Contribution from the Department of Chemistry,
West Virginia University, Morgantown, West Virginia 26506

# Crystal and Molecular Structure of Tris(dibenzylideneacetone)dipalladium(0)

CORTLANDT G. PIERPONT* and MARGARET C. MAZZA

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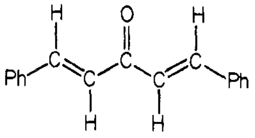
The complex $Pd_2(C_{17}OH_{14})_3$ has been isolated as its methylene chloride solvate. The crystal and molecular structure of the complex has been determined from three-dimensional X-ray data collected by the $\theta$–$2\theta$ scan technique. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional $R$ factor of 0.068 for 2911 observed reflections. The complex crystallizes in space group $P\bar{1}$ of the triclinic system in a cell of dimensions $a = 12.400$ (5) Å, $b = 15.149$ (5) Å, $c = 12.956$ (5) Å, $\alpha = 115.01$ (5)°, $\beta = 95.23$ (5)°, $\gamma = 97.30$ (5)°, and $V = 2159$ Å$^3$. There are two formula weights per unit cell ($\rho_{\text{exptl}} = 1.53$ (1) g cm$^{-3}$; $\rho_{\text{calcd}} = 1.54$ g cm$^{-3}$). Each ligand bridges the two metal atoms, coordinated to each through the pentadienone olefin groups. Two of the ligands are in the s-cis,trans conformation while the third is in the s-cis,cis form. The olefin groups in the latter ligand have been forced apart by the Pd(1)–Pd(2) separation (3.237 (5) Å).

## Introduction

Complexes of the group VIII metals with $d^{10}$ electronic configurations have been of considerable catalytic interest.[1] Of the zerovalent members of this series far less work has been done with Pd than Ni or Pt. This is due in part to the reduced stability of Pd(0) complexes and the lower affinity of the Pd atom for $\pi$-acceptor ligands of the type normally used to stabilize nucleophilic metal complexes.[2]

In 1970 the synthesis of the interesting and useful complex bis(dibenzylideneacetone)palladium(0), $Pd(DBA)_2$, was reported.[3] In contrast to other $d^{10}$ group VIII metal systems the synthesis is remarkably simple and the complex air stable. Since the initial report of this work various substitution and addition reactions have been reported along with an investigation of the potential utility of the complex as a homogeneous catalyst.[4,5] The complex is also an extremely useful precursor to other Pd(0) complexes. The DBA ligands in the complex are labile with complete dissociation to Pd metal occurring in boiling benzene. We have reported that recrystallization of $Pd(DBA)_2$ from methylene chloride yields the complex $Pd_2(DBA)_3 \cdot CH_2Cl_2$.[6] More recent work has indicated the formation of solvated $Pd_2(DBA)_3$ in other solvent media and suggests that $Pd(DBA)_2$ may rather be the DBA solvate of $Pd_2(DBA)_3$.[4] We have examined the addition of DBA to $Pd_2(DBA)_3$ and isolated the complex $Pd(DBA)_3$.[7] The kinetics of this ligand addition may be easily followed spectroscopically and does not suggest the formation of stable complexes of intermediate stoichiometry.



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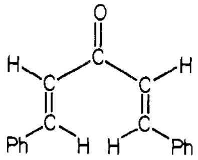

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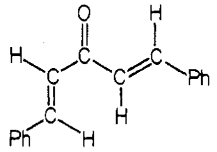
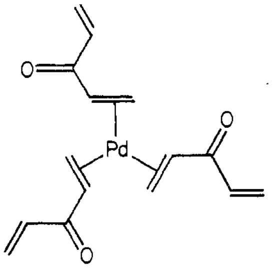


III

The structural properties of the DBA complexes have proven to be interesting. The DBA molecule may adopt three conformeric forms, the s-trans,trans (I), s-cis,cis (II), and the s-cis,trans (III). The close proximity of the olefin hydrogen atoms in II suggests that it would be less stable than forms I and III. While I has not yet been observed as a ligand, structural work on the Pd-DBA complexes confirms the stability of the s-cis,trans conformer. The complex $Pd(DBA)_3$ has been shown to have a trigonal coordination geometry about the metal with each DBA bonded to the metal through one olefin group and each ligand in the s-cis,trans configuration (IV). Structural work on the chloroform[4] and benzene[8] solvates of $Pd_2(DBA)_3$ has indicated that the complex in both cases contains three s-cis,trans DBA ligands bridging the two metal atoms coordinated through their olefin groups. The methylene chloride solvate of $Pd_2(DBA)_3$, however, has two DBA ligands in the s-cis,trans form while the third is in the s-cis,cis conformer.[6] We wish to present herein the complete account of the crystal and molecular structure of $Pd_2(DBA)_3 \cdot CH_2Cl_2$.



IV

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[1] P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. I and II, Academic Press, New York, N. Y., 1971.

[2] (a) E. P. Kundig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, 95, 7234 (1973); (b) R. S. Nyholm, *Proc. Chem. Soc., London*, 273 (1961).

[3] Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *J. Chem. Soc. D*, 1065 (1970).

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[5] (a) K. Moseley and P. M. Maitlis, *J. Chem. Soc. D*, 982 (1971); (b) K. Moseley and P. M. Maitlis, *ibid.*, 1604 (1971); (c) T. Ito, Y. Takahashi, and Y. Ishii, *J. Chem. Soc., Chem. Commun.*, 629 (1972); (d) W. J. Cherwinski, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, 52, C61 (1973).

[6] M. C. Mazza and C. G. Pierpont, *J. Chem. Soc., Chem. Commun.*, 207 (1973).

[7] M. C. Mazza and C. G. Pierpont, *Inorg. Chem.*, 12, 2955 (1973).

[8] M. Clay and C. G. Pierpont, unpublished results. Crystal data for $Pd_2(DBA)_3 \cdot C_6H_6$: monoclinic, $P2_1/c$, $a = 13.745$ (5) Å, $b = 23.589$ (5) Å, $c = 15.434$ (5) Å, $\beta = 66.04$ (3)°. When the refinement reached $R = 0.085$ with isotopic thermal parameters for all atoms, it was clear that the structure suffered from a similar disorder problem found for $Pd_2(DBA)_3 \cdot CHCl_3$.[4]

## Experimental Section

Wine red crystals of $Pd_2(DBA)_3$ were formed by allowing a methylene chloride solution of $Pd(DBA)_2$ to evaporate slowly in air. Elemental analyses revealed the presence of one molecule of $CH_2Cl_2$ per molecule of complex.

**Crystal Data.** Precession and Weissenberg photographs taken on the crystals of $Pd_2(DBA)_3 \cdot CH_2Cl_2$ indicated the triclinic system. A crystal of dimensions 0.243 × 0.210 × 0.312 mm was mounted along the $a^*$ axis and aligned on a Picker automated diffractometer. The centered locations of 18 reflections gave a cell of refined dimensions $a = 12.400$ (5) Å, $b = 15.149$ (5) Å, $c = 12.956$ (5) Å, $\alpha = 115.01$ (5)°, $\beta = 95.23$ (5)°, $\gamma = 97.30$ (5)°, and $V = 2159$ Å$^3$. An experimental density of 1.53 (1) g cm$^{-3}$ is in agreement with a calculated density of 1.54 g cm$^{-3}$ for two formula weights of composition $Pd_2(C_{17}OH_{14})_3 \cdot CH_2Cl_2$ per unit cell. Space group $P\bar{1}$ was assumed for further work on the crystal. The mosaic spread of the crystal was determined using the narrow-source, open-counter $\omega$-scan technique[9] and found to be acceptably low at 0.06°. An independent set of intensity data was collected by the $\theta$-$2\theta$ scan technique using Zr-filtered Mo K$\alpha$ radiation at a takeoff angle of 1.5°. A receiving aperture of dimensions 4.5 × 4.5 mm was positioned 24 cm from the crystal. A symmetrical scan range in $2\theta$ was used from ±0.6° of the Mo K$\alpha$ peak. The data set was collected within the angular range $5° \leqslant 2\theta \leqslant 47°$. During data collection the intensities of six standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 2% during the time required to collect the data. Data were processed in the usual way with the values of $I$ and $\sigma(I)$ corrected for Lorentz and polarization effects. The intensities of a total of 4605 reflections were measured of which 2911 were observed to be greater than $2\sigma$. Since the crystal was approximately equidimensional and the linear absorption coefficient small ($\mu = 9.6$ cm$^{-1}$), no correction was applied for absorption effects.

**Solution and Refinement of the Structure.** The structure was solved using conventional Patterson, least-squares, and Fourier methods. The positions of Pd(1) and Pd(2) were determined from a Patterson synthesis while all other nonhydrogen atoms were located from a difference Fourier calculated from the phases of the two metal atoms. Three cycles of least-squares refinement with isotropic thermal parameters assigned to all atoms and phenyl rings treated as rigid groups ($d$(C–C) = 1.392 Å) with single-group thermal parameters gave discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ of $R_1 = 0.090$ and $R_2 = 0.106$. During refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights $w$ were taken as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F^2)$ were calculated according to the formula of Reed, *et al.*,[10] with a value of 0.03 for the uncertainty parameter. Only the reflections for which $F_o^2 \geqslant 2\sigma(F_o^2)$ were included in the refinement. In all calculations the atomic scattering factors for the nonhydrogen atoms were those of Cromer and Waber[11] while hydrogen scattering factors were taken from the tabulation of Stewart, *et al.*[12] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Pd and Cl atoms taken from the report of Cromer and Liberman.[13] Three more cycles of refinement with anisotropic thermal parameters assigned to nongroup atoms and individual isotropic thermal parameters to group atoms converged with discrepancy factors of $R_1 = 0.068$ and $R_2 = 0.072$. The positions of the methylene chloride hydrogen atoms were then determined from a difference Fourier and included in the refinement with the idealized positions of the phenyl hydrogen atoms ($d$(C–H) = 0.98 Å). The hydrogen atoms of the pentadienone groups could not be located. The fixed contributions of the ring hydrogens and the refined contributions of the methylene chloride hydrogens gave discrepancy indices of $R_1 = 0.068$ and $R_2 = 0.069$. On the final cycle of refinement no parameter changed by more than 30% of its standard deviation with the largest shifts occurring for the olefin carbon atoms of the pentadienone groups. The final positional and thermal parameters of the structure are given in Table I. Derived positional and thermal parameters for the group atoms are given in Table II. The root-mean-square vibrational amplitudes of anisotropically refined atoms are given in Table III and a table of the final $F_o$ and $|F_c|$ values for the 2911 reflections used in the refinement is available.[14]

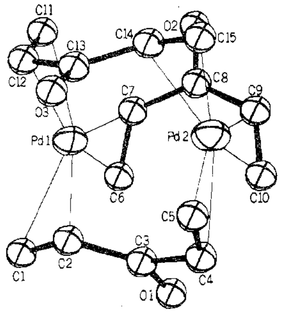

Figure 1. Perspective view of the inner coordination geometry of the $Pd_2(DBA)_3$ molecule.

## Discussion of the Structure

The $Pd_2(DBA)_3$ molecule consists of Pd atoms separated by 3.237 (5) Å, each trigonally coordinated bonding to the olefin groups of three bridging dibenzylideneacetone ligands. A perspective view of the inner coordination geometry of the complex is shown in Figure 1. In Figure 2 a stereoview of the entire molecule is given. Two of the DBA ligands are in the s-cis,trans conformation while the third is in the s-cis,cis form. Weakly hydrogen bonded to the oxygen of the s-cis,cis ligand is the methylene chloride molecule (O(2)· · · H(1) = 2.00 (5) Å). Intramolecular bond distances and angles for the structure are presented in Table IV.

While the atoms of the carbonyl and phenyl groups of the DBA ligands occupy well-defined positions in the molecule, the olefin carbon atoms show considerable anisotropy within the ligand plane (Figure 3). This appears to arise from a vibrational disorder within the pentadienone group caused by the combination of a relatively short nonbonding Pd(1)-Pd(2) separation and the stereochemical restrictions of the diene bridges.[15] Previous structural work on the chloroform solvate of $Pd_2(DBA)_3$ indicated similar results which led to an anomalously short average olefin C–C distance of 1.20 (3) Å.[4] In the present structure ligand distortion of this type would be expected to be most severe for the s-cis,cis ligand. Ideally the separation between parallel olefin groups in this conformation would be approximately 2.6 Å, much shorter than the Pd(1)-Pd(2) distance (3.237 (5) Å). Angular values of 129 (2), 135 (3), and 125 (2)° within the interior of this group formed by atoms C(6) through C(10) (Figure 1) together with values of 3.04 (2) and 3.67 (2) Å for separations C(7)· · ·C(9) and C(6)· · ·C(10) clearly show that the olefin groups have been forced apart to accommodate the separation between metal atoms. As expected the olefin bond distances in this ligand are each unusually short with values of 1.24 (2) Å while the distances to the carbonyl carbon atom are lengthened to values of 1.61 (2) and 1.67 (2) Å. The resilient flexibility of the s-cis,trans ligands of the structure with olefin groups distorted by the Pd(1)-Pd(2) separation is probably also responsible for the large vibrational motion of the other olefin atoms of the molecule and the short C(4)-C(5) distance.

It is of interest that the s-cis,cis DBA ligand prefers to bond to the metals in the strained conformeric form rather than the less strained s-cis,trans form found in the chloroform

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[9] T. C. Furnas, "Single Crystal Orienter Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

[10] J. Reed, A. J. Schultz, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, 12, 2949 (1973).

[11] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[13] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

[14] See paragraph at end of paper regarding supplementary material.

[15] Monobonded Pd-Pd distances are normally found with the range of values 3.32–3.56 Å.[1]

**Table I.** Final Structural Parameters for $Pd_2(C_{17}H_{14}O)_3 \cdot CH_2Cl_2$[a]

Atomic Positional and Anisotropic Thermal Parameters

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$[b] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pd(1) | −0.22012 (8) | 0.03881 (7) | 0.24124 (9) | 0.0042 (1) | 0.0070 (1) | 0.0072 (1) | 0.0011 (1) | −0.0001 (1) | 0.0030 (1) |
| Pd(2) | −0.26641 (8) | −0.17662 (7) | 0.02102 (10) | 0.0051 (1) | 0.0068 (1) | 0.0083 (1) | 0.0013 (1) | 0.0002 (1) | 0.0033 (1) |
| Cl(1) | 0.26069 (6) | −0.2312 (4) | 0.1479 (5) | 0.0287 (10) | 0.0185 (6) | 0.0201 (8) | 0.0103 (6) | 0.0064 (7) | 0.0085 (6) |
| Cl(2) | 0.2909 (5) | −0.03412 (4) | 0.3229 (5) | 0.0220 (8) | 0.0157 (5) | 0.0227 (8) | −0.0001 (5) | −0.0039 (6) | 0.0099 (6) |
| Me | 0.2497 (14) | −0.1108 (12) | 0.1749 (13) | 0.0166 (19) | 0.0116 (15) | 0.0088 (20) | 0.0047 (14) | −0.0025 (15) | 0.0036 (14) |
| C(1) | −0.3757 (16) | 0.1186 (17) | 0.2329 (22) | 0.0077 (7) | 0.0165 (21) | 0.0267 (36) | 0.0049 (18) | 0.0007 (19) | 0.0099 (25) |
| C(2) | −0.3936 (18) | 0.0212 (19) | 0.1709 (37) | 0.0061 (18) | 0.0147 (23) | 0.0620 (77) | 0.0059 (19) | −0.0055 (31) | 0.0079 (41) |
| C(3) | −0.3898 (12) | −0.0232 (14) | 0.0360 (21) | 0.0033 (11) | 0.0071 (15) | 0.0145 (31) | 0.0022 (10) | −0.0001 (14) | 0.0040 (16) |
| C(4) | −0.4248 (17) | −0.1380 (18) | −0.0336 (31) | 0.0055 (17) | 0.0152 (25) | 0.0493 (54) | 0.0020 (17) | −0.0041 (23) | 0.0187 (35) |
| C(5) | −0.4473 (19) | −0.2132 (19) | −0.0144 (31) | 0.0064 (19) | 0.0191 (28) | 0.0408 (49) | 0.0047 (21) | −0.0006 (24) | 0.0071 (34) |
| O(1) | −0.3690 (8) | 0.0174 (9) | −0.0219 (11) | 0.0054 (8) | 0.0108 (10) | 0.0108 (17) | 0.0018 (7) | −0.0002 (8) | 0.0082 (11) |
| C(6) | −0.1396 (23) | 0.1225 (22) | 0.1534 (31) | 0.0203 (36) | 0.0200 (30) | 0.0398 (53) | 0.0011 (25) | 0.0154 (38) | 0.0145 (33) |
| C(7) | −0.0712 (20) | 0.0765 (23) | 0.1745 (31) | 0.0148 (25) | 0.0294 (38) | 0.0404 (51) | 0.0130 (23) | 0.0186 (29) | 0.0322 (40) |
| C(8) | −0.0511 (13) | −0.0333 (11) | 0.0965 (15) | 0.0049 (12) | 0.0081 (12) | 0.0106 (22) | 0.0000 (10) | 0.0008 (13) | 0.0036 (13) |
| C(9) | −0.1102 (15) | −0.1255 (22) | −0.0324 (25) | 0.0065 (16) | 0.0303 (36) | 0.0318 (47) | 0.0033 (20) | 0.0071 (22) | 0.0294 (38) |
| C(10) | −0.1948 (26) | −0.1251 (23) | −0.0909 (30) | 0.0243 (38) | 0.0300 (35) | 0.0461 (59) | 0.0069 (31) | 0.0123 (40) | 0.0250 (38) |
| O(2) | 0.0225 (8) | −0.0527 (18) | 0.1423 (9) | 0.0048 (8) | 0.0135 (10) | 0.0139 (15) | 0.0035 (7) | 0.0000 (8) | 0.0086 (10) |
| C(11) | −0.2494 (16) | −0.2954 (13) | 0.0957 (17) | 0.0171 (23) | 0.0099 (15) | 0.0141 (25) | 0.0046 (15) | 0.0012 (19) | 0.0054 (16) |
| C(12) | −0.2142 (15) | −0.1984 (13) | 0.1740 (15) | 0.0149 (20) | 0.0098 (14) | 0.0055 (21) | 0.0006 (14) | −0.0021 (16) | 0.0061 (14) |
| C(13) | −0.2763 (13) | −0.1398 (12) | 0.2662 (15) | 0.0059 (13) | 0.0085 (13) | 0.0092 (22) | 0.0016 (11) | 0.0005 (13) | 0.0040 (13) |
| C(14) | −0.2260 (13) | −0.0440 (13) | 0.3557 (15) | 0.0061 (13) | 0.0097 (14) | 0.0149 (24) | −0.0013 (11) | −0.0034 (14) | 0.0056 (15) |
| C(15) | −0.1178 (16) | −0.0031 (12) | 0.3602 (13) | 0.0160 (21) | 0.0127 (16) | 0.0064 (20) | 0.0049 (15) | 0.0016 (16) | 0.0088 (15) |
| O(3) | −0.3732 (10) | −0.1717 (9) | 0.2708 (10) | 0.0106 (12) | 0.0176 (13) | 0.0133 (16) | 0.0001 (10) | 0.0018 (11) | 0.0097 (12) |
| H(1) | 0.161 (5) | −0.120 (6) | 0.141 (6) | 4.1 (5) | | | | | |
| H(2) | 0.287 (7) | −0.073 (8) | 0.140 (7) | 7.2 (8) | | | | | |

Group Positional Parameters

| Group[c] | $x_c$ | $y_c$ | $z_c$ | $\phi$ | $\theta$ | $\rho$ |
|---|---|---|---|---|---|---|
| R(1) | −0.1340 (5) | 0.3296 (5) | 0.2907 (6) | −2.173 (11) | −2.205 (7) | 2.285 (11) |
| R(2) | −0.4107 (5) | 0.2086 (5) | 0.4657 (6) | −0.874 (17) | 1.955 (7) | 2.102 (16) |
| R(3) | −0.5319 (5) | −0.4152 (5) | −0.1552 (6) | 2.442 (13) | −2.091 (7) | −1.829 (12) |
| R(4) | −0.2442 (5) | −0.2893 (5) | −0.3214 (6) | −2.663 (6) | −3.062 (7) | −1.093 (6) |
| R(5) | −0.1323 (6) | −0.4278 (5) | −0.0641 (5) | 1.885 (7) | 2.796 (7) | −2.236 (6) |
| R(6) | −0.0074 (6) | 0.1846 (4) | 0.5524 (5) | −1.807 (7) | 2.638 (6) | 2.288 (6) |

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] $x_c, y_c, z_c$ are the fractional coordinates of the rigid group centers. The angles $\phi, \theta, \rho$ are in radians and have previously been defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

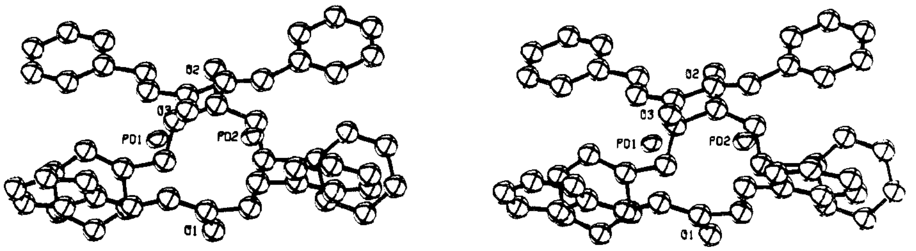

**Figure 2.** Stereoscopic view of the entire $Pd_2(DBA)_3$ molecule.

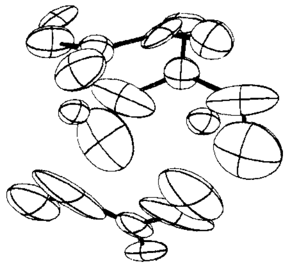

**Figure 3.** View of the inner coordination geometry of $Pd_2(DBA)_3$ similar to Figure 1 with anisotropic thermal ellipsoids for all atoms. The ellipsoids enclose 50% of the electron density.

and benzene solvates of the complex. Trends observed for olefin coordination in trigonal complexes of Ni(0), Pd(0), and Pt(0) may account for this. While olefin complexes of the divalent metal ions of this series are consistently found to have the C–C bond oriented normal to the plane of a square-planar complex,[16] olefin bonding in the trigonal complexes of the $d^{10}$ metal atoms is nearly always within 20° of the complex plane.[17] This result may indicate that metal-olefin $\pi$ bonding is most effective with in-plane metal d orbitals in trigonal complexes of the $d^{10}$ metals. Effects governing the conformational properties of the DBA ligands in $Pd_2(DBA)_3$ are complicated and include such contributions as contacts within the DBA ligand and interligand steric effects about the metal as well as optimization of metal-olefin $\pi$ bonding. However, with other factors ignored the s-cis,cis conformational form of the DBA ligand with both olefin groups oriented approximately in the trigonal planes of the metal atoms would be expected to $\pi$ bond more effectively than the other conformational forms which

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(16) For example: W. C. Hamilton, K. A. Klanderman, and R. Spratley, *Acta Crystallogr.*, 25, 5172 (1969).

(17) For example: J. F. Francis, A. McAdam, and J. A. Ibers, *J. Organometal. Chem.*, 29, 131 (1971).

**Table II.** Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms

| Atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| | | Ring R1 | | |
| R1C(1) | −0.1491 (17) | 0.4275 (7) | 0.3413 (9) | 7.8 (4) |
| R1C(2) | −0.1900 (13) | 0.3674 (9) | 0.2252 (9) | 8.6 (4) |
| R1C(3) | −0.0930 (10) | 0.3897 (6) | 0.4069 (7) | 6.7 (4) |
| R1C(4) | −0.1190 (17) | 0.2316 (7) | 0.2402 (9) | 6.2 (4) |
| R1C(5) | −0.0780 (12) | 0.2918 (9) | 0.3563 (9) | 6.2 (4) |
| R1C(6) | −0.1750 (10) | 0.2694 (7) | 0.1746 (7) | 7.9 (4) |
| | | Ring R2 | | |
| R2C(1) | −0.3777 (25) | 0.3107 (5) | 0.5097 (11) | 6.9 (4) |
| R2C(2) | −0.4228 (13) | 0.2702 (8) | 0.5780 (7) | 7.3 (4) |
| R2C(3) | −0.3657 (17) | 0.2492 (8) | 0.3974 (10) | 6.2 (4) |
| R2C(4) | −0.4438 (25) | 0.1065 (5) | 0.4218 (11) | 6.9 (4) |
| R2C(5) | −0.3987 (12) | 0.1470 (7) | 0.3535 (7) | 5.9 (3) |
| R2C(6) | −0.4558 (17) | 0.1681 (9) | 0.5314 (10) | 7.8 (4) |
| | | Ring R3 | | |
| R3C(1) | −0.5716 (18) | −0.5164 (6) | −0.2188 (10) | 6.6 (4) |
| R3C(2) | −0.5200 (9) | −0.4625 (7) | −0.2707 (6) | 6.9 (4) |
| R3C(3) | −0.5835 (14) | −0.4691 (8) | −0.1033 (10) | 7.8 (5) |
| R3C(4) | −0.4923 (18) | −0.3141 (6) | −0.0916 (10) | 5.3 (3) |
| R3C(5) | −0.5439 (10) | −0.3680 (8) | −0.0397 (6) | 6.7 (4) |
| R3C(6) | −0.4803 (13) | −0.3614 (8) | −0.2071 (10) | 6.3 (3) |
| | | Ring R4 | | |
| R4C(1) | −0.2873 (9) | −0.3595 (8) | −0.4336 (7) | 8.3 (4) |
| R4C(2) | −0.3113 (8) | −0.2644 (9) | −0.3934 (10) | 9.3 (5) |
| R4C(3) | −0.2202 (9) | −0.3843 (5) | −0.3617 (10) | 7.7 (4) |
| R4C(4) | −0.2011 (8) | −0.2191 (7) | −0.2092 (7) | 5.9 (4) |
| R4C(5) | −0.1771 (7) | −0.3141 (8) | −0.2495 (9) | 5.5 (3) |
| R4C(6) | −0.2682 (9) | −0.1942 (6) | −0.2812 (10) | 7.7 (5) |
| | | Ring R5 | | |
| R5C(1) | −0.0813 (10) | −0.4975 (7) | −0.1432 (8) | 8.6 (5) |
| R5C(2) | −0.0180 (6) | −0.4123 (8) | −0.0539 (10) | 7.8 (4) |
| R5C(3) | −0.1956 (9) | −0.5130 (6) | −0.1535 (8) | 8.2 (5) |
| R5C(4) | −0.1833 (8) | −0.3582 (7) | 0.0150 (7) | 6.0 (4) |
| R5C(5) | −0.2466 (6) | −0.4434 (8) | −0.0744 (9) | 7.1 (4) |
| R5C(6) | −0.0690 (8) | −0.3426 (5) | 0.0252 (7) | 6.5 (4) |
| | | Ring R6 | | |
| R6C(1) | 0.0508 (9) | 0.2734 (6) | 0.6405 (7) | 7.1 (4) |
| R6C(2) | −0.0628 (9) | 0.2493 (6) | 0.6317 (8) | 8.7 (5) |
| R6C(3) | 0.1062 (6) | 0.2088 (8) | 0.5612 (9) | 6.5 (4) |
| R6C(4) | −0.0656 (8) | 0.0959 (6) | 0.4644 (7) | 5.4 (3) |
| R6C(5) | 0.0481 (8) | 0.1200 (6) | 0.4732 (7) | 5.7 (3) |
| R6C(6) | −0.1210 (6) | 0.1605 (8) | 0.5437 (9) | 6.6 (4) |

**Table III.** Root-Mean-Square Amplitudes of Vibration (Å) for $Pd_2(C_{17}H_{14}O)_3 \cdot CH_2Cl_2$

| Atom | Min | Intermed | Max |
|---|---|---|---|
| Pd(1) | 0.167 (3) | 0.229 (3) | 0.257 (3) |
| Pd(2) | 0.189 (3) | 0.243 (3) | 0.251 (3) |
| Cl(1) | 0.36 (3) | 0.36 (3) | 0.48 (3) |
| Cl(2) | 0.32 (3) | 0.36 (3) | 0.48 (3) |
| Me | 0.17 (2) | 0.28 (2) | 0.41 (3) |
| C(1) | 0.21 (2) | 0.37 (2) | 0.43 (3) |
| C(2) | 0.13 (2) | 0.35 (2) | 0.71 (3) |
| C(3) | 0.13 (2) | 0.25 (2) | 0.32 (2) |
| C(4) | 0.16 (2) | 0.30 (2) | 0.59 (3) |
| C(5) | 0.20 (2) | 0.39 (2) | 0.58 (3) |
| O(1) | 0.15 (2) | 0.23 (2) | 0.34 (2) |
| C(6) | 0.27 (2) | 0.43 (2) | 0.53 (3) |
| C(7) | 0.14 (2) | 0.25 (2) | 0.61 (3) |
| C(8) | 0.19 (2) | 0.27 (2) | 0.29 (2) |
| C(9) | 0.09 (2) | 0.24 (2) | 0.59 (3) |
| C(10) | 0.35 (2) | 0.44 (2) | 0.53 (3) |
| O(2) | 0.15 (2) | 0.28 (2) | 0.36 (2) |
| C(11) | 0.27 (2) | 0.31 (2) | 0.36 (2) |
| C(12) | 0.11 (2) | 0.29 (2) | 0.36 (2) |
| C(13) | 0.20 (2) | 0.26 (2) | 0.28 (2) |
| C(14) | 0.18 (2) | 0.30 (2) | 0.35 (2) |
| C(15) | 0.06 (2) | 0.31 (2) | 0.36 (2) |
| O(3) | 0.25 (2) | 0.28 (2) | 0.42 (3) |

**Table IV.** Principal Interatomic Distances and Angles for $Pd_2(C_{17}H_{14}O)_3 \cdot CH_2Cl_2$

| | | Distances, Å | |
|---|---|---|---|
| Pd(1)–C(1) | 2.421 (11) | C(7)–C(8) | 1.61 (2) |
| Pd(1)–C(2) | 2.196 (12) | C(8)–C(9) | 1.67 (2) |
| Pd(1)–C(6) | 2.237 (12) | C(9)–C(10) | 1.24 (2) |
| Pd(1)–C(7) | 2.218 (11) | C(8)–O(2) | 1.18 (1) |
| Pd(1)–C(11) | 2.312 (11) | C(11)–C(12) | 1.37 (1) |
| Pd(1)–C(12) | 2.251 (11) | C(12)–C(13) | 1.50 (1) |
| Pd(2)–C(4) | 2.256 (11) | C(13)–C(14) | 1.44 (1) |
| Pd(2)–C(5) | 2.198 (11) | C(14)–C(15) | 1.39 (1) |
| Pd(2)–C(9) | 2.269 (12) | C(13)–O(3) | 1.25 (1) |
| Pd(2)–C(10) | 2.124 (12) | Me–Cl(1) | 1.73 (1) |
| Pd(2)–C(14) | 2.399 (12) | Me–Cl(2) | 1.75 (1) |
| Pd(2)–C(15) | 2.197 (11) | Me–H(1) | 1.12 (5) |
| Pd(1)–Pd(2) | 3.237 (5) | Me–H(2) | 0.98 (5) |
| C(1)–C(2) | 1.33 (1) | O(2)- -H(1) | 2.00 (5) |
| C(2)–C(3) | 1.58 (2) | O(2)- -Me | 3.10 (2) |
| C(3)–C(4) | 1.56 (2) | C(2)- -C(4) | 2.68 (2) |
| C(4)–C(5) | 1.27 (2) | C(12)- -C(14) | 2.56 (2) |
| C(3)–O(1) | 1.18 (1) | C(7)- -C(9) | 3.04 (2) |
| C(6)–C(7) | 1.24 (2) | C(6)- -C(10) | 3.67 (2) |

| | | Angles, Deg | |
|---|---|---|---|
| C(1)–C(2)–C(3) | 119 (2) | C of M(C(1),C(2))–Pd(1)– | 118 (2) |
| C(2)–C(3)–O(1) | 129 (2) | C of M(C(6),C(7)) | |
| C(2)–C(3)–C(4) | 116 (2) | C of M(C(1),C(2))–Pd(1)– | 120 (2) |
| O(1)–C(3)–C(4) | 115 (2) | C of M(C(11),C(12)) | |
| C(3)–C(4)–C(5) | 139 (3) | C of M(C(6),C(7))–Pd(1)– | 122 (2) |
| C(6)–C(7)–C(8) | 129 (2) | C of M(C(11),C(12)) | |
| C(7)–C(8)–O(2) | 111 (2) | C of M(C(4),C(5))–Pd(2)– | 121 (2) |
| C(7)–C(8)–C(9) | 135 (3) | C of M(C(9),C(10)) | |
| O(2)–C(8)–C(9) | 114 (2) | C of M(C(4),C(5))–Pd(2)– | 118 (2) |
| C(8)–C(9)–C(10) | 125 (2) | C of M(C(14),C(15)) | |
| C(11)–C(12)–C(13) | 125 (2) | C of M(C(9),C(10))–Pd(2)– | 121 (2) |
| C(12)–C(13)–O(3) | 123 (2) | C of M(C(14‘C(15)) | |
| C(12)–C(13)–C(14) | 121 (2) | | |
| O(3)–C(13)–C(14) | 116 (2) | | |
| C(13)–C(14)–C(15) | 121 (2) | | |

**Table V.** Dihedral Angles between Planes for $Pd_2(C_{17}H_{14}O)_3 \cdot CH_2Cl_2$

| Planes | Angle, deg |
|---|---|
| C(2), C(3), C(4)–C(7), C(8), C(9) | 116 (3) |
| C(2), C(3), C(4)–C(12), C(13), C(14) | 122 (3) |
| C(7), C(8), C(9)–C(12), C(13), C(14) | 122 (3) |
| C(1), C(2), Pd(1)–trigonal plane[a] | 67 (3) |
| C(6), C(7), Pd(1)–trigonal plane | 21 (3) |
| C(11), C(12), Pd(1)–trigonal plane | 17 (3) |
| C(4), C(5), Pd(2)–trigonal plane | 37 (3) |
| C(9), C(10), Pd(2)–trigonal plane | 9 (3) |
| C(14), C(15), Pd(2)–trigonal plane | 80 (3) |

[a] Trigonal plane of the complex defined by the centers of mass of the three coordinated olefin groups to the corresponding palladium atom.

would have at least one olefin group oriented out of the plane. Additionally, if in-plane π bonding was not a primary effect in determining the conformational properties of the DBA ligands, the s-trans,trans form would probably prevail since it allows maximum separation between Pd atoms. It is both interesting and surprising that the flexibility of the DBA ligand allows such configurational options in the $Pd_2(DBA)_3$ complexes.

Planes defined by the inner carbon atoms of each pentadienone ligand form dihedral angles with each other which average to 120 (3)° (Table V). This, together with the average angle of 120 (2)° formed by the centers of mass of each coordinated olefin group about each associated metal, strongly reflects the trigonal coordination geometry about each metal. By defining the trigonal plane about each metal in terms of the centers of mass of the coordinated olefins dihedral angles formed by the metal-olefin plane and the trigonal plane of the complex may be determined. With the

**Table VI.** Equations of Weighted Least-Squares Planes[a] and Deviations of the Atoms from the Planes for $Pd_2(C_{17}H_{14}O)_3 \cdot CH_2Cl_2$

| Atom | Distance, Å | Atom | Distance, Å |
|---|---|---|---|
| Plane through Pentadienone Group C(1)-C(5)<br>$12.06X - 4.16Y + 1.74Z = 4.55$ | | | |
| C(1) | −0.02 (2) | C(4) | −0.01 (2) |
| C(2) | 0.02 (2) | C(5) | 0.00 (2) |
| C(3) | 0.01 (1) | O(1) | −0.00 (1) |
| Pd(1) | 2.15[b] | Pd(2) | 2.11[b] |
| Plane through Pentadienone Group C(6)-C(10)<br>$7.91X + 7.97Y - 9.63Z = 1.60$ | | | |
| C(6) | 0.02 (3) | C(9) | 0.01 (2) |
| C(7) | −0.02 (2) | C(10) | −0.01 (3) |
| C(8) | −0.00 (2) | O(2) | 0.00 (1) |
| Pd(1) | 2.15[b] | Pd(2) | 2.12[b] |
| Plane through Pentadienone Group C(11)-C(15)<br>$4.18X - 11.62Y + 10.63Z = -3.32$ | | | |
| C(11) | −0.01 (2) | C(14) | −0.03 (2) |
| C(12) | 0.00 (1) | C(15) | 0.02 (1) |
| C(13) | −0.02 (2) | O(3) | 0.01 (1) |
| Pd(1) | 2.13[b] | Pd(2) | 2.16[b] |

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). Equations given in triclinic coordinates. [b] Not included in the calculation of the plane.

conformational geometries of the ligands as observed two olefin groups are directed roughly normal to the trigonal plane while the other four are much closer to the plane (Table V). A structural feature normally associated with olefin coordination to nucleophilic metals is the direction of substituents back from the olefin plane, away from the olefin-metal bond.[16,17] This is generally viewed to reflect a decrease in the C-C bond order and has been found to occur for ethylene as well as for olefins with electron-withdrawing substituents.[18] The coordinated dibenzylideneacetone ligands in both $Pd_2(DBA)_3$ and $Pd(DBA)_3$, however, show only minor deviations from planarity reflecting weak palladium-olefin bonding (Table VI). The Pd-C distances in $Pd_2(DBA)_3$ are relatively long, averaging to 2.26 (1) Å but varying significantly over values from 2.124 (12) to 2.421 (11) Å. This average value agrees well with the average Pd-C distance of 2.25 (1) Å in $Pd(DBA)_3$. These features are consistent with the observed lability of the DBA ligands in these complexes.

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**Registry No.** $Pd_2(DBA)_3 \cdot CH_2Cl_2$, 51364-52-4.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1891.

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Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

# Molecular Structure of $\eta^2$-(*cis*-2,3-Dicarbomethoxymethylenecyclopropane)iron Tetracarbonyl (*cis*-Feist's Ester Iron Tetracarbonyl). An Olefin-Iron Complex Stabilized by Relief of Strain

THOMAS H. WHITESIDES,* ROBERT W. SLAVEN, and JOSEPH C. CALABRESE

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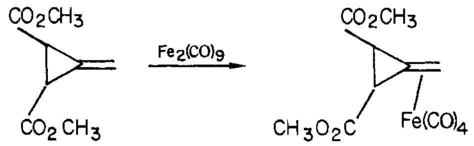
The structure of $\eta^2$-*cis*-2,3-dicarbomethoxymethylenecyclopropane)iron tetracarbonyl ($C_{12}H_{10}FeO_8$) has been determined by X-ray crystallographic techniques. The compound crystallizes in the orthorhombic space group *Pcmn*, with lattice constants $a = 7.047$ (1) Å, $b = 13.690$ (3) Å, and $c = 14.510$ (2) Å; $V = 1399.9$ (4) Å$^3$, $Z = 4$. Full-matrix anisotropic least-squares refinement on the diffractometer-collected intensities of 882 independent reflections resulted in a final conventional $R$ value of 4.3%. The refined structure shows several interesting features. The iron atom is located on the same side of the three-membered ring as the ester groups, and intramolecular distances suggest substantial steric congestion between the ester carbonyl groups and the $Fe(CO)_4$ unit. Considerable rehybridization has occurred at the olefinic linkage in the three-membered ring, and the geometry around the iron atom is interpreted as being intermediate between trigonal bipyramidal and octahedral. The bonding in the complex, and its remarkable stability, are discussed in terms of relief of angle strain accompanying the rehybridization, and the mechanistic implications of the observed stereochemistry are considered.

## Introduction

In a recent paper concerning the reaction of iron carbonyls with the cis and trans isomers of Feist's ester (2,3-dicarbomethoxymethylenecyclopropane, **1**), we[1] reported the isolation of two complexes to which we ascribed the structure **2**, *i.e.*, the tetracarbonyl iron complex of the corresponding olefin. Because Krull[2] had reported obtaining compounds with very similar physical properties from similar reactions, to which however he assigned a different structure, and because the structure of these small-ring species is inherently interesting, we undertook an investigation of one of our



**1** **2**

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[2] (a) I. S. Krull, paper presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973; (b) *J. Organometal. Chem.*, 57, 363 (1973). We thank Professor Krull for a preprint of his article.