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Palladium(0) Complexes of Dibenzylideneacetone. Formation and Molecular Structure of Tris(dibenzylideneacetone)palladium(0)

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The complex $Pd(C_{17}OH_{14})_3$ has been prepared and isolated as the benzene solvate. From three-dimensional X-ray data collected by the θ-2θ scan technique the crystal and molecular structure of the complex has been determined. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional *R* factor of 0.084 for 2449 nonzero reflections. The complex crystallizes in space group $P\bar{1}$ of the triclinic system in a cell of dimensions $a = 13.684$ (5) Å, $b = 15.938$ (5) Å, $c = 16.094$ (5) Å, $\alpha = 122.92$ (5)°, $\beta = 127.45$ (5)°, $\lambda = 63.82$ (5)°, and $V = 2307$ Å^3. There are two formula weights per unit cell ($\rho_{\text{exptl}} = 1.26$ (1) g/cm^3; $\rho_{\text{calcd}} = 1.276$ g/cm^3). Each pentadienone ligand is coordinated to the metal through one olefin group. The coordination geometry about the Pd atom is essentially trigonal with the molecule having approximate C_3 symmetry.

Introduction

Organopalladium complexes have been of interest as homogeneous catalysts and models for catalytic reactions. A review of organopalladium chemistry, however, will reveal that practically all work in this area has been performed on complexes of Pd(II).[1] This appears to be related to the scarcity of Pd(0) organometallic complexes and the relative instability of those which are known. Few reports have appeared on Pd(0)-olefin complexes in contrast to the great interest in Ni(0)- and Pt(0)-olefin complexes and their use as catalytic agents. Attempts to prepare the bis(1,5-cyclooctadiene) complex of Pd(0) using procedures found to be successful for similar Ni(0) and Pt(0) compounds have failed.[2] The ethylene complex $Pd(P(C_6H_5)_3)_2(C_2H_4)$ has been reported but appears to be less stable than the Ni or Pt analogs.[3] These results may be interpreted in terms of the view that Pd(0) has a much lower affinity for olefin coordination than Ni or Pt.[4]

Recently Takahashi, *et al.*, noted that addition of sodium acetate to a solution of $PdCl_4^{2-}$ and dibenzylideneacetone (DBA) (1,5-diphenyl-3-pentadienone) gave the complex $Pd(DBA)_2$.[5] Subsequent reports by Maitlis have extended this work to Pt and have indicated that these compounds may be useful as alkyne oligomerization catalysts.[6] Additionally, the absence of ^{195}Pt coupling to olefin protons in the nmr of $Pt(DBA)_2$ has been interpreted to indicate DBA coordination through carbonyl groups.

We have noted previously that $Pd(DBA)_2$ dissociates in solution giving the binuclear complex $Pd_2(DBA)_3$.[7] The metal atoms in this molecule have trigonal coordination geometries with the pentadienone ligands bridging and bonding through olefin groups. We wish to report herein the formation of the complex $Pd(DBA)_3$ by addition of excess DBA to $Pd(DBA)_2$, thus indicating the existence of the reversible series of Pd-DBA complexes

$$Pd_2(DBA)_3 \overset{DBA}{\rightleftarrows} Pd(DBA)_2 \overset{DBA}{\rightleftarrows} Pd(DBA)_3$$

Synthesis and Properties of the Complex

A fourfold excess of dibenzylideneacetone was added to a benzene solution of $Pd(DBA)_2$.[8] The solution was heated and reduced in volume. The color gradually changed from the dark red of $Pd(DBA)_2$ to dark brown. For the present study the solution was allowed to evaporate entirely giving orange-brown crystals of $Pd(DBA)_3$ among yellow crystals of DBA. An elemental analysis of the complex indicated the presence of one benzene solvate molecule per molecule of complex. The complex $Pd(DBA)_3$ readily dissociates in solution in the absence of excess DBA giving $Pd(DBA)_2$. Attempts to wash crystals isolated in this way resulted in loss of the benzene solvate and crystal decomposition. The infrared spectrum of the complex shows a band predominantly ν(C=O) at 1651 cm^{-1}, with olefin bands at 1598, 1580, and 1531 cm^{-1}.

Collection and Reduction of the X-Ray Data

A crystal of the complex $Pd(DBA)_3 \cdot C_6H_6$ was isolated and prepared for the crystallographic study. The crystal was coated with an amorphous resin to retard loss of the benzene solvate. On the basis of Weissenberg and precession photographs of the *hk*0, *hk*1, *h*0*l*, *h*1*l*, 0*kl*, and 1*kl* zones it was established that the complex crystallizes in the triclinic system. The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 20 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 13.684$ (5) Å, $b = 15.938$ (5) Å, $c = 16.094$ (5) Å, $\alpha = 122.92$ (5)°, $\beta = 127.45$ (5)°, $\gamma = 63.82$ (5)°, and $V = 2307$ Å^3. An experimental density of 1.26 (1) g/cm^3 obtained by the flotation method agrees with a calculated value of 1.276 g/cm^3 for two $Pd(C_{17}OH_{14})_3 \cdot C_6H_6$ formula weights per unit cell. Space group $P\bar{1}$ (C_i^1, No. 2)[9] was chosen for the refinement. A crystal of dimensions 0.21 × 0.23 × 0.35 mm was mounted along the *a** axis and prepared for data collection. The mosaic spread of the crystal was determined

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Table I. Final Structural Parameters for $Pd(C_{17}H_{14}O)_3 \cdot C_6H_6$

Atomic Positional and Anisotropic Thermal Parameters

Atom	X^a	Y	Z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	−0.1172 (1)[b]	0.0212 (1)	0.1971 (1)	0.0074 (1)	0.0062 (2)	0.0047 (1)	−0.0015 (1)	0.0030 (1)	0.0009 (1)
C(1)	−0.4039 (14)	−0.1743 (15)	−0.1503 (14)	0.0085 (18)	0.0013 (24)	0.0074 (17)	0.0013 (14)	0.0039 (14)	0.0023 (15)
C(2)	−0.3635 (15)	−0.0848 (17)	−0.0725 (15)	0.0095 (20)	0.0051 (27)	0.0066 (17)	−0.0006 (16)	0.0053 (16)	0.0002 (14)
C(3)	−0.3601 (19)	−0.0381 (30)	0.0456 (30)	0.0070 (20)	0.0037 (31)	0.0269 (41)	−0.0013 (18)	0.0011 (22)	0.0017 (23)
C(4)	−0.3222 (17)	0.0643 (27)	0.1240 (18)	0.0051 (19)	0.0072 (34)	0.0113 (20)	−0.0037 (16)	0.0023 (14)	−0.0020 (18)
C(5)	−0.2914 (20)	0.1215 (28)	0.1137 (19)	0.0065 (22)	0.0030 (37)	0.0128 (21)	−0.0038 (19)	0.0016 (17)	0.0008 (20)
O(1)	−0.3877 (12)	−0.0960 (16)	0.0574 (10)	0.0093 (14)	0.0023 (26)	0.0086 (11)	−0.0013 (12)	0.0010 (10)	−0.0010 (11)
C(6)	−0.0819 (16)	−0.3181 (18)	0.0536 (16)	0.0110 (22)	0.0119 (30)	0.0099 (19)	−0.0061 (19)	0.0036 (17)	0.0002 (18)
C(7)	−0.0878 (18)	−0.2306 (16)	0.1371 (19)	0.0149 (27)	0.0031 (27)	0.0214 (30)	−0.0023 (20)	0.0015 (25)	−0.0011 (21)
C(8)	0.0140 (20)	−0.1711 (18)	0.2122 (16)	0.0139 (28)	0.0045 (30)	0.0121 (22)	−0.0024 (22)	0.0027 (21)	0.0020 (18)
C(9)	0.0013 (16)	−0.0707 (15)	0.3012 (14)	0.0131 (23)	0.0044 (23)	0.0085 (17)	−0.0004 (16)	0.0021 (17)	0.0011 (15)
C(10)	−0.1084 (16)	−0.0259 (14)	0.3082 (12)	0.0123 (22)	0.0070 (23)	0.0049 (14)	−0.0025 (16)	0.0045 (15)	−0.0006 (12)
O(2)	0.1180 (11)	−0.2123 (10)	0.2135 (10)	0.0097 (15)	0.0075 (17)	0.0117 (13)	0.0006 (11)	0.0057 (11)	0.0022 (10)
C(11)	−0.0663 (15)	−0.2066 (14)	−0.1193 (12)	0.0116 (21)	0.0051 (22)	0.0045 (14)	−0.0030 (16)	0.0034 (14)	−0.0005 (13)
C(12)	−0.0259 (16)	−0.1392 (16)	−0.0098 (13)	0.0118 (23)	0.0018 (28)	0.0085 (18)	−0.0026 (18)	0.0058 (17)	0.0007 (16)
C(13)	−0.0849 (17)	−0.0322 (19)	0.0098 (16)	0.0080 (20)	0.0057 (30)	0.0099 (20)	0.0009 (19)	0.0063 (17)	0.0046 (19)
C(14)	−0.0392 (14)	0.0510 (15)	0.1294 (13)	0.0055 (17)	0.0114 (27)	0.0035 (13)	−0.0024 (16)	0.0010 (13)	0.0026 (14)
C(15)	0.0605 (17)	0.0245 (15)	0.2207 (16)	0.0130 (25)	0.0051 (26)	0.0123 (21)	−0.0041 (18)	0.0082 (20)	0.0021 (17)
O(3)	−0.1702 (11)	−0.0022 (9)	−0.0692 (10)	0.0109 (14)	0.0062 (15)	0.0101 (12)	0.0002 (10)	0.0049 (11)	0.0043 (10)

Group Positional Parameters

Group[c]	x_c	y_c	z_c	ϕ	θ	ρ
R(1)	−0.2816 (8)	−0.4445 (7)	−0.1228 (7)	−3.627 (12)	2.329 (8)	−2.406 (11)
R(2)	−0.1324 (7)	0.1579 (6)	0.4889 (6)	2.088 (8)	−3.014 (8)	1.114 (7)
R(3)	0.1808 (8)	0.1790 (7)	0.4462 (7)	0.810 (9)	−3.072 (9)	0.927 (7)
R(4)	0.0428 (7)	−0.4248 (7)	−0.1783 (7)	−1.748 (12)	−2.369 (8)	−0.823 (11)
R(5)	−0.2665 (6)	0.3302 (7)	0.2597 (6)	−3.212 (10)	−2.242 (9)	1.613 (10)
R(6)	−0.4177 (6)	−0.2666 (7)	−0.3699 (7)	2.994 (7)	3.043 (11)	−1.510 (7)
BZ	0.4667 (8)	−0.2521 (9)	0.1596 (6)	1.717 (22)	−2.362 (8)	−2.949 (17)

[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 ϕ, θ, ρ are in radians and have been previously defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

using the narrow-source open-counter ω-scan technique.[10] The average width at half-height was found to be acceptably low at 0.21°. An independent set of intensity data was collected by the θ–2θ scan technique using Zr-filtered Mo Kα 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. An unsymmetrical scan range in 2θ was used from −0.6 to +0.7° of the Mo Kα peak with allowances made for the Kα_1–Kα_2 separation at higher 2θ values. The data set was collected within the angular range $5° \leqslant 2\theta \leqslant 50°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded about 10,000 counts/sec during the scan. The attenuators used were brass foil of thickness chosen to give an approximate attenuation factor of 2.5. 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 3% 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 4070 reflections were measured of which 2449 were observed to be greater than 2σ. Since the crystal was approximately equidimensional and the linear absorption coefficient small ($\mu = 4.4$ cm^{-1}), no correction was applied for absorption effects.

Solution and Refinement of the Structure

The position of the Pd atom was determined from a three-dimensional Patterson function. After a cycle of least-squares refinement of the positional and isotropic thermal parameters of the atom and a single scale factor, the discrepancy indices $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$ were 0.55 and 0.59, respectively. The positions of the remaining atoms of the structure were determined from successive cycles of least-squares refinement followed by Fourier syntheses.

The complete trial structure was refined by a least-squares procedure in which 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 estimated from counting statistics according to the formula given by Corfield, *et al.*,[11] with a value of 0.03 for the uncertainty parameter. Only the 2449 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,[12] while the hydrogen scattering factors were taken from the tabulation of Stewart, *et al.*[13] 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 atom taken from the report by Cromer.[14] Throughout the refinement the phenyl rings and benzene solvate molecule were treated as rigid groups of D_{6h} symmetry (d(C–C) = 1.392 Å) in the manner described previously. Three cycles of least-squares refinement with isotropic temperature factors assigned to nongroup atoms, single thermal parameters assigned to each group, and one scale factor reduced the discrepancy factors to $R_1 = 0.119$ and $R_2 = 0.164$. 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 $R_1 = 0.084$ and $R_2 = 0.091$. The positions of the hydrogen atoms of the phenyl rings were then included (d(C–H) = 0.98 Å) in a subsequent structure factor calculation. The discrepancy factors remained unchanged. No parameter changed by more than 20% of its standard deviation on the final cycle of refinement. The estimated standard deviation of an observation of unit weight is 2.14. A final difference Fourier map showed residual electron density equivalent to about 30% the height of a carbon atom in the vicinity of the solvate benzene molecule. The final positional and thermal parameters of the structure are given in Table I. Derived positional and thermal parameters of the groups are given in Table II. Table III contains root-mean-square vibrational amplitudes of anisotropically refined atoms. A table of the final F_o and $|F_c|$ values for the 2449 reflections used in the refinement is available.[15]

Description and Discussion of the Structure

The $Pd(DBA)_3$ molecule consists of a trigonally coordinated Pd atom bonded to olefin groups of three dibenzylideneace-

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

Atom	*x*	*y*	*z*	*B*, Å^2
		Ring R1		
R1C(1)	−0.1668 (10)	−0.4787 (13)	−0.1194 (12)	8.4 (6)
R1C(2)	−0.1881 (11)	−0.3850 (11)	−0.0403 (11)	5.8 (5)
R1C(3)	−0.2604 (13)	−0.5382 (8)	−0.2019 (9)	8.4 (6)
R1C(4)	−0.3963 (9)	−0.4103 (13)	−0.1262 (11)	6.6 (5)
R1C(5)	−0.3751 (13)	−0.5041 (11)	−0.2053 (11)	7.8 (6)
R1C(6)	−0.3028 (10)	−0.3508 (8)	−0.0437 (8)	5.0 (4)
		Ring R2		
R2C(1)	−0.1479 (13)	0.2487 (8)	0.5737 (9)	6.4 (5)
R2C(2)	−0.0432 (11)	0.2211 (9)	0.5631 (9)	7.1 (5)
R2C(3)	−0.2371 (9)	0.1855 (10)	0.4995 (11)	6.7 (5)
R2C(4)	−0.1169 (12)	0.0671 (7)	0.4041 (9)	5.3 (5)
R2C(5)	−0.2216 (10)	0.0947 (9)	0.4147 (10)	6.3 (5)
R2C(6)	−0.0277 (9)	0.1303 (10)	0.4783 (11)	6.0 (5)
		Ring R3		
R3C(1)	0.2398 (13)	0.2508 (10)	0.5546 (8)	6.0 (5)
R3C(2)	0.2916 (10)	0.1485 (12)	0.5304 (10)	8.9 (6)
R3C(3)	0.1290 (13)	0.2813 (8)	0.4705 (13)	8.6 (6)
R3C(4)	0.1218 (12)	0.1072 (10)	0.3378 (8)	5.3 (4)
R3C(5)	0.0700 (10)	0.2095 (11)	0.3620 (12)	7.1 (5)
R3C(6)	0.2326 (12)	0.0767 (8)	0.4219 (12)	6.9 (5)
		Ring R4		
R4C(1)	0.0927 (18)	−0.5276 (8)	−0.2102 (12)	7.6 (5)
R4C(2)	−0.0116 (14)	−0.4901 (9)	−0.2916 (8)	7.7 (6)
R4C(3)	0.1470 (12)	−0.4623 (11)	−0.0968 (10)	7.8 (6)
R4C(4)	−0.0071 (17)	−0.3220 (8)	−0.1464 (10)	5.3 (4)
R4C(5)	0.09717 (12)	−0.3595 (9)	−0.0648 (7)	5.5 (5)
R4C(6)	−0.0614 (12)	−0.3874 (11)	−0.2598 (9)	7.2 (5)
		Ring R5		
R5C(1)	−0.2538 (18)	0.4315 (8)	0.3293 (12)	5.2 (4)
R5C(2)	−0.2553 (15)	0.3888 (11)	0.2268 (13)	7.2 (5)
R5C(3)	−0.2651 (9)	0.3730 (10)	0.3622 (7)	5.3 (5)
R5C(4)	−0.2792 (18)	0.2289 (8)	0.1901 (11)	4.7 (4)
R5C(5)	−0.2778 (15)	0.2717 (10)	0.2926 (12)	4.6 (4)
R5C(6)	−0.2679 (9)	0.2874 (11)	0.1572 (7)	6.7 (5)
		Ring R6		
R6C(1)	−0.4236 (12)	−0.3128 (13)	−0.4749 (8)	8.0 (6)
R6C(2)	−0.4042 (11)	−0.2127 (12)	−0.4063 (13)	8.1 (6)
R6C(3)	−0.4371 (11)	−0.3667 (8)	−0.4385 (11)	7.2 (5)
R6C(4)	−0.4118 (10)	−0.2205 (12)	−0.2649 (8)	5.7 (5)
R6C(5)	−0.4312 (11)	−0.3205 (12)	−0.3335 (13)	6.1 (5)
R6C(6)	−0.3983 (10)	−0.1665 (7)	−0.3013 (12)	5.7 (4)
		Ring BZ		
BZC(1)	0.4680 (33)	−0.3465 (10)	0.1462 (24)	10.6 (7)
BZC(2)	0.5465 (18)	−0.3365 (13)	0.1254 (15)	8.2 (6)
BZC(3)	0.3882 (21)	−0.2621 (17)	0.1804 (16)	9.8 (7)
BZC(4)	0.4654 (32)	−0.1577 (10)	0.1730 (23)	8.7 (6)
BZC(5)	0.3869 (17)	−0.1677 (14)	0.1938 (15)	6.4 (5)
BZC(6)	0.5452 (20)	−0.2421 (16)	0.1388 (16)	8.7 (6)

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Pd	0.176 (3)	0.208 (3)	0.265 (3)
C(1)	0.08 (2)	0.23 (2)	0.25 (2)
C(2)	0.17 (2)	0.24 (2)	0.28 (2)
C(3)	0.18 (2)	0.20 (2)	0.58 (3)
C(4)	0.13 (2)	0.23 (2)	0.42 (3)
C(5)	0.09 (2)	0.23 (2)	0.36 (2)
O(1)	0.12 (2)	0.22 (2)	0.39 (2)
C(6)	0.20 (2)	0.29 (2)	0.38 (2)
C(7)	0.15 (2)	0.28 (2)	0.57 (3)
C(8)	0.19 (2)	0.27 (2)	0.39 (2)
C(9)	0.19 (2)	0.24 (2)	0.39 (2)
C(10)	0.16 (2)	0.27 (2)	0.31 (2)
O(2)	0.21 (2)	0.27 (2)	0.35 (2)
C(11)	0.15 (2)	0.26 (2)	0.27 (2)
C(12)	0.08 (2)	0.23 (2)	0.27 (2)
C(13)	0.15 (2)	0.19 (2)	0.28 (2)
C(14)	0.15 (2)	0.20 (2)	0.33 (2)
C(15)	0.08 (2)	0.25 (2)	0.32 (2)
O(3)	0.21 (2)	0.27 (2)	0.27 (2)

Table IV. Principle Interatomic Distances (Å) and Angles (deg) for $Pd(C_{17}H_{14}O)_3 \cdot C_6H_6$

		Distances	
Pd–C(4)	2.211 (19)	C(9)–C(10)	1.39 (2)
Pd–C(5)	2.262 (22)	C(8)–O(2)	1.27 (2)
Pd–C(9)	2.202 (20)	C(11)–C(12)	1.35 (2)
Pd–C(10)	2.213 (20)	C(12)–C(13)	1.47 (2)
Pd–C(14)	2.231 (18)	C(13)–C(14)	1.53 (2)
Pd–C(15)	2.242 (17)	C(14)–C(15)	1.39 (2)
C(1)–C(2)	1.35 (2)	C(13)–O(3)	1.25 (2)
C(2)–C(3)	1.54 (4)	Pd- - -C(3)	2.88 (2)
C(3)–C(4)	1.50 (4)	Pd- - -C(8)	2.85 (2)
C(4)–C(5)	1.37 (4)	Pd- - -C(13)	2.91 (2)
C(3)–O(1)	1.27 (3)	Pd- - -O(1)	3.70 (1)
C(6)–C(7)	1.32 (2)	Pd- - -O(2)	3.70 (1)
C(7)–C(8)	1.47 (2)	Pd- - -O(3)	3.71 (1)
C(8)–C(9)	1.49 (2)		
		Angles	
C(1)–C(2)–C(3)	118 (2)	C(12)–C(13)–O(3)	123 (2)
C(2)–C(3)–O(1)	114 (3)	C(12)–C(13)–C(14)	121 (2)
C(2)–C(3)–C(4)	115 (3)	O(3)–C(13)–C(14)	116 (2)
O(1)–C(3)–C(4)	131 (4)	C(13)–C(14)–C(15)	119 (2)
C(3)–C(4)–C(5)	131 (3)		
C(6)–C(7)–C(8)	119 (2)	[C of M(C(4),C(5))]–Pd–[C of M(C(9),C(10))][a]	122 (3)
C(7)–C(8)–O(2)	120 (2)		
C(7)–C(8)–C(9)	118 (2)	[C of M(C(4),C(5))]–Pd–[C of M(C(14),C(15))]	116 (3)
O(2)–C(8)–C(9)	120 (2)		
C(8)–C(9)–C(10)	122 (2)	[C of M(C(9),C(10))]–Pd–[C of M(C(14),C(15))]	121 (3)
C(11)–C(12)–C(13)	117 (2)		

[a] C of M refers to the center of mass of the olefin carbon atoms indicated.

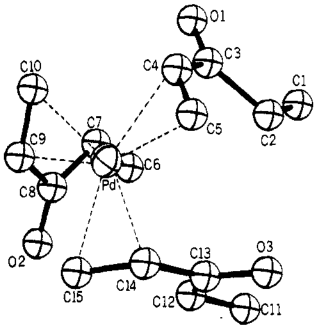

Figure 1. Perspective view of the $Pd(C_{17}OH_{14})_3$ molecule with phenyl rings omitted for clarity.

tone ligands. A perspective view of the coordination geometry is shown in Figure 1. In Figure 2 a stereoscopic view of the entire molecule is given. Intramolecular bond distances and angles are presented in Table IV.

Palladium(0) Coordination Geometry. As may be seen from the figures the Pd(DBA)$_3$ molecule possesses approximately threefold symmetry with angles formed by the centers of each coordinated olefin about the metal averaging to 119 (3)°. The DBA ligands are all in the asymmetric syn, trans conformation with coordination to the metal through the syn olefin. Palladium–carbon distances for the coordinated olefins average to a value of 2.23 (2) Å, significantly longer than values found for Pd(II)-olefin complexes. Distances of 2.159 (4) and 2.166 (4) Å have been found for the norbornadiene complex $(C_7H_{10})PdCl_2$[16] while values of 2.15 (2) and 2.14 (3) Å have been reported for the olefin group in the complex $(C_3H_5NHC(OCH_3)S)PdCl_2$.[17] It is of interest to note that while the Pd(0)-olefin distances are longer than those of Pd(II), the metallic radius of Pd is shorter (1.28 Å) than the planar covalent radius of Pd(II) (1.32 Å).[18]

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[17] P. Porta, *J. Chem. Soc. A*, 1217 (1971).

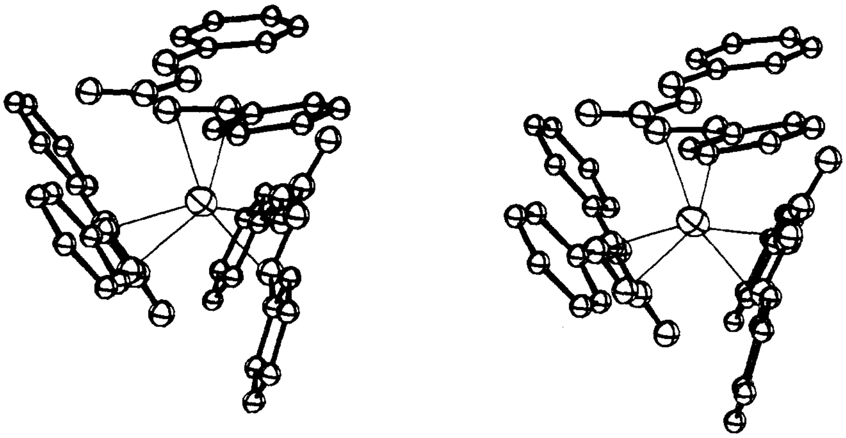

Figure 2. View of the $Pd(C_{17}OH_{14})_3$ molecule showing the planarity of the pentadienone ligands and the approximate threefold symmetry of the molecule. These drawings constitute a stereopair and should be viewed with a hand viewer.

Metal-olefin distances observed for Ni(0) and Pt(0) also seem to reflect stronger bonding than distances in the present structure. The $Pt(P(C_6H_5)_3)_2$(olefin) complexes have been extensively studied with Pt–C distances ranging from 2.01 (3) Å for *cis*-dichlorodicyanoethylene to 2.11 (3) Å for unsubstituted ethylene.[19] In contrast to the present result Pt(0)-olefin complexes show expectedly shorter Pt–C distances than Pt(II) systems where values of 2.13–2.14 Å have been reported.[20] For the Ni(0) complexes $Ni(P(C_6H_5)_3)_2(C_2H_4)$,[21] $Ni(P(C_6H_{11})_3)(C_2H_4)_2$,[22] and (1,5,9-cyclododecatriene)nickel(0)[23] Ni–C distances within the range 1.99 (1)–2.04 (1) Å have been found. With a metallic radius of 1.15 Å for Ni these bond lengths may be viewed to represent stronger metal-olefin bonding for Ni(0) than for Pd(0).

Dihedral angles formed by the planes including the two olefin carbons and the Pd with the trigonal plane of the complex are included in Table V and average to a value of 18 (3)°. The long Pd–C distances in $Pd(DBA)_3$ and weak Pd-olefin bonding agree with the rapid dissociation of the complex observed in solution.

Dibenzylideneacetone Ligands. The C–C distances for the coordinated olefin groups average to a value of 1.38 (2) Å compared with 1.34 (2) Å for the uncoordinated olefin groups. Single C–C bond lengths average to 1.50 (3) Å while carbonyl distances average to 1.26 (2) Å. The slight elongation of the C=O bonds over an expected value of 1.21 Å agrees with the relatively low value of ν(C=O) and may reflect slight delocalization over the pentadienone groups. Least-squares planes including the pentadienone atoms (Table VI) indicate only small variations from planarity. Dihedral angles (Table V) between planes defined by the inner carbon atoms of the pentadienone groups indicate minor deviations from ideal C_3 symmetry for the molecule.

Table V. Dihedral Angles between Planes

Plane 1–plane 2	Angle, deg
[C(2), C(3), C(4)]–[C(7), C(8), C(9)]	127 (3)
[C(2), C(3), C(4)]–[C(12), C(13), C(14)]	119 (3)
[C(7), C(8), C(9)]–[C(12), C(13), C(14)]	113 (3)
[C(4), C(5), Pd]–[trigonal plane][a]	21 (3)
[C(9), C(10), Pd]–[trigonal plane]	16 (3)
[C(14), C(15), Pd]–[trigonal plane]	16 (3)

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

Table VI. Equations of Weighted Least-Squares Planes[a] and Deviations of the Atoms from the Planes

Atom	Distance, Å	Atom	Distance, Å
Plane through Pentadienone Group C(1)–C(5) $9.18x - 4.36y + 1.09z = 3.09$			
C(1)	−0.03 (2)	C(5)	0.00 (3)
C(2)	0.04 (2)	O(1)	0.01 (2)
C(3)	0.00 (2)	Pd	2.13[b]
C(4)	−0.02 (2)		
Plane through Pentadienone Group C(6)–C(10) $-4.38x - 12.46y + 14.00z = -5.10$			
C(6)	−0.02 (2)	C(10)	0.01 (2)
C(7)	0.07 (3)	O(2)	0.02 (1)
C(8)	−0.06 (2)	Pd	2.09[b]
C(9)	0.00 (2)		
Plane through Pentadienone Group C(11)–C(15) $13.40x + 9.52y - 11.50z = 1.52$			
C(11)	0.04 (2)	C(15)	0.03 (2)
C(12)	−0.04 (2)	O(3)	0.02 (1)
C(13)	−0.03 (2)	Pd	2.11[b]
C(14)	−0.01 (2)		

[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.

Structural changes generally observed to occur for coordinated olefins are elongation of the carbon-carbon bond and bending of bonded substituents away from the metal-olefin bond. The relatively small change in olefin bond length on coordination and rigid planarity of the DBA ligands (including the phenyl rings) further reflect the weak nature of the bonding to the metal.

Palladium(0)-Olefin Bonding. A significant feature of metal-olefin bonding is the return of the charge to olefin π^* levels by interaction with filled metal d orbitals. Coordinated olefins are generally regarded to be weak σ donors but strong π acceptor ligands. It is of interest that olefin groups bonded to planar complexes of d^8 metals tend to be oriented normal to the plane while trigonal d^{10} complexes commonly have olefin ligands directed close to the trigonal plane.[19a] This

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trend may result, in part, from the involvement of in-plane metal d orbitals with both σ and π bonding to ligands.

Nickel(0) and platinum(0) have been shown from various studies to be stronger π-bonding metals than their d^8 divalent ions.[24,25] Structurally shorter M–C distances and longer C–C distances would be expected for olefin complexes of the zerovalent metals of this series relative to their divalent analogs. Although comparative data are only available for Pt, such seems to be the case. The present structural result suggests that Pd(0) behaves in an anomalous way. Estimates of d_π bonding ability for the d^{10} series Ni(0), Pd(0), and Pt(0) have been related to the $d^{10} \rightarrow d^9p^1$ promotion energy of the atom.[25] Values of 1.72, 4.23, and 3.28 eV for the respective metal atoms clearly suggest that of the series Pd would be the least effective d_π metal.[4] The relatively long Pd–C bond lengths, short coordinated olefin C–C distances, and ligand planarity of $Pd(DBA)_3$ strongly indicate a lower affinity for olefin coordination for Pd(0).

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Registry No. $Pd(DBA)_3 \cdot C_6H_6$, 41812-89-9.

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, 20× 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-73-2955.

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Bonding in Sulfur Dioxide Complexes Active toward Oxygenation. Molecular Structure of the Benzene Solvate of Tris(triphenylphosphine)(sulfur dioxide)platinum

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The crystal and molecular structure of tris(triphenylphosphine)(sulfur dioxide)platinum has been determined as its benzene solvate from three-dimensional X-ray data. Crystals of the complex are hexagonal, space group $P6_3$, with unit cell parameters $a = 18.722$ (6) Å, $c = 10.008$ (5) Å, and $V = 3038$ Å^3. Refinement by least-squares procedures using 375 independent reflections gave a final R factor of 0.067. There are two molecules of complex per unit cell ($\rho_{exptl} = 1.18$ (5), $\rho_{calcd} = 1.168$ g/cm^3) with crystallographically required threefold symmetry. The benzene solvate has been found to have a fractional occupancy of approximately 0.5. The complex is four coordinate, essentially trigonal pyramidal in geometry with the SO_2 in the apical position (P–Pt–P = 118.4 (4), P–Pt–S = 97.2 (2)°). Oxygen atoms of the SO_2 are disordered about the threefold axis. Bonding between the Pt and phosphine ligands is relatively strong (Pt–P = 2.280 (9) Å) while SO_2 coordination is weak (Pt–S = 2.399 (13) Å). The open trigonal base of the pyramid exposes the basic metal to electrophilic attack.

Introduction

Structural studies on sulfur dioxide adducts of transition metal complexes have indicated that bonding between the metal center and the SO_2 molecule can occur in two forms.[1-3] The M–SO_2 group in the complex $[RuCl(NH_3)_4(SO_2)]^+$ was found to have a strong Ru–S bond collinear with the SO_2 plane.[1] Recent work on the complexes $MCl(SO_2)(P(C_6H_5)_3)_2(CO)$ (M = Rh, Ir) has indicated an entirely different coordination geometry for the M–SO_2 group.[2,3] Significantly longer M–S bond lengths were found with the SO_2 plane bent severely away from the direction of the M–S bond. The SO_2 has been viewed to add oxidatively to the metal in these latter complexes with the change in electronic structure of the sulfur resulting in the bent bonding configuration. The M–S bond in this coordination configuration is qualitatively similar to the N–S bond found in amine–SO_2 charge-transfer complexes where the SO_2 group bonds as a Lewis acid.[4] The SO_2 in $[RuCl(NH_3)_4(SO_2)]^+$, however, bonds as a Lewis base with considerable M–SO_2 π bonding.

The coordination of SO_2 to nucleophilic transition metals has attracted recent attention with the interest in the metal-catalyzed oxygenation of SO_2 to SO_4^{2-}.[5] Virtually all molecular oxygen complexes have been found to react with SO_2 to form coordinated sulfate while a few select SO_2 complexes react with O_2 to give SO_4^{2-}. The complexes $M(SO_2)(P(C_6H_5)_3)_{2,3}$ (M = Pd, Pt) have been found to undergo oxygenation forming $M(SO_4)(P(C_6H_5)_3)_2$.[6,7] Recently $Ru(CO)_2(P(C_6H_5)_3)_2(SO_2)$ and $Ru(Cl)(SO_2)(NO)(P(C_6H_5)_3)_2$ have been reported to form $Ru(SO_4)(CO)_2(P(C_6H_5)_3)_2$[8] and $Ru(SO_4)(Cl)(NO)(P(C_6H_5)_3)_2$[9] on exposure to air. In order to attempt to correlate the activity of coordinated SO_2 with its bonding properties to metals the molecular structure of one of the more active members of this series, the benzene solvate of $Pt(SO_2)(P(C_6H_5)_3)_3$, has been determined crystallographically.

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