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Preparation, Structure, and Role of Tetrakis(methoxycarbonyl)palladiacyclopentadiene Cyclic Diolefin Complexes in Selective Palladium-Catalyzed Cyclocotrimerization of Acetylenes with Olefins

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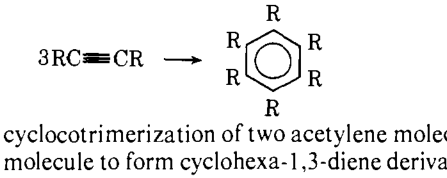
Abstract: Tetrakis(methoxycarbonyl)palladiacyclopentadiene cyclic diolefin complexes, Pd[$C_4(COOCH_3)_4$]L, for L = 1,5-cyclooctadiene and norbornadiene have been prepared. The latter complex has been characterized crystallographically. The material crystallizes with two molecules in space group $C_i{}^1$-$P\bar{1}$ in a cell of dimensions a = 10.560 (2), b = 10.583 (2), c = 9.710 (2) Å, α = 99.33 (1), β = 113.24 (1), and γ = 85.53 (2)°. The structure has been refined by standard methods to a conventional R index of 0.027, based on 3646 reflections above background. There is a nearly symmetrical coordination of the diolefin to the palladium atom of the metallocycle. The olefinic C═C bond lengths of 1.352 (4) Å in the norbornadiene fragment together with spectroscopic results suggest a net transfer of electrons from the electron-rich norbornadiene to the metallocycle which has electron-withdrawing substituents. The fact that the diolefin bonds more strongly to the metallocycle than does an activated acetylene is brought to bear on mechanisms of cyclotrimerization of acetylenes and cyclocotrimerization of two acetylene and one olefin molecule. The parent oligomeric Pd[$C_4(COOCH_3)_4$] complex is an efficient catalyst for the cyclocotrimerization of two dimethylacetylenedicarboxylate molecules with norbornadiene to give 1,2,3,4-tetrakis(methoxycarbonyl)benzene. Use of norbornene in place of norbornadiene leads to the palladium-catalyzed stereoselective production of a cyclohexa-1,3-diene derivative in 94% yield.

The catalytic cyclotrimerization of acetylenes to form benzene derivatives (reaction 1) has been intensively investigated.[2-4]



(1)

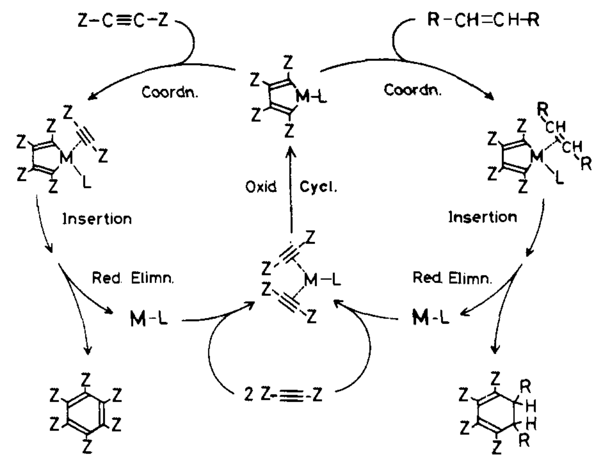
The cyclocotrimerization of two acetylene molecules with an olefin molecule to form cyclohexa-1,3-diene derivatives (reaction 2) has also been the subject of a number of studies,[5-9]

(2)

but apparently no highly selective, catalytically efficient reactions have been found. This is because reaction 1 is commonly a competitive, fatal side reaction for (2). These two reactions have been postulated to proceed, at least in some instances, via a metallocyclopentadiene complex as the key intermediate,[4,7] as shown in Scheme I. Thus, in principle, high selectivity for the cyclocotrimerization reaction of acetylenes and an olefin may be achieved if the olefin binds much more strongly to the metallocyclopentadiene than does the acetylene. Indeed, Chalk[5] has reported the selective cyclocotrimerization between terminal or conjugated acetylenes and N-substituted maleimides. Such activated olefins are expected to bond very strongly to the metallocycle.

Another approach for preventing reaction 1, the cyclo-

Scheme I



trimerization of acetylenes, is to use a metallocycle which contains strongly electron-withdrawing groups in conjunction with an electron-donating olefin. Such a metallocycle should show a preference for the olefin over the electron-withdrawing acetylene. We have found this approach to be successful. In this paper we describe first the preparation of a model of what we believe to be the key intermediate in the palladium mediated cyclocotrimerization between two molecules of dimethylacetylenedicarboxylate (DMAD), an activated acetylene, and one molecule of an electron-donating olefin, such as norbornadiene (NBD) or norbornene (NB). This model complex, $Pd[C_4(COOCH_3)_4](NBD)$, has been studied spectroscopically and crystallographically. Next we show how reactions between DMAD and NBD or DMAD and NB in the presence of $Pd[C_4(COOCH_3)_4]$ bear on the mechanism of the cyclocotrimerization reaction. Finally, we describe the palladium-catalyzed cyclocotrimerization of DMAD and NB. This reaction is stereoselective and proceeds almost quantitatively.

Experimental Section

Preparations. All reactions were carried out under dry dinitrogen gas. Norbornadiene (NBD) was purified by the distillation of the commercial reagent. Norbornene (NB) as a commercial reagent was used without further purification. Dimethylacetylenedicarboxylate (DMAD) was prepared according to the reported method.[10] Tetrakis(methoxycarbonyl)palladiacyclopentadiene (I) was prepared from $Pd_2(dba)_3 \cdot CHCl_3$[11] (dba = dibenzylidene acetone) with an excess of DMAD.[12,13] The NMR spectra were recorded with a JEOL C-60HL spectrometer using tetramethylsilane as an internal standard in $CDCl_3$. The infrared spectra were measured with a JASCO DS-403G spectrometer.

Preparation of $Pd[C_4(COOCH_3)_4](NBD)$ (IIa). To an acetone (7 ml) suspension of I (96 mg; 2.5 mmol), NBD (0.04 ml) was added slowly with vigorous stirring at room temperature. The reaction mixture gradually turned to a greenish brown, homogeneous solution. After stirring 30 min at room temperature, the solution was concentrated to 0.5 ml under reduced pressure. Ethyl ether (1 ml) and 2 drops of NBD were added. After 2 days at 0 °C IIa was precipitated as yellow brown prisms: mp 130–132 °C dec; IR (KBr) 1713, 1692 ($\nu_{C=O}$), 1231 cm^{-1} (ν_{C-O}); NMR ($CDCl_3$) δ 2.03 (t, 2, CH_2, $J = 0.8$ Hz), 3.65 (s, 6, ester CH_3), 3.67 (s, 6, ester CH_3), 4.07 (m, 2, bridgehead), 6.49 (t, 4, vinyl, $J = 2.0$ Hz). Anal. Calcd for $C_{19}H_{20}O_8Pd$: C, 47.27; H, 4.18. Found: C, 47.32; H, 4.42.

Preparation of $Pd[C_4(COOCH_3)_4](COD)$ (IIb). To a methylene chloride (5 ml) suspension of I (66.8 mg; 0.17 mmol), 0.025 ml of 1,5-cyclooctadiene (COD) was added dropwise. The reaction proceeded instantaneously to give a homogeneous, yellowish brown solution. The solution was stirred for 1 h and trace palladium metal was filtered off. The filtrate was condensed to 0.5 ml under reduced pressure and ethyl ether was added to the resulting oil until darkening occurred. The solution was kept in a refrigerator overnight to yield orange crystals of IIb in 73% yield: mp 151–152 °C; IR (KBr) 1720, 1709, 1691 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 2.82 (m, 8, CH_2), 3.62 (s, 6, CH_3O), 3.68 (s, 6, CH_3O), 5.79 (br s, 4, =CH). Anal. Calcd for $C_{20}H_{24}O_8Pd$: C, 48.16; H, 4.85. Found: C, 47.97; H, 4.85.

Catalytic Reaction between DMAD and NBD. To a benzene (3 ml) solution of DMAD (420 mg; 3.00 mmol) and NBD (135 mg; 1.5 mmol) was added I (39 mg; 0.10 mmol). The mixture was kept at 45 °C for 4 days. The mixture was concentrated under reduced pressure to cause the precipitation of 1,2,3,4-tetrakis(methoxycarbonyl)benzene (III), whih was separated by filtration. The filtrate was again concentrated and a second crop of III was collected. This procedure was repeated three times to give 35% total yield of III: mp 127–128 °C; NMR ($CDCl_3$) δ 3.81 and 3.83 (2 s, 12 H, CH_3O), 7.88 (s, 2, aromatic). Anal. Calcd for $C_{14}H_{14}O_8$: C, 54.20; H, 4.55. Found: C, 53.77; H, 4.51.

Thin layer chromatography (silica gel-benzene, then chloroform) of the residual oil indicated the presence of dicyclopentadiene, 2,3-bis(methoxycarbonyl)norbornadiene, and the remaining III, all of which were identified unequivocally by comparison with authentic samples.

Preparation of the Cycloadduct of NB and 2 DMAD (V) by Palladium-Catalyzed Cyclocotrimerization. When a benzene (5 ml) solution of NB (3.30 mmol), DMAD (3.37 mmol), and I (0.05 mmol) was kept in a sealed tube for 20 h at 45 °C, a palladium mirror deposited on the walls of the tube. The liquid phase was separated and evaporated under reduced pressure to yield crude V quantitatively. This crude product was purified by column chromatography on silica gel (Merck 7734) with a 2 × 12 cm column using chloroform as eluent. A 94% recovery of pure V was achieved: mp 66.5–68.0 °C; IR (liquid film) 1733 and 1720 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.30 (m, 1, H_a), 1.54 (m, 4, H_c), 1.68 (m, 1, H_b), 2.34 (d of t, 2, $J = 0.75$, 1.50 Hz, H_d), 2.92 (d, 2, $J = 0.75$ Hz, H_e), 3.71 and 3.68 (2 s, 12, ester CH_3). Anal. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86. Found: C, 60.44; H, 5.83.

Crystallographic Procedures. Preliminary optical and x-ray examination indicated that the dark yellow prismatic crystals of IIa belong to the triclinic system. This was confirmed by a cell reduction and by successful refinement of the structure in space group C_i^1-$P\bar{1}$.

With the crystal mounted approximately along the y axis the unit cell parameters were determined from a least-squares refinement of the setting angles of 12 reflections in the range $51 < 2\theta$ (Cu Kα_1) $< 64°$.[14] Intensity data[14] were collected for unique ($k \geq 0$) reflections on a Picker FACS-I diffractometer. Details are given in Table I. Data were processed in the usual way, using a value of p of 0.04,[14] and were then corrected for absorption effects[15] to yield 3646 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ to be used in subsequent calculations.

From a sharpened, origin-removed Patterson synthesis the Pd position was easily located. All nonhydrogen atoms were located on a subsequent difference Fourier synthesis. Two cycles of isotropic refinement and one cycle of anisotropic refinement led to an R index of 0.042. A subsequent difference Fourier calculation revealed the positions of all hydrogen atoms, confirming our choice of the centrosymmetric space group $P\bar{1}$. The idealized positions of the hydrogen atoms were used as fixed contributions in the subsequent calculations. Two more cycles of anisotropic refinement of 254 variables (including an isotropic extinction parameter) for 3646 observations led to values of R and R_w (on F) of 0.027 and 0.039, respectively. The error in an observation of unit weight is 1.66 electrons. In a final difference Fourier synthesis the highest residual is 0.51 e/Å^3, compared with a typical peak of 5 e/Å^3 for previously found carbon atoms. All but one of the unobserved reflections satisfied the condition $|F_c^2 - F_o^2| < 4\sigma(F_o^2)$. There were no trends of the quantity $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, diffractometer setting angles, or Miller indices. The final positional and thermal parameters for the nonhydrogen atoms are given in Table II. Table III contains the idealized H atom parameters.[16] The root-mean-square amplitudes of vibration of the individual nonhydrogen atoms are given in Table IV.[16] A listing of observed and calculated structure amplitudes is available.[16]

Results and Discussion

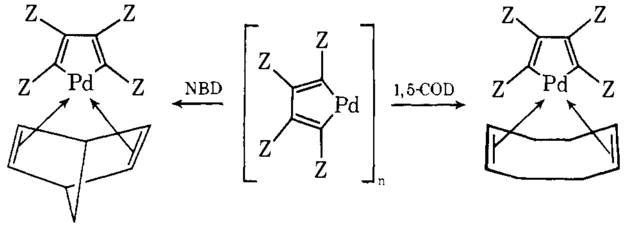
Preparation and Spectroscopy. Tetrakis(methoxycarbonyl)palladiacyclopentadiene (I), $Pd[C_4(COOCH_3)_4]$, is readily prepared from the reaction of $Pd_2(dba)_3$[11] with excess DMAD.[12,13] The compound is probably an oligomer which can be cleaved by various neutral ligands.[12,13] Although the complex is thought to be an intermediate in the palladium-

Table I. Summary of Crystal Data and Intensity Collection

Compd	Pd[$C_4(COOCH_3)_4$](NBD)
Formula	$C_{19}H_{20}O_8Pd$
Formula weight	482.766 amu
a	10.560 (2) Å
b	10.583 (2) Å
c	9.710 (2) Å
α	99.33 (1)°
β	113.24 (1)°
γ	85.53 (2)°
Z	2
Density	1.629 g/cm³ (calcd), 1.62 (2) g/cm³ (exptl)
Space group	C_i^1-$P\bar{1}$
Crystal dimensions	0.45 × 0.19 × 0.11 mm
Crystal shape	Triclinic prism with {001}, {100}, {10$\bar{1}$}, {01$\bar{1}$} faces well developed.
Crystal volume	0.0073 mm³
Temperature	22°C
Radiation	Cu Kα_1 (λ 1.54056Å) prefiltered with 1 mil of Ni foil
Transmission factors	0.141–0.553
μ	81.65 cm⁻¹
Receiving aperture	3.2 mm wide by 3.2 mm high, 32 cm from the crystal
Takeoff angle	3.1°
Scan speed	2° in 2θ/min
Scan range	0.75 below Kα_1 to 0.75 above Kα_2 between 4° < 2θ < 110°; 0.95 below Kα_1 to 0.85 above Kα_2 between 110 < 2θ < 125°; 1.4 below Kα_1 to 0.9 above Kα_2 between 125 < 2θ < 160°
Final number of variables	254
Unique data used ($F_O^2 > 3\sigma(F_O^2)$)	3646
Error in observation of unit weight	1.66 e

catalyzed trimerization of DMAD to yield hexamethyl mellitate,[13] the presence of electron-withdrawing groups on the metallocycle suggested to us that the complex should bind an electron-donating olefin much more strongly than it would DMAD. Indeed, this is the case: whereas the DMAD adduct cannot be isolated, it is possible to isolate and characterize very stable adducts with electron-donating olefins. Both the COD and NBD adducts have been isolated and characterized, the latter by a complete x-ray structure determination.

1,5-Cyclooctadiene reacts readily with I to give Pd[$C_4(COOCH_3)_4$](COD) (IIb). The olefinic protons in the NMR spectrum of IIb occur at δ 5.79, a low-field shift on coordination (δ 5.49 for free COD). This is consistent with the electron-accepting property of I.



IIa I IIb

Z = COOMe

When norbornadiene (NBD) was added dropwise to an acetone suspension of I, Pd[$C_4(COOCH_3)_4$](NBD) (IIa) was obtained in 51% yield. The analysis and infrared spectrum of IIa, $\nu_{C=O}$ at 1713 and 1692 cm⁻¹, are consistent with the structure depicted and established by x-ray analysis. The olefinic proton signals of the vinylic protons in the NMR spectrum of IIa occur at δ 6.49 as a triplet (4 H, J = 2.0 Hz), which is only slightly higher than free NBD (δ 6.67). Fur-

Table II. Positional and Thermal Parameters for the Atoms of Pd[$C_4(COOCH_3)_4$] (NBD)

ATOM	X[a]	Y	Z	B11[b]	B22	B33	B12	B13	B23
PD	-0.032559(16)	0.194663(17)	0.094477(17)	8.74(3)	10.08(3)	10.15(3)	-0.91(2)	3.76(2)	1.71(2)
O(1)	-0.08198(30)	0.22230(27)	-0.27187(25)	20.07(39)	18.27(34)	11.48(27)	-8.19(30)	0.85(26)	3.30(24)
O(2)	0.01200(24)	0.41547(20)	-0.18727(22)	14.84(27)	10.55(21)	12.75(26)	1.23(19)	4.20(21)	4.14(19)
O(3)	0.34818(25)	0.46051(21)	0.08283(25)	16.43(30)	11.28(22)	15.84(30)	-5.94(21)	6.74(25)	-1.93(21)
O(4)	0.28796(20)	0.30455(18)	-0.11517(20)	12.05(21)	10.15(19)	11.97(23)	-2.67(16)	6.30(19)	-0.01(16)
O(5)	0.49125(23)	0.25546(32)	0.28044(26)	9.79(23)	26.50(44)	13.84(30)	2.08(25)	4.89(22)	0.64(29)
O(6)	0.42040(21)	0.32519(22)	0.46679(20)	10.63(22)	16.50(27)	9.71(22)	-2.26(19)	2.78(18)	-0.40(19)
O(7)	0.13101(32)	0.20921(38)	0.48731(27)	18.66(39)	33.36(57)	13.33(32)	2.78(38)	9.02(30)	6.15(34)
O(8)	0.28002(34)	0.07136(23)	0.43024(26)	28.08(51)	11.82(25)	13.06(30)	2.05(29)	6.75(31)	4.24(22)
C(1)	0.06576(27)	0.27044(25)	-0.01334(28)	9.97(26)	9.09(24)	10.22(30)	-0.39(20)	3.83(23)	2.03(21)
C(2)	0.19954(25)	0.29760(23)	0.06861(26)	9.17(24)	7.96(21)	9.90(27)	-0.22(18)	3.66(21)	1.11(19)
C(3)	0.25214(24)	0.26546(24)	0.22447(25)	8.78(23)	8.70(22)	9.15(26)	0.46(18)	3.12(20)	0.91(19)
C(4)	0.15986(27)	0.21100(27)	0.25834(27)	10.11(26)	10.80(27)	8.95(27)	-0.32(21)	3.20(22)	1.38(21)
C(5)	-0.00805(27)	0.29757(28)	-0.17084(29)	9.43(26)	12.04(30)	10.67(31)	-0.93(22)	3.13(24)	2.77(23)
C(6)	-0.04931(43)	0.44644(40)	-0.33933(41)	17.99(51)	15.84(45)	15.19(47)	2.52(38)	4.81(39)	7.83(37)
C(7)	0.28710(25)	0.36317(24)	0.01589(27)	9.07(24)	8.91(23)	10.68(28)	-0.75(19)	3.29(22)	1.23(20)
C(8)	0.35571(39)	0.37029(36)	-0.18545(39)	17.00(45)	15.17(40)	16.32(45)	-4.95(34)	9.75(39)	0.60(33)
C(9)	0.40059(27)	0.28081(27)	0.32374(27)	9.52(26)	11.27(28)	10.22(29)	-0.51(21)	3.06(23)	1.56(22)
C(10)	0.56116(40)	0.33915(53)	0.57144(40)	13.02(41)	26.32(71)	11.89(40)	-4.56(43)	-0.09(33)	-0.13(41)
C(11)	0.18772(33)	0.16628(34)	0.40459(30)	12.90(34)	15.26(38)	9.70(31)	-2.97(29)	3.25(27)	1.80(27)
C(12)	0.30294(88)	0.01530(50)	0.56553(55)	54.1(17)	16.17(60)	16.85(65)	3.24(79)	10.97(84)	7.59(51)
C(13)	-0.29782(30)	0.23979(27)	0.10531(38)	11.44(30)	8.78(25)	21.05(49)	-0.95(22)	9.02(33)	-1.09(27)
C(14)	-0.17109(32)	0.18554(30)	0.22264(33)	12.96(33)	11.85(31)	14.25(37)	-2.66(25)	7.82(30)	-0.45(26)
C(15)	-0.15378(33)	0.06330(29)	0.16454(36)	13.22(34)	10.26(28)	16.83(43)	-0.60(25)	7.66(33)	3.06(27)
C(16)	-0.27035(31)	0.03772(26)	0.00879(36)	12.22(31)	7.76(24)	18.45(44)	-1.43(22)	7.10(31)	-0.42(25)
C(17)	-0.24007(28)	0.12417(29)	-0.08705(31)	9.33(26)	11.14(28)	12.54(34)	-1.05(21)	3.49(24)	0.55(24)
C(18)	-0.25751(28)	0.24610(28)	-0.02976(35)	8.78(26)	9.67(26)	16.66(41)	-0.46(21)	3.66(27)	2.90(26)
C(19)	-0.38597(30)	0.11768(29)	0.04257(39)	11.04(31)	10.39(28)	21.03(50)	-2.45(23)	7.90(34)	-0.49(30)

[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: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10³.

Table V. Bond Distances (Å) in $Pd[C_4(COOCH_3)_4](NBD)$

Pd–C(1)	2.019 (3)	C(5)–O(1)	1.202 (3)
Pd–C(4)	2.026 (3)	C(7)–O(3)	1.206 (3)
Av	2.023 (3)	C(9)–O(5)	1.186 (3)
		C(11)–O(7)	1.196 (4)
Pd–C(14)	2.280 (3)	Av	1.198 (4)
Pd–C(15)	2.304 (3)	C(5)–O(2)	1.327 (3)
Pd–C(17)	2.290 (3)	C(7)–O(4)	1.325 (3)
Pd–C(18)	2.268 (3)	C(9)–O(6)	1.330 (3)
Av	2.286 (7)	C(11)–O(8)	1.326 (4)
		Av	1.327 (4)
Pd–C(14,15)	2.189	C(6)–O(2)	1.441 (4)
Pd–C(17,18)	2.177	C(8)–O(4)	1.442 (3)
C(1)–C(2)	1.347 (4)	C(10)–O(6)	1.434 (4)
C(3)–C(4)	1.339 (4)	C(12)–O(8)	1.455 (5)
C(14)–C(15)	1.354 (4)	Av	1.443 (5)
C(17)–C(18)	1.349 (4)		
Av	1.347 (4)	C(13)–C(19)	1.545 (4)
		C(16)–C(19)	1.544 (4)
C(1)–C(5)	1.482 (4)	Av	1.545 (4)
C(4)–C(11)	1.481 (4)	C(13)–C(14)	1.519 (5)
C(2)–C(7)	1.479 (3)	C(13)–C(18)	1.542 (4)
C(3)–C(9)	1.486 (3)	C(15)–C(16)	1.525 (5)
C(2)–C(3)	1.479 (3)	C(16)–C(17)	1.537 (4)
Av	1.481 (4)	Av	1.531 (5)

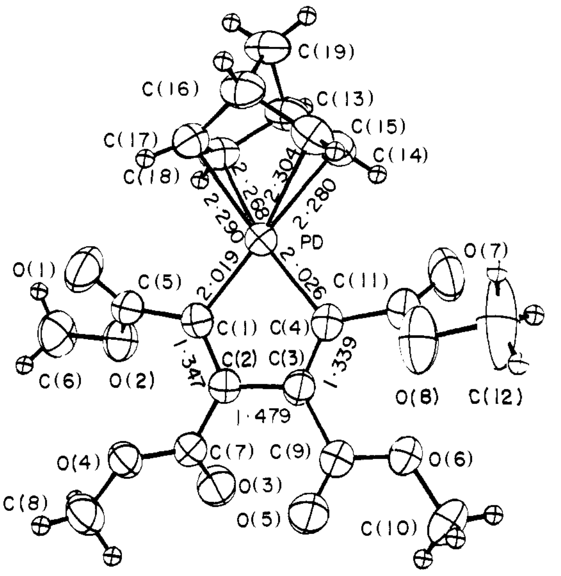


Figure 1. A perspective drawing of the $Pd[C_4(COOCH_3)_4](NBD)$ molecule showing the labeling scheme and principal distances. The 50% probability ellipsoids are displayed, except for the hydrogen atoms, which are artificially small.

Table VI. Bond Angles (deg) in $Pd(C_4(COOCH_3)_4)(NBD)$

C(1)–Pd–C(4)	79.7 (1)	C(14)–C(13)–C(19)	99.1 (2)
C(1)–Pd–C(14)	158.8 (1)	C(18)–C(13)–C(19)	99.1 (2)
C(4)–Pd–C(18)	157.5 (1)	C(15)–C(16)–C(19)	99.2 (2)
C(1)–Pd–C(15)	164.5 (1)	C(17)–C(16)–C(19)	99.6 (2)
C(4)–Pd–C(17)	166.0 (1)	Av	99.3 (2)
C(1)–Pd–C(17)	106.4 (1)		
C(4)–Pd–C(15)	107.4 (1)	C(13)–C(14)–C(15)	107.1 (3)
C(1)–Pd–C(18)	104.0 (1)	C(14)–C(15)–C(16)	106.7 (3)
C(4)–Pd–C(14)	104.2 (1)	C(16)–C(17)–C(18)	106.7 (2)
C(14)–Pd–C(15)	34.4 (1)	C(13)–C(18)–C(17)	106.8 (2)
C(17)–Pd–C(18)	34.4 (1)	Av	106.8 (3)
C(14)–Pd–C(17)	74.8 (1)		
C(15)–Pd–C(18)	74.9 (1)	C(13–C(19)–C(16)	92.8 (2)
C(14)–Pd–C(18)	64.6 (1)		
C(15)–Pd–C(17)	63.7 (1)	C(1)–C(5)–O(1)	123.6 (3)
C(1)–Pd–C(14,15)	172.8	C(2)–C(7)–O(3)	123.8 (2)
C(4)–Pd–C(17,18)	172.6	C(3)–C(9)–O(5)	123.8 (2)
C(1)–Pd–C(17,18)	106.0	C(4)–C(11)–O(7)	123.7 (3)
C(4)–Pd–C(14,15)	106.6	Av	123.7 (3)
C(14,15)–Pd–C(17,18)	67.5	C(1)–C(5)–O(2)	112.8 (2)
Pd–C(1)–C(2)	115.7 (2)	C(2)–C(7)–O(4)	112.3 (2)
Pd–C(4)–C(3)	115.6 (2)	C(3)–C(9)–O(6)	112.4 (2)
Pd–C(1)–C(5)	121.2 (2)	C(4)–C(11)–O(8)	111.9 (3)
Pd–C(4)–C(11)	119.2 (2)	Av	112.4 (3)
C(2)–C(1)–C(5)	123.1 (2)		
C(3)–C(4)–C(11)	125.2 (2)	O(1)–C(5)–O(2)	123.5 (3)
C(1)–C(2)–C(3)	114.3 (2)	O(3)–C(7)–O(4)	123.9 (2)
C(2)–C(3)–C(4)	114.6 (2)	O(5)–C(9)–O(6)	123.8 (2)
C(1)–C(2)–C(7)	124.4 (2)	O(7)–C(11)–O(8)	124.4 (3)
C(4)–C(3)–C(9)	124.9 (2)	Av	123.9 (3)
C(3)–C(2)–C(7)	121.1 (2)		
C(2)–C(3)–C(9)	120.2 (2)	C(5)–O(2)–C(6)	116.1 (3)
		C(7)–O(4)–C(8)	116.3 (2)
C(14)–C(13)–C(18)	105.0 (2)	C(9)–O(6)–C(10)	116.1 (3)
C(15)–C(16)–C(17)	104.7 (2)	C(11)–O(8)–C(12)	114.6 (4)
Av	104.9 (2)	Av	115.8 (4)

thermore, the bridgehead protons of free NBD at δ 3.49 shift substantially to low field (δ 4.07; Δ = 0.58 ppm) on coordination. The chemical shifts of the two ester protons in IIa (σ 3.65 and 3.67) are at higher field than those of the parent complex I (δ 3.58 and 3.62). All of these spectroscopic results suggest that net transfer of electrons from the strained olefin to the metallocycle has occurred.

Crystallographic Results. The structural results are completely consistent with the spectroscopic results. A perspective view of $Pd[C_4(COOCH_3)_4](NBD)$ is given in Figure 1 along with selected distances. Table V contains the bond distances and Table VI the bond angles. The crystal structure consists of well separated molecules; a stereoview of the unit cell is given in Figure 2. Table VII contains the best, weighted least-squares planes through the molecule. Although there is no imposition of crystallographic symmetry, the Pd–NBD segment of the molecule is highly symmetric, as judged by the fact that planes 1, 2, and 3 are nearly perpendicular to one another. The metallocycle itself is essentially planar, the largest deviation from planarity being 0.03 Å. The carbomethoxy groups are approximately related by a noncrystallographic twofold axis through atoms Pd and C(19).

In Table VIII we compare the structural parameters of the present PdC_4 metallocycle with other five-membered metallocycles.[17-21] Within the stated standard deviations, the agreement among the ring systems, which contain different metals and different substituent groups, is remarkably good.

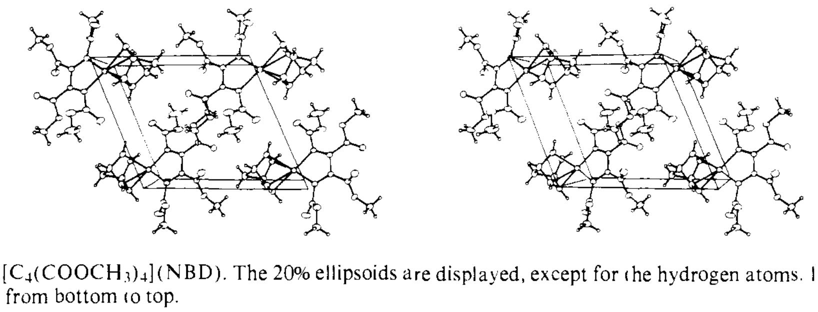


Figure 2. The unit cell of $Pd[C_4(COOCH_3)_4](NBD)$. The 20% ellipsoids are displayed, except for the hydrogen atoms. In the drawing the x axis goes from left to right, the z axis from bottom to top.

Table VII. Best Weighted Least-Squares Planes

Plane equation: $Ax + By + Cz = D$ (in triclinic coordinates)

Plane no.	A	B	C	D
1	−0.364	−4.223	8.737	0.015
2	−2.610	9.222	3.116	2.175
3	10.280	2.808	−2.847	−1.872
4	3.613	−8.971	−3.167	−2.163
5	3.003	−9.147	−3.117	−2.244

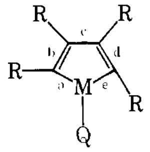
Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
Pd	0.0000 (2)[a]	0.0000 (0)	1.815	−0.0001 (2)	0.072
O(1)	−3.300	−0.758	2.427	0.734	
O(2)	−3.410	1.042	3.695	−0.928	
O(3)	−1.363	1.422	6.508	−0.973	
O(4)	−2.412	−0.476	6.015	0.836	
O(5)	1.178	−0.227	6.841	0.758	
O(6)	2.537	1.182	5.778	−0.714	
O(7)	3.311	0.932	2.419	−0.784	
O(8)	3.341	0.906	3.726	1.172	
C(1)	−1.298	0.106	3.345	0.017 (3)	0.010 (3)
C(2)	−0.745	0.263	4.563	−0.003 (2)	−0.011 (3)
C(3)	0.733	0.315	4.570	−0.018 (3)	
C(4)	1.293	0.159	3.372	0.030 (3)	
C(5)	−2.762	0.058	3.111	0.006	
C(6)	−4.847	1.014	3.584	−0.945	
C(7)	−1.514	0.475	5.798	−0.108	
C(8)	−3.329	−0.266	7.096	0.714	
C(9)	1.482	0.379	5.857	0.066	
C(10)	3.341	1.270	6.966	−0.662	
C(11)	2.749	0.130	3.117	0.068	
C(12)	4.751	−1.062	3.419	1.329	
C(13)	0.001 (4)	1.142	−0.817	−1.398	
C(14)	1.209	0.677	0.000 (4)	−0.825	
C(15)	1.211	0.677	0.000 (4)	0.519	
C(16)	0.001 (3)	1.094	−0.827	0.820	
C(17)	−1.213	0.674	0.000 (3)	0.458	
C(18)	−1.221	0.674	0.000 (3)	−0.881	
C(19)	−0.001 (4)	0.052	−1.887	−0.424	
C(14,15)[b]	1.210	0.000 (0)	0.000	−0.153	0.015 (3)
C(17,18)	−1.217	0.000 (0)	0.000	−0.212	−0.014 (3)

Dihedral Angles, deg

1–2	90.2	2–4	174.1
1–3	89.5	2–5	177.7
1–4	88.4	3–4	82.9
1–5	89.1	3–5	86.4
2–3	91.3	4–5	3.6

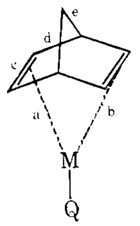
[a] Errors are shown only for those atoms used to define the plane. [b] C(14, 15) is the center of the C(14)–C(15) bond; C(17, 18) is the center of the C(17)–C(18) bond.

Table VIII. Comparison of the Structural Data of Some Metallocycles



	$RhCl[Sb(C_6H_5)_3]_2[C_4(CF_3)_4]\cdot CH_2Cl_2$	$RhCl(H_2O)[As(CH_3)_3]_2[C_4(CF_3)_4]$	$Co(C_5H_5)[P(C_6H_5)_3][C_4(C_6F_5)_4]$	$Ti[C_4(C_6H_5)_4](C_5H_5)_2$	$Hf[C_4(C_6H_5)_4](C_5H_5)_2$	$Pd[C_4(COOCH_3)_4](Ph_3PC_5H_4)$	$Pd[C_4(COOCH_3)_4](NBD)$
M	Rh	Rh	Co	Ti	Hf	Pd	Pd
R	CF_3	CF_3	C_6F_5	C_6H_5	C_6H_5	$COOCH_3$	$COOCH_3$
Q	Cl, $SbPh_3$, $SbPh_3$	Cl, H_2O, $AsMe_3$, $AsMe_3$	π-C_5H_5, PPh_3	π-C_5H_5, π-C_5H_5	π-C_5H_5, π-C_5H_5	$Ph_3PC_5H_4$	NBD
Ref	17	18	19	20	20	21	Present structure
a	2.000 (10)	2.047 (16)	1.995 (11)	2.172 (5)	2.22 (2)	1.955 (5)	2.019 (3)
b	1.330 (16)	1.311 (24)	1.326 (15)	1.369 (6)	1.39 (3)	1.38 (1)	1.347 (4)
c	1.388 (14)	1.433 (26)	1.467 (16)	1.495 (6)	1.51 (3)	1.44 (1)	1.479 (3)
d	1.367 (15)	1.346 (23)	1.335 (15)	1.370 (6)	1.36 (2)	1.37 (1)	1.339 (4)
e	1.964 (11)	1.998 (16)	1.993 (11)	2.147 (5)	2.18 (2)	1.984 (5)	2.026 (3)
a–e	77.2 (4)	80.2 (6)	82.4 (4)	80.3 (2)	78.7 (8)	80.2 (3)	79.7 (1)
a–b	116.4 (7)	114.3 (12)	112.1 (8)	111.0 (3)	114.1 (8)	116.5 (5)	115.7 (2)
b–c	116.1 (9)	114.9 (15)	116.8 (9)	118.5 (4)	114 (2)	113.8 (5)	114.3 (2)
c–d	111.4 (10)	117.4 (15)	114.8 (9)	117.4 (4)	120 (2)	113.8 (5)	114.6 (2)
d–e	118.8 (7)	113.2 (12)	113.1 (7)	112.5 (3)	113.1 (8)	116.5 (5)	115.6 (2)

Table IX. Comparison of the Structural Data of Some Norbornadiene π-Complexes

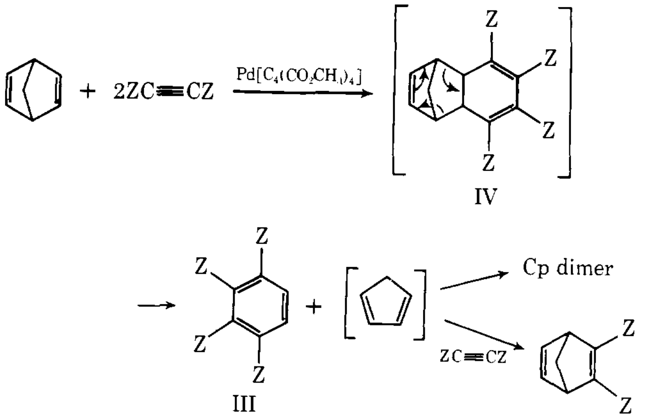


	$PdCl_2(NBD)$	$Co(SnCl_3)$-$(CO)_2(NBD)$	$Co_2(CO)_6$-(NBD)	$Ir(SnCl_3)[P(CH_3)_2(C_6H_5)]_2$-(NBD)	$Pd[C_4(COOCH_3)_4]$-(NBD)	$RuCl_2(C_6H_5NH_2)_2(NBD)$
M	Pd	Co	Co	Ir	Pd	Ru
Q	Cl, Cl	CO, CO, $SnCl_3$	CO, CO, CO	PMe_2Ph, PMe_2Ph, $SnCl_3$		Cl, Cl, $C_6H_5NH_2$, $C_6H_5NH_2$
Ref	23	24	25	26	Present structure	27
a	2.049	2.050	2.049	2.068	2.189	2.066
b	2.056	1.959	2.056	2.123	2.177	2.066
c	1.366 (10)	1.396 (15)	1.373 (8)	1.400 (9)	1.352 (4)	1.385 (6)
d	1.553 (6)	1.550 (15)	1.525 (8)	1.528 (10)	1.531 (5)	1.537 (6)
e	1.547 (6)	1.560 (14)	1.547 (9)	1.525 (10)	1.545 (4)	1.524 (12)
a–b	71.0	72.1	71.3	67.6	67.5	70.0
c–d	107.0 (4)	106.7 (9)	106.7 (5)	105.7 (6)	106.8 (3)	105.9 (1)
d–d	100.3 (3)	99.5 (8)	101.2 (7)	99.5 (5)	104.9 (2)	100.9 (5)
d–e	100.0 (4)	100.6 (9)	100.3 (5)	101.9 (6)	99.7 (2)	101.0 (5)
e–e	94.5	94.2 (7)	93.4 (4)	93.6 (5)	92.8 (2)	93.9 (5)

In a few of the structures there appears to be possible asymmetry in the metal-carbon bonds, as noted earlier.[17,18,22] The fact that $Pd[C_4(COOCH_3)_4]Q$, with Q = $Ph_3PC_5H_4$, shows apparent asymmetry, but with Q = NBD does not suggest, to us that packing forces, rather than electronic effects, are the probable cause of the asymmetry. In the Q = $Ph_3PC_5H_4$ complex the Pd atom has a formal oxidation state of −1; in the Q = NBD complex the oxidation state is 0. The differences in Pd-C distances are consistent with this assignment.

In Table IX we summarize data on different π-bonded NBD structures.[23-27] Again the agreement is excellent. Electron transfer to an olefin lengthens the C=C bond.[28] In the present structure the C=C bond length is shorter than in the other π-bound NBD molecules and is equal to that in free NBD.[29] Moreover, the bonding of the NBD to the metal in the present structure appears to be weaker, as judged by the distance of metal to double-bond center. Thus the structural results are completely consistent with the spectroscopic evidence for electron transfer from the olefin to the metallocycle.

Cyclocotrimerization Catalyzed by I. The high stability of the cyclic diolefin complexes IIa and IIb suggested to us the possibility of a successful cyclocotrimerization between two molecules of DMAD and one molecule of an electron-rich olefin. When a benzene solution of DMAD and NBD (in 2/1 molar ratio) was kept at 45 °C for 4 days in the presence of a catalytic amount of $Pd[C_4(COOCH_3)_4]$ (I), 1,2,3,4-tetrakis(methoxycarbonyl)benzene (III) was isolated in 35% yield.



IV

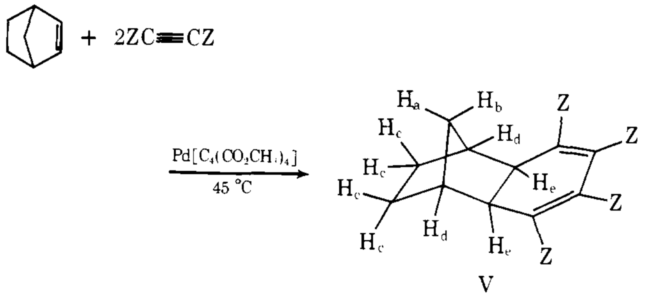
III

Z = COOMe

The formation of hexamethyl mellitate, the cyclic trimer of DMAD, was completely inhibited as expected from the fact that in other experiments $Pd[C_4(COOCH_3)_4](DMAD)$ proved too unstable to isolate.

The formation of III presumably results from subsequent cycloreversion[30,31] of the intermediate cyclic cotrimer (IV). This view is supported by the presence of dicyclopentadiene and 2,3-bis(methoxycarbonyl)norbornadiene in the reaction mixture, suggestive of the generation of cyclopentadiene. When the norbornadiene complex IIa itself was treated with a twice molar amount of DMAD in $CDCl_3$ for 1 h at 55 °C, III was formed in quantitative yield (estimated by the characteristic aryl proton at δ 7.88) with the concurrent precipitation of I in nearly 80% yield. This result strongly suggests that IIa is the correct intermediate in the catalytic cyclotrimerization reaction.

If these views are correct, then by judicious choice of the electron-rich olefin it should be possible to prevent the cycloreversion process and obtain a cyclohexa-1,3-diene derivative. Indeed, we have found that $Pd[C_4(CCOCH_3)_4]$ catalyzes stereoselectively the cyclocotrimerization of two molecules of DMAD with norbornene (NB). When a benzene solution of NB, DMAD, and a catalytic amount of $Pd[C_4(COOCH_3)_4]$ (I) was kept at 45 °C for 20 h, the expected cycloadduct (V)



V

Z = COOMe

from two molecules of DMAD and NB was isolated in 94% yield, based on DMAD. No trace of hexamethyl mellitate was detected. Complex V is formed stereoselectively as the exo adduct, as judged by the large differences in chemical shifts between H_a (δ 1.30) and H_b (δ 1.68) and the small coupling constant (J = 0.8 Hz) between H_d and H_e.

Conclusion

The results presented here are consistent with Scheme I, in which a metallocyclopentadiene molecule is the key intermediate in the cyclocotrimerization of two molecules of acetylene and one molecule of olefin to form cyclohexa-1,3-diene derivatives. By judicious choice of an electron-withdrawing metallocycle and an electron-donating olefin it is possible to suppress the competing cyclotrimerization reaction of three molecules of acetylene to obtain a catalytic, stereoselective production of the cyclohexa-1,3-diene.

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Supplementary Material Available: the idealized H atom parameters (Table III), the amplitudes of vibration on individual nonhydrogen atoms (Table IV), and a listing of observed and calculated structure amplitudes (27 pages). Ordering information is given on any current masthead page.

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Cofacial Dimer of a Dihydrooctaaza[14]annulene Complex Containing a Nickel–Nickel Bond and Related Monomeric Complexes

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Abstract: Oxidative dehydrogenation of the bis-α-diimine macrocyclic complex, $[\mathrm{Ni(C_{10}H_{20}N_8)}]^{2+}$, under basic conditions results in a four-electron oxidation of the ligand and deprotonation of each six-membered chelate ring to yield a molecular dimeric complex, $[\mathrm{Ni(C_{10}H_{14}N_8)}]_2$. A single-crystal x-ray structure analysis (space group $C2/c$; $a = 16.597$ (9), $b = 18.534$ (9), $c = 13.233$ (7) Å; $\cos\beta = -0.8121$ (2); $\rho_{\text{calcd}} = 1.718$ g/cm^3, $\rho_{\text{expl}} = 1.70$ (2) g/cm^3; $Z = 4$) has revealed an eclipsed cofacial dimeric complex with nickel-nickel bond length of 2.788 (2) Å. The close approach of the eclipsed macrocyclic ligands, 3.00 Å, necessitates ascribing bonding between the two macrocyclic ligands in addition to the metal-metal bond. The dimer units are stacked along the c axis of the unit cell with adjacent dimer units having a nickel-nickel separation of 3.800 (3) Å. The octaaza[14]annulene ligand has a delocalized double-bond arrangement comparable to that expected for an aromatic system. A monomeric isomer of this complex having a syn–anti α-diimine arrangement and C_{2h} molecular symmetry has also been isolated. A comparison of the solid state and solution electronic spectra indicates some interaction in the solid state for the C_{2h} isomer. A crystal structure analysis of the C_{2h} isomer (space group, $P\bar{1}$; $a = 8.433$ (1), $b = 8.408$ (2), $c = 4.860$ (1) Å; $\alpha = 75.94$ (1), $\beta = 68.25$ (1), $\gamma = 81.73$ (1)°; $\rho_{\text{calcd}} = 1.632$ g/cm^3, $\rho_{\text{expt}} = 1.628$; $Z = 1$) reveals a localized double-bond arrangement. The molecules are packed in a parallel fashion with a Ni–Ni separation of 4.860 Å and interplanar separations of 3.373 Å for adjacent molecules. The nickel–nitrogen distances, 1.784 (1) and 1.820 (1) Å, are unusually short for Ni(II).

The significant role of highly conjugated and completely conjugated macrocyclic ligands in biological processes suggests that highly conjugated synthetic macrocyclic ligands may confer unusual properties on coordinated metals as well. Naturally occurring macrocyclic ligands have nitrogen-to-center (N–Ct) distances in the range of 2.0–2.05 Å,[1] a range compatible with ideal first-row transition metal–nitrogen distances. The N–Ct distance associated with completely conjugated 14-membered macrocyclic ligands are expected to be in the range 1.80–1.90 Å, significantly shorter than

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