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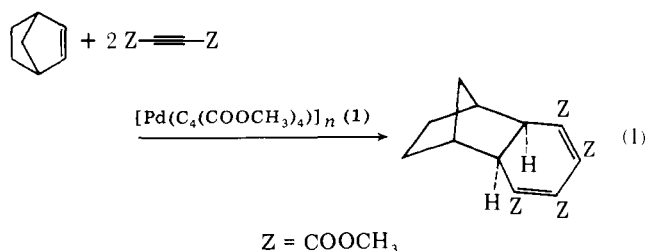
Effects of Donor Molecules on the Palladium-Catalyzed Cyclocotrimerization of Acetylenes with Olefins. Preparation of Dimeric Tetrakis(methoxycarbonyl)palladiacyclopentadiene(base) Complexes and the Structure with Base = 2,6-Lutidine

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Abstract: A tetrakis(methoxycarbonyl)cyclohexadiene annulation of norbornene, cyclopentene, and cyclohexene with two molecules of dimethyl acetylenedicarboxylate (DMAD) is effectively catalyzed by a combination of an oligomeric palladiacyclopentadiene complex, $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)]_n$ (**1**), with 1 equiv of triphenylphosphine. The reaction of **1** with L = pyridine, α -picoline, 2,5-lutidine, 2,6-lutidine, or triphenylphosphine led to new dimeric complexes of formula $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}]_2$. In these complexes there is intermolecular coordination through the carbonyl oxygen atom of the α -methoxycarbonyl group as deduced from spectroscopic results and as shown in an X-ray structure determination of the L = 2,6-lutidine complex. This complex crystallizes with four dimers in space group $C_{2h}^5-P2_1/c$ of the monoclinic system in a cell of dimensions $a = 16.967$ (4) Å, $b = 14.362$ (3) Å, $c = 18.410$ (5) Å, $\beta = 112.05$ (1)°. The structure has been refined by full-matrix least-squares methods to values of R and R_w of 0.036 and 0.050, respectively, based on 440 variables and 8287 observations. Acceleration of the rate of cyclocotrimerization of two DMAD molecules with norbornene by the addition of 1 equiv of triphenylphosphine to the catalyst, **1**, and the formation of the dimeric complex are explained in terms of a common three-coordinate intermediate, " $\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}$ ", which is effectively trapped by an entering cycloolefin in the palladium-catalyzed cyclohexadiene annulation.

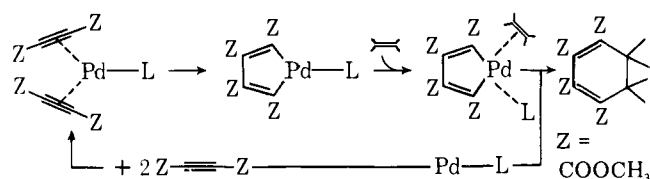
Metallo-cycles have attracted considerable interest because they are often key intermediates in various homogeneous catalytic reactions. For example, metalocyclobutane is an important intermediate in olefin metathesis,² transition metal mediated $[\sigma_2 + \sigma_2]$ skeletal isomerization,³ and $[\sigma_2 + \pi_2]$ cycloadditions⁴ of strained molecules. Metalocyclopentadiene complexes, $[\text{M}(\text{C}_4\text{R}_4)\text{L}]_n$, are key intermediates in cyclooligomerization⁵⁻⁹ or cycloooligomerization¹⁰⁻¹⁶ of various acetylenes using low-valent transition-metal catalysts. Recently we reported that tetrakis(methoxycarbonyl)palladiacyclopentadiene cyclic olefin complexes are key intermediates for a formally $[\pi_2 + \pi_2 + \pi_2']$ cycloooligomerization between two molecules of dimethyl acetylenedicarboxylate (DMAD) and an electron-donating olefin, such as norbornene (NB) or norbornadiene.¹⁶ The oligomeric $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)]_n$ (**1**) species is a catalyst for the cyclocotrimerization of two DMAD molecules with one NB molecule (eq 1). The reaction proceeds



without formation of hexamethyl mellitate, the cyclo-trimerization product of three molecules of DMAD. A plausible mechanism¹⁶ of this palladium-catalyzed cyclocotrimerization reaction is shown in Scheme I, where L is DMAD or a cyclic olefin present as a reactant in the catalytic system.

We have now found that the rate of reaction 1 is markedly increased, after a slight induction period, if triphenylphosphine

Scheme 1



is added to the reaction mixture. The present paper reports these studies, as well as an investigation of the reactions of **1** with various ligands L, including L = PPh₃. Isolable species or proposed intermediates to be discussed include Pd(C₄(COOCH₃)₄)(NB)L (**2**), [Pd(C₄(COOCH₃)₄)L]₂ (**3**), Pd(C₄(COOCH₃)₄)L₂ (**4**), and Pd(C₄(COOCH₃)₄)L (**5**). The nature of the dimeric compound **3d**, with L = 2,6-lutidine, has been established from a single-crystal X-ray study.

Experimental Section

Physical Measurements. Infrared spectra (KBr pellets) were recorded on a JASCO DS 403G spectrometer. ¹H NMR spectra were obtained at 60 MHz on a JEOL C-60HL spectrometer, and chemical shifts were determined relative to internal tetramethylsilane. Molecular weights were measured on a Hitachi Perkin-Elmer Model 115 instrument by vapor pressure osmometry in chloroform. Gas chromatography was performed on a Shimadzu GC-4B instrument equipped with TC detectors.

Materials. The oligomeric palladiacyclopentadiene complex, [PdC₄(COOCH₃)₄]_n (**1**), was prepared from Pd(dibenzylideneacetone)₃(CHCl₃)¹⁷ with an excess of DMAD according to a modified procedure reported previously.^{8,9}

Preparation of [Pd(C₄(COOCH₃)₄)L]₂ (3**), L = Pyridine, **3a**.** To a dichloromethane (8 mL) suspension of **1** (68.88 mg, 0.1664 mmol) a dichloromethane (2 mL) solution of pyridine (13.99 mg, 0.1768 mmol) was added with stirring at room temperature. The mixture turned gradually from a yellow-green suspension to an orange-yellow solution. After 5 h of stirring at room temperature, a trace of metallic palladium was filtered off, and the solution was concentrated under reduced pressure to ca. 3 mL. Ethyl ether (15 mL) was added to the concentrate, and the mixture was kept in a refrigerator for 2 days. The crystals of **3a** were filtered and then washed with excess ethyl ether. The yield was 81.4%, mp 204–205 °C dec. Anal. Calcd for C₃₄H₃₄N₂O₁₆Pd₂: C, 43.47; H, 3.65. Found: C, 43.35; H, 3.59. Mol wt: calcd, 939.5; found, 950.5 amu.

Compound **3a** was also prepared in 93% yield by the disproportionation of **1** (35.25 mg, 0.0902 mmol) and Pd(C₄(COOCH₃)₄)(pyridine)₂ (**4a**, 46.99 mg, 0.08562 mmol) in dichloromethane (5 mL) at room temperature for 3 h.

L = α-Picoline, **3b.** A dichloromethane (2 mL) solution of α-picoline (19.40 mg, 0.2083 mmol) was added to a dichloromethane (5 mL) suspension of **1** (83.36 mg, 0.2134 mmol) and was then stirred at room temperature for 24 h. The resultant yellow-orange solution was filtered in order to remove metallic palladium. The solution was concentrated under reduced pressure to ca. 1.5 mL and ethyl ether (2 mL) was added. The mixture was kept in a refrigerator overnight; orange-yellow crystals of **3b** as the CH₂Cl₂ solvate were then isolated in 98% yield by filtration, mp 195–196 °C dec. Anal. Calcd for C₃₆H₃₈N₂O₁₆Pd₂·CH₂Cl₂: C, 41.75; H, 3.79. Found: C, 42.41; H, 3.67. Mol wt: calcd, 967.5; found, 1054 amu.

L = 2,5-Lutidine, **3c.** A dichloromethane (1 mL) solution of 2,5-lutidine (31.43 mg, 0.2933 mmol) was added to a dichloromethane (4 mL) suspension of **1** (115.2 mg, 0.2951 mmol). After 2 h of stirring at room temperature the resultant green solution was filtered and was concentrated to ca. 0.5 mL. Addition of ethyl ether (3 mL) caused precipitation of **3c** (97.4% yield), mp 197–202 °C dec. Anal. Calcd for C₃₈H₄₂N₂O₁₆Pd₂: C, 45.85; H, 4.45. Found: C, 46.53; H, 4.45. Mol wt: calcd, 995.6; found, 1032 amu.

L = 2,6-Lutidine, **3d.** To a dichloromethane (4 mL) suspension of **1** (57.92 mg, 0.1483 mmol), a dichloromethane (1 mL) solution of 2,6-lutidine (15.73 mg, 0.1468 mmol) was added with stirring at room temperature. The mixture turned immediately to a dark green solution. After removal of trace palladium metal, the solution was concentrated under reduced pressure to ca. 1 mL. Addition of ethyl ether (3 mL) caused precipitation of yellow crystals (82.6% yield), mp 197–200 °C dec. Anal. Calcd for C₃₈H₄₂N₂O₁₆Pd₂: C, 45.85; H, 4.25.

Found: C, 45.82; H, 4.41. Mol wt: calcd, 995.56; found, 961.25 amu.

L = PPh₃, **3e.** A mixture of **1** (296.34 mg, 0.7586 mmol), triphenylphosphine (200.10 mg, 0.7629 mmol), and dichloromethane (20 mL) was stirred for 24 h at room temperature to give an orange-yellow solution. After removal of metallic palladium the solution was concentrated to ca. 1 mL in vacuo and ethyl ether was added (1 mL). The mixture was kept in a refrigerator overnight. The resultant yellow crystals are the dichloromethane solvate of **3e** (NMR δ 5.26, 2 H, s), mp 138–140 °C dec. Anal. Calcd for C₆₁H₅₆Cl₂O₁₆P₂Pd₂: C, 50.51; H, 3.90. Found: C, 50.46; H, 3.96. Mol wt: calcd, 1305; found, 1250 amu.

Complex **3e** was also prepared by the following disproportionation procedure. A dichloromethane (10 mL) suspension of **1** (1.73 mmol) and Pd(C₄(COOCH₃)₄)(PPh₃)₂^{8,9} (**4e**, 1.68 mmol) was stirred at room temperature for 10 min. Workup of the resultant yellow-green solution yielded **3e** in 96% yield.

Preparation of Pd(C₄(COOCH₃)₄)L₂ (4**), L = Pyridine (**4a**).** A dichloromethane (8 mL) suspension of **1** (83.55 mg, 0.2139 mmol) was added with stirring to a dichloromethane (2 mL) solution of pyridine (130.86 mg, 1.654 mmol) at room temperature. Trace metallic palladium was removed from the yellow-green solution which was then concentrated to ca. 1 mL under reduced pressure. Addition of ethyl ether gave pale yellow prisms of **4a** in 97% yield, mp 219–220 °C dec. Anal. Calcd for C₂₂H₂₂N₂O₈Pd: C, 48.15; H, 4.04. Found: C, 48.32; H, 3.48.

L = α-Picoline (4b**).** Compound **4b** was prepared similarly as yellow-green prisms in 90% yield using **1** (88.52 mg, 0.2260 mmol), α-picoline (1 mL), and dichloromethane (10 mL), mp 225–227 °C dec. Anal. Calcd for C₂₄H₂₆N₂O₈Pd: C, 49.97; H, 4.72. Found: C, 50.17; H, 4.43.

L = 2,5-Lutidine (4c**).** Complex **4c** was prepared by adding a dichloromethane (2 mL) solution of 2,5-lutidine (11.31 mg) to a dichloromethane (2 mL) solution of **3c** (33.78 mg, 0.0679 mmol) at room temperature followed by stirring for 2 h. A workup similar to that used for **4a** gave **4c** in 76% yield, mp 201–205 °C dec. Anal. Calcd for C₂₈H₃₀N₂O₈Pd: C, 51.62; H, 5.00. Found: C, 51.41; H, 4.87.

L = 2,6-Lutidine (4d**).** To a dichloromethane (8 mL) suspension of **1** (61.10 mg, 0.1564 mmol) was added a dichloromethane (2 mL) solution of excess 2,6-lutidine (1 mL). The mixture turned to a yellow-green solution after 15 min. Complex **4d** was isolated in 86% yield as yellow needles, mp 153–154 °C dec. Anal. Calcd for C₂₈H₃₀N₂O₈Pd: C, 51.62; H, 4.63. Found: C, 51.41; H, 4.87.

L = Triphenylphosphine (4e**).** Compound **4e** was prepared in 91% yield by the literature method⁸ using **1** (104.47 mg, 0.2674 mmol), PPh₃ (154.23 mg, 0.5880 mmol), and dichloromethane (25 mL), mp 151–152 °C dec (150 °C).⁸ Anal. Calcd for C₄₈H₄₂O₂P₂Pd: C, 62.99; H, 4.63. Found: C, 63.16; H, 4.71.

Rate Measurements. The effect of triphenylphosphine on the rate of cyclocotrimerization of two DMAD molecules with one NB molecule, as catalyzed by **1**, was determined from the remaining DMAD as detected by GLC (stainless steel column, 2.5 mm × 3.0 m length, packed with about 25% Apiezon grease L on 60–80 mesh Shimalite). As a typical run, the catalytic annulation of NB with 1 equiv of PPh₃ is described. Triphenylphosphine (0.0253 mg, 0.097 mmol) and **1** (0.0376 mg, 0.096 mmol) were placed in a 20-mL flask fitted with a three-way stopcock. The flask was purged with argon, and benzene (3.50 mL) was added to form **4e** immediately. Norbornene (0.145 g, 1.54 mmol), DMAD (0.428 g, 3.01 mmol), and decalin (an internal standard of GLC, 0.355 g) were added. The flask was put in a temperature bath kept at 65 °C. A sample was withdrawn with a microsyringe at appropriate intervals and was analyzed by GLC (carrier gas, H₂; the retention time of DMAD was 2.5 min at 130 °C). After all DMAD was consumed (3 h), the product, 5,10-endo-dihydro-6,7,8,9-tetrakis(methoxycarbonyl)benzonorbornene, separated by column chromatography (silica gel, Merck 7734 with a benzene-chloroform mixed solvent), was obtained in 95% yield. The spectroscopic data of the product were consistent with an authentic sample reported previously.

Catalytic Annulation of Cyclopentene with DMAD. A benzene (3 mL) suspension of **1** (0.0125 g, 0.0319 mmol) and triphenylphosphine (0.0082 g, 0.0312 mmol) were placed in a tube. Cyclopentene (0.770 g, 11.3 mmol) and DMAD (0.431 g, 3.04 mmol) were added and the tube was sealed. The mixture was kept at 40 °C for 100 h. The resultant reddish-brown solution was concentrated, and the remaining oil was separated by column chromatography with silica gel (Merck 7734, benzene and chloroform as eluents). The annulation product,

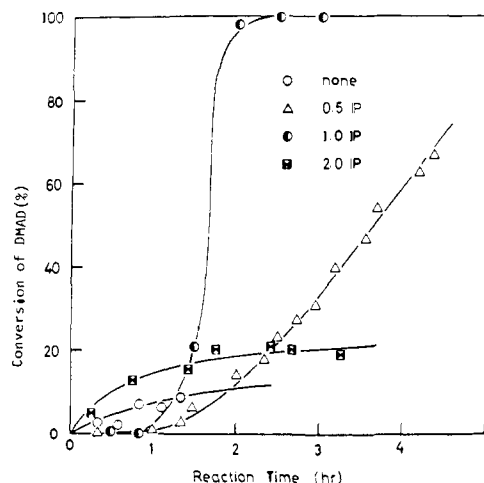


Figure 1. The effect of added equivalents of PPh_3 on the rate of reaction 1.

2,3,8,9-tetrahydro-4,5,6,7-tetrakis(methoxycarbonyl)indene, was isolated as a colorless oil (0.266 g) in 50% yield: IR (CCl_4) 1735 cm^{-1} ($\text{C}=\text{O}$); NMR (CCl_4) δ 1.68 (m, 2 H), 2.65–2.05 (br m, 4 H, homoallylic), 3.18 (d, 2 H, allylic), 3.75 and 3.80 (s, each 6 H, COOCH_3). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_8$: C, 57.95; H, 5.72. Found: C, 57.71; H, 5.55.

Catalytic Annulation of Cyclohexene with DMAD. A benzene (3 mL) solution of **1** (0.0118 g, 0.0302 mmol) and triphenylphosphine (0.0016 g, 0.0215 mmol) was mixed with cyclohexene (0.810 g, 9.86 mmol) and DMAD (0.430 g, 3.03 mmol). The mixture was kept in a sealed tube at 55°C for 4 days. A chromatographic separation similar to that above gave hexahydro-1,2,3,4-tetrakis(methoxycarbonyl)naphthalene in 56% yield (0.298 g) as a colorless oil: IR (CCl_4) 1726 cm^{-1} ($\text{C}=\text{O}$); NMR (CCl_4) δ 1.2–2.1 (br m, 8 H), 2.80 (t, 2 H, allylic), 3.74 (s, 12 H, COOCH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_8$: C, 59.01; H, 6.05. Found: C, 59.46; H, 6.06.

X-ray Diffraction Study of $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(2,6\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_2]$ (3d**).** Crystals of **3d** suitable for the structure determination were obtained by dissolving the material in dichloromethane and then slowly adding diethyl ether. Preliminary film data from a single crystal mounted in air revealed Laue symmetry $2/m$ and systematic absences characteristic of space group $C_{2h}^2\text{-}P2_1/c$. Based on the setting angles of 12 manually centered reflections ($30^\circ < 2\theta(\text{Mo K}\alpha_1) < 32^\circ$) the cell constants of Table I were obtained. Data were collected at room temperature on a Picker FACS-I diffractometer using methods standard in this laboratory.¹⁸ Some of the details of data collection and reduction are given in Table I.

The structure was solved in a straightforward way, using procedures and computer programs described before.¹⁸ From a sharpened, origin-removed Patterson function the positions of the two Pd atoms were evident. The other nonhydrogen atoms were found through the usual combination of least-squares refinement and difference Fourier techniques. The atoms of the two pyridine rings of the lutidine ligands were treated as rigid groups. After one cycle of anisotropic refinement of the independent nonhydrogen atoms, together with isotropic refinement of the atoms of the two rigid groups, the hydrogen atoms of the 12 methyl groups were apparent on a subsequent difference Fourier map. These positions were idealized, using a C–H bond length of 0.95 \AA and assigning $B(\text{H}) = B(\text{C}) + 1\text{ \AA}^2$. The positions of the hydrogen atoms on the pyridine rings were idealized in a similar manner. The fixed contributions of these hydrogen atoms were included in subsequent calculations. The final cycle of full-matrix least-squares refinement converged to values of R and R_w of 0.036 and 0.050, respectively, and to an error in an observation of unit weight of 1.64 electrons, for the 440 variables and 8287 observations. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices showed nothing unusual. Of those reflections having $F_o^2 < 3\sigma(F_o^2)$ which were omitted from the refinement, only three have $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$. Peaks in the final difference Fourier map range in height from -0.9 (1) to $+0.9$ (1) $\text{e}/\text{\AA}^3$.

Final positional and thermal parameters are tabulated in Tables II and III. The idealized positions of the hydrogen atoms are given in

Table I. Crystal Data and Data Collection Procedures for $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(2,6\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_2]$

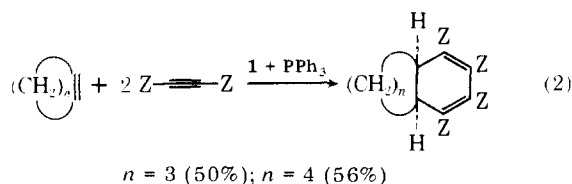
compd	$[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(2,6\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_2]$
formula	$\text{C}_{38}\text{H}_{42}\text{N}_2\text{Pd}_2\text{O}_{16}$
mol wt	995.56 amu
<i>a</i>	16.967 (4) \AA
<i>b</i>	14.362 (3) \AA
<i>c</i>	18.410 (5) \AA
β	112.05 (1) $^\circ$
<i>V</i>	4158.1 \AA^3
<i>Z</i>	4
space group	$C_{2h}^2\text{-}P2_1/c$
ρ_c	1.590 g/cm^3
ρ_o	1.57 (2) g/cm^3
bounding planes	$\{10\bar{1}\}, \{100\}, \{011\}, \{001\}$
crystal volume	0.0687 mm^3
linear absorption coefficient (Mo $\text{K}\alpha$)	9.23 cm^{-1}
transmission factors	0.697–0.787
takeoff angle	2.7°
aperture	3.2 mm wide by 4.7 mm high 32 cm from crystal
scan range	0.6° below Mo $\text{K}\alpha_1$ peak to 0.6° above Mo $\text{K}\alpha_2$ peak
scan speed	2.0° $2\theta/\text{min}$
collection range	$\pm h, +k, +l$ $3^\circ \leq 2\theta(\text{Mo K}\alpha_1) \leq 55^\circ$
number of data	10 302 total; 8287 unique with $F_o^2 > 3\sigma(F_o^2)$ ($p = 0.04$)

Table IV.¹⁹ Table V gives the root-mean-square amplitudes of vibration.¹⁹ Values of $10|F_o|$ vs. $10|F_c|$ for those reflections used in the refinement are given in Table VI.¹⁹

Results

The selective cyclocotrimerization of two molecules of DMAD and one molecule of norbornene is catalyzed by an oligomeric palladiacyclopentadiene complex, $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)]_n$ (**1**), to give stereoselectively an exo-annulation product.¹⁶ When triphenylphosphine is added to the system, the reaction rate is enhanced considerably after a slight induction period, as shown in Figure 1. The rate enhancement is maximum when 1 equiv of triphenylphosphine is added to the catalytic complex **1**. However, when 2 equiv is added, the reaction rate is still higher than it is without triphenylphosphine.

Addition of triphenylphosphine not only accelerates the rate of the catalysis but also broadens the choice of the olefin component. In fact, the catalytic annulation of cyclopentene or cyclohexene with two molecules of DMAD proceeds readily (reaction 2) in the presence of **1** and an equimolar amount of



triphenylphosphine. These two cyclic olefins do not cyclocotrimerize with DMAD at all in the absence of triphenylphosphine.

As a means of assessing the effects of PPh_3 on the catalytic system, PPh_3 , as well as several other donor ligands, was reacted with **1**. When the ratio of donor ligand to **1** was 1:1, complexes of the general formula $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}]_2$ (**3a–e**) were obtained in good yield, whereas in the presence of excess L complexes^{8,9} of the type $\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}_2$ (**4a–e**) were obtained. The spectroscopic data on these complexes are listed in Table VII. The strong bands in the carbonyl

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(2,6\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_2]$

ATOM	X ^A	Y	Z	B ^B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
POA	0.141039(14)	0.073356(16)	0.368020(13)	23.52(10)	31.23(13)	20.07(9)	-0.08(8)	9.52(7)	2.66(7)
POB	0.299642(14)	0.116984(16)	0.571377(13)	21.16(10)	28.04(12)	23.18(9)	-1.02(8)	8.90(7)	0.16(7)
O(11A)	0.18961(13)	0.03916(15)	0.56846(12)	28.4(9)	36.3(11)	21.4(7)	-7.3(8)	12.3(7)	-4.3(7)
O(21A)	0.09138(16)	-0.07221(17)	0.53179(14)	42.1(11)	50.5(14)	31.2(9)	-19.6(10)	23.7(8)	-10.3(9)
O(31A)	0.14407(18)	-0.27151(17)	0.44747(16)	55.4(14)	36.6(13)	38.9(11)	-13.0(11)	10.6(10)	0.9(10)
O(41A)	0.24340(17)	-0.19041(19)	0.54000(14)	51.0(13)	49.9(15)	25.2(9)	-12.4(11)	4.3(8)	9.4(9)
O(51A)	0.18511(22)	-0.20754(21)	0.23701(15)	86.5(20)	56.9(18)	30.9(10)	10.9(15)	20.9(12)	-4.7(11)
O(61A)	0.25379(18)	-0.25294(20)	0.36010(16)	47.4(13)	55.3(16)	36.9(11)	16.2(12)	13.8(10)	-5.0(11)
O(71A)	0.08096(18)	-0.01042(24)	0.17071(15)	46.1(13)	107.0(24)	23.5(9)	5.7(14)	5.9(9)	1.6(12)
O(81A)	0.22233(17)	-0.00024(19)	0.21492(14)	49.5(13)	57.0(16)	32.0(9)	7.5(12)	24.8(9)	12.2(10)
C(11A)	0.15486(18)	-0.03252(21)	0.44314(16)	24.7(12)	31.4(15)	18.8(9)	-1.7(11)	9.0(9)	1.1(10)
C(21A)	0.17412(20)	-0.11581(21)	0.42085(17)	24.6(12)	33.2(15)	20.9(10)	-3.3(11)	9.4(9)	0.0(10)
C(31A)	0.17680(21)	-0.11525(22)	0.34178(18)	28.3(13)	36.7(16)	23.0(11)	-3.3(12)	11.8(10)	-3.7(11)
C(41A)	0.15912(19)	-0.03174(23)	0.30601(17)	26.2(13)	39.4(16)	21.1(10)	-2.1(12)	10.2(9)	-2.0(11)
C(51A)	0.14883(19)	-0.01865(20)	0.51931(17)	24.0(12)	30.8(14)	22.8(10)	-1.3(11)	11.2(9)	1.5(10)
C(61A)	0.18510(21)	-0.20165(23)	0.46873(18)	30.3(14)	36.3(16)	23.0(11)	0.7(12)	11.3(10)	1.9(11)
C(71A)	0.20367(22)	-0.19568(24)	0.30586(20)	36.7(14)	36.9(17)	29.5(12)	-5.3(13)	19.1(11)	-4.4(12)
C(81A)	0.14896(24)	-0.01579(25)	0.22353(19)	42.3(17)	45.6(18)	23.1(11)	4.2(14)	15.2(11)	0.5(12)
ME(11A)	0.0844(3)	-0.0647(3)	0.60782(23)	70.6(24)	87.(3)	40.6(15)	-40.5(21)	41.3(17)	-21.2(17)
ME(21A)	0.2558(4)	-0.2688(3)	0.59199(26)	92.(3)	74.(3)	37.3(17)	-5.6(25)	3.0(18)	27.9(19)
ME(31A)	0.2649(3)	-0.33360(28)	0.3332(3)	54.9(24)	46.2(20)	63.3(23)	14.2(18)	26.5(19)	-6.2(17)
ME(41A)	0.2158(4)	0.0249(4)	0.13658(26)	95.(3)	86.(3)	44.6(17)	19.8(20)	47.5(21)	25.7(20)
ME(51A)	-0.01505(23)	0.1704(3)	0.24012(23)	29.9(15)	81.(3)	35.6(15)	7.6(17)	7.8(12)	17.1(18)
ME(61A)	0.29477(23)	0.1705(3)	0.33811(26)	29.9(15)	76.6(29)	46.8(18)	-13.3(17)	10.3(13)	-4.3(18)
O(11B)	0.10087(13)	0.17752(15)	0.43162(13)	24.6(9)	35.4(11)	28.1(8)	1.1(8)	9.5(7)	-0.7(8)
O(21B)	0.11200(15)	0.29606(17)	0.51241(16)	28.7(10)	48.6(14)	46.6(11)	3.5(10)	15.1(9)	-13.4(10)
O(31B)	0.29983(21)	0.45313(21)	0.46465(24)	48.3(16)	49.2(16)	108.2(22)	-8.2(13)	9.2(15)	34.5(15)
O(41B)	0.17752(19)	0.37727(19)	0.40478(19)	38.9(13)	51.3(17)	60.0(14)	4.2(12)	3.7(11)	23.1(12)
O(51B)	0.49651(19)	0.38463(20)	0.58402(17)	51.9(14)	65.9(17)	44.4(12)	-30.3(13)	18.5(11)	-12.1(12)
O(61B)	0.44966(18)	0.33303(19)	0.46101(15)	48.9(13)	54.5(16)	37.0(10)	-15.8(12)	18.7(10)	-0.8(10)
O(71B)	0.54127(18)	0.17422(25)	0.59555(19)	35.6(12)	99.4(25)	56.7(14)	13.9(14)	21.8(11)	0.8(15)
O(81B)	0.50283(17)	0.14440(22)	0.69579(17)	33.5(12)	77.5(19)	41.3(11)	-6.5(12)	2.4(9)	14.5(12)
C(11B)	0.23865(20)	0.23056(22)	0.51319(18)	25.2(12)	31.1(14)	26.4(11)	1.4(11)	10.3(9)	-0.7(10)
C(21B)	0.28777(21)	0.29703(23)	0.50021(20)	27.4(13)	31.1(16)	32.4(12)	-0.6(12)	9.4(10)	1.6(11)
C(31B)	0.37938(20)	0.27813(23)	0.53919(20)	25.8(13)	33.6(16)	32.4(13)	-3.0(12)	10.4(10)	-1.8(11)
C(41B)	0.39712(20)	0.19879(22)	0.58107(19)	24.5(12)	31.4(15)	30.7(12)	-1.9(11)	9.9(10)	-1.3(11)
C(51B)	0.14534(20)	0.23326(22)	0.48092(19)	26.6(13)	31.5(15)	26.5(11)	2.4(11)	11.3(10)	1.7(11)
C(61B)	0.25738(25)	0.38410(26)	0.45522(25)	35.9(17)	41.3(19)	49.0(18)	0.5(15)	14.5(14)	13.4(15)
C(71B)	0.44715(21)	0.33900(23)	0.53218(21)	28.3(13)	33.4(16)	35.6(14)	-3.8(12)	10.5(11)	-0.5(12)
C(81B)	0.48712(21)	0.17152(25)	0.62316(22)	30.3(14)	36.7(18)	36.9(14)	-4.2(13)	7.4(11)	-2.2(13)
ME(11B)	0.01989(21)	0.3039(3)	0.4827(3)	29.2(13)	73.7(28)	76.5(25)	11.9(16)	22.7(15)	-21.6(21)
ME(21B)	0.13825(28)	0.4603(3)	0.3619(3)	52.0(21)	67.5(25)	92.7(28)	19.7(19)	7.3(20)	48.8(23)
ME(31B)	0.5173(3)	0.3831(3)	0.4484(3)	67.4(25)	64.1(27)	61.7(23)	-17.2(21)	42.3(21)	1.3(20)
ME(41B)	0.58774(27)	0.1054(4)	0.73587(28)	39.4(18)	84.(4)	57.1(20)	5.2(20)	-10.4(15)	19.0(22)
ME(51B)	0.35943(27)	0.0232(3)	0.74147(21)	49.4(20)	60.4(24)	27.2(12)	1.6(18)	15.4(13)	5.5(14)
ME(61B)	0.38402(24)	-0.01811(27)	0.48882(21)	33.6(16)	53.9(22)	34.3(14)	2.8(15)	15.4(12)	-3.8(14)

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^B THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $\exp[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23})]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^4$.

Table III. Derived Parameters for the Rigid Group Atoms of $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(2,6\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_2]$

ATOM	X	Y	Z	B ^B _A	ATOM	X	Y	Z	B ^B _A
NA	0.13976(13)	0.17509(13)	0.28647(11)	2.86(5)	NB	0.37484(12)	-0.00264(12)	0.61734(11)	2.79(4)
C(91A)	0.06614(10)	0.20964(16)	0.23615(13)	3.61(6)	C(91B)	0.39548(15)	-0.03221(15)	0.69124(10)	3.42(6)
C(101A)	0.06042(13)	0.27692(18)	0.17977(14)	5.05(8)	C(101B)	0.44776(17)	-0.10866(17)	0.72297(10)	4.47(8)
C(111A)	0.13537(18)	0.31069(17)	0.17499(14)	6.03(10)	C(111B)	0.48084(16)	-0.15772(15)	0.67549(14)	4.99(9)
C(121A)	0.21255(14)	0.27550(19)	0.22691(16)	5.23(9)	C(121B)	0.46002(16)	-0.12790(16)	0.59843(13)	4.29(7)
C(131A)	0.21119(10)	0.20829(16)	0.28109(13)	3.75(7)	C(131B)	0.40717(14)	-0.05055(15)	0.57250(9)	3.18(6)

GROUP	X ^A _C	Y _C	Z _C	DELTA ^B	EPSILON	ETA
RING 1	0.13758(10)	0.24241(11)	0.23113(9)	-1.5793(15)	3.0993(15)	-2.3362(16)
RING 2	0.42746(10)	-0.07962(10)	0.64620(9)	0.6425(15)	3.0005(12)	1.5661(17)

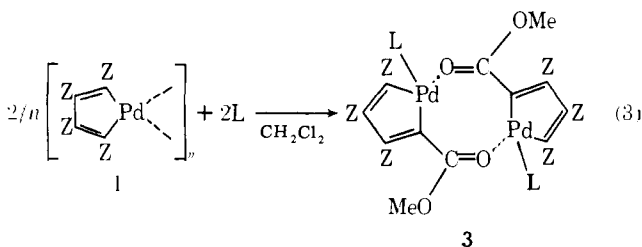
^A X, Y, AND Z ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^B THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETAS (DEGREES) HAVE BEEN DEFINED PREVIOUSLY: S.J., LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

Table VII. Spectroscopic Results on [Pd(C₄(COOCH₃)₄)L₂] (3) and Pd(C₄(COOCH₃)₄)L₂ (4) Complexes

complex	chemical shifts, δ ppm (CDCl ₃)							$\nu(\text{C}=\text{O})$, cm ⁻¹ (KBr)		
	α -COOCH ₃	β -COOCH ₃	H(2)	H(3)	H(4)	CH ₃	free	bridging		
[Pd(C ₄ (COOCH ₃) ₄)(C ₅ H ₅ N)] ₂ (3a)	3.19 (6 H, s)	3.24 (6 H, s)	3.68 (6 H, s)	3.71 (6 H, s)	8.66 (4 H, dd)	7.35 (4 H, m)	7.68 (2 H, dd)	1724	1618	
Pd(C ₄ (COOCH ₃) ₄)(C ₅ H ₅ N) ₂ (4a) ^d	3.10 (6 H, s)			3.58 (6 H, s)	8.54 (4 H, dd)	7.25 (4 H, m)	7.71 (2 H, m)	1720	1695	
[Pd(C ₄ (COOCH ₃) ₄)-(2-MeC ₅ H ₄ N) ₂] (3b)	3.12 (6 H, s)	3.22 (6 H, s)		3.68 (12 H, s)	8.75 (2 H, dd)	7.12 (2 H, m)	7.64 (2 H, m)	1725	1621	
Pd(C ₄ (COOCH ₃) ₄)(2-Me-C ₅ H ₄ N) ₂ (4b)	3.08 (6 H, s)			3.62 (6 H, s)	8.67 (2 H, dd)	7.21 (4 H, m)	7.63 (2 H, m)	2.95 3.02 (6 H, s)	1713	
[Pd(C ₄ (COOCH ₃) ₄)(2,5-Me ₂ C ₅ H ₃ N) ₂] (3c)	3.11 (3 H, s)	3.19 (3 H, s)		3.66 (12 H, s)	8.54 (2 H, m)	7.00 (2 H, br)	6.80- 7.30 (2 H, m)	2.30 (5) 2.85 (2) (12 H, s)	1724 1710	1622
Pd(C ₄ (COOCH ₃) ₄)(2,5-Me ₂ C ₅ H ₃ N) ₂ (4c)	3.06 (6 H, s)			3.59 (6 H, s)	8.47 (2 H, m)	7.00 (2 H, br)	6.80- 7.20 (2 H, m)	2.27 (6 H, s) 2.91 (3 H, s) 2.85 (3 H, s)	1722 1704	
[Pd(C ₄ (COOCH ₃) ₄)(2,6-Me ₂ C ₅ H ₃ N) ₂] (3d)	3.16 (6 H, s)	3.22 (6 H, s)		3.62 (12 H, s)		7.02 (4 H, dd)	7.50 (2 H, dd)	3.06 (6 H, s) 3.08 (6 H, s)	1724 1704	1622
Pd(C ₄ (COOCH ₃) ₄)(2,6-Me ₂ C ₅ H ₃ N) ₂ (4d)	dissociation of 2,6-lutidine ^b								1722 1706	
[Pd(C ₄ (COOCH ₃) ₄)(PPh ₃) ₂ ·CH ₂ Cl ₂] (3e) ^c	2.59 (6 H, s)	3.12 (6 H, s)	3.39 (6 H, s)	3.78 (6 H, s)	7.63 (12 H, m)		7.41 (18 H, m)	1723 1707	1618	
Pd(C ₄ (COOCH ₃) ₄)(PPh ₃) ₂ (4e)	2.71		3.62		7.17 (30 H, br m)			1718 1698		

^a s, singlet; dd, doublet of doublet; m, multiplet. ^b See text. ^c δ 5.26 (2 H, s; CH₂Cl₂). ^d Measured in dichloromethane because of solubility.

stretching region between 1696 and 1722 cm⁻¹ are characteristic of the Pd(C₄(COOCH₃)₄) skeleton. The strong, lower frequency bands, also in the carbonyl stretching region, at 1618–1622 cm⁻¹ may reasonably be assigned to methoxycarbonyl groups involved in intermolecular coordination of the monomer species to form the dimers. From the NMR data of Table VII it is seen that the methyl proton signals of the α -methoxycarbonyl group split into two singlets in complexes 3a–e. The splittings of these proton signals from the β -methoxycarbonyl group are smaller in 3a and 3e and are not observed at all in 3b and 3c. We thus conclude that one of the α -methoxycarbonyl groups, rather than a β -methoxycarbonyl group, is involved in intermolecular coordination (eq 3). Mo-



seley and Maitlis⁸ proposed a possible structure of the oligomeric complex 1 involving bridging through the two oxygen atoms of the carbonyl groups on the β -methoxycarbonyl substituents; however, their evidence did not eliminate the possibility that the α -methoxycarbonyl, rather than the β -methoxycarbonyl, groups might be involved.

These deductions from spectroscopic data have been confirmed by the determination of the crystal and molecular structure of [Pd(C₄(COOCH₃)₄)(2,6-(CH₃)₂C₅H₃N)₂] (3d).

The crystal structure consists of well-separated dimers. A view of one such dimer is shown in Figure 2. A tabulation of important distances and angles is given in Table VIII. Indeed dimer formation occurs through bridges involving the oxygen atom of the carbonyl group on one of the α -methoxycarbonyl groups of each monomer unit. In the dimer thus formed each Pd atom maintains nearly square-planar geometry. The central eight-membered ring Pd–C–C–O–Pd–C–C–O is distinctly nonplanar. The ring has approximately a boat configuration as indicated by the least-squares plane data and the conformational angles of Table IX. However, each of the PdC₄ rings maintains its expected planarity, the largest deviation from planarity being 0.08 Å. The dihedral angle between the two PdC₄ rings is 95.6°.

There is exceptionally good agreement in the metrical details of the A and B portions of the present dimer (Table VIII). Moreover, the Pd(C₄(COOCH₃)₄) portion of each monomer is in excellent agreement with that portion of the Pd(C₄(COOCH₃)₄)(norbornadiene)¹⁶ structure. Table X presents such a comparison for the Pd–C₄ rings. The absence of delocalization or aromatic character in the PdC₄ rings is again apparent from the bond length alternation. In principle such delocalization could occur in a d⁸ complex.²⁰ There are very slight variations in the angles within the metallocycle. However, the only large differences occur in the Pd–C distances; these distances undoubtedly are sensitive to the nature of the trans ligands. In particular, in the present complex note the significantly longer Pd–C distance trans to the N atom of the donor ligand.

An attempt to measure the NMR spectrum of Pd(C₄(COOCH₃)₄)(2,6-lutidine)₂ (4d) resulted in a complex spectrum composed of a mixture of 4d (δ 2.96 s of 2-methyl), dimeric 3d, and free 2,6-lutidine (δ 2.51 s, 6.93 dd, 7.43 m).

Table VIII. Selected Distances (Å) and Angles (deg) in $[\text{Pd}(\text{C}_4(\text{COOMe})_4)(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})]_2$

distance	A ^a	B ^a	angle	A	B	angle	A	B
Pd-C(1)	2.009 (3)	2.012 (3)	C(1)-Pd-C(4)	79.5 (1)	79.2 (1)	C(1)-C(2)-C(6)	123.2 (3)	126.1 (3)
Pd-C(4)	1.985 (3)	1.982 (3)	C(1)-Pd-O(1)	97.5 (1)	98.0 (1)	C(3)-C(2)-C(6)	123.2 (3)	120.7 (3)
Pd-N	2.089 (2)	2.118 (2)	C(1)-Pd-N	172.3 (1)	169.4 (1)	C(2)-C(1)-C(5)	121.9 (3)	123.7 (3)
PdA-O(1)B	2.162 (2)		C(4)-Pd-O(1)	170.5 (1)	173.6 (1)	C(2)-C(3)-C(7)	124.3 (3)	123.9 (3)
PdB-O(1)A	2.159 (2)		C(4)-Pd-N	94.6 (1)	95.0 (1)	C(4)-C(3)-C(7)	121.6 (3)	122.2 (3)
C(1)-C(2)	1.344 (4)	1.346 (4)	O(1)-Pd-N	89.1 (1)	88.6 (1)	C(3)-C(4)-C(8)	123.9 (3)	119.2 (3)
C(2)-C(3)	1.473 (4)	1.472 (4)	Pd-C(1)-C(2)	116.3 (2)	116.1 (2)	Pd-C(4)-C(8)	119.3 (2)	123.5 (2)
C(3)-C(4)	1.347 (4)	1.345 (5)	C(1)-C(2)-C(3)	113.4 (3)	113.2 (3)			
C(1)-C(5)	1.457 (4)	1.468 (4)	C(2)-C(3)-C(4)	113.8 (3)	113.8 (3)	C(9)-N-C(13)	116.8 ^b	
C(2)-C(6)	1.486 (4)	1.482 (5)	C(3)-C(4)-Pd	116.8 (2)	116.8 (2)	N-C(9)-C(10)	123.9 ^b	
C(3)-C(7)	1.485 (4)	1.488 (5)	Pd-C(1)-C(5)	121.8 (2)	119.9 (2)	N-C(13)-C(12)}	118.5 ^b	
C(4)-C(8)	1.480 (4)	1.482 (5)	C(1)-C(5)-O(1)	125.2 (3)	123.3 (3)	C(9)-C(10)-C(11)}	118.5 ^b	
C(5)-O(1)	1.232 (4)	1.233 (4)	C(5)-O(1)-Pd	127.5 (2)	128.2 (2)	C(13)-C(12)-C(11)}	118.3 ^b	
C(6)-O(3)	1.200 (4)	1.199 (5)	C(1)-C(5)-O(2)	114.1 (3)	114.7 (3)	C(10)-C(11)-C(12)	117.2 (2)	116.3 (2)
C(7)-O(5)	1.198 (4)	1.201 (4)	C(2)-C(6)-O(4)	111.6 (3)	112.2 (3)	N-C(9)-Me(5)	117.3 (3)	117.3 (2)
C(8)-O(7)	1.200 (4)	1.206 (5)	C(3)-C(7)-O(6)	111.4 (3)	111.1 (3)	N-C(13)-Me(6)	118.9 (2)	119.9 (2)
C(5)-O(2)	1.328 (4)	1.310 (4)	C(4)-C(8)-O(8)	113.2 (3)	112.6 (3)	C(10)-C(9)-Me(5)	118.8 (2)	118.8 (2)
C(6)-O(4)	1.324 (4)	1.328 (5)	C(2)-C(6)-O(3)	124.9 (3)	123.6 (4)	C(12)-C(13)-Me(6)	120.7 (2)	123.5 (2)
C(7)-O(6)	1.326 (4)	1.329 (4)	C(3)-C(7)-O(5)	125.4 (3)	125.6 (3)	Pd-N-C(9)	122.4 (1)	119.7 (1)
C(8)-O(8)	1.332 (4)	1.320 (5)	C(4)-C(8)-O(7)	123.2 (3)	124.7 (4)	Pd-N-C(13)		
O(2)-Me(1)	1.452 (4)	1.454 (4)	O(1)-C(5)-O(2)	120.7 (3)	121.8 (3)			
O(4)-Me(2)	1.441 (4)	1.448 (4)	O(3)-C(6)-O(4)	123.5 (3)	124.2 (4)			
O(6)-Me(3)	1.437 (4)	1.445 (4)	O(5)-C(7)-O(6)	123.2 (3)	123.2 (3)			
O(8)-Me(4)	1.450 (4)	1.461 (5)	O(7)-C(8)-O(8)	123.4 (3)	122.7 (3)			
C(9)-Me(5)	1.515 (5)	1.512 (5)	C(5)-O(2)-Me(1)	117.0 (3)	118.0 (3)			
C(13)-Me(6)	1.513 (4)	1.513 (4)	C(6)-O(4)-Me(2)	115.6 (3)	117.4 (3)			
N-C(9)-C(13)	1.340 ^b		C(7)-O(6)-Me(3)	117.1 (3)	116.5 (3)			
C(9)-C(10),	1.395 ^b		C(8)-O(8)-Me(4)	115.8 (3)	114.2 (3)			
C(11)-C(10),-C(12)								
C(12)-C(13)								

^a A and B denote the "A" and "B" atoms of the dimer. ^b The NC₅ portion of the pyridine ring was treated as a rigid group having these dimensions, as determined by microwave spectroscopy (B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1968)).

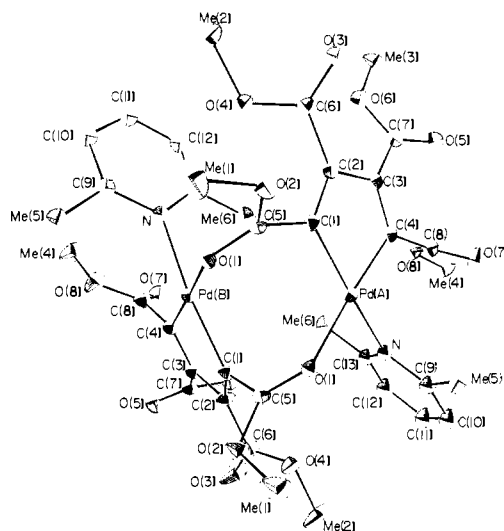
Table IX. Metrical Details on the Pd-C-C-O-Pd-C-C-O Ring

equation of best weighted least-squares plane	
$15.404x - 4.487y - 11.046z + 2.248 = 0$	
deviations (Å) from this plane	
Pd(A) 0.0259 (2); C(1A) -0.116 (3); C(5A) -1.113 (3); O(1A) -1.287 (2);	
Pd(B) 0.0269 (2); C(1B) -0.779 (3); C(5B) -1.873 (3); O(1B) -1.763 (2)	
torsion angles, deg	
Pd(A)-C(1A)-C(5A)-O(1A)	-52.8 (4)
C(1A)-C(5A)-O(1A)-Pd(B)	-14.1 (4)
C(5A)-O(1A)-Pd(B)-C(1B)	92.6 (3)
O(1A)-Pd(B)-C(1B)-C(5B)	-3.8 (3)
Pd(B)-C(1B)-C(5B)-O(1B)	-60.4 (4)
C(1B)-C(5B)-O(1B)-Pd(A)	-8.0 (5)
C(5B)-O(1B)-Pd(A)-C(1A)	91.7 (3)
O(1B)-Pd(A)-C(1A)-C(5A)	-8.1 (2)

Table X. Comparisons of the Geometries of the PdC₄ Skeleton

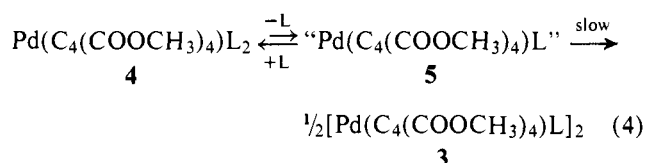
	$\text{Pd}(\text{C}_4(\text{COOCH}_3)_4\text{-norbornadiene})^a$	$[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4\text{-}(2,6\text{-lutidine}))_2]^b$
<i>a</i> , Å	2.023 (3)	2.011 (3)
<i>b</i> , Å	1.343 (4)	1.984 (3)
<i>c</i> , Å	1.479 (3)	1.346 (4)
α , deg	79.7 (1)	79.4 (1)
β , deg	115.7 (2)	116.5 (2)
γ , deg	114.5 (2)	113.6 (3)

^a Reference 16. ^b Average values from present work.

**Figure 2.** A drawing of the $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(2,6\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})]_2$ molecule. Hydrogen atoms have been omitted. Other atoms are drawn at the 20% probability level for thermal vibration. The labeling scheme is shown.

This indicates that **4d**, although stable in the solid state, dissociates one molecule of sterically hindered 2,6-lutidine in solution to give a mixture of about 83% of dimer **3d** and 17% of monomer **4d** at room temperature. This observation suggests the possibility that one molecule of donor ligand is liberated from $\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}_2$ (**4**) to give the corresponding coordinatively unsaturated monomer, " $\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}$ " (**5**), which dimerizes through the intermolecular carbonyl

bridging of the α -methoxycarbonyl group to give $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4\text{L})_2]$ (**3**).



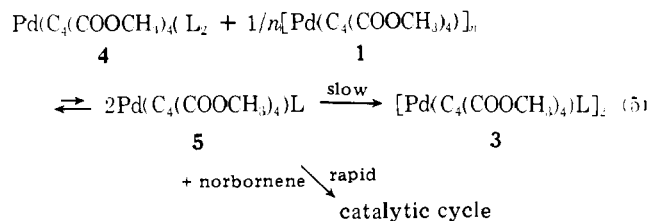
Similar phenomena are observed in the initial stages of the reactions between oligomer **1** and donor ligands. At the early stage of the reaction between **1** and equimolar triphenylphosphine, for example, the mixture is composed of unreacted **1** and monomeric $\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)(\text{PPh}_3)_2$ (**4e**) which slowly disproportionates to **3e**. This disproportionation process is confirmed by the direct reaction between **1** and **4e** which in 10 min at 25 °C gives **3e** in 96% yield.

The dimeric complex **3e** is a surprisingly poor catalyst for the cyclohexadiene annulation of norbornene with an excess of DMAD; only 29% of DMAD is consumed with 6% of **3e** at 45 °C for 9 days. Under these conditions all DMAD is converted to the adduct with either **1** alone or with a combination of **1** and an equivalent amount of triphenylphosphine. The catalytic inactivity of **3e** suggests that the intermolecular bridging of the α -methoxycarbonyl groups in the dimeric complex **3e** is stable to ligand cleavage by an entering cyclic olefin.

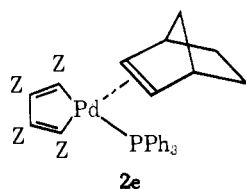
Discussion

In the presence of $[\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)]_n$ (**1**) a catalytic cyclocotrimerization of two molecules of DMAD with one molecule of NB occurs (reaction 1). The rate of this reaction is increased markedly, after a slight induction period, if PPh_3 is added to the reaction mixture. The observations detailed above enable us to offer a plausible explanation for these facts.

The presence of the following disproportionation process (eq 5) is consistent with the appearance of the induction period (Figure 1).

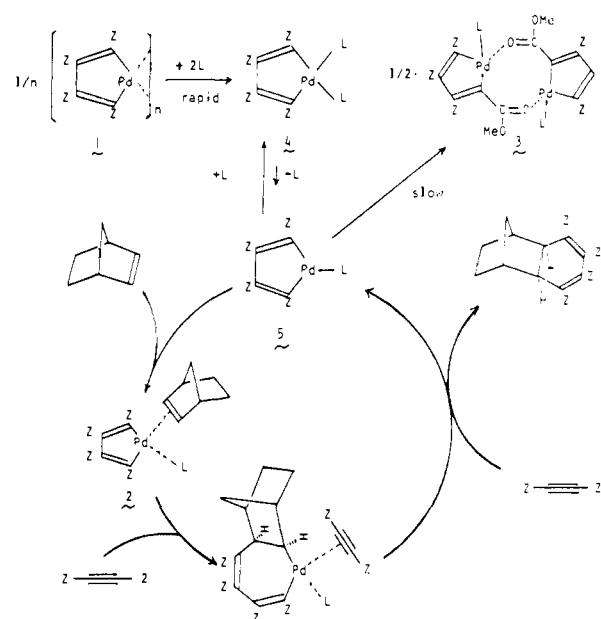


The induction period corresponds to the time required for generating an active three-coordinate intermediate, " $\text{Pd}(\text{C}_4(\text{COOCH}_3)_4)\text{L}$ " (**5**), which is either rapidly intercepted by an existing cyclic olefin or is slowly dimerized to the catalytically inactive dimeric complex **3**. The relation between the catalytic cyclohexadiene annulation and the formation of **3a-e** is shown in Scheme II, where these two reactions have **5** as a common intermediate. If one engages in mechanistic speculation, then the accelerating effect of PPh_3 on reaction **1** is plausibly explained in terms of the intermediate **2e**. The Pd-C



bond trans to PPh_3 in **2e** is more susceptible to the insertion of the coordinated olefin because of the translabilizing influence of this donor ligand. Such an influence was evident in the Pd-C bond lengths in **3d**.

Scheme II



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Supplementary Material Available: Table IV, idealized positions of the hydrogen atoms, Table V, root-mean-square amplitudes of vibration, and Table VI, a listing of structure amplitudes (61 pages). Ordering information is given on any current masthead page.

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