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The Structure of Bis(triphenylphosphine)(dibenzoylhydrazido)platinum, $Pt[P(C_6H_5)_3]_2[C_6H_5CONNCOC_6H_5]\cdot C_2H_5OH$

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The compound bis(triphenylphosphine)(dibenzoylhydrazido)platinum crystallizes from dichloromethane–ethanol as the solvated species $Pt[P(C_6H_5)_3]_2[C_6H_5CONNCOC_6H_5]\cdot C_2H_5OH$. The structure of this complex has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic space group C_i^1-$P1$ with cell dimensions $a = 13.329$ (6), $b = 15.312$ (7), $c = 12.466$ (5) Å; $\alpha = 99.95$ (2), $\beta = 113.60$ (2), $\gamma = 97.78$ (2)°. Observed and calculated densities for two molecules per unit cell are 1.45 (±0.02) and 1.49 g cm^{-3}, respectively. Least-squares refinement has led to a final value of the conventional R index (on F) of 0.037 for the 3906 reflections having $F^2 > 3\sigma(F^2)$. The coordination around the platinum atom is distorted square planar. The dibenzoylhydrazide, acting as a bidentate ligand, coordinates through an oxygen atom and a nitrogen atom, resulting in a five-membered, Pt–N(2)–N(1)–C(1)–O(1), ring. The Pt–O(1) distance is 2.016 (5) Å and the Pt–N(2) distance is 2.047 (6) Å. The Pt–P distances trans to O(1) and N(2) are 2.258 (2) and 2.268 (2) Å, respectively. The N(1)–N(2) distance is 1.401 (9) Å while the N(1)–C(1) and C(1)–O(1) distances are 1.286 (10) and 1.318 (10) Å, respectively. There is a hydrogen bond between the ethanol molecule and the exocyclic oxygen atom of the dibenzoylhydrazide ligand, the O· · ·O bond length being 2.776 (13) Å.

Introduction

It is now well established that substituted diazenes may coordinate to transition metals by a variety of means. The substituent groups may or may not be bonded to the metal, and the diazene moiety may be bonded by one of two means. The first[1,2] involves π bonding where the two nitrogen atoms are equidistant from the metal and electron density is transferred from diazene π-bonding orbitals to the metal and from the metal into π-antibonding orbitals. The second[3,4] involves the lone-pair electrons of one of the nitrogen atoms in the formation a σ bond with the metal.

As part of a continuing study of the coordination of diazenes to transition metals[1,2] it was felt that an investigation of coordinated diazenes with substituents other than aryl or alkyl groups would be of interest. The literature contains several reports[5-7] of transition metal complexes of diazenes with carbonyl substituents. These are of interest because the carbonyl introduces another possible coordination site.

In the first of these, $IrCl(CO)(NCO_2Et)_2(PPh_3)_2$ (where $Ph = C_6H_5$ and $Et = C_2H_5$), reported by Green, *et al.*,[5] an equatorial, symmetrical π-bonded structure with axial phosphines was assigned on the basis of nmr results. The ethyl resonances were observed to be nonequivalent and this was rationalized by citing the nonequivalence of the CO and Cl, which share the equatorial plane with the diazene. A second complex, $Pt(NCO_2Et)_2(PPh_3)_2$,[5] is expected to be planar so a symmetric π bond would lead to the equivalent ethyl resonances observed.

Kasenally treated dibenzoylhydrazine with $PtCl_2(PPh_3)_2$ and also with *mer*-$Rh(PMe_2Ph)_3Cl_3$ (where $Me = CH_3$) to give what was formulated as the reduced species bis(triphenylphosphine)(dibenzoyldiazene)platinum[6] and the bridged species $[Rh(CO)(PMe_2Ph)]_2(PhCON{=}NCOPh)$,[6,7] respectively. On the basis of infrared, Raman, and nmr spectroscopy, these species were also assigned symmetric π-bonded structures. The related species bis(triphenylphosphine)(diacetyldiazene)platinum[6] was assigned a σ-bonded structure with an acetyl oxygen atom completing a five-membered ring with the platinum. This proposed structure is confirmed by preliminary results of a crystallographic study.[8]

A related compound, the benzoylhydrazine adduct of cuprous chloride, has been the subject of a crystallographic investigation[9] which revealed a σ-bonded metallocycle involving the lone-pair electrons of the nitrogen and oxygen atoms. In this complex no reduction has taken place so it is therefore a coordinated hydrazine rather than a coordinated diazene.

The compound bis(triphenylphosphine)(dibenzoyldiazene)platinum was chosen for a crystallographic investigation because of its similarity to the compound bis(tri-*p*-tolylphosphine)(diphenyldiazene)nickel, whose structure had been determined in this laboratory.[2] Here we show that in the complex the diazene is not bonded in the symmetric π manner and indeed that the compound is more properly described as a platinum(II)-dibenzoylhydrazido derivative, rather than as a platinum(0)-dibenzoyldiazene derivative.

Experimental Section

The compound $Pt(PPh_3)_2(PhCONNCOPh)$, which was kindly supplied by Dr. A. S. Kasenally, crystallizes from 4:1 ethanol–dichloromethane with one molecule of ethanol in the lattice. The small clear yellow crystals display from six to twenty faces. Precession photographs using Cu Kα radiation show only a center of inversion, indicating that the crystals belong to the triclinic system.

The eight faces of the crystal selected for data collection belonged to the $\{010\}$, $\{001\}$, $\{100\}$, and $\{10\bar{1}\}$ forms. The distances between centrosymmetrically related faces as measured by a microscope fitted with a micrometer eyepiece are 0.0244, 0.0174, 0.0156, and 0.0092 cm, respectively.

All intensity measurements were made with a Picker FACS-I computer-controlled four-circle X-ray diffractometer equipped with a scintillation counter and pulse height analyzer. Cell constants and their standard deviations were derived[10] from a least-squares refine-

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[10] In addition to various local programs for the CDC 6400, computer programs used in this work include local versions of Dewar's FAME program, Zalkin's FORDAP Fourier program, Cahen's AGNOST absorption program, Busing and Levy's ORFFE function and error program, and Johnson's ORTEP thermal ellipsoid plotting program. Our least-squares program NUCLS, in its nongroup form closely resembles the Busing–Levy ORFLS program.

Table I. Positional and Anisotropic Thermal Parameters for Individual Atoms of $Pt(PPh_3)_2(PhCONNCOPh)\cdot C_2H_5OH$[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	−0.05441 (3)	0.23186 (2)	−0.05645 (3)	41.5 (4)	32.8 (2)	64.1 (4)	9.1 (2)	21.9 (3)	13.8 (2)
P(1)	0.0676 (2)	0.2167 (1)	−0.1384 (2)	52 (1)	36 (1)	80 (2)	12 (1)	30 (2)	16 (1)
P(2)	−0.2146 (2)	0.1932 (1)	−0.2313 (2)	52 (2)	33 (1)	71 (2)	13 (1)	25 (2)	15 (1)
O(1)	−0.1510 (4)	0.2669 (4)	0.0262 (5)	47 (5)	51 (3)	65 (6)	7 (3)	25 (4)	1 (3)
O(2)	0.2100 (5)	0.2319 (4)	0.1152 (5)	58 (5)	62 (4)	90 (6)	21 (4)	32 (5)	14 (4)
O(3)[c]	0.4181 (7)	0.2086 (6)	0.1315 (8)	154 (9)	153 (6)	259 (10)	65 (6)	87 (8)	78 (6)
N(1)	0.0183 (6)	0.3271 (5)	0.1943 (6)	59 (7)	45 (4)	73 (7)	14 (4)	26 (6)	12 (4)
N(2)	0.0608 (5)	0.2814 (4)	0.1204 (6)	45 (6)	42 (4)	66 (6)	11 (4)	20 (5)	14 (4)
C(1)	−0.0891 (8)	0.3151 (6)	0.1384 (8)	63 (10)	40 (5)	76 (10)	13 (5)	35 (8)	18 (6)
C(2)	0.1680 (7)	0.2714 (6)	0.1746 (8)	53 (9)	34 (5)	89 (10)	7 (5)	18 (8)	22 (6)
C(3)[c]	0.5619 (12)	0.1360 (9)	0.2310 (12)	223 (15)	114 (9)	215 (16)	38 (9)	72 (13)	45 (10)
C(4)[c]	0.4517 (12)	0.1501 (9)	0.2169 (12)	170 (16)	109 (10)	428 (17)	86 (10)	176 (13)	76 (10)

[a] Numbers in parentheses here and throughout the paper are estimated standard deviations in the least significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The values of β have been multiplied by 10^4. [c] Atoms of the ethanol molecule of crystallization.

Table II. Positional Parameters for Rigid Groups of $Pt(PPh_3)_2(PhCONNCOPh)\cdot C_2H_5OH$

Group	x_c[a]	y_c	z_c	δ	ϵ	η
Ring 1	−0.2166 (3)	0.4028 (3)	0.2452 (3)	−1.090 (4)	−2.782 (3)	2.332 (4)
Ring 2	0.3140 (4)	0.3431 (3)	0.4299 (4)	1.894 (6)	−2.458 (4)	1.722 (5)
Ring 3	−0.0222 (3)	0.2046 (3)	−0.4246 (4)	2.936 (4)	3.028 (4)	−1.203 (4)
Ring 4	0.1634 (3)	0.0349 (3)	−0.1283 (3)	−1.019 (6)	2.136 (4)	−0.271 (6)
Ring 5	0.2594 (4)	0.4014 (3)	−0.0306 (3)	−2.312 (4)	2.766 (4)	3.093 (4)
Ring 6	−0.2249 (3)	0.3582 (3)	−0.3579 (4)	−0.793 (7)	−2.176 (4)	−2.320 (7)
Ring 7	−0.4257 (3)	0.1814 (3)	−0.1668 (3)	−2.896 (4)	−2.859 (4)	0.752 (4)
Ring 8	−0.2790 (4)	−0.0072 (3)	−0.4025 (4)	−2.142 (4)	−2.691 (4)	−0.600 (5)

[a] These quantities have been defined previously (see ref 15).

ment of the setting angles of twelve reflections which had been centered on the Cu Kα_1 peak, λ 1.54056 Å, using a narrow source. The unit cell parameters are a = 13.329 (6); b = 15.312 (7); c = 12.466 (5) Å; α = 99.95 (2), β = 113.60 (2), γ = 97.78 (2)°; V= 2236.5 Å^3. The density calculated for two molecules of complex and two molecules of ethanol per unit cell is 1.49 g/cm^3, which agrees with the experimental value of 1.45 (±0.02) g/cm^3 measured by flotation in dichloromethane–chloroform. The mosaicity of the crystal was measured by means of a narrow-source, open-counter ω-scan technique and found acceptable.

Intensities were measured by the θ–2θ scan technique using nickel-filtered Cu radiation at a takeoff angle of 2.4°. At this angle the intensity of a reflection is about 80% of the maximum value as a function of takeoff angle. Peaks were scanned in 2θ from 0.8° below the Cu Kα_1 peak to 0.8° above the Cu Kα_2 peak with backgrounds measured at each end of the scan. The counter was positioned 30 cm from the crystal and was preceded by an aperture of 2.5 mm × 2.5 mm. The pulse height analyzer was set to admit 90% of the Cu Kα peak and copper foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan. All reflections were scanned at 2°/min. Background counts of 10 sec were taken at each end of the scan range out to 2θ = 45°, 20 sec out to 2θ = 90°, and 40 sec for the remainder out to 2θ = 97°. Beyond this point there were few reflections of significant intensity.

The intensities of six standard reflections were measured after every 100 reflections. The standard deviations of these reflections, computed on the basis of the agreement among the 50 observations made for each standard, were 1.5–2 times the deviations based on counting statistics alone, but there was no trend in the variations.

All data were processed as described previously.[11] A value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. Of the 4493 observed reflections, 3906 unique reflections obeyed the condition $F_o^2 > 3\sigma(F_o^2)$ and only these reflections were used in subsequent calculations. An analysis of 211 Friedel pairs ($h0l$) showed an average deviation of only 1.2%. Hence the centrosymmetric space group $P\bar{1}$ was assumed.

Solution and Refinement of Structure

Refinement of the structure was carried out by full-matrix least-squares techniques.[10] Throughout the refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight, w, is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices R and R_w are defined as $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The atomic scattering factors for Pt, P, O, N, and C were from the tabulation in ref 12; the values for hydrogen were those of Stewart, *et al.*[13] The anomalous dispersion terms of Cromer[14] for Pt, P, O, and N were applied to the calculated structure factors.

From a Patterson synthesis it was possible to locate the platinum and two phosphorus positions in the asymmetric unit. Two other less intense peaks were found near the platinum, but because they were too far apart for the reported N=N π bond, they were not included. One cycle of refinement followed by a difference Fourier synthesis led to positions for all nonhydrogen atoms except those of the ethanol. The agreement indices R and R_w were 0.259 and 0.339 after the first cycle of refinement. The next and all further cycles of refinement were computed with the eight phenyl rings constrained[15] to rigid groups with C-C bond distances of 1.397 Å and D_{6h} symmetry. R and R_w were 0.197 and 0.228, respectively, for a cycle in which all

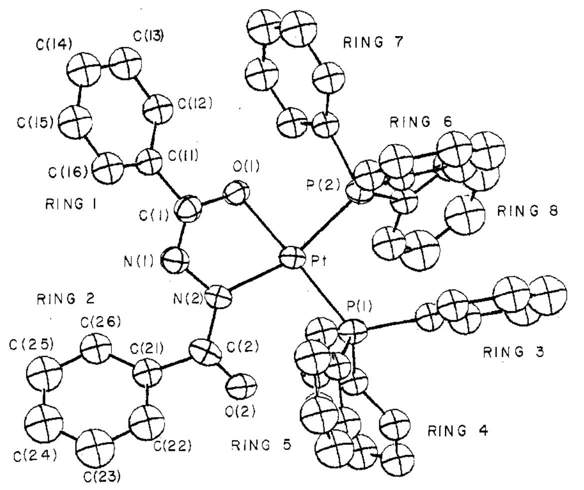

Figure 1. A drawing of the $Pt(PPh_3)_2(PhCONNCOPh)$ molecule with H atoms omitted for the sake of clarity. The vibrational ellipsoids are drawn at the 50% probability level.

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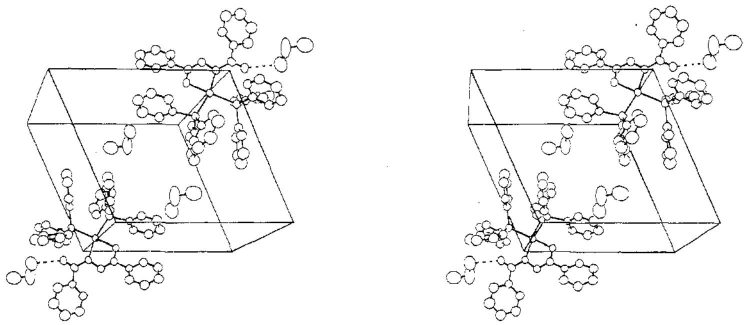

Figure 2. A stereoview of the unit cell of $Pt(PPh_3)_2(PhCONNCOPh){\cdot}C_2H_5OH$. Two extra molecules of C_2H_5OH are drawn to illustrate the hydrogen bond interactions. H atoms are omitted. The vibrational ellipsoids are drawn at the 50% probability level. The x axis goes from left to right, the y axis goes into the paper, and the z axis goes from bottom to top.

Table III. Positional and Isotropic Thermal Parameters for Phenyl Carbon Atoms

Atom	x	y	z	B, Å^2
C(11)	−0.1527 (4)	0.3586 (4)	0.1979 (5)	3.2 (2)
C(12)	−0.2691 (4)	0.3261 (3)	0.1474 (4)	4.2 (2)
C(13)	−0.3330 (3)	0.3703 (4)	0.1947 (5)	4.9 (2)
C(14)	−0.2806 (5)	0.4470 (4)	0.2924 (5)	5.3 (2)
C(15)	−0.1642 (5)	0.4794 (3)	0.3429 (5)	5.4 (2)
C(16)	−0.1002 (3)	0.4353 (4)	0.2957 (5)	4.7 (2)
C(21)	0.2389 (5)	0.3121 (4)	0.3076 (4)	3.9 (2)
C(22)	0.3513 (5)	0.3520 (4)	0.3415 (5)	5.8 (2)
C(23)	0.4264 (4)	0.3831 (5)	0.4638 (6)	7.0 (3)
C(24)	0.3891 (5)	0.3742 (5)	0.5523 (4)	6.8 (3)
C(25)	0.2768 (6)	0.3343 (5)	0.5184 (5)	5.9 (2)
C(26)	0.2017 (4)	0.3032 (4)	0.3961 (5)	4.4 (2)
C(31)	0.0166 (5)	0.2104 (4)	−0.3010 (4)	3.6 (2)
C(32)	0.0179 (5)	0.2898 (3)	−0.3420 (5)	4.6 (2)
C(33)	−0.0210 (6)	0.2839 (4)	−0.4656 (6)	6.3 (3)
C(34)	−0.0610 (6)	0.1988 (5)	−0.5482 (4)	7.4 (3)
C(35)	−0.0623 (6)	0.1195 (4)	−0.5072 (5)	6.6 (3)
C(36)	−0.0234 (6)	0.1253 (3)	−0.3836 (6)	4.9 (2)
C(41)	0.1267 (5)	0.1162 (3)	−0.1291 (5)	3.5 (2)
C(42)	0.0986 (5)	0.0565 (4)	−0.0671 (5)	3.8 (2)
C(43)	0.1353 (5)	−0.0247 (3)	−0.0663 (5)	4.9 (2)
C(44)	0.2001 (5)	−0.0463 (3)	−0.1275 (6)	5.6 (2)
C(45)	0.2282 (5)	0.0133 (4)	−0.1894 (5)	5.1 (2)
C(46)	0.1915 (5)	0.0946 (4)	−0.1902 (5)	4.4 (2)
C(51)	0.1786 (4)	0.3197 (3)	−0.0734 (5)	3.5 (2)
C(52)	0.1492 (4)	0.4025 (4)	−0.0485 (6)	4.5 (2)
C(53)	0.2299 (6)	0.4841 (3)	−0.0056 (6)	5.8 (2)
C(54)	0.3401 (5)	0.4830 (4)	0.0123 (6)	6.6 (3)
C(55)	0.3695 (4)	0.4003 (5)	−0.0126 (6)	6.9 (3)
C(56)	0.2888 (5)	0.3186 (4)	−0.0555 (6)	5.4 (2)
C(61)	−0.2191 (5)	0.2831 (3)	−0.3078 (5)	3.3 (2)
C(62)	−0.2632 (5)	0.2702 (3)	−0.4332 (5)	5.4 (2)
C(63)	−0.2690 (6)	0.3452 (5)	−0.4833 (4)	6.8 (3)
C(64)	−0.2307 (6)	0.4333 (4)	−0.4080 (6)	5.8 (2)
C(65)	−0.1866 (6)	0.4463 (3)	−0.2827 (5)	5.5 (2)
C(66)	−0.1808 (5)	0.3712 (4)	−0.2326 (4)	4.3 (2)
C(71)	−0.3371 (4)	0.1866 (4)	−0.2000 (5)	3.2 (2)
C(72)	−0.4052 (5)	0.2494 (3)	−0.2220 (5)	4.6 (2)
C(73)	−0.4938 (5)	0.2442 (4)	−0.1888 (6)	6.2 (2)
C(74)	−0.5144 (5)	0.1763 (4)	−0.1336 (6)	5.7 (2)
C(75)	−0.4463 (5)	0.1135 (4)	−0.1116 (6)	5.1 (2)
C(76)	−0.3576 (5)	0.1186 (3)	−0.1448 (5)	4.2 (2)
C(81)	−0.2509 (5)	0.0816 (3)	−0.3316 (5)	3.3 (2)
C(82)	−0.3420 (5)	0.0555 (4)	−0.4460 (5)	4.7 (2)
C(83)	−0.3701 (5)	−0.0333 (5)	−0.5169 (5)	6.9 (3)
C(84)	−0.3071 (7)	−0.0960 (4)	−0.4734 (6)	7.5 (3)
C(85)	−0.2160 (6)	−0.0698 (4)	−0.3591 (6)	7.6 (3)
C(86)	−0.1879 (5)	.0190 (4)	−0.2882 (5)	5.3 (2)

nongroup atoms were assigned isotropic thermal parameters and each of the groups an overall thermal parameter. The observed intensities were corrected for absorption, with calculated transmission factors ranging from 0.338 to 0.555, based on $\mu = 69.2$ cm^{-1}. A cycle of isotropic refinement followed by a cycle in which all nongroup atoms were allowed to vibrate anisotropically while group atoms were restricted to isotropic vibration resulted in values of R and R_w of 0.099 and 0.124, respectively. Phenyl hydrogen atom positions were calculated from the group parameters using a C–H distance of 1.00 Å.

Table IV. Idealized Positional Coordinates for Hydrogen Atoms[a]

Atom	x	y	z
H(3-1)	0.621	0.196	0.254
H(3-2)	0.552	0.105	0.140
H(3-3)	0.589	0.096	0.281
H(4-1)	0.398	0.098	0.189
H(4-2)	0.466	0.188	0.301
H(O(3))	0.343	0.217	0.126
H(12)	−0.307	0.271	0.078
H(13)	−0.416	0.347	0.159
H(14)	−0.326	0.479	0.326
H(15)	−0.126	0.534	0.412
H(16)	−0.017	0.458	0.331
H(22)	0.378	0.359	0.278
H(23)	0.506	0.413	0.488
H(24)	0.442	0.397	0.640
H(25)	0.250	0.328	0.581
H(26)	0.121	0.274	0.371
H(32)	0.047	0.350	−0.283
H(33)	−0.010	0.340	−0.495
H(34)	−0.089	0.194	−0.637
H(35)	−0.091	0.058	−0.567
H(36)	−0.024	0.068	−0.354
H(42)	0.052	0.072	−0.023
H(43)	0.115	−0.068	−0.022
H(44)	0.226	−0.105	−0.127
H(45)	0.274	−0.002	−0.233
H(46)	0.211	0.137	−0.235
H(52)	0.070	0.403	−0.060
H(53)	0.209	0.543	0.013
H(54)	0.398	0.542	0.043
H(55)	0.448	0.400	−0.001
H(56)	0.310	0.259	−0.074
H(62)	−0.292	0.207	−0.487
H(63)	−0.301	0.336	−0.573
H(64)	−0.234	0.487	−0.444
H(65)	−0.158	0.509	−0.229
H(66)	−0.149	0.380	−0.143
H(72)	−0.391	0.298	−0.262
H(73)	−0.544	0.289	−0.205
H(74)	−0.578	0.172	−0.110
H(75)	−0.461	0.065	−0.072
H(76)	−0.309	0.074	−0.129
H(82)	−0.387	0.100	−0.477
H(83)	−0.435	−0.052	−0.599
H(84)	−0.327	−0.160	−0.525
H(85)	−0.171	−0.115	−0.329
H(86)	−0.122	0.037	−0.207

[a] A C–H or O–H distance of 1.00 A was assumed, as was tetrahedral geometry for nonphenyl hydrogen atoms. The numbers of the hydrogen atoms indicate the carbon atom to which they were attached, except in the case of the hydrogen attached to O(3).

The hydrogen atoms were given isotropic thermal parameters equal to the values of the carbon atoms to which they were attached. A fixed contribution from these hydrogen atoms was added to structure factor calculations in two further cycles of refinement which led to agreement indices of R and R_w of 0.058 and 0.096.

At this point an analysis of agreement indices as a function of 2θ revealed that agreement at low angles was poor. A difference Fourier map displayed three peaks that could be attributed to an ethanol of

Table VII. Selected Distances (Å) in $Pt(PPh_3)_2(PhCONNCOPh){\cdot}C_2H_5OH$

Bond distances				Nonbonded distances	
Pt-P(1)	2.258 (2)	O(1)-C(1)	1.318 (10)	O(1)-N(1)	2.306 (9)
Pt-P(2)	2.268 (2)	C(1)-C(11)	1.483 (14)	O(2)-N(2)	2.241 (9)
Pt-O(1)	2.016 (5)	C(1)-N(1)	1.286 (10)	N(1)-C(2)	2.356 (12)
Pt-N(2)	2.047 (6)	N(1)-N(2)	1.401 (9)	N(2)-C(1)	2.216 (11)
P(1)-C(31)	1.841 (5)	N(2)-C(2)	1.357 (11)	O(1)-C(12)	2.721 (9)
P(1)-C(41)	1.822 (6)	C(2)-O(2)	1.223 (10)	O(1)-P(2)	2.934 (6)
P(1)-C(51)	1.817 (5)	C(2)-C(21)	1.503 (9)	O(2)-C(51)	2.822 (10)
P(2)-C(61)	1.800 (6)	O(3)-C(4)	1.481 (15)	O(3)-C(3)	2.367 (16)
P(2)-C(71)	1.819 (7)	C(4)-C(3)	1.459 (17)	O(3)-H· · ·O(2)	2.776 (13)
P(2)-C(81)	1.808 (5)				

Table VIII. Selected Intramolecular Bond Angles (deg) in $Pt(PPh_3)_2(PhCONNCOPh){\cdot}C_2H_5OH$

P(1)-Pt-P(2)	97.7 (1)	N(2)-C(2)-O(2)	120.5 (8)
N(2)-Pt-P(1)	97.9 (2)	C(21)-C(2)-O(2)	118.7 (8)
O(1)-Pt-P(2)	86.2 (2)	C(1)-C(11)-C(12)	118.3 (5)
O(1)-Pt-N(2)	77.6 (2)	C(1)-C(11)-C(16)	121.4 (5)
Pt-O(1)-C(1)	111.2 (5)	C(2)-C(21)-C(22)	115.9 (7)
O(1)-C(1)-N(1)	124.6 (8)	C(2)-C(21)-C(26)	123.7 (6)
O(1)-C(1)-C(11)	114.6 (8)	C(3)-C(4)-O(3)	107.2 (14)
C(11)-C(1)-N(1)	120.7 (7)	Pt-P(1)-C(31)	117.7 (2)
C(1)-N(1)-N(2)	111.0 (7)	Pt-P(1)-C(41)	116.9 (3)
N(1)-N(2)-Pt	113.6 (5)	Pt-P(1)-C(51)	108.4 (2)
N(1)-N(2)-C(2)	117.3 (7)	Pt-P(2)-C(61)	109.1 (2)
C(2)-N(2)-Pt	129.0 (6)	Pt-P(2)-C(71)	110.5 (2)
N(2)-C(2)-C(21)	120.7 (9)	Pt-P(2)-C(81)	118.8 (2)

crystallization. One of these was about 2.8 Å from O(2), suggesting a hydrogen bond interaction. One cycle of refinement in which the carbon and oxygen atoms of the ethanol were varied isotropically and all other atoms were varied as in the previous cycle resulted in $R = 0.042$ and $R_w = 0.060$. A subsequent difference Fourier map led to reasonable positions for the hydrogen atoms on the methylene and methyl carbon atoms despite the very large thermal motion exhibited by the C and O atoms. These positions were idealized using C-H and O-H = 1.0 Å and tetrahedral geometry. The H atom in the presumed O-H· · ·O bond could not be located on the difference map. However, its presence was assumed and its position idealized. The fixed contributions from these idealized hydrogen atoms and the phenyl group hydrogen atoms were added to structure factor calculations in one final cycle of refinement in which all nonhydrogen nongroup atoms were varied anisotropically. The final values of R and R_w were 0.037 and 0.053, respectively.

Refinement was discontinued at this point because all major parameter shifts were associated with the ethanol with no significant shifts in the parameters of the platinum complex. Further refinement would have improved the ethanol parameters but this is an expensive means of determining the structure of ethanol.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of setting angles, magnitude of $|F_o|$, and Miller indices revealed no unusual trends. No correction for extinction was necessary. The error in an observation of unit weight is 1.97 e. The maximum density on a final difference Fourier synthesis is 1.09 e/Å^3; this may be compared with the range of 2.6-4.1 e/Å^3 for the peaks of the ethanol molecule in the previous map.

The final atomic positional and thermal parameters along with their standard deviations as estimated from the inverse matrix are given in Table I. Table II lists the positional parameters of the eight phenyl rings and Table III lists the carbon atom positions derived from the data of Table II, together with the corresponding isotropic thermal parameters. The idealized hydrogen atom positions are given in Table IV. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table V;[16] only the reflections which were used in the refinement are listed in this table.

Description of the Structure and Discussion

Table IX. Selected Interplanar and Vector Plane–Normal Angles (deg) in $Pt(PPh_3)_2(PhCONNCOPh){\cdot}C_2H_5OH$

	Dihedral Angles[a]		
Pt P(1) P(2) Pt O(1) N(2)	8.9 (2)	N(1) N(2) C(2) N(2) C(2) C(21)	−2.7 (12)
Pt P(1) N(2) Pt P(2) O(1)	−170.9 (2)	N(2) C(2) O(2) C(23) C(21) C(25)	−42.2 (4)
O(1) C(1) N(1) O(15) C(1) C(13)	−20.4 (5)	N(2) C(2) C(21) C(2) C(21) C(26)	47.5 (12)
O(1) C(1) C(11) C(1) C(11) C(12)	17.5 (11)	O(1) C(1) N(1) C(1) N(1) N(2)	−0.6 (13)
Pt N(2) N(1) O(2) C(2) C(21)	179.2 (10)	C(1) N(1) N(2) N(1) N(2) C(2)	−166.1 (8)
Pt N(2) C(2) N(2) C(2) O(2)	3.8 (14)	Pt O(1) C(1) O(1) C(1) N(1)	−9.6 (12)
	Vector Plane–Normal Angles		
C(11) C(1) O(1) C(1) N(1)	91.4 (14)	N(1) N(2) Pt N(2) C(2)	−86.5 (11)
N(1) C(1) O(1) C(1) C(11)	88.7 (13)	N(2) C(2) O(2) C(2) C(21)	92.2 (13)
C(2) N(2) N(1) N(2) Pt	87.0 (9)	O(2) C(2) N(2) C(2) C(21)	87.8 (14)
		C(21) C(2) N(2) C(2) O(2)	−92.2 (13)

[a] For a definition of the angles, see ref 2 or W. R. Busing, K. O Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

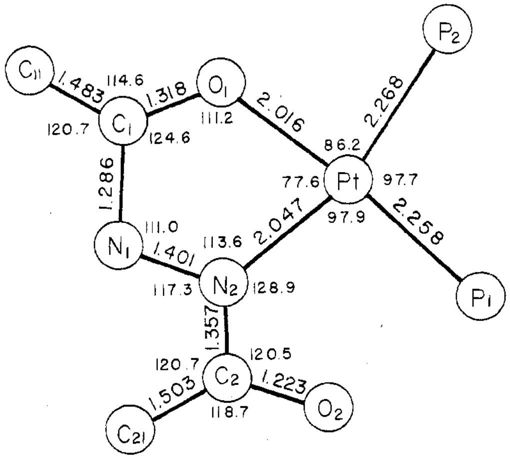

Figure 3. A sketch of the inner coordination sphere of $Pt(PPh_3)_2$-(PhCONNCOPh) showing important bond distances and angles. See Tables VII and VIII for estimated standard deviations on these quantities.

The structure consists of monomolecular units with two molecules of ethanol filling the void in the center of each cell. Figure 1 presents the labeling scheme for the complex and Figure 2 presents a stereoscopic view of the packing. Figures 1 and 2 display the 50% probability ellipsoids for thermal motion. The root-mean-square amplitudes of vibration are listed in Table VI.[16] The numbering of all rings starts at the α-carbon atom and works around the ring. Hydrogen atoms have the same number as the carbon atom to which they are attached. Intermolecular contacts are normal, the shortest between refined atomic positions being the O(2)· · ·H-O(3) distance of 2.776 (13) Å. Selected interatomic distances and angles are presented in Tables VII and

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(16) See paragraph at end of paper regarding supplementary material.

Table X. Deviations (Å) from weighted Least-Squares Planes of Atoms Used to Determine the Planes[a]

	Plane				
	1	2	3	4	5
Pt	−0.0025 (3)	0.0002 (4)	0.0000 (4)		
P(1)	0.038 (2)				
P(2)	0.015 (2)				
O(1)	0.253 (6)	−0.074 (6)		0.001 (6)	−0.104 (6)
O(2)			0.007 (7)		−0.005 (7)
N(1)		0.084 (8)	0.000 (8)	0.002 (8)	0.146 (8)
N(2)	0.140 (7)	−0.117 (7)	0.025 (7)	−0.001 (7)	0.152 (7)
C(1)		0.083 (10)		−0.003 (10)	0.007 (10)
C(2)			−0.009 (10)		0.002 (10)
C(11)					−0.003 (6)
C(21)			−0.010 (6)		−0.103 (7)

Plane	*A*	*B*	*C*	*D*
1	−0.062	15.160	−3.397	3.713
2	1.276	14.565	−5.571	3.622
3	4.125	13.489	−6.322	3.260
4	2.246	13.724	−7.177	3.135
5	3.250	13.694	−6.699	3.092

[a] Plane equation: $Ax + By + Cz - D = 0$ with x, y, and z in triclinic coordinates.

VIII and in Figure 3. Table IX presents data on selected dihedral angles.

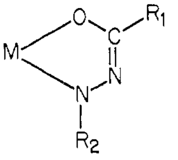
The structure does not contain a diazene symmetrically bonded to Pt but rather contains an unsymmetric chelate involving one nitrogen atom and the oxygen atom of the opposite benzoyl group bound to Pt. The complex is best described as square planar, as indicated by the dihedral angles between various planes defined by the inner coordinate sphere (Table IX), but there is a distinct distortion toward square pyramidal with Pt at the apex, as can be discerned from Figure 2 and from the least-squares plane 1 of Table X. The Pt-P(1) distance trans to O(1) of 2.258 (2) Å is slightly shorter than the Pt-P(2) distance trans to N(1) (2.268 (2) Å). Variation of the P-C distances is statistical, with an average value of 1.817 (6) Å. The average Pt-P-C angle is 113.6 (19)° with variations caused by interactions between the phosphine phenyl groups.

The metallocycle formed by the chelating O-C-N-N has an envelope conformation as indicated by plane 2 in Table X. The atoms O(1), C(1), N(1), and N(2) are coplanar (number 4, Table X) and the platinum atom is 0.330 (9) Å from this plane. The Pt-O(1) and Pt-N(2) bond lengths are 2.016 (5) and 2.047 (6) Å, respectively. The N(1)-N(2) bond has lengthened to 1.401 (9) Å, similar to that of a hydrazine (1.40 Å) rather than that of a diazene (1.24 Å). It is interesting to note that in the structure of chlorobis(benzoylhydrazine)copper(I)[9] this distance has an average value of 1.436 Å suggesting that in the present structure there is still some slight degree of multiple-bond character left.

The endocyclic O(1)–C(1) bond has lengthened from a normal C=O distance, such as 1.233 (10) Å for the exocyclic C(2)–O(2) distance, past that of a coordinated C=O value of 1.257 Å in the copper complex to 1.318 (10) Å. The endocyclic C(1)–N(1) bond of 1.286 (10) Å has shortened toward that of a double bond. For comparison, the value in the copper complex is 1.326 Å and the exocyclic N(2)–C(2) distance is 1.357 (11) Å. These changes in bond lengths suggest fractional bond orders and delocalized electron density through the chelate ring. Though there is undoubtedly a resonance equilibrium between the two species in Figure 4, the equilibrium lies to the right. Thus it would be better to consider the complex to be Pt(II) with an enolized dibenzoylhydrazido moiety, rather than as a Pt(0) complex with an unsymmetrically bound dibenzoyldiazene.

The results of this study indicate that further investigation of reported diazene systems involving carbonyls is warranted. A symmetric π bond in these systems cannot be ruled out, but it is unlikely for several reasons. First, the only reported π complexes of diazenes are in low-oxidation-state, electron-rich metals which would allow a considerable degree of π back-donation. Under these conditions, oxidation of the

Table XI. Some Reported Metallocycles Containing N-N-C-O Chelates



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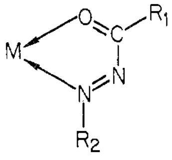

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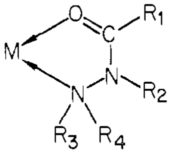

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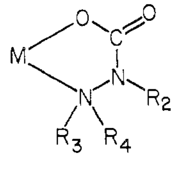

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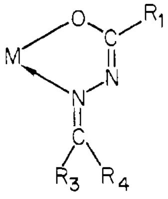

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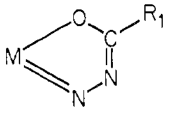

6

Type	Metal	R_1	R_2	R_3	R_4	Ref
1	Pt^{II}	C_6H_5	$C{=}O(C_6H_5)$			This work
	Pt^{II}	C_2H_5	$C{=}O(C_2H_5)$			6, 8
	Mo^{IV}	C_6H_5	H			8
2	Mo^{III}	p-$C_6H_4CH_3$	C_6H_5			17
	Os^{II}	Alkyl	Aryl			18
3	Cu^{I}	C_6H_5	H	H	H	9
	Cu^{II}, Zn^{II}	NH_2	H	H	H	19
4	Mn^{II}		H	H	H	20
5	Re^{V}	Aryl		Alkyl	Alkyl	21
6	Re^{V}	Aryl				22

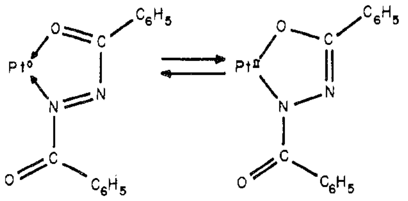

Figure 4. Representation of platinum(0) dibenzoyldiazene and platinum(II) dibenzoylhydrazido resonance forms. In the present structure the equilibrium lies to the right.

metal by the carbonyldiazene is very likely. Second, even if the metal is not oxidized by the ligand, five-membered chelate rings tend to be energetically favorable. Thus, unsymmetrical chelating would again be favored.

It should be possible to prepare a complex with an unsymmetrically bound dibenzoyldiazene by going to metals in higher oxidation states. There would then be less need for electron transfer to the ligand. This form would be of interest structurally because there is a growing list[6,8,9,17-22] (Table XI) of metallocycles with a metal-O-C-N-N ring having varying degrees of saturation and substitution. In spite of this variety, there is still no reported structure of a dibenzoyldiazene complex in which distances found are indicative of an N=N bond. Dibenzoyldiazene and other similar disubstituted diazenes are potentially bridging, bidentate ligands with one metal bound to N(1) and O(2) while the second metal is bound to N(2) and O(1). This is a likely structure for the reported[6] rhodium complex. There would thus be two Rh(I) rather than the two Rh(0) atoms, and the complex would still be symmetric as indicated by spectroscopy. These and other related systems are currently under investigation.

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Registry No. $Pt[P(C_6H_5)_3]_2[C_6H_5CONNCOC_6H_5]\cdot C_2H_5OH$, 41202-93-1.

Supplementary Material Available. Tables V and VI, showing structure factor amplitudes and root-mean-square amplitudes of vibration, 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-73-2290.

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Structure of Tetrahydridotetrakis(methyldiphenylphosphine)molybdenum(IV)

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The molecular and crystal structures of tetrahydridotetrakis(methyldiphenylphosphine)molybdenum(IV), $H_4Mo[CH_3P(C_6H_5)_2]_4$, have been determined from counter data by single-crystal X-ray techniques. The coordination polyhedron around the eight-coordinate molybdenum atom is a somewhat distorted variant of the D_{2d}-$\bar{4}2m$ dodecahedron with hydrogen atoms forming an elongated tetrahedron (A sites) and phosphorus atoms a flattened tetrahedron (B sites). The molecular structure has no imposed symmetry but nearly has idealized $C_2(2)$ point symmetry leading to two Mo–P distances (2.433 (2) and 2.503 (8) Å). All four hydride hydrogen atoms were located and refined giving an average Mo–H distance of 1.70 (3) Å. The ligand selection of the A and B sites as well as the distortion of the coordination polyhedra appear to arise from interligand steric factors. The MoP_4 coordination is midway between a regular tetrahedron and a square-planar configuration. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions of $a = 12.174$ (4), $b = 22.057$ (9), $c = 19.642$ (11) Å, and $\beta = 119.68$ (4)°. The density for four molecules per cell is 1.31 g/cm³. The final R value is 0.071 after least-squares refinement with 3667 reflections.

Introduction

Eight-coordinate complexes are becoming quite commonplace, yet their stereochemistry is not well understood. A half-dozen or so different coordination geometries have been considered for discrete eight-coordinate complexes, and X-ray structures have established the existence of several of these in the solid state. The whole area of eight-coordinate complexes has been reviewed extensively.[1-6]

Many of the systematics with respect to structures in this area are due to Hoard, *et al.*,[7-10] the basic analysis by Hoard and Silverton being most notable.[5] The metal–ligand coordination in eight-coordinate complexes is dominated by the D_{4d}-$\bar{8}2m$ square antiprism and D_{2d}-$\bar{4}2m$ dodecahedron. Both polyhedra appear to be about equally acceptable for an MX_8 complex from the viewpoints of maximization of bonding,[5,11,12] minimization of repulsions,[4,5,13] or crystal-

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