLC and the structures were determined spectroscopically to be **4f**. Carbonylation of the *endo* face was realized in this case.¹



2.7. Reaction of carbon monoxide with bicyclo[2.1.1]hex-2-ene (**1g**)

The reaction of carbon monoxide with **1g** gave brown solids in a moderate yield after the preliminary work-up. Molecular weight ranged from 600 to 1000 (by GPC). Strong absorptions at $1750\text{--}1770$ and 1700 cm^{-1} in the IR spectrum indicated the presence of lactonic and ketonic carbonyl groups. The ^{13}C NMR spectra showed many poorly resolved absorptions. The broad peaks attributed to lactone and ketone groups appeared at 176 and 210 ppm, respectively. It is conceivable that higher oligomers having lactone and ketone structures in the backbone were produced.

We propose a mechanism initiated by a Pd–H species for the cooligomerization reaction. The insertion of a strained double bond into a Pd–H bond from the *exo* face followed by carbon monoxide insertion into the resulting Pd–alkyl bond affords a Pd–acyl species X. Another insertion of alkene into the Pd–acyl bond produces a Pd–alkyl species Y having a five-membered cyclic structure with internal coordination of the carbonyl group. The stereochemistry of the insertion has been established for norbornene, norbornadiene and dicyclopentadiene where the palladium and the acyl group lie on the *exo* face [19].



Because of the steric inaccessibility of the available β -hydrogen atoms, subsequent decomposition of the inserted product does not occur. Then carbon monoxide insertion into the Pd–alkyl bond in Y

¹ This type of carbonylation for 1,5-diene system has been reported: [18].

takes place to give a Pd–acyl species Z [20]. It is recognized that olefin insertion into a Pd–acyl bond is the rate limiting step in the two-step chain growth sequence involving alternate insertions of alkene and carbon monoxide into an initial Pd–H bond [21]. So the intermediate Z may suffer enolization to undergo cyclization affording the observed enol lactone **2**.² Another insertion of alkene and carbon monoxide followed by enolization–cyclization would give rise to the 3-unit product **3**, the γ -lactone with spiroketal structure. The paucity of higher cooligomers indicates that the subsequent alkene insertion is not easy probably because of steric reasons. Control experiments revealed that the complex $[\text{Pd}(\text{MeCN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$ could hardly catalyze the reaction of carbon monoxide with monocyclic olefins. Thus cyclopentene gave cyclopentenyl cyclopentyl ketone in only 8% yield [19]. Moreover cyclohexene gave no carbonylation products. Higher reactivity of the strained alkenes towards the insertion into a Pd–alkyl bond is the key of this reaction [23].

3. Experimental

3.1. General method

¹H and ¹³C NMR spectra were recorded in CDCl₃ at 500 and 125 MHz, respectively, on a Bruker DRX-500 instrument with Me₄Si as the internal standard. Assignment of spectra was achieved using 2D-method (COSY, HETCOL). IR spectra were run on a JASCO FT/IR 350 spectrometer. GLC analyses were performed with 0.25 mm × 30 m columns packed with TC5. Preparative HPLCs were done with Lab-Quatec MP-311. GPC measurements were performed with a TOSO CCPE instrument. MS (CI) spectra were recorded at Tohoku University Instrumental Analysis Center for Chemistry. MS (EI) spectra were recorded on a Shimadzu GCMS-2000 instrument.

3.2. Materials

The cationic palladium complex $[\text{Pd}(\text{MeCN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$ was prepared according to the reported procedure [24]. The alkenes were purchased (**1a**, **1b**, **1c**) or prepared (**1d** [25], **1e** [26], **1f** [25], **1g** [27]) according to the literature methods.

3.3. General procedure for the reaction of carbon monoxide with strained alkenes 1

Into a 50 ml stainless steel autoclave were added 0.04 mmol of $[\text{Pd}(\text{MeCN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$, 10 ml of MeCN and 2 mmol of alkene **1** under nitrogen atmosphere. The reaction vessel was then pressurized with 10 atm of carbon monoxide. The reaction was allowed to proceed at 100°C for 5 h. After the reaction, the resulting solution was taken up in diethyl ether and passed through a short florisil[®] column to remove palladium complexes.

3.3.1. Reaction of carbon monoxide with norbornene (**1a**)

The crude products obtained (white solids, 204 mg, 81%) were subjected to column chromatography on silica gel eluting with hexane/ethyl acetate (10/1) to give the 2:2 and 3:3 cooligomers in 9 and 66% yield, respectively. Analytical samples of 2:2 cooligomers **2a** were obtained by preparative GLC as an *E*, *Z* mixture.

² Enol lactone formation by palladium catalyzed carbonylation of *o*-bromoacetophenone derivatives is precedented: [22].

3.3.1.1. 2:2 Cooligomer **2a**. IR (KBr), 1781, 1721 cm^{-1} . ^{13}C NMR (CDCl_3), δ 177.4, 142.3, 141.8, 120.6, 120.4, 27–49. MS (CI), m/z 245 ($M + 1$), MS (EI), m/z 93, 215, 244(M^+). Calcd. for $(\text{C}_7\text{H}_{10} \cdot \text{CO})_2$: C; 78.65; H; 8.25. Found: C; 77.47, H; 8.01%.

3.3.1.2. 3:3 Cooligomer **3a**. The product was found to be composed of more than 8 isomers (by GLC). IR (KBr), 1775, 1727 cm^{-1} . ^1H NMR (CDCl_3), δ 1.0–3.0 (m). ^{13}C NMR (CDCl_3), δ 177, 146, 117, 116, 26–59. MS (CI), m/z 367 ($M + 1$). MS (EI), m/z 93, 337, 338, 366 (M^+). Calcd. for $(\text{C}_7\text{H}_{10} \cdot \text{CO})_3$: C; 78.65, H, 8.25. Found: C; 75.99, H; 8.11%.

3.3.2. Reaction of carbon monoxide with dicyclopentadiene (**1b**)

The crude products obtained (white solids, 306 mg, 96%) were subjected to column chromatography on silica gel eluting with hexane/ethyl acetate (10/1) to give the 2-unit and 3-unit products in 44 and 18% yield, respectively.

3.3.2.1. 2:2 Cooligomer **2b**. The product is a mixture of 8 isomers (by GLC). IR (KBr), 1790, 1721 cm^{-1} . ^1H NMR (CDCl_3), δ 1.36–3.23 (m, 20H), 5.32–5.75 (m, 4H). ^{13}C NMR (CDCl_3), δ 178, 143–144, 130–132, 116–118, 27–54. MS (CI), m/z 321 ($M + 1$). MS(EI), m/z 66, 93, 253, 254, 320 (M^+). Calcd. for $(\text{C}_{10}\text{H}_{12} \cdot \text{CO})_2$: C; 82.46, H; 7.77. Found: C; 81.73, H; 7.72%.

3.3.2.2. 3:3 Cooligomer **3b**. The product was found to be composed of many isomers (by GLC). IR (KBr), 1775, 1735, 1719 cm^{-1} . ^1H NMR (CDCl_3), δ 1.2–3.2 (m, 30H), 5.3–5.8 (m, 6H). ^{13}C NMR (CDCl_3), δ 178–179, 147–149, 130–136, 116–120, 109–112, 27–61. MS (CI), m/z 481 ($M + 1$). MS (EI), m/z 67, 93, 253, 321, 369, 413, 480 (M^+). Calcd. for $(\text{C}_{10}\text{H}_{12} \cdot \text{CO})_3$: C; 82.46, H; 7.77. Found: C; 80.20, H; 7.88%.

3.3.3. Reaction of carbon monoxide with norbornadiene (**1c**)

The crude products were yellow solids (128 mg, 24% assuming a 1:1 reaction). The molecular weight by GPC measurement ranged from 800 to 1200. IR (KBr), 1778, 1722, 1702 cm^{-1} . ^1H NMR (CDCl_3), δ 1.1–3.4 (m, br.), 6.0–6.3 (m, br.). The ratio was approximately 5:1. ^{13}C NMR (CDCl_3), δ 175, 139–137, 132, 128, 10–49.

3.3.4. Reaction of carbon monoxide with bicyclo[2.2.2]oct-2-ene (**1d**)

A total of 178 mg (69%) of product was obtained, which was composed of two 2:2 cooligomers in a ratio of 43:57 (by GLC). Analytical samples were obtained by preparative HPLC (ODS-120A, methanol/ H_2O = 80/20).

3.3.4.1. (*Z*)-5-Bicyclo[2.2.2]octylidene-4-oxa-3-oxotricyclo[5.2.2.0^{2,6}]undecane (*Z*)-**2d**. Minor component. mp 120–123°C. IR (KBr), 1777, 1705 cm^{-1} . ^1H NMR (CDCl_3), δ 1.40–1.60 (m, 16H), 1.80 (s, 1H), 1.94 (s, 1H), 2.05–2.16(m, 3H), 2.78 (s, 1H), 2.84 (dd, 1H, $J = 11.2, 4.0$ Hz), 3.07 (d, 1H, $J = 11.2$ Hz). ^{13}C NMR (CDCl_3), δ 177.84, 142.70, 118.29, 43.32, 39.57, 30.86, 26.85, 25.74, 25.72, 25.62, 25.50, 25.45, 25.43, 24.71, 24.65, 24.09, 21.84, 20.65. MS(EI), m/z 41 (21), 79 (39), 107 (21), 136 (21), 243 (29), 272 (100, M^+). Calcd. for $(\text{C}_8\text{H}_{12} \cdot \text{CO})_2$: C; 79.37, H; 8.88. Found C; 78.80, H; 8.98%.

3.3.4.2. (*E*)-**2d**. Major component. mp 104–108°C. IR (KBr), 1788, 1707 cm^{-1} . ^1H NMR (CDCl_3), δ 1.40–1.70 (m, 16H), 1.73 (s, 1H), 1.77–1.80 (m, 1H), 2.07 (s, 1H), 2.15 (s, 1H), 2.28–2.38 (m, 2H), 2.83 (dd, 1H, $J = 11.2, 4.0$ Hz), 3.12 (d, 1H, $J = 11.2$ Hz). ^{13}C NMR (CDCl_3), δ 177.95, 143.01,

118.43, 43.32, 39.22, 31.20, 28.11, 27.28, 26.28, 25.97, 25.69, 25.56, 25.47, 25.00, 24.84, 24.01, 21.76, 20.61. MS (EI), m/z 41 (22), 79 (44), 107 (24), 136 (25), 243 (30), 272 (100, M^+). Calcd. for $(C_8H_{12} \cdot CO)_2$: C; 79.37, H; 8.88. Found: C; 79.06, H; 8.83%.

3.3.5. Reaction of carbon monoxide with dibenzobicyclo[2.2.2]octatriene (**1e**)

The reaction of carbon monoxide (20 atm) with **1e** (1 mmol) at 100°C for 10 h in 5 ml acetonitrile in the presence of 2 mol% of the cationic palladium complex afforded 97 mg (41%) of two 2:2 cooligomers **2e** after purification by column chromatography on silica gel (hexane/ $CHCl_3$ = 1/1). The ratio was 39:61 (by 1H NMR). Calcd. for $(C_{16}H_{12} \cdot CO)_2$: C; 87.90, H; 5.21. Found: C; 85.85, H; 5.77%. Analytical samples were obtained by preparative HPLC.

3.3.5.1. 2:2 Cooligomer (*Z*)-**2e**. Minor component. mp 225°C (dec.). IR (KBr), 1791, 1708 cm^{-1} . 1H NMR ($CDCl_3$), δ 2.16–2.21 (m, 1H), 2.26–2.31 (m, 1H), 3.30 (dd, 1H, J = 9.8, 3.7 Hz), 3.76–3.79 (m, 1H), 4.38–4.40 (m, 1H), 4.71 (d, 1H, J = 3.7 Hz), 4.82 (d, 1H, J = 3.1 Hz), 5.06 (s, 1H), 6.64 (d, 1H, J = 7.4 Hz), 6.84 (t, 1H, J = 7.4 Hz), 7.02 (t, 1H, J = 7.4 Hz), 7.05–7.40 (m, 11H), 7.56 (d, 1H, J = 7.2 Hz), 7.66 (d, 1H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$), δ 173.65, 143.90, 138.65–143.19 (8 signals) 122.94–126.79 (16 signals), 114.91, 48.54, 47.92, 47.19, 45.61, 44.36, 43.73, 32.69.

3.3.5.2. 2:2 Cooligomer (*E*)-**2e**. Major component. mp 202°C (dec.). IR (KBr), 1793, 1707 cm^{-1} . 1H NMR ($CDCl_3$), δ 2.45–2.50 (m, 1H), 2.75–2.80 (m, 1H), 3.18–3.25 (m, 2H), 4.43 (d, 1H, J = 3.3 Hz), 4.57 (s, 1H), 4.68 (d, 1H, J = 3.0 Hz), 5.06 (s, 1H), 6.38 (d, 1H, J = 7.4 Hz), 6.82 (t, 1H, J = 7.4 Hz), 7.0–7.4 (m, 14H). ^{13}C NMR ($CDCl_3$), δ 173.66, 142.71, 138.56–143.27 (8 signals), 123.09–126.79 (16 signals), 114.27, 47.64, 46.43, 45.71, 44.75, 44.56, 43.77, 32.44.

3.3.6. Reaction of carbon monoxide with tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (**1f**)

A total yield of 340 mg of yellow oil was obtained. Isolation by column chromatography on silica gel (hexane/ethyl acetate = 10/1) gave 70 mg (18%) of 2:2 cooligomers **2f** which were composed of many isomers. Mixture of two 1:1 codimers **4** in a ratio of 58:42 (124 mg, 32%) was also obtained. Calcd. for $C_{12}H_{16} \cdot CO$: C; 82.94, H; 8.57. Found: C; 82.21, H; 8.84%. Isolation by HPLC (ODS-120A, MeOH/ H_2O = 80/20) gave the 1:1 codimer **4f**.

3.3.6.1. 2:2 Cooligomers **2f**. IR (neat), 1790, 1710 cm^{-1} . MS (EI), m/z 79, 91, 295, 296, 376 (M^+).

3.3.6.2. 1:1 Codimer **4f**: major component. IR (neat), 1740, 1655 cm^{-1} . 1H NMR ($CDCl_3$), δ 1.45–1.55 (m, 2H), 1.67–1.78 (m, 3H), 1.78–1.93 (m, 3H), 1.97–2.04 (m, 1H), 2.10–2.18 (m, 1H), 2.30–2.38 (m, 1H), 2.44–2.56 (m, 2H), 2.78–2.84 (m, 1H), 5.80–5.86 (m, 1H), 5.88–5.95 (m, 1H). ^{13}C NMR ($CDCl_3$), δ 219.94, 127.61, 123.93, 47.83, 46.75, 36.05, 33.27, 32.55, 31.41, 28.89, 27.96, 26.95, 19.23. MS (EI), m/z 67 (53), 77 (31), 79 (100), 91 (30), 131 (27), 144 (23), 188 (30, M^+).

3.3.6.3. 1:1 Codimer **4f**: minor component. IR (neat), 1738, 1655 cm^{-1} . 1H NMR ($CDCl_3$), δ 1.42–1.55 (m, 2H), 1.58–1.79 (m, 3H), 1.84–1.94 (m, 2H), 1.98–2.04 (m, 1H), 2.15–2.22 (m, 1H), 2.26–2.38 (m, 3H), 2.47–2.62 (m, 2H), 5.44–5.50 (m, 1H), 5.74–5.80 (m, 1H). ^{13}C NMR ($CDCl_3$), δ 224.31, 130.23, 126.51, 47.25, 45.82, 36.37, 36.24, 34.20, 29.96, 27.91, 26.88, 23.04, 19.18. MS (EI), m/z 67 (27), 77 (41), 79 (100), 91 (38), 107 (47), 131 (27), 188 (72, M^+).

3.3.7. Reaction of carbon monoxide with bicyclo[2.1.1]hex-2-ene (**1g**)

A total yield of 194 mg of brown solids was obtained after the usual work-up.

3.3.7.1. Carbon monoxide-**1g** cooligomers. IR (KBr), 1750–1770, 1700 cm^{-1} . ^1H NMR (CDCl_3), δ 0.8–3.7 (m), 5.5–5.8 (m), 7.6–7.9 (m). The ratio was approximately 28:1:2. ^{13}C NMR (CDCl_3), δ 210, 176, 127–135, 25–58.

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