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Structures of Two Metal–Cyclobutenyl Isomers of $[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$[1]

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The structures of two organopalladium isomers of empirical composition $C_{30}H_{25}OPdCl$ (designated[4] as complexes A and C), prepared by the reactions of palladium compounds with diphenylacetylene, have been determined from three-dimensional X-ray work. The basic structure of both compounds is found to consist of two dimeric molecules in a unit cell of formula $[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$ with a molecular crystallographic center of symmetry such that each palladium of a rhombic Pd_2Cl_2 fragment is symmetrically bonded to the allylic part of a nonplanar cyclobutenyl ring. Crystals of complex A are monoclinic with dimensions $a = 9.90$ Å., $b = 20.75$ Å., $c = 13.75$ Å., $\beta = 118° 40'$, and with space group $P2_1/c$. Crystals of complex C are monoclinic with dimensions $a = 13.17$ Å., $b = 13.57$ Å., $c = 14.05$ Å., $\beta = 92° 30'$, and with space group $P2_1/n$. The dimeric molecules are found to be geometrical isomers (*endo* and *exo* forms) with the phenyl and ethoxy groups attached to the tetrahedral cyclobutenyl ring carbon interchanged; with respect to the palladium(II) the ethoxy group in complex A is in the *endo* position, while in complex C it is in the *exo* position. The detailed molecular features of these compounds are compared to each other and to related compounds including a cyclobutenyl–nickel complex and the cyclobutenium cation.

Introduction

The present X-ray investigation of two palladium isomers of empirical formula $C_{30}H_{25}OPdCl$ was prompted by our structural analysis of the Criegee–Ludwig–King complex,[5,6] $C_{13}H_{17}NiC_5H_5$, which was shown to be the first proven example of a cyclobutenyl–metal complex.[7]

The synthesis of one of these isomers was first reported by Malatesta, *et al.*,[8] who, in the reaction of diphenylacetylene with palladium(II) chloride, obtained an orange-red, stable, diamagnetic complex of composition $[C_{30}H_{25}OPdCl]_x$. Malatesta, *et al.*,[8] proposed a dimeric structure in which a substituted cyclobutene moiety is bonded *via* a σ-type and a π-type bond to each palladium. Guy and Shaw[9] later assumed it to be a cyclobutenyl–palladium complex. Blomquist and Maitlis[4] prepared the same substance (designated by them as complex A) by the reaction of bis(benzonitrile)-palladium(II) chloride with diphenylacetylene in ethanol and proposed an acyclic structure.

In addition, Blomquist and Maitlis[4] isolated from the reaction of the cyclobutadiene–palladium chloride complex, $[(C_{14}H_{10})_2PdCl_2]_x$, with ethanol a yellow insoluble substance (complex C) of the same empirical formula as complex A but with different chemical and physical properties for which they suggested a cyclobutenyl–metal model. Further studies of the chemical behavior of these compounds recently were reported by Maitlis and Games[10] and by Vallarino and Santarella.[11] In order to characterize unambiguously the constitution of these insoluble compounds, structural studies of complexes A and C were carried out, which in accord with our prognostications based on our structural results for the cyclobutenyl–nickel complex[6] revealed both complexes to be geometrical isomers (*endo* and *exo* forms) of a dimeric palladium–cyclobutenyl complex.

Experimental

Samples of complexes A and C, kindly furnished to us by Professor Maitlis of McMaster University (Ontario, Canada), did not yield sufficiently large crystals for X-ray study. Consequently, samples of both complexes were prepared in our laboratories by the Blomquist–Maitlis procedure.[4]

The average diameters of the crystals used for obtaining intensity data with Mo Kα radiation were 0.02 and 0.03 cm. for complexes A and C, respectively. Since the corresponding values of μR are only 0.10 and 0.15, respectively, the absorption corrections were neglected. The densities of the crystals were measured by flotation in mixtures of bromobenzene and methylene chloride.

The unit cell lengths were determined from precession photographs calibrated with sodium chloride; the angle β for each complex was measured from precession pictures.

Multiple-film equi-inclination Weissenberg photographs were obtained for eleven reciprocal layers ($0kl$–$10kl$) for complex A and for fourteen reciprocal layers ($hk0$–$hk13$) for complex C with Zr-filtered Mo Kα radiation. The intensities of 2461 independent reflections for complex A and 1764 reflections for complex C were estimated visually with the aid of calibrated standard intensity spots made with the same crystals and reduced in the normal manner to structure amplitudes.

Crystal Data

Complex A.—$[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$, mol. wt. 1086.7. Crystals are monoclinic with $a = 9.90 \pm 0.02$ Å., $b = 20.75 \pm 0.04$ Å., $c = 13.75 \pm 0.03$ Å., $\beta = 118° 40' \pm 10'$; volume of unit cell = 2479 Å.^{3}; $\rho_{obsd} = 1.46$ g. cm.$^{-3}$ *vs.* $\rho_{calcd} = 1.46$ g. cm.$^{-3}$ for two dimeric molecules per unit cell. The total number of electrons per unit cell, $F(000) = 1104$. The linear absorption coefficient for Mo Kα radiation (λ 0.7107

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[4] A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

[5] R. Criegee and P. Ludwig, *Chem. Ber.*, **94**, 2038 (1961).

[6] R. B. King, *Inorg. Chem.*, **2**, 528 (1963).

[7] W. Oberhansli and L. F. Dahl, *ibid.*, **4**, 150 (1965).

[8] L. Malatesta, G. Santarella, L. M. Vallarino, and F. Zingalis, *Atti. accad. nazl. Lincei, Rend., Classe sci. fis. mat. nat.*, **27**, 230 (1959); L. Malatesta, G. Santarella, L. Vallarino and F. Zingales, *Angew. Chem.*, **72**, 34 (1960).

[9] R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, 77 (1962).

[10] P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964).

[11] L. M. Vallarino and G. Santarella, *Gazz. chim. ital.*, **94**, 252 (1964).

Table I

Individual Atomic Parameters of Complex A with Standard Deviations from (a) Anisotropic–Isotropic Least-Squares Refinement; (b) Rigid Body Least-Squares Refinement with Individual Isotropic Temperature Factors

Atom		x	y	z	B, Å.^{2}	$10^4\sigma_x$	$10^4\sigma_y$	$10^4\sigma_z$	σB, Å.^{2}
Pd	(a)	−0.0228	−0.0679	0.0619	*a*	1.4	0.4	1.0	
	(b)	−0.0226	−0.0679	0.0618	1.81	1.1	0.5	1.0	0.05
Cl	(a)	−0.1636	−0.0185	−0.1202	*a*	5.3	2.1	3.8	
	(b)	−0.1632	−0.0190	−0.1209	2.81	3.6	1.7	3.1	0.11
O	(a)	0.1070	−0.1869	0.0404	3.72	15	6.2	11	0.25
	(b)	0.1093	−0.1863	0.0424	3.31	9.8	4.7	8.4	0.32
C_1	(a)	0.0251	−0.1911	0.0990	1.83	17	7.2	13	0.29
	(b)	0.0241	−0.1912	0.0992	1.68	14	7.0	13	0.33
C_2	(a)	0.0586	−0.1398	0.1933	1.87	17	7.0	12	0.26
	(b)	0.0599	−0.1385	0.1937	1.46	14	7.0	12	0.31
C_3	(a)	−0.1034	−0.1264	0.1465	1.67	17	6.8	12	0.26
	(b)	−0.1060	−0.1261	0.1456	1.28	14	6.8	12	0.30
C_4	(a)	−0.1332	−0.1575	0.0430	1.64	17	7.0	12	0.26
	(b)	−0.1330	−0.1594	0.0442	1.29	14	7.0	12	0.29
C_5	(a)	0.0152	−0.2606	0.1283	2.55	20	8.1	14	0.30
	(b)	0.0213	−0.2614	0.1295	2.28				0.37
C_6	(a)	−0.0293	−0.2750	0.2034	5.59	29	12	20	0.51
	(b)	−0.0275	−0.2772	0.2061	4.57				0.57
C_7	(a)	−0.0387	−0.3494	0.2244	10.20	51	21	33	1.02
	(b)	−0.0382	−0.3415	0.2302	11.25				1.31
C_8	(a)	−0.0085	−0.3920	0.1727	7.44	38	16	27	0.62
	(b)	−0.0002	−0.3900	0.1777	6.91				0.81
C_9	(a)	0.0456	−0.3723	0.1119	6.78	34	14	24	0.61
	(b)	0.0485	−0.3743	0.1011	6.78				0.81
C_{10}	(a)	0.0644	−0.3099	0.0813	4.40	25	11	18	0.42
	(b)	0.0593	−0.3099	0.0770	4.88				0.60
C_{11}	(a)	0.1915	−0.1285	0.3026	2.28	18	7.7	14	0.29
	(b)	0.1918	−0.1288	0.3014	2.08				0.35
C_{12}	(a)	0.3125	−0.1712	0.3493	4.86	26	11	19	0.49
	(b)	0.3149	−0.1717	0.3473	4.78				0.57
C_{13}	(a)	0.4487	−0.1551	0.4497	6.32	31	14	22	0.56
	(b)	0.4413	−0.1585	0.4499	5.44				0.67
C_{14}	(a)	0.4364	−0.1002	0.5036	6.25	32	14	24	0.59
	(b)	0.4446	−0.1024	0.5066	6.06				0.71
C_{15}	(a)	0.3075	−0.0627	0.4599	5.74	31	12	22	0.53
	(b)	0.3215	−0.0595	0.4607	5.38				0.62
C_{16}	(a)	0.2017	−0.0688	0.3613	4.42	25	11	18	0.41
	(b)	0.1951	−0.0727	0.3581	4.22				0.49
C_{17}	(a)	−0.2014	−0.0996	0.1894	2.62	19	8.5	14	0.36
	(b)	−0.2023	−0.0989	0.1899	2.51				0.38
C_{18}	(a)	−0.1940	−0.1244	0.2871	4.17	25	10	18	0.42
	(b)	−0.1941	−0.1261	0.2852	4.63				0.57
C_{19}	(a)	−0.2776	−0.0991	0.3329	6.32	32	14	22	0.61
	(b)	−0.2881	−0.1029	0.3269	5.49				0.66
C_{20}	(a)	−0.3922	−0.0507	0.2753	5.24	29	12	20	0.49
	(b)	−0.3902	−0.0526	0.2734	3.58				0.48
C_{21}	(a)	−0.3940	−0.0262	0.1813	6.12	32	13	22	0.56
	(b)	−0.3983	−0.0255	0.1781	7.33				0.87
C_{22}	(a)	−0.2972	−0.0448	0.1380	4.82	27	12	19	0.43
	(b)	−0.3044	−0.0487	0.1364	4.97				0.61
C_{23}	(a)	−0.2725	−0.1725	−0.0605	1.60	17	6.9	12	0.25
	(b)	−0.2726	−0.1716	−0.0625	1.25				0.28
C_{24}	(a)	−0.4177	−0.1502	−0.0857	4.21	25	10	17	0.45
	(b)	−0.4161	−0.1462	−0.0883	3.42				0.46
C_{25}	(a)	−0.5399	−0.1590	−0.1950	5.11	27	12	19	0.47
	(b)	−0.5422	−0.1578	−0.1918	4.44				0.56
C_{26}	(a)	−0.5172	−0.1947	−0.2634	5.88	30	12	21	0.54
	(b)	−0.5247	−0.1948	−0.2695	4.07				0.52
C_{27}	(a)	−0.3838	−0.2147	−0.2411	6.56	34	14	23	0.62
	(b)	−0.3812	−0.2202	−0.2437	6.66				0.81
C_{28}	(a)	−0.2573	−0.2070	−0.1385	5.76	30	13	21	0.52
	(b)	−0.2551	−0.2086	−0.1402	5.39				0.64
C_{29}	(a)	0.2570	−0.1609	0.0894	5.64	30	13	21	0.56
	(b)	0.2597	−0.1628	0.0890	5.27	14	7.0	12	0.63
C_{30}	(a)	0.3087	−0.1519	0.0037	8.27	42	17	28	0.74
	(b)	0.3112	−0.1566	0.0042	6.21	14	7.0	12	0.76

Table I (*Footnotes*)

[a] For the Pd and Cl atoms anisotropic temperature factors of the form: $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used; the resulting thermal coefficients (with standard deviations in parentheses) are as given below.

	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Pd	83(4.1)	9.8(0.3)	46(1.0)	7.9(0.7)	34(1.0)	−5.2(0.5)
Cl	102(7.8)	16(1.1)	53(3.6)	17(2.2)	11.4(4.0)	−10.6(1.6)

For the completely isotropic refinement the thermal parameters for Pd and Cl were 2.00 ± 0.05 and 2.94 ± 0.11 Å.^{2}, respectively.

Å.) is 9.8 cm.$^{-1}$. Systematic absences, $\{h0l\}$ for l odd and $\{0k0\}$ for k odd, show the probable space group to be $P2_1/c$ (C_{2h}^5). All atoms occupy the general fourfold set of positions (4e): $\pm[x, y, z;\ \bar{x}, {}^1/_2 + y, {}^1/_2 - z]$.[12]

Complex C.—$[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$, mol. wt. 1086.7. Crystals are monoclinic with $a = 13.17 \pm 0.03$ Å., $b = 13.57 \pm 0.03$ Å., $c = 14.05 \pm 0.03$ Å., $\beta = 92° 30' \pm 10'$; volume of unit cell = 2506 Å.^{3}; $\rho_{obsd} = 1.46$ g. cm.$^{-3}$ *vs.* $\rho_{calcd} = 1.45$ g. cm.$^{-3}$ for two dimeric molecules per unit cell. $F(000) = 1104$ electrons per unit cell. The linear absorption coefficient for Mo Kα radiation is 9.8 cm.$^{-1}$. Systematic absences, $\{h0l\}$ for $h + l$ odd and $\{0k0\}$ for k odd, show the probable space group to be $P2_1/n(C_{2h}^5)$. All atoms occupy the fourfold set of general positions (4e): $\pm[x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z]$.[12]

The subsequent structural determinations of complexes A and C verified the assigned space groups. Since for both complexes A and C the unit cell contains only two dimeric molecules, each molecule lies on a crystallographic center of symmetry.

Determination of the Structures

The structural determination of complex A, which required the location of one palladium, one chlorine, one oxygen, and thirty carbon atoms, involved the usual combination of three-dimensional Patterson, Fourier, and least-squares methods. The atomic positions were refined by the computation of four cycles with the Busing–Martin–Levy full-matrix least-squares program[13] for which individual isotropic temperature factors and separate reciprocal layer scale factors were employed. Final reliability values of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 13.3\%$ and $R_2 = [(\Sigma w||F_o| - |F_c||^2)^{1/2}/(\Sigma w|F_o|^2)^{1/2} \times 100 = 16.6\%$ were obtained. The parameter shifts observed in the last cycle were all less than one standard deviation. The weights (w) for the individual reflections were assigned as follows: $\sqrt{w} = 20/F_o$ if $I_0 \geq \sqrt{10}I_0(\text{min.})$; $\sqrt{w} = 2I_0^2/F_oI_0(\text{min.})^2$ if $I_0 < \sqrt{10}I_0(\text{min.})$. For the calculation of structure factors the atomic scattering factors given by Thomas and Umeda,[14] Dawson,[15] Berghuis, *et al.*,[16] and Hoerni and Ibers[17] were used for palladium, chlorine, carbon, and oxygen, respectively. The refined structure was confirmed by calculation of a three-dimensional difference map. Except for considerable anisotropy around the chlorine and palladium atoms all the residual peaks were less than 1.0 electron/Å.^{3}. In order to correct for this anisotropy of the two heavy atoms, a least-squares refinement with anisotropic thermal coefficients for these atoms and isotropic thermal parameters for the light atoms then was carried out. This mixed anisotropic–isotropic refinement resulted in reliability values of $R_1 = 11.2\%$ and $R_2 = 13.9\%$. All atomic coordinates for this anisotropic heavy metal refinement differed by less than two standard deviations from their corresponding values for the completely isotropic refinement.

The structural analysis of complex C followed closely the procedures employed for complex A. The final isotropic least-squares refinement yielded reliability factors of $R_1 = 12.7\%$ and $R_2 = 15.0\%$. Since a final three-dimensional electron density difference map revealed considerably less thermal anisotropy of the palladium and the chlorine than that found for complex A, no anisotropic refinement of complex C was performed.

Tables I and II give the final positional and thermal parameters of atoms in complexes A and C together with their standard deviations as obtained from the least-squares refinements.[18] Intramolecular distances and bond angles calculated from the final positional parameters with the Busing–Levy function and error program[19] in which all standard deviations are obtained from a full variance–covariance matrix are listed in Tables III and IV. Equations of planes formed by several sets of atoms and the distances of these and other atoms from the planes were calculated with the Smith program.[18,20] All Fourier and Patterson maps were computed with the Blount program.[21]

Even though the data-to-parameter ratio for each complex is greater than 10:1, the individual bond lengths and angles in the phenyl rings for both complexes vary considerably about the mean values of 1.39 Å. and 120°, and most of them display relatively high σ values (Tables III and IV). The range of C–C bond lengths is 1.26–1.58 Å., and the inner phenyl angles

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(12) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

(13) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory, 1962.

(14) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(15) B. Dawson, *Acta Cryst.*, **13**, 403 (1960).

(16) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(17) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(18) Calculated and observed structure factors together with equations of molecular planes and perpendicular distances (Å.) of atoms from these planes are deposited as Document No. 8262 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting \$2.50 for photoprints or \$1.75 for 35-mm. microfilm in advance payable to: Chief, Photoduplication Service, Library of Congress.

(19) W. R. Busing and H. A. Levy, "A Fortran Function and Error Program," Oak Ridge National Laboratory, 1962.

(20) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

(21) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," University of Wisconsin, 1962.

TABLE II

INDIVIDUAL ATOMIC PARAMETERS OF COMPLEX C WITH STANDARD DEVIATIONS FROM (a) ISOTROPIC LEAST-SQUARES REFINEMENT; (b) RIGID BODY LEAST-SQUARES REFINEMENT WITH INDIVIDUAL ISOTROPIC TEMPERATURE FACTORS

Atom		x	y	z	B, Å.^{2}	$10^4\sigma_x$	$10^4\sigma_y$	$10^4\sigma_z$	σ_B, Å.^{2}
Pd	(a)	0.4594	−0.4198	0.5871	3.25	1.4	1.4	1.2	0.07
	(b)	0.4594	−0.4198	0.5871	3.30	0.9	0.9	0.7	0.07
Cl	(a)	0.3786	−0.5292	0.4692	4.08	4.9	5.2	4.7	0.14
	(b)	0.3787	−0.5294	0.4692	4.13	2.8	2.9	2.5	0.14
O	(a)	0.3803	−0.3422	0.8459	4.11	12	13	12	0.35
	(b)	0.3809	−0.3418	0.8467	4.06	7	7	7	0.36
C_1	(a)	0.4098	−0.3817	0.7609	4.23	19	20	18	0.55
	(b)	0.4109	−0.3809	0.7619	4.41	11	11	10	0.59
C_2	(a)	0.3371	−0.3651	0.6719	2.60	16	16	14	0.41
	(b)	0.3371	−0.3648	0.6721	2.76	11	11	10	0.43
C_3	(a)	0.4027	0.2845	0.6415	4.18	19	19	18	0.52
	(b)	0.4032	−0.2839	0.6417	3.94	11	11	10	0.52
C_4	(a)	0.4878	−0.3223	0.7030	2.66	16	16	15	0.42
	(b)	0.4879	−0.3220	0.7034	2.82	11	11	10	0.44
C_5	(a)	0.4464	−0.4864	0.7903	3.35	17	17	17	0.48
	(b)	0.4475	−0.4855	0.7900	3.57				0.51
C_6	(a)	0.5086	−0.4925	0.8674	5.20	23	23	23	0.61
	(b)	0.5135	−0.4956	0.8696	5.24				0.64
C_7	(a)	0.5506	−0.5926	0.9005	6.07	26	28	31	1.14
	(b)	0.5471	−0.5886	0.8981	6.28				1.06
C_8	(a)	0.5124	−0.6718	0.8452	7.56	28	28	28	0.87
	(b)	0.5148	−0.6717	0.8471	7.26				0.85
C_9	(a)	0.4470	−0.6634	0.7688	7.30	28	29	27	0.86
	(b)	0.4488	−0.6616	0.7675	6.75				0.80
C_{10}	(a)	0.4138	−0.5647	0.7335	6.68	20	22	21	0.60
	(b)	0.4152	−0.5685	0.7390	6.17				0.74
C_{11}	(a)	0.2328	−0.3949	0.6550	3.72	18	18	18	0.50
	(b)	0.2336	−0.3955	0.6544	3.86				0.52
C_{12}	(a)	0.1876	−0.3787	0.5676	5.59	23	22	22	0.65
	(b)	0.1859	−0.3776	0.5657	5.20				0.63
C_{13}	(a)	0.0802	−0.3993	0.5502	6.28	25	24	25	0.71
	(b)	0.0830	−0.3986	0.5505	6.53				0.75
C_{14}	(a)	0.0262	−0.4375	0.6226	7.81	28	28	28	0.90
	(b)	0.0278	−0.4376	0.6239	7.59				0.89
C_{15}	(a)	0.0755	−0.4566	0.7125	6.94	26	27	27	0.80
	(b)	0.0755	−0.4556	0.7126	6.88				0.81
C_{16}	(a)	0.1805	−0.4356	0.7267	5.44	22	21	21	0.62
	(b)	0.1784	−0.4346	0.7279	6.00				0.71
C_{17}	(a)	0.3797	−0.2019	0.5579	4.09	19	19	18	0.53
	(b)	0.3790	−0.2033	0.5763	4.37				0.57
C_{18}	(a)	0.4494	−0.1780	0.5121	6.88	25	27	26	0.78
	(b)	0.4400	−0.1681	0.5053	9.12				1.16
C_{19}	(a)	0.4322	−0.0784	0.4616	16.40	57	50	62	1.95
	(b)	0.4120	−0.0834	0.4548	32.15				4.51
C_{20}	(a)	0.3262	−0.0349	0.4777	12.90	47	44	51	1.49
	(b)	0.3229	−0.0340	0.4752	14.51				1.78
C_{21}	(a)	0.2633	−0.0722	0.5255	9.44	35	35	36	1.05
	(b)	0.2619	−0.0692	0.5461	12.90				1.88
C_{22}	(a)	0.2899	−0.1504	0.5858	4.47	20	21	19	0.56
	(b)	0.2899	−0.1538	0.5967	5.43				0.71
C_{23}	(a)	0.5832	−0.2739	0.7292	4.02	19	20	18	0.52
	(b)	0.5836	−0.2737	0.7306	4.03				0.53
C_{24}	(a)	0.5889	−0.1741	0.7427	7.90	28	30	28	0.92
	(b)	0.5888	−0.1718	0.7407	7.86				0.94
C_{25}	(a)	0.6870	−0.1272	0.7762	8.78	36	34	36	1.10
	(b)	0.6798	−0.1273	0.7710	9.24				1.10
C_{26}	(a)	0.7607	−0.1845	0.7902	8.34	32	33	31	0.94
	(b)	0.7656	−0.1847	0.7912	8.80				1.02
C_{27}	(a)	0.7669	0.2887	0.7824	8.46	31	32	32	0.98
	(b)	0.7605	−0.2867	0.7810	8.94				1.06
C_{28}	(a)	0.6675	−0.3291	0.7532	7.76	30	29	30	0.89
	(b)	0.6695	−0.3312	0.7508	8.08				0.91
C_{29}	(a)	0.3380	−0.2410	0.8391	5.39	22	23	21	0.62
	(b)	0.3369	−0.2413	0.8398	6.03	11	11	10	0.71
C_{30}	(a)	0.3034	−0.2091	0.9390	6.51	25	24	25	0.77
	(b)	0.3031	−0.2100	0.9384	6.36	11	11	10	0.76

TABLE III
INTRAMOLECULAR DISTANCES (Å.) OF COMPLEX A AND COMPLEX C WITH STANDARD DEVIATIONS

	Complex A		Complex C	
Bond	Anisotropic–isotropic	Rigid body	Isotropic	Rigid body
Pd–Pd[a]	3.432 ± 0.006	3.429 ± 0.005	3.479 ± 0.008	3.479 ± 0.006
Pd–Cl	2.432 ± 0.008	2.435 ± 0.007	2.435 ± 0.009	2.436 ± 0.006
Pd–Cl[a]	2.418 ± 0.007	2.422 ± 0.005	2.408 ± 0.010	2.407 ± 0.006
Pd–Cl	2.606 ± 0.016	2.608 ± 0.015	2.607 ± 0.025	2.619 ± 0.015
Pd–C_2	2.177 ± 0.016	2.164 ± 0.015	2.176 ± 0.022	2.178 ± 0.015
Pd–C_3	2.086 ± 0.019	2.093 ± 0.014	2.136 ± 0.026	2.141 ± 0.015
Pd–C_4	2.109 ± 0.016	2.146 ± 0.015	2.118 ± 0.021	2.126 ± 0.015
Cl–Cl[a]	3.427 ± 0.011	3.440 ± 0.013	3.370 ± 0.016	3.369 ± 0.011
C_1–C_2	1.586 ± 0.023	1.603 ± 0.021	1.558 ± 0.033	1.575 ± 0.021
C_1–C_3	2.156 ± 0.026	2.164 ± 0.019	2.133 ± 0.036	2.140 ± 0.020
C_2–C_3	1.441 ± 0.022	1.471 ± 0.018	1.469 ± 0.033	1.476 ± 0.021
C_2–C_4	2.062 ± 0.017	2.074 ± 0.021	2.096 ± 0.030	2.098 ± 0.021
C_3–C_4	1.458 ± 0.024	1.461 ± 0.022	1.477 ± 0.033	1.475 ± 0.022
C_4–C_1	1.543 ± 0.021	1.518 ± 0.019	1.562 ± 0.034	1.554 ± 0.021
C_1–C_5	1.512 ± 0.024	1.517 ± 0.016	1.551 ± 0.035	1.544 ± 0.017
C_5–C_6	1.337 ± 0.040		1.332 ± 0.038	
C_6–C_7	1.582 ± 0.052		1.532 ± 0.045	
C_7–C_8	1.257 ± 0.064		1.406 ± 0.050	
C_8–C_9	1.258 ± 0.059		1.352 ± 0.045	
C_9–C_{10}	1.400 ± 0.039		1.487 ± 0.045	
C_{10}–C_5	1.416 ± 0.033		1.386 ± 0.037	
C_2–C_{11}	1.466 ± 0.019	1.445 ± 0.016	1.441 ± 0.031	1.436 ± 0.016
C_{11}–C_{12}	1.377 ± 0.027		1.359 ± 0.041	
C_{12}–C_{13}	1.432 ± 0.030		1.452 ± 0.042	
C_{13}–C_{14}	1.395 ± 0.044		1.369 ± 0.051	
C_{14}–C_{15}	1.364 ± 0.038		1.418 ± 0.052	
C_{15}–C_{16}	1.260 ± 0.029		1.417 ± 0.040	
C_{16}–C_{11}	1.454 ± 0.029		1.362 ± 0.038	
C_3–C_{17}	1.466 ± 0.030	1.468 ± 0.014	1.457 ± 0.035	1.456 ± 0.016
C_{17}–C_{18}	1.406 ± 0.033		1.369 ± 0.035	
C_{18}–C_{19}	1.364 ± 0.046		1.538 ± 0.072	
C_{19}–C_{20}	1.436 ± 0.036		1.542 ± 0.079	
C_{20}–C_{21}	1.380 ± 0.045		1.200 ± 0.069	
C_{21}–C_{22}	1.404 ± 0.048		1.393 ± 0.052	
C_{22}–C_{17}	1.433 ± 0.028		1.383 ± 0.035	
C_4–C_{23}	1.463 ± 0.017	1.478 ± 0.016	1.451 ± 0.032	1.457 ± 0.016
C_{23}–C_{24}	1.387 ± 0.029		1.369 ± 0.043	
C_{24}–C_{25}	1.418 ± 0.027		1.498 ± 0.049	
C_{25}–C_{26}	1.300 ± 0.043		1.252 ± 0.049	
C_{26}–C_{27}	1.273 ± 0.044		1.421 ± 0.050	
C_{27}–C_{28}	1.375 ± 0.032		1.461 ± 0.051	
C_{28}–C_{23}	1.356 ± 0.037		1.369 ± 0.041	
O–Cl	1.394 ± 0.028	1.401 ± 0.017	1.380 ± 0.031	1.378 ± 0.018
O–C_{29}	1.412 ± 0.030	1.398 ± 0.016	1.483 ± 0.034	1.484 ± 0.018
C_{29}–C_{30}	1.505 ± 0.058	1.485 ± 0.020	1.555 ± 0.047	1.533 ± 0.020

[a] Atoms in other half of dimeric unit related by the center of symmetry.

TABLE IV
BOND ANGLES OF COMPLEX A AND COMPLEX C WITH STANDARD DEVIATIONS

	Complex A		Complex C	
Angle	Anisotropic–isotropic	Rigid body	Isotropic	Rigid body
Cl–Pd–Cl′	89.9 ± 0.2	90.1 ± 0.2	88.2 ± 0.3	88.2 ± 0.2
Pd–Cl–Pd′	90.1 ± 0.2	89.8 ± 0.2	91.8 ± 0.2	91.8 ± 0.2
Cl–Pd–C_2	160.7 ± 0.4	161.1 ± 0.4	105.6 ± 0.6	105.7 ± 0.4
Cl′–Pd–C_4	164.4 ± 0.5	163.9 ± 0.4	107.6 ± 0.6	107.6 ± 0.4
Cl′–Pd–C_2	108.2 ± 0.5	107.6 ± 0.4	164.9 ± 0.7	164.8 ± 0.4
Cl–Pd–C_4	103.7 ± 0.5	104.1 ± 0.4	164.0 ± 0.4	164.0 ± 0.4
Cl–Pd–C_3	129.5 ± 0.5	128.9 ± 0.4	128.2 ± 0.6	128.5 ± 0.4
Cl′–Pd–C_3	133.0 ± 0.5	133.0 ± 0.4	133.9 ± 0.6	133.6 ± 0.4
Pd–C_2–C_3	66.9 ± 0.9	67.2 ± 0.8	68.6 ± 1.2	68.7 ± 0.8
Pd–C_4–C_3	68.9 ± 0.9	67.9 ± 0.8	70.3 ± 1.2	70.3 ± 0.8
Pd–C_3–C_2	73.7 ± 0.9	72.4 ± 0.8	71.5 ± 1.2	71.4 ± 0.8
Pd–C_3–C_4	70.5 ± 0.9	71.8 ± 0.8	69.1 ± 1.1	69.2 ± 0.8
C_2–Pd–C_4	57.4 ± 0.9	57.5 ± 0.8	58.4 ± 1.3	58.3 ± 0.8
O–C_1–C_5	110.1 ± 1.4	108.6 ± 1.0	102.8 ± 1.9	103.4 ± 1.0
O–C_1–C_2	118.6 ± 1.3	116.3 ± 1.1	116.9 ± 2.0	116.7 ± 1.2
O–C_1–C_4	114.7 ± 1.4	115.9 ± 1.2	117.8 ± 2.1	118.5 ± 1.2
C_2–C_1–C_5	116.0 ± 1.4	117.3 ± 1.1	121.3 ± 2.0	120.5 ± 1.1
C_4–C_1–C_5	112.6 ± 1.4	113.9 ± 1.1	114.0 ± 1.9	113.8 ± 1.1
C_2–C_1–C_4	82.4 ± 1.1	83.3 ± 1.0	84.4 ± 1.7	84.2 ± 1.1
C_1–O–C_{29}	121.3 ± 1.7	124.3 ± 1.1	115.0 ± 1.8	115.1 ± 1.1
O–C_{29}–C_{30}	110.4 ± 2.4	111.2 ± 1.2	108.9 ± 2.3	109.8 ± 1.1
C_1–C_2–C_3	90.7 ± 1.3	89.4 ± 1.1	89.6 ± 1.7	89.0 ± 1.0
C_1–C_4–C_3	91.8 ± 1.3	93.2 ± 1.2	89.1 ± 1.8	89.8 ± 1.1
C_2–C_3–C_4	90.7 ± 1.3	90.0 ± 1.0	90.7 ± 1.8	90.6 ± 1.2
C_1–C_2–C_{11}	132.7 ± 1.4	131.8 ± 1.1	129.7 ± 1.9	130.2 ± 1.2
C_3–C_2–C_{11}	133.5 ± 1.5	134.7 ± 1.2	136.8 ± 2.0	137.2 ± 1.3
C_1–C_4–C_{23}	130.4 ± 1.4	132.0 ± 1.2	133.1 ± 1.9	132.0 ± 1.2
C_3–C_4–C_{23}	134.3 ± 1.5	133.2 ± 1.0	128.1 ± 2.1	128.3 ± 1.2
C_2–C_3–C_{17}	134.7 ± 1.6	133.5 ± 1.3	130.0 ± 2.2	128.7 ± 1.3
C_4–C_3–C_{17}	134.2 ± 1.6	136.0 ± 1.2	139.3 ± 2.3	140.7 ± 1.3
C_1–C_5–C_{10}	119.2 ± 1.7		117.7 ± 2.1	
C_1–C_5–C_6	120.4 ± 1.8		116.5 ± 2.3	
C_5–C_6–C_7	115.5 ± 2.6		120.2 ± 2.7	
C_6–C_7–C_8	122.2 ± 3.9		113.2 ± 2.9	
C_7–C_8–C_9	116.0 ± 3.6		125.1 ± 3.7	
C_8–C_9–C_{10}	131.4 ± 3.1		120.5 ± 3.4	
C_9–C_{10}–C_5	114.0 ± 2.3		114.8 ± 2.5	
C_{10}–C_5–C_6	120.2 ± 1.9		125.8 ± 2.6	
C_2–C_{11}–C_{16}	119.6 ± 1.6		120.0 ± 2.2	
C_2–C_{11}–C_{12}	121.9 ± 1.7		118.7 ± 2.3	
C_{11}–C_{12}–C_{13}	120.4 ± 2.2		120.4 ± 2.7	
C_{12}–C_{13}–C_{14}	114.9 ± 2.6		118.8 ± 3.0	
C_{13}–C_{14}–C_{15}	122.2 ± 2.9		119.9 ± 3.3	
C_{14}–C_{15}–C_{16}	122.4 ± 2.7		119.7 ± 3.2	
C_{15}–C_{16}–C_{11}	118.9 ± 2.2		119.9 ± 2.6	
C_{16}–C_{11}–C_{12}	118.4 ± 1.9		121.2 ± 2.5	
C_3–C_{17}–C_{18}	120.4 ± 1.7		118.0 ± 2.5	
C_3–C_{17}–C_{22}	120.7 ± 1.8		119.6 ± 2.4	
C_{17}–C_{18}–C_{19}	122.4 ± 2.2		115.5 ± 3.9	
C_{18}–C_{19}–C_{20}	120.5 ± 2.7		112.6 ± 5.6	
C_{19}–C_{20}–C_{21}	115.3 ± 2.6		124.9 ± 6.0	
C_{20}–C_{21}–C_{22}	126.2 ± 2.6		120.0 ± 4.9	
C_{21}–C_{22}–C_{17}	115.8 ± 2.2		122.0 ± 3.0	
C_{22}–C_{17}–C_{18}	118.7 ± 1.9		122.3 ± 2.7	
C_4–C_{23}–C_{28}	118.1 ± 1.8		119.9 ± 2.8	
C_4–C_{23}–C_{24}	123.6 ± 1.6		121.7 ± 2.6	
C_{23}–C_{24}–C_{25}	118.5 ± 2.1		120.4 ± 3.5	
C_{24}–C_{25}–C_{26}	118.9 ± 2.5		115.9 ± 4.2	
C_{25}–C_{26}–C_{27}	122.1 ± 2.9		130.8 ± 4.4	
C_{26}–C_{27}–C_{28}	122.6 ± 3.0		109.9 ± 3.7	
C_{27}–C_{28}–C_{23}	118.7 ± 2.6		124.9 ± 3.6	
C_{28}–C_{23}–C_{24}	118.2 ± 2.0		117.9 ± 3.0	

differ by as much as 11° from the normal hexagon angle. These inaccuracies in determining the phenyl carbon coordinates (also reflected by the σ values in Tables I and II) are especially great for the *meta* and *para* carbons and no doubt are due to the high thermal motion in the phenyl rings relative to that in the more rigid cyclobutenyl ring–palladium chloride system. Substantiation of this effect is given by the temperature factors (Tables I and II) which generally are highest for these *meta* and *para* phenyl carbons.

It was decided to continue additional least-squares refinements in which the four asymmetric phenyl rings in each complex were constrained to their well-known geometry. A full-matrix least-squares program for rigid body refinement written by Scheringer[22] was used. This program, which allows only one isotropic thermal parameter per rigid body group (not realistic for the phenyl rings), was modified[23] for the final least-squares cycles to allow the refinement of an individual isotropic temperature factor for each atom in the rigid body phenyl rings. Each phenyl ring is described by three translational parameters and three angular parameters which relate the origin and orientation of the internal axial system of the ring to the crystallographic axes. The use of these six parameters together with individual atomic thermal parameters for each phenyl ring decreased for each complex the total number of nonhydrogen positional and isotropic thermal parameters from 132 to 84.

For each complex four cycles were needed to reduce all the parameter shifts to less than one standard deviation. The final R_1 values for the rigid body refinements

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(22) C. Scheringer, *Acta Cryst.*, **16**, 546 (1963).

(23) We are indebted to Dr. Milton D. Glick (formerly of this laboratory) for carrying out this modification and for assisting in the rigid body refinement of both complexes.

TABLE V

FINAL GROUP PARAMETERS FROM RIGID BODY REFINEMENT OF COMPLEXES A AND C WITH INDIVIDUAL ISOTROPIC THERMAL PARAMETERS. ENCLOSED IN PARENTHESES ARE THE STANDARD DEVIATIONS OF THE LEAST SIGNIFICANT FIGURES[a]

Group	x_r	y_r	z_r	φ	θ	ρ
			Complex A			
C_6H_5 (I) (C_5–C_{10})	0.0213 (10)	−0.2614 (3)	0.1295 (8)	45.9° (4)	−43.6° (2)	−92.0° (4)
C_6H_5 (II) (C_{11}–C_{16})	0.1918 (7)	−0.1288 (4)	0.3014 (5)	−24.5° (3)	11.3° (3)	60.3° (3)
C_6H_5 (III) (C_{17}–C_{22})	−0.2023 (9)	−0.0989 (4)	0.1899 (7)	67.3° (2)	20.2° (3)	45.2° (3)
C_6H_5 (IV) (C_{23}–C_{28})	−0.2726 (7)	−0.1716 (5)	−0.0625 (5)	155.6° (2)	−10.0° (3)	−33.0° (3)
			Complex C			
C_6H_5 (I) (C_5–C_{10})	0.4475 (7)	−0.4855 (5)	0.7900 (6)	−39.4° (4)	−35.5° (3)	−96.2° (4)
C_6H_5 (II) (C_{11}–C_{16})	0.2336 (4)	−0.3955 (7)	0.6544 (5)	99.0° (2)	−11.8° (3)	19.1° (3)
C_6H_5 (III) (C_{17}–C_{22})	0.3790 (7)	−0.2033 (6)	0.5763 (6)	154.5° (4)	55.6° (3)	−8.2° (5)
C_6H_5 (IV) (C_{23}–C_{28})	0.5836 (5)	−0.2737 (6)	0.7306 (7)	−70.2° (4)	25.7° (2)	84.6° (4)

[a] The internal orthogonal axial system x', y', z' for each phenyl ring in complexes A and C is as follows: the origin (or base point) x_r, y_r, z_r is at the phenyl carbon attached to the cyclobutenyl ring; one axis (x' or y') passes through the two ring carbons *ortho* to the base point carbon; the second axis passes through the origin and the *para* ring carbon; z' is the vector product of x' and y' normal to the phenyl ring. The three rotational angles φ, θ, and ρ refer to the orientation of the internal axial system with respect to the crystallographic axes.[22]

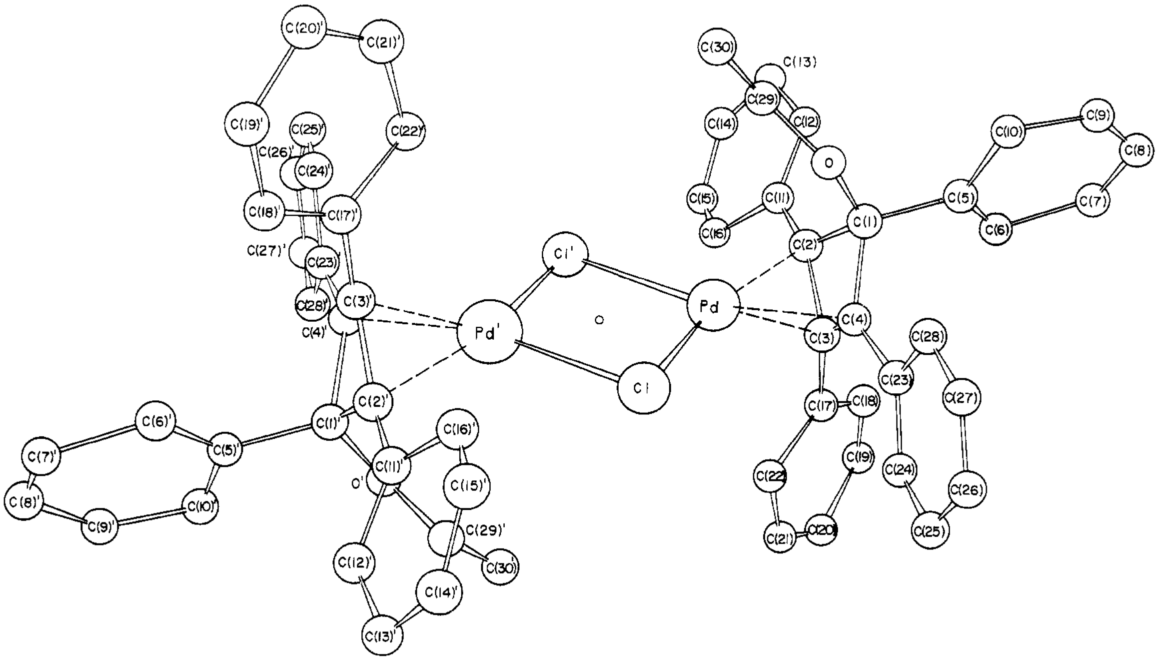

Figure 1.—Molecular configuration of *endo*-1-ethoxy-1,2,3,4-tetraphenylcyclobutenyl–palladium(II) chloride dimer, $[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$ (complex A).

of complexes A and C were 13.6 and 13.3%, respectively. The group parameters are listed in Table V. The individual atomic parameters corresponding to the rigid body refinement are given in Tables I and II. Comparison of the bond lengths (Table III) and angles (Table IV) shows in general for the rigid body refinement a decrease in standard deviations of the parameters and considerably better internal agreement of the molecular parameters. For example, the presumably equivalent Pd–C_2 and Pd–C_4 bonds which for complex A differed by at least 0.06 Å. for the regular refinement now agree within 0.02 Å. As expected, the resulting molecular parameters from the anisotropic–isotropic refinement of complex A in general are closer to the corresponding parameters from the rigid body refinement than to those from the completely isotropic nonrigid body refinement of complex A (not given in Tables III and IV to conserve space). Since the calculated model for the rigid body refinement (by which the positions of the phenyl groups are varied as a whole) then should represent more closely the true nature of the complex, the molecular parameters based on this relatively new crystallographic technique are given in the Discussion unless otherwise specified. The advantages of this type of refinement have been utilized successfully in other structural investigations.[22,24]

Discussion

The structures of the isomeric complexes A and C consist of discrete dimeric units of $[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$ in which each palladium of a rhombic $(PdCl)_2$ fragment is symmetrically bonded to the allylic part of a 1-ethoxy-1,2,3,4-tetraphenylcyclobutenyl system such that the required crystallographic molecular symmetry is C_i-$\bar{1}$. A comparison of Figures 1 and 2 (which are

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(24) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

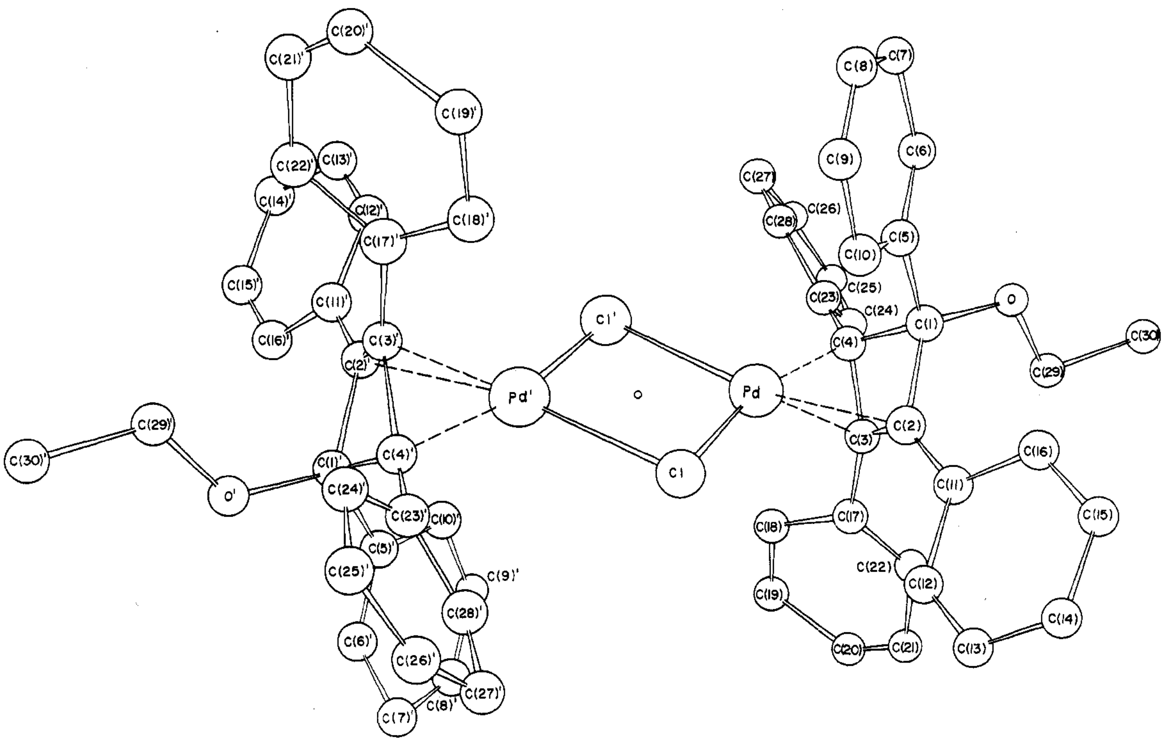

Figure 2.—Molecular configuration of *exo*-1-ethoxy-1,2,3,4-tetraphenylcyclobutenyl–palladium(II) chloride dimer, $[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$ (complex C).

configurations of complexes A and C, respectively, drawn from the coordinates provided by the Blount projection program[21]) shows that complexes A and C are a pair of geometrical isomers with interchanged phenyl and ethoxy groups on the tetrahedral cyclobutenyl carbon C_1. With respect to the location of the ethoxy group relative to the palladium, complex A can be classified as the *endo* form and complex C as the *exo* form. Except for this isomerism and different relative orientations in the solid state of the phenyl rings attached to the other cyclobutenyl ring carbons, the two complexes possess similar molecular parameters. In this discussion concerning the two structures, the molecular parameters of complex A are given first followed by the corresponding values in parentheses for complex C.

The planar $(PdCl)_2$ fragment possesses long symmetrical Pd–Cl distances of 2.43 Å. (av.) (2.42 Å. (av.)) comparable to those of 2.41 Å. (av.) found in $[(C_3H_5)PdCl]_2$.[25,26] A similar lengthening is observed for the Pd–Cl bridging distances *trans* to the olefinic groups in $[(\text{styrene})PdCl_2]_2$ (*i.e.*, 2.39 Å. *vs.* 2.32 Å. for the bridging Pd–Cl distances *trans* to the terminal Pd–Cl bonds)[27,28]; the normal Pd–Cl bridging distances in $PdCl_2$ are 2.31 Å.[29]

The symmetrical orientation of the allylic fragment of the cyclobutenyl ring system with respect to the $(PdCl)_2$ bridge system is shown from the similar Pd–C distances of 2.16 (2.18) and 2.15 (2.13) Å. for the terminal allylic carbons and 2.09 (2.14) Å. for the central allylic carbon. The average distance of the allylic carbons from the palladium of 2.13 (2.15) Å. is in agreement with the average value of 2.11 Å. found in $[(C_3H_5)PdCl]_2$. The nonbonding distance from the palladium to the tetrahedral cyclobutenyl ring carbon of 2.61 (2.62) Å. results from the nonplanarity of the cyclobutenyl ring system; this salient feature will be discussed later.

The plane of the three allylic carbons forms a dihedral angle of 95° (95°) with the $(PdCl)_2$ plane, which shows the orientation of the allylic carbons to be more nearly perpendicular with respect to the $(PdCl)_2$ plane than that observed for $[(C_3H_5)PdCl]_2$, for which the corresponding dihedral angle is 110° (av.).[25,26] As also observed for $[(C_3H_5)PdCl]_2$, the plane of the $(PdCl)_2$ bridge system in each of the $[(C_6H_5)_4C_4OC_2H_5]_2Pd_2Cl_2$ isomers cuts the allylic bonds (C_2–C_3 and C_3–C_4) much closer to the two terminal carbons; the central allylic carbon (C_3) is approximately 0.8 Å. above and the terminal carbons (C_2 and C_4) about 0.2 Å. below the $(PdCl)_2$ plane. This similar stereochemical arrangement of the allylic carbons, which are now constrained as part of a four-membered ring, also is consistent with the premise made for $[(C_3H_5)PdCl]_2$[25] that these isomeric cyclobutenyl–palladium complexes can be considered formally to arise from the bonding of a palladium(II) with an allylic anion which functions as a bidentate group by occupying two square-planar coordination sites. The closest intermolecular distances of 3.4 Å. for C···C contacts in complexes A and C support the view that these molecular crystals are held to-

(25) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, **3**, 43 (1965).

(26) A. E. Smith, *Acta Cryst.*, in press.

(27) J. R. Holden and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955).

(28) N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 131–138.

(29) A. F. Wells, *Z. Krist.*, **100**, 189 (1938).

gether primarily by the usual van der Waals forces.

Of interest is a close examination of the type and amount of distortion of the otherwise planar cyclobutenyl ring system on interaction with the palladium(II). For these purposes a detailed comparison is made of the molecular parameters or complexes A and C with those of the cyclobutenyl–nickel compound, $[(CH_3)_4C_4C_5H_5]NiC_5H_5$, and those of the uncoordinated 1-chloro-1,2,3,4-tetraphenylcyclobutenium cation crystallized as $[(C_6H_5)_4C_4Cl]^+SnCl_5^-$. Schematic drawings of the three metal complexes are given in Figure 3; bond lengths and angles of the cyclobutenyl rings for these compounds and the cyclobutenium cation are presented in Figure 4. The recent structural determination of $[(C_6H_5)_4C_4Cl]^+SnCl_5^-$ By Bryan[30] revealed a planar cyclobutenium ring coplanar with the two phenyl rings attached to the terminal carbons of the allylic fragment, which implies stability due to extensive charge delocalization.

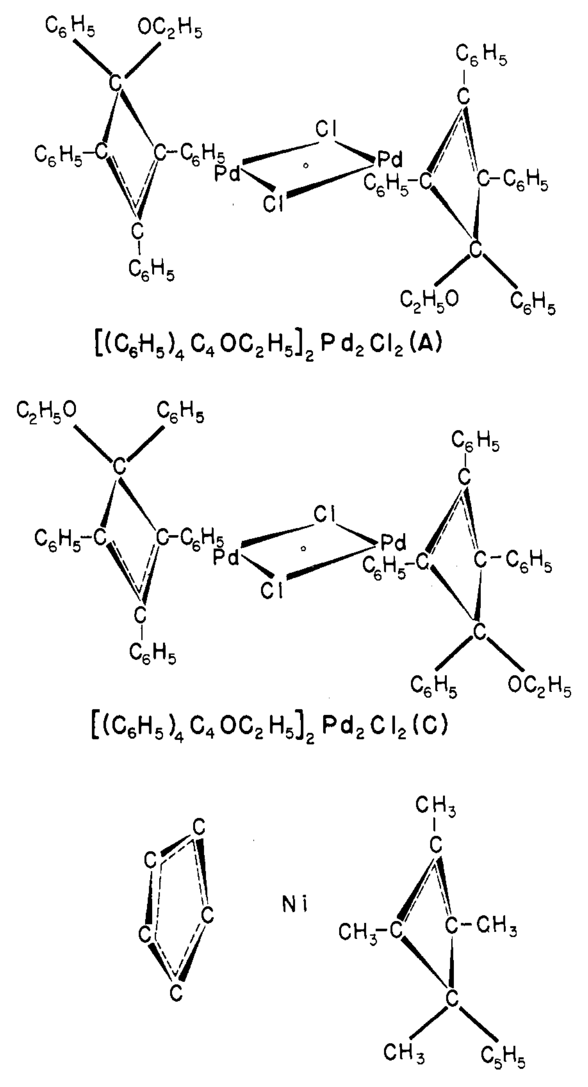

Figure 3.—Schematic diagrams of the nickel and two palladium cyclobutenyl complexes.

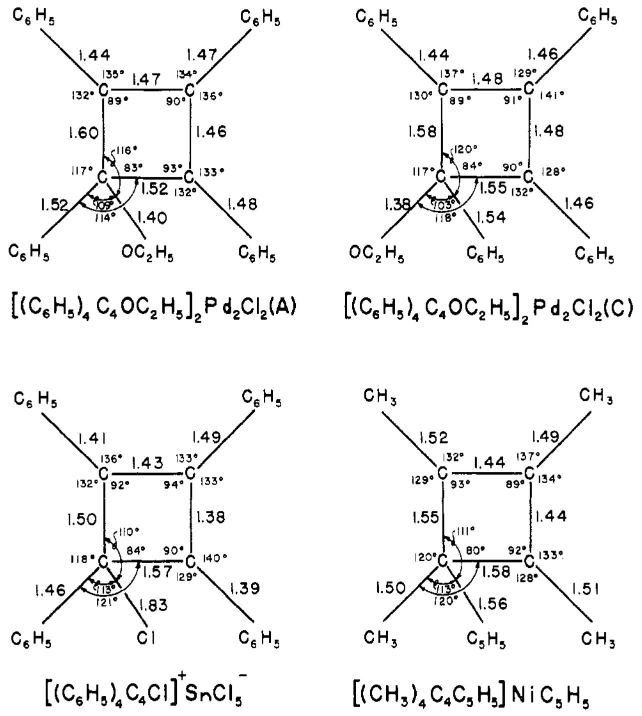

Figure 4.—Comparison of molecular ring parameters for the three cyclobutenyl–metal complexes and the cyclobutenium cation.

In contrast, the cyclobutenyl ring system for each of the palladium and nickel complexes is nonplanar in that the tetrahedral ring carbon is bent out of the allylic carbon plane away from the metal (Figure 3). The dihdral angle formed between the plane of the three allylic carbons and the plane of the two terminal allylic carbons and tetrahedral carbon is 21.8° (26.6°) for complex A (C); a similar dihedral angle of 24.9° was found for the cyclobutenyl ring in the nickel complex.[7] This distortion can be rationalized mainly from steric considerations as due to the repulsion between the metal and tetrahedral carbon such that the nonbonding distance is increased to a reasonable value (*i.e.*, 2.61 Å. for complex A, 2.62 Å. for complex C, and 2.55 Å. for $[(CH_3)_4C_4C_5H_5]NiC_5H_5$). Further deformation of the σ-framework of the allylic fragment coordinated to the palladium in complexes A and C is revealed by the phenyl carbons C_{11}, C_{17}, and C_{23} attached to the allylic carbons C_2, C_3, and C_4, respectively, being displaced from the plane of the allylic carbons by 0.12 (0.03) Å., 0.13 (0.02) Å., and 0.04 (0.24) Å. in the direction away from the palladium. These latter effects may be a consequence both of the unsymmetrical perturbation of the π-electron charge distribution by the palladium and of the intra- and intermolecular interactions of the phenyl groups. The different relative orientations of the phenyl rings in complexes A and C, readily observed in Figures 1 and 2, are given by the dihedral angles of 94° (49°), 34° (34°), 129° (48°), and 7° (40°) formed between the plane of the allylic fragment and the phenyl rings bonded to carbons C_1 to C_4, respectively.

Noteworthy is that the average allylic C–C bonds of

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[30] R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964); R. F. Bryan, private communication to L. F. Dahl, 1964.

1.47 (1.48) Å. for complex A (C) agree within experimental error with the average value of 1.44 Å. for the nickel complex. The average value of 1.46 Å. for the three metal complexes appears to be significantly longer than the average values of 1.36 and 1.38 Å. found for the open allylic fragment in $[(C_3H_5)PdCl]_2$.[25,26] These longer allylic bonds for the cyclobutenyl–metal complexes may be inherent in the strained four-membered carbon ring system and do not necessarily reflect a difference in the strength of interaction between the metal and the two types of allylic fragments present. This conclusion is supported by the average allylic C–C bond length of 1.41 Å. found[30] for the uncomplexed cyclobutenium cation in $[(C_6H_5)_4C_4Cl]^+SnCl_5^-$.

The average bond length of the allylic carbons to the phenyl carbons in complex A (C) is 1.46 (1.45) Å., whereas a bond length of 1.52 (1.54) Å. is observed between the cyclobutenyl tetrahedral carbon and its bonded phenyl carbon. The cyclobutenyl ring bond angles for the three metal complexes (Figure 4) are similar to those in the cyclobutenium ring, and all are reduced by equivalent amounts from the *ideal* strain-free values. For all four rings (Figure 4) the bonds from the ring carbons to the attached allylic ring substituents essentially bisect the external angles (*i.e.*, ~133 ± 8°). The small differences in bond lengths and angles for the metal-complexed cyclobutenyl systems compared to those for the planar cyclobutenium cation no doubt are due to the rigidity of the four-membered ring system.

Of interest also is a comparison of the directions of the lines perpendicular to the planes defined by the three bonding carbon neighbors of each of the allylic carbons. For an ideally trigonally hybridized carbon these lines define the direction of the p_π-type orbitals. A determination of the angles between these lines allows a qualitative estimate of the amount of electron delocalization retained in the cyclobutenyl system in complexes A and C and $[(CH_3)_4C_4C_5H_5]NiC_5H_5$. The results of such a calculation are given below for the three cyclobutenyl–metal systems

Angle	Complex A	Complex C	$[(CH_3)_4C_4C_5H_5]NiC_5H_5$
P_{C_3}–P_{C_2}	14.2°	15.4°	16.5°
P_{C_3}–P_{C_4}	16.0°	14.5°	16.4°
P_{C_2}–P_{C_4}	6.9°	4.9°	2.2°

Here P_{C_2} and P_{C_4} represent the perpendicular lines extending from the planes of attached carbons for the terminal allylic carbons and P_{C_3} the line from the central carbon. The results of these calculations again show the similarities in the three transition metal–cyclobutenyl systems. The small differences observed among corresponding angles are not significant. There is a symmetrical distortion of the σ-framework such that the normals through the terminal allylic carbons remain essentially parallel. It is concluded that considerable electron delocalization in the allylic portion of the cyclobutenyl ring is retained on forming these metal complexes.

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CONTRIBUTION FROM THE HERBERT JONES CHEMICAL LABORATORY,
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The Structure of a Self-Condensation Product of *o*-Aminobenzaldehyde in the Presence of Nickel Ions[1]

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The structure of the closed tridentate macrocyclic ligand nickel complex, tribenzo[*b,f,j*][1.5.9]triazacycloduodecinenickel nitrate, has been determined by X-ray diffraction. The nickel is in an octahedral configuration with the three nitrogens of the macrocyclic ligand occupying a face of the octahedron. Two waters and a nitrate fill the remainder of the positions. A second nitrate is not bound directly to the nickel but connected to the complex by a system of hydrogen bonds.

Introduction

This work was undertaken to determine the structure of the nickel complex of tribenzo[*b,f,j*][1.5.9]triazacycloduodecine (hereafter called TRI) with the composition $Ni(TRI)(H_2O)_2(NO_3)_2$ (see Figure 1). At the time this work was undertaken the structure of the TRI ligand and the details of the coordination around the nickel ion were not known.[2] Melson and

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[1] This research was supported by a grant from the Public Health Service.

[2] G. L. Eichhorn and R. A. Latif, *J. Am. Chem. Soc.*, **76**, 5180 (1954); G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).