# Crystal and Molecular Structure of a (Dibenzylideneacetone)platinum Dimer with Partial Pt Occupancy

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*Received February 24, 1992*

The crystal and molecular structure of a platinum dibenzylideneacetone (dba) complex is described and is a dimer with three bridging dba ligands. The coordination environment for the two metals is different, and one of the metal positions is partially occupied. The resultant formula derived from the structure is $Pt_{1.44}(dba)_3 \cdot CH_2Cl_2$. The crystal data for $C_{52}H_{44}Cl_2O_3Pt_{1.44}$ are space group $P\bar{1}$ with $a$ = 12.982 (4) Å, $b$ = 14.891 (6) Å, $c$ = 12.274 (4) Å, $\alpha$ = 96.95 (1)°, $\beta$ = 95.81 (1)°, $\gamma$ = 114.77°, $V$ = 2107.7 (2) Å$^3$, and $Z$ = 2. This is the first X-ray structure for a platinum dibenzylideneacetone compound. $^{195}$Pt NMR measurements indicate that in solution the compound adopts a fully occupied dimeric structure with two nonequivalent platinum centers.

We have explored platinum compounds for their use as improved hydrosilylation catalysts. We reported that higher activity would be expected from zerovalent platinum compounds containing olefinic ligands.[4] One class of compounds investigated was the platinum dibenzylideneacetone (dba) compounds.

Several reports have appeared concerning platinum compounds with the dba ligand. There has been some contradiction as to the stoichiometry and structure of some of the Pt(dba) complexes. The Maitlis group first prepared $Pt(dba)_2$[5,6] and $Pt(dba)_3$.[5] A single-crystal X-ray structure for the Pd analog established a dimeric structure with bridging dba ligands.[7] Subsequent NMR analyses on the Pt complexes have suggested that $Pt(dba)_2$ was actually $Pt_2(dba)_3 \cdot dba$, with olefin to Pt coordination.[8] Recent spectroscopic studies for $Pt_2(dba)_3 \cdot x$ (x = solvent or dba) assigned the vis/uv spectra as MLCT transitions and the Raman spectra to weak Pt–Pt interactions.[9] The lack of X-ray crystal data for the platinum dba compounds prompted us to attempt such an analysis. We report here the formation of a Pt(dba) complex with a new stoichiometry and structure.

## Results and Discussion

The compound $Pt_{1.44}(dba)_3 \cdot CH_2Cl_2$ was obtained by employing a modified literature procedure for preparation of the dimer $Pt_2(dba)_3 \cdot x$ (x = solvent of crystallization)[5,6] followed by recrystallization from $CH_2Cl_2/CH_3OH$. Spectroscopic data for the compound was consistent with Pt(dba) coordination on the basis of the perturbation of the conjugated bands from the carbonyl–olefin region in the infrared spectrum for the compound. $^1$H NMR data showed free dba as well as coordinated dba; coordinated dba was identified by the upfield shifts observed upon coordination to Pt, Figure 1.

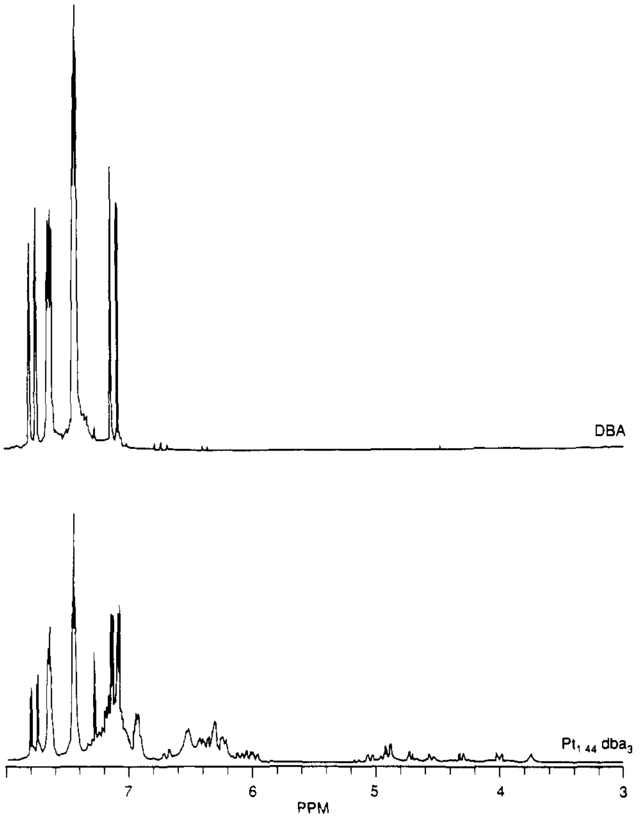

**Figure 1.** $^1$H NMR spectra comparing free dba to $Pt_{1.44}(dba)_3$.

**Table I.** Crystallographic Data for $Pt_{1.44}(dba)_3 \cdot CH_2Cl_2$

| | |
|---|---|
| $Pt_{1.44}C_{51}H_{42}O_3 \cdot CH_2Cl_2$ | formula weight 1178.00[a] |
| $a$ = 12.982 (4) Å | space group $P1$ (No. 2) |
| $b$ = 14.891 (6) Å | $T$ = –155 °C |
| $c$ = 12.274 (4) Å | $\lambda$ = 0.710 69 Å |
| $\alpha$ = 96.95 (1)° | $\rho_{calc}$ = 1.683 g cm$^{-3}$ |
| $\beta$ = 95.85 (1)° | $\mu$ = 68.706 cm$^{-1}$ [a] |
| $\gamma$ = 114.77 (2)° | transmission coeff 0.48/0.87 |
| $V$ = 2107.8 (9) Å$^3$ | $R(F)$ = 0.071[b] |
| $Z$ = 2 | $R_w(F)$ = 0.064[c] |

[a] Based on full occupancy of Pt. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w(F) = (\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2)^{1/2}$.

The most remarkable and unexpected feature of the structure was the partial occupancy of one of the Pt positions as observed in the single-crystal X-ray structure. Table I gives the crystallographic data, Table II gives the fractional coordinates, and

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**Table II.** Fractional Coordinates and Isotropic Thermal Parameters for $Pt_{1.44}(dba)_3 \cdot CH_2Cl_3$[a]

| atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| PT(1) | 2390 (1) | 360 (1) | 2791 (1) | 17 |
| PT(2) | 238 (1) | -1747 (1) | 2386 (1) | 20 |
| C(3) | -823 (19) | -4463 (16) | 2635 (19) | 44 |
| C(4) | -1605 (19) | -5101 (14) | 3158 (17) | 43 |
| C(5) | -1450 (18) | -4921 (15) | 4306 (17) | 42 |
| C(6) | -555 (19) | -4116 (16) | 4920 (17) | 43 |
| C(7) | 238 (15) | -3467 (13) | 4347 (18) | 36 |
| C(8) | 83 (17) | -3632 (15) | 3210 (17) | 35 |
| C(9) | 939 (21) | -2978 (17) | 2530 (18) | 47 |
| C(10) | 1695 (17) | -2124 (14) | 2899 (18) | 39 |
| C(11) | 2572 (12) | -1511 (13) | 2209 (12) | 17 |
| O(12) | 2621 (11) | -1859 (10) | 1283 (10) | 35 |
| C(13) | 3404 (15) | -500 (15) | 2742 (15) | 29 |
| C(14) | 3561 (14) | -37 (14) | 3805 (15) | 27 |
| C(15) | 4618 (13) | 943 (13) | 4405 (14) | 26 |
| C(16) | 4710 (14) | 1210 (14) | 5525 (15) | 30 |
| C(17) | 5586 (15) | 2088 (15) | 6081 (15) | 33 |
| C(18) | 6385 (15) | 2682 (15) | 5515 (19) | 40 |
| C(19) | 6304 (15) | 2393 (15) | 4370 (16) | 35 |
| C(20) | 5410 (15) | 1547 (14) | 3808 (14) | 26 |
| C(21) | -2296 (19) | -3802 (21) | 173 (17) | 45 |
| C(22) | -2755 (19) | -4795 (18) | -229 (15) | 41 |
| C(23) | -2054 (20) | -5161 (13) | -657 (16) | 39 |
| C(24) | -918 (19) | -4562 (18) | -761 (16) | 40 |
| C(25) | -479 (17) | -3556 (16) | -360 (15) | 38 |
| C(26) | -1150 (32) | -3152 (17) | 133 (16) | 66 |
| C(27) | -817 (23) | -1989 (24) | 559 (18) | 70 |
| C(28) | 136 (18) | -1408 (22) | 700 (15) | 86 |
| C(29) | 391 (14) | -222 (14) | 1115 (12) | 23 |
| O(30) | -341 (11) | 66 (10) | 1272 (9) | 33 |
| C(31) | 1581 (15) | 546 (16) | 1233 (13) | 33 |
| C(32) | 2510 (21) | 434 (16) | 1033 (15) | 45 |
| C(33) | 3657 (16) | 1304 (16) | 941 (13) | 37 |
| C(34) | 4449 (17) | 1075 (14) | 555 (14) | 31 |
| C(35) | 5499 (16) | 1799 (17) | 507 (14) | 33 |
| C(36) | 5784 (15) | 2771 (15) | 824 (16) | 33 |
| C(37) | 4974 (18) | 3060 (14) | 1212 (17) | 38 |
| C(38) | 3883 (15) | 2320 (17) | 1273 (13) | 32 |
| C(39) | -2656 (17) | -3229 (16) | 3247 (15) | 35 |
| C(40) | -3746 (18) | -3806 (14) | 2737 (19) | 42 |
| C(41) | -4313 (16) | -3431 (20) | 2059 (16) | 46 |
| C(42) | -3772 (21) | -2445 (20) | 1912 (18) | 52 |
| C(43) | -2640 (20) | -1843 (15) | 2484 (17) | 41 |
| C(44) | -2090 (15) | -2258 (15) | 3125 (18) | 36 |
| C(45) | -839 (27) | -1674 (22) | 3778 (23) | 76 |
| C(46) | -116 (17) | -871 (17) | 3764 (18) | 43 |
| C(47) | 988 (13) | -351 (12) | 4486 (14) | 18 |
| O(48) | 1343 (10) | -634 (10) | 5245 (9) | 32 |
| C(49) | 1819 (19) | 706 (18) | 4313 (14) | 44 |
| C(50) | 1570 (17) | 1252 (16) | 3582 (15) | 38 |
| C(51) | 2305 (16) | 2343 (13) | 3684 (15) | 29 |
| C(52) | 3468 (17) | 2856 (15) | 4168 (14) | 31 |
| C(53) | 4054 (16) | 3866 (15) | 4043 (15) | 35 |
| C(54) | 3498 (18) | 4336 (14) | 3522 (18) | 36 |
| C(55) | 2368 (20) | 3815 (16) | 3071 (18) | 41 |
| C(56) | 1775 (15) | 2819 (15) | 3117 (15) | 32 |
| CL(57) | 8515 (5) | 2469 (4) | 2368 (5) | 51 |
| CL(58) | 6822 (5) | 376 (4) | 2064 (5) | 57 |
| C(59) | 8264 (19) | 1222 (17) | 2395 (15) | 45 |

[a] Fractional coordinates are ×$10^4$ for non-hydrogen atoms and ×$10^3$ for hydrogen atoms. $B_{iso}$ values are ×10. Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton.

Tables III and IV give selected bond distances and angles. The compound adopts an apparent binuclear structure with three bridging dba units; however, the second Pt position is only present 44% of the time (Figure 2).[11]

The two metals occupy significantly different coordination environments. The three olefins around Pt(1) assume a nearly planar configuration while those around Pt(2) are perpendicular to the coordination plane. The planar arrangement is the one typically observed in Pt(O) olefin complexes.[10-12] In addition, each dba molecule is in the s-cis,trans conformation (Figure 2), with Pt(1) bound to three s-trans olefins and Pt(2) bound to three s-cis olefins. This conformational arrangement is different from those in the palladium dibenzylideneacetone dimers (s-cis,trans, s-cis,trans, and s-trans,cis for $Pd_2(dba)_3 \cdot CHCl_3$,[7c], and s-cis,trans,

**Table III.** Selected Bond Distances (Å) for $Pt_{1.44}(dba)_3 \cdot CH_2Cl_2$

| | | | |
|---|---|---|---|
| Pt(1)–C(13) | 2.189 (16) | Pt(2)–C(46) | 2.214 (16) |
| Pt(1)–C(14) | 2.180 (15) | C(13)–C(14) | 1.354 (23) |
| Pt(1)–C(31) | 2.192 (14) | C(31)–C(32) | 1.330 (25) |
| Pt(1)–C(32) | 2.193 (18) | C(49)–C(50) | 1.383 (25) |
| Pt(1)–C(49) | 2.162 (15) | C(9)–C(10) | 1.229 (25) |
| Pt(1)–C(50) | 2.219 (18) | C(27)–C(28) | 1.150 (30) |
| Pt(2)–C(9) | 2.380 (19) | C(45)–C(46) | 1.170 (30) |
| Pt(2)–C(10) | 2.240 (16) | C(11)–O(12) | 1.209 (17) |
| Pt(2)–C(27) | 2.409 (21) | C(29)–O(30) | 1.216 (19) |
| Pt(2)–C(28) | 2.190 (19) | C(47)–O(48) | 1.192 (17) |
| Pt(2)–C(45) | 2.335 (23) | | |

**Table IV.** Selected Bond Angles (deg) for $Pt_{1.44}(dba)_3 \cdot CH_2Cl_2$

| | |
|---|---|
| C(15)–C(14)–C(13) | 126.1 (15) |
| C(14)–C(13)–C(11) | 128.4 (15) |
| C(33)–C(32)–C(31) | 124.1 (19) |
| C(29)–C(31)–C(32) | 128.9 (20) |
| C(51)–C(50)–C(49) | 120.8 (17) |
| C(50)–C(49)–C(47) | 126.0 (18) |
| C(8)–C(9)–C(10) | 124.3 (21) |
| C(9)–C(10)–C(11) | 122.7 (20) |
| C(26)–C(27)–C(28) | 119.0 (30) |
| C(27)–C(28)–C(29) | 115.0 (30) |
| C(44)–C(45)–C(46) | 132.0 (30) |
| C(45)–C(46)–C(47) | 118.3 (16) |

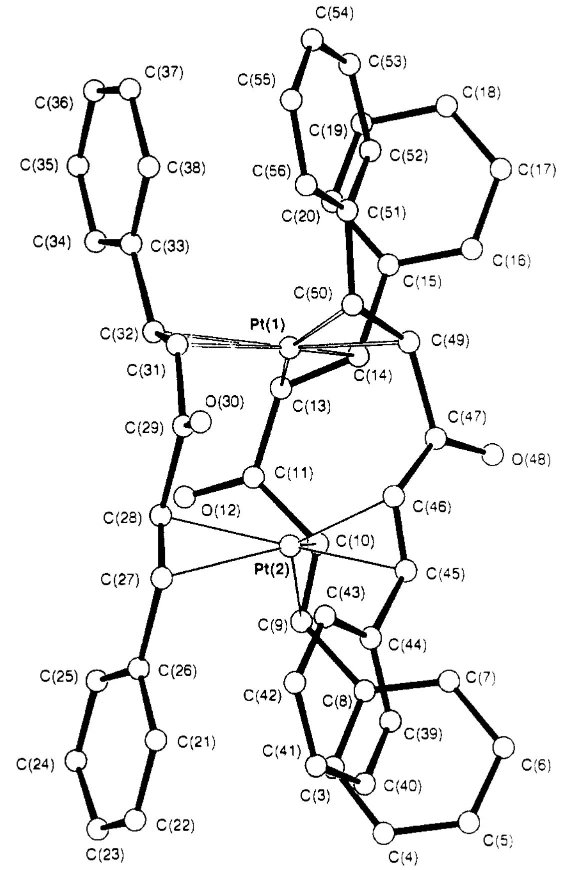

**Figure 2.** A ball and stick representation of $Pt_{1.44}(dba)_3 \cdot CH_2Cl_2$. Pt(2) is the partially occupied position. The s-trans bonds are between C(13) and C(14), C(31) and C(32), and C(49) and C(50). The s-cis bonds are between C(9) and C(10), C(27) and C(28), and C(45) and C(46).

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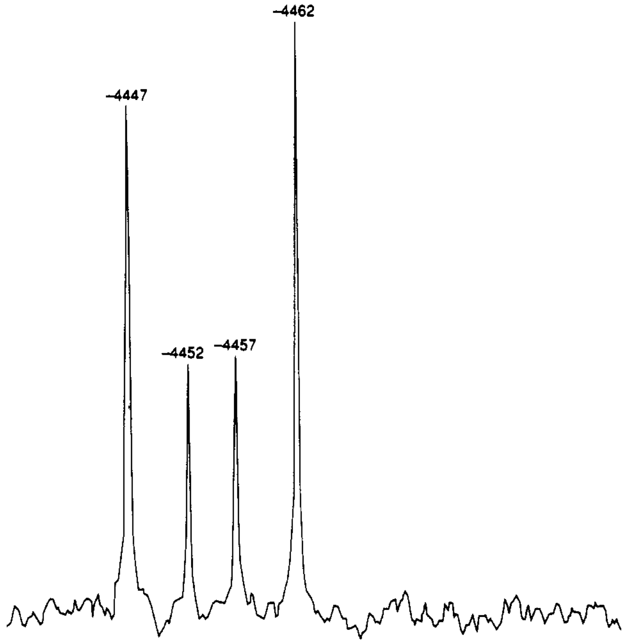

**Figure 3.** $^{195}$Pt NMR spectrum ($(CD_3)_2CO$) at 64.12 MHz for $Pt_{1.44}(dba)_3$. Chemical shifts are upfield from the external standard $Na_2PtCl_6$ (0 ppm).

s-cis,trans, and s-trans,trans for $Pd_2(dba)_3{\cdot}CH_2Cl_2$[7b]). The Pt–C and olefinic C–C bond lengths around Pt(2) are averages for the occupied and unoccupied sites so no conclusions can be drawn regarding the metal–ligand interaction of Pt(2). Consistent with the predictions from Raman spectroscopy of a weak Pt–Pt interaction,[9] the Pt–Pt measured distance in the title compound was 3.14 Å (Pd–Pd bond 3.24 Å in the Pd(dba) analog).[7] There was no evidence of coordination of Pt to the carbonyl group.

The solution $^{195}$Pt NMR spectrum (Figure 3) shows only two nonequivalent platinums coupled to each other (34% abundant, spin $^1/_2$) which indicates that only the fully occupied dimer is present in solution. The spectrum, which is the same at ambient temperature and −50 °C, is due to an ab spin system with line spacings of 354 and 282 Hz. The outer lines predicted for the ab system will be $^1/_9$ the intensity of the two inner lines and apparently not observed. The calculated $J_{Pt-Pt} = 1282$ Hz. The origin of the nonequivalence of the Pt atoms could be due to the same conformational differences observed in the solid state; however, other nonequivalent conformational arrangements are possible.[8] The absence of a $^{195}$Pt signal for the single occupied molecule $Pt(dba)_3$ indicates that dimerization and liberation of free dba occur in solution.

$$0.44Pt_2(dba)_3 + 0.56Pt(dba)_3 \rightarrow 0.72Pt_2(dba)_3 + 0.84dba$$

Vapor-phase osmometry in $CH_2Cl_2$ gave an average molecular weight of 1016 amu (calcd for $Pt_{1.44}(dba)_3$, 983 amu).

Evidence was sought for paramagnetism resulting from the Pt partial occupancy. The molecule remained diamagnetic down to 10 K.[13] Thus, the deep purple color of this compound appeared to be due to MLCT transitions,[9] and not due to unpaired electrons. The results presented here represent novel stoichiometry and structure for compounds of this type. The consequences of this unique structural pattern on catalytic activity are under investigation.

## Experimental Section

**General Procedure.** All solvents were reagent grade and were used as received. Dibenzylideneacetone (99%, Aldrich), potassium tetrachloroplatinate (Strem), sodium acetate (99%, Aldrich), and tetrabutylammonium chloride (96%, Aldrich) were also used as received. $^1$H NMR spectra were recorded on a GE Model QE-300 NMR spectrometer at 300.15 MHz. $^{195}$Pt NMR spectra were recorded on a Varian XL300 spectrometer at 64.12 MHz. IR spectra were recorded on a Perkin-Elmer Model 598 IR spectrometer. Elemental analyses were performed in-house or by Galbraith Labs.

**$Pt_2(dba)_3$.** Sodium acetate (2.8 g, 34.1 mmol), dba (3.1 g, 13.2 mmol), and $Bu_4NCl$ (1.6 g, 5.7 mmol) were dissolved in MeOH (160 mL) by refluxing the mixture in air. Finely ground $K_2PtCl_4$ (0.79 g, 1.9 mmol) was dissolved in hot $H_2O$ (10 mL) and then slowly added to the above solution. The mixture was refluxed for 2 hours and then concentrated to ~50 mL and cooled to room temperature. The solids were isolated by filtration and washed with water and then MeOH to remove salts and unreacted dba. The crude product was dissolved in hot THF (150 mL) and filtered and the volume reduced to ca. 10 mL by evaporation. MeOH (ca. 20 mL) was added slowly, and after cooling for 1 h the product was isolated by filtration, washed with MeOH, and dried under vacuum (0.72 g, 69%). Anal. Calcd for $C_{51}H_{42}O_3Pt_2$: C, 56.04; H, 3.87. Found: C, 55.75; H, 3.93. The crystals used for the structure were obtained by dissolving the above powder in $CH_2Cl_2$ and layering on MeOH. Slow evaporation enriched the mixture in MeOH, and the crystals were obtained. Anal. Calcd for $C_{92}H_{44}Cl_2O_3Pt_{1.44}$: Pt, 26.29; C, 58.44; H, 4.15. Found: Pt, 26.2 (average of two measurements); C, 61.15; H, 4.65. IR (KBr pellet) (dba): 1650 (s), 1625 (m), 1590 (vs), 1575 (sh), 1500 (m), 1450 (m) cm$^{-1}$. IR (KBr pellet) ($Pt_{1.44}(dba)_3$): 1650 (s), 1640 (s, sh), 1590 (vs), 1575 (sh), 1550 (m), 1510 (sh), 1500 (w) cm$^{-1}$.

**Acknowledgment.** We thank Elizabeth Williams and Steven Tetrick for their help in analyzing the $^{195}$Pt NMR data. Dr. Israel Jacobs carried out and interpreted the magnetic measurements.

**Supplementary Material Available:** Textual presentation of crystal and diffractometer data and tables of crystallographic data, fractional coordinates and isotropic thermal parameters for H atoms, anisotropic thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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(13) Solid measured with an EGG-Princeton Applied Research vibrating sample magnetometer in a magnetic field of up to 2 T. The low temperature was achieved using a Janis Research Co. variable-temperature liquid helium research dewar.