Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Structural Studies of Triazenido Complexes. 2.[1] Monodentate Coordination of 1,3-Diphenyltriazenide in *cis*-Bis(triphenylphosphine)bis(1,3-diphenyltriazenido)platinum(II) Benzene Solvate, *cis*-$[Pt(C_6H_5N_3C_6H_5)_2(P(C_6H_5)_3)_2]\cdot C_6H_6$

LEO D. BROWN and JAMES A. IBERS*

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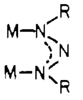
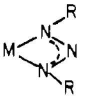
The structure of *cis*-bis(triphenylphosphine)bis(1,3-diphenyltriazenido)platinum(II) benzene solvate has been determined crystallographically. The square-planar platinum complex is the first definitive example of the monodentate bonding mode for the triazenido ligand. The two crystallographically independent diphenyltriazenido ligands show good agreement in their bond lengths and angles. The average Pt–N distance is 2.089 (6) Å with average N–N lengths of 1.336 (6) Å for the bond adjacent to the Pt and 1.278 (6) Å for the bond away from the metal atom; the N–N–N angle averages 113.9 (5)°. A comparison is made with other reported structures of triazenido complexes. The red-orange crystals of the platinum complex belong to space group $P2_1/n$ with $a = 10.797$ (1), $b = 23.048$ (3), $c = 22.034$ (3) Å; $\beta = 91.08$ (1)°; $V = 5482$ Å^3; $Z = 4$; $\rho_{\text{calcd}} = 1.44$, $\rho_{\text{obsd}} = 1.43$ g cm^{-3}. The intensity data were collected by counter methods. The structure refined to a conventional R index of 0.045 for the 7923 independent data for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

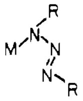
Great interest in the bonding properties of the triazenido ligand has developed in the past few years. The triazenido group may act as a bridging ligand between two metal centers (I), a bidentate group (II), or a monodentate ligand (III).



I



II



III

Whereas the bridging and bidentate bonding modes have been studied extensively and numerous structures reported,[1-13] the monodentate form has until now eluded structural characterization. Monodentate bonding for the triazenido ligand was first suggested in 1959 to account for the properties of some Pd(II) complexes.[14] Recently, on the basis of ir spectral data, Robinson and co-workers[15] categorized a series of triazenido complexes of the platinum metals as bidentate (class A, II) and monodentate (class B, III). This infrared basis for the structural assignment is the subject of some dispute.[16] In order to establish definitively the bonding mode in these "class B" complexes, we have undertaken the x-ray crystal structure of one of them, *cis*-$Pt(dpt)_2(PPh_3)_2$ (dpt = 1,3-diphenyltriazenido, Ph = C_6H_5). Our results provide the first reported example of the monodentate mode of bonding for the triazenido ligand.[17]

Experimental Section

The platinum triazenido complex was prepared by literature methods.[15a] Red-orange crystals of the cis isomer were slowly deposited from the benzene reaction mixture by addition of methanol. Elemental analysis (C, H, N) of the crystals suggested the presence of a benzene of solvation (later found in the structure analysis). Anal. Calcd for $C_{66}H_{56}N_6P_2Pt$: C, 66.60; H, 4.74; N, 7.06. Found: C, 66.67; H, 4.46; N, 6.98.

Precession and Weissenberg photographs displayed Laue symmetry $2/m$ and systematic absences $0k0$, $k \neq 2n$, and $h0l$, $h + l \neq 2n$, consistent with space group C_{2h}^5-$P2_1/n$. The crystal chosen for the intensity data collection was attached to a glass fiber approximately along the crystallographic a axis. The crystal was a parallelepiped bounded by {001}, {010}, and {100}. The angle settings of 18 hand-centered reflections on a Picker FACS-I automated diffractometer (Cu Kα_1 radiation and in the range $95° > 2\theta > 85°$) were used in a least-squares analysis[18] for determination of the cell constants. Table I lists the refined cell constants and other information about the crystal.

Table I. Crystal Data for *cis*-$[Pt(dpt)_2(PPh_3)_2]\cdot C_6H_6$

Mol formula	$C_{66}H_{56}N_6P_2Pt$
Formula wt	1190.26 amu
Cell constants^a	$a = 10.797$ (1) Å $b = 23.048$ (3) Å $c = 22.034$ (3) Å $\beta = 91.08$ (1)° $V = 5482$ Å^3
Space group	C_{2h}^5-$P2_1/n$
Z	4
Density	1.44 (calcd), 1.43 (exptl) g cm^{-3}
Crystal dimensions	0.519 × 0.279 × 0.467 mm
Crystal vol	6.12 × 10^{-2} mm^3
Absorption coeff, μ^a	57.44 cm^{-1}

^{a} Cu Kα_1 (λ 1.540 562 Å) at 22 °C ambient temperature.

The intensity data were collected in the θ–2θ scan mode using Ni-filtered Cu Kα radiation. The takeoff angle was 3.4°. The counter was situated 32 cm from the crystal with an aperture setting 2.4 mm high and 2.6 mm wide. The scan rate was 2°/min from 0.65° below the Kα_1 peak to 0.65° above the Kα_2 peak. Stationary-crystal, stationary-counter background counts of 10 s each were taken at the beginning and end of each scan. Copper foil attenuators were automatically inserted if the counting rate approached 7000 counts/s. During data collection the intensities of six standard reflections were measured after every 100 reflections. No significant variation was observed in the standards throughout the data collection. Unique data were collected out to $2\theta = 125°$, past which point relatively few were strong. The processing of the data was carried out as described previously[18] using a value of p of 0.04. Of the 9566 data that were collected, 7923 independent reflections were found to have intensity above background ($I_o > 3\sigma(I_o)$) and were used in the subsequent solution and refinement of the structure.

The structure was solved by standard Patterson and difference Fourier techniques.[19] The position of the platinum atom was easily found from a three-dimensional, origin-removed, sharpened Patterson map. Additional least-squares and difference Fourier calculations revealed the positions of the remaining nonhydrogen atoms. In the full-matrix least-squares refinements the function minimized is $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $w = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors used in all calculations were taken from the usual source.[20] Anomalous dispersion terms for the platinum and phosphorus atoms are those of Cromer and Liberman.[21] The ten phenyl rings in the complex and the benzene of crystallization were refined as rigid groups[22] (D_{6h} symmetry, C–C = 1.395 Å) with isotropic thermal parameters assigned to the individual group atoms. With all of the isotropic nonhydrogen atoms present, the structure refined to $R = 0.074$ and $R_w = 0.119$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of *cis*-$[Pt(C_6H_5N_3C_6H_5)_2(P(C_6H_5)_3)_2]\cdot C_6H_6$

ATOM	X^A	Y	Z	B11^B	B22	B33	B12	B13	B23
PT	0.655634(19)	0.253421(8)	0.568458(10)	52.87(32)	13.35(7)	13.33(8)	0.92(6)	0.45(10)	0.95(3)
P(1)	0.50732(13)	0.287078(61)	0.632204(60)	63.0(12)	17.27(27)	14.40(26)	3.10(45)	1.86(45)	0.03(22)
P(2)	0.53275(15)	0.242037(59)	0.482648(74)	58.6(13)	16.31(27)	14.13(32)	0.10(43)	0.15(51)	0.59(21)
N(1)	0.77586(58)	0.25114(17)	0.64380(27)	74.5(55)	17.8(12)	16.0(13)	2.3(14)	-5.0(21)	2.19(71)
N(2)	0.78157(42)	0.20504(20)	0.68026(20)	69.7(44)	18.4(10)	16.6(10)	2.2(17)	-2.7(16)	1.6(8)
N(3)	0.70277(45)	0.16512(20)	0.66725(21)	88.5(50)	18.5(10)	17.8(11)	0.3(18)	2.0(18)	2.4(8)
N(4)	0.80822(42)	0.23570(20)	0.51469(21)	50.4(39)	16.3(8)	16.4(11)	-1.5(15)	6.3(16)	0.8(8)
N(5)	0.85359(39)	0.27771(20)	0.47954(20)	56.6(40)	16.8(9)	17.2(10)	-2.5(15)	2.9(16)	1.6(8)
N(6)	0.79452(41)	0.32536(19)	0.48363(20)	67.1(42)	15.2(9)	19.3(11)	3.1(15)	1.9(17)	1.45(77)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table III. Derived Parameters for the Rigid-Group Atoms of *cis*-$[Pt(C_6H_5N_3C_6H_5)_2(P(C_6H_5)_3)_2]\cdot C_6H_6$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
PH1C1	0.85406(35)	0.29692(14)	0.66319(17)	3.45(10)	PH6C4	0.44481(46)	0.48234(13)	0.59890(23)	6.45(17)
PH1C2	0.87589(39)	0.34192(18)	0.62241(14)	4.60(12)	PH6C5	0.54229(40)	0.45329(17)	0.57145(20)	5.86(16)
PH1C3	0.95390(44)	0.38767(16)	0.63916(18)	5.84(15)	PH6C6	0.55764(33)	0.39377(18)	0.58032(19)	4.45(12)
PH1C4	1.01009(40)	0.38843(16)	0.69669(21)	6.01(16)	PH7C1	0.36202(33)	0.24738(15)	0.63276(22)	3.66(12)
PH1C5	0.98827(41)	0.34343(19)	0.73747(15)	5.23(14)	PH7C2	0.36876(35)	0.18886(16)	0.64862(22)	4.94(13)
PH1C6	0.91025(40)	0.29768(16)	0.72071(16)	4.46(12)	PH7C3	0.26120(46)	0.15538(14)	0.64981(23)	6.13(16)
PH2C1	0.71730(44)	0.11648(16)	0.70679(20)	4.21(11)	PH7C4	0.14689(36)	0.18043(21)	0.63512(26)	7.18(20)
PH2C2	0.79151(44)	0.11662(19)	0.75930(22)	6.67(18)	PH7C5	0.14015(32)	0.23895(22)	0.61926(26)	6.35(18)
PH2C3	0.80122(48)	0.06670(25)	0.79488(19)	7.82(22)	PH7C6	0.24771(41)	0.27243(14)	0.61808(23)	4.96(13)
PH2C4	0.73671(55)	0.01664(20)	0.77793(23)	7.25(19)	PH8C1	0.60533(39)	0.24553(17)	0.40743(16)	3.86(12)
PH2C5	0.66250(50)	0.01649(17)	0.72541(25)	6.97(19)	PH8C2	0.69138(40)	0.20252(15)	0.39386(17)	4.17(11)
PH2C6	0.65280(42)	0.06641(21)	0.68984(18)	5.73(15)	PH8C3	0.74931(38)	0.20265(17)	0.33780(20)	5.26(14)
PH3C1	0.87642(34)	0.18325(13)	0.51274(17)	3.20(9)	PH8C4	0.72118(46)	0.24579(20)	0.29532(17)	6.20(20)
PH3C2	0.98582(37)	0.17804(16)	0.48050(18)	4.89(13)	PH8C5	0.63512(47)	0.28879(18)	0.30890(18)	5.92(16)
PH3C3	1.05403(33)	0.12669(19)	0.48351(21)	6.02(16)	PH8C6	0.57720(38)	0.28867(15)	0.36495(20)	4.73(13)
PH3C4	1.01284(40)	0.08053(15)	0.51877(22)	5.73(15)	PH9C1	0.39931(28)	0.29029(14)	0.47465(17)	3.14(9)
PH3C5	0.90344(41)	0.08573(14)	0.55102(19)	5.19(14)	PH9C2	0.27757(33)	0.27011(12)	0.47594(18)	3.80(10)
PH3C6	0.83523(31)	0.13709(17)	0.54800(17)	4.20(11)	PH9C3	0.17916(25)	0.30910(17)	0.47048(20)	4.52(12)
PH4C1	0.84439(35)	0.36820(14)	0.44372(16)	3.58(10)	PH9C4	0.20248(32)	0.36825(15)	0.46373(20)	5.15(14)
PH4C2	0.84609(39)	0.42520(17)	0.46502(14)	4.66(13)	PH9C5	0.32421(38)	0.38843(12)	0.46244(20)	5.29(14)
PH4C3	0.89644(43)	0.46921(13)	0.42972(19)	5.27(14)	PH9C6	0.42263(28)	0.34944(15)	0.46790(19)	4.35(12)
PH4C4	0.94510(42)	0.45623(15)	0.37311(18)	5.08(14)	PH10C1	0.47221(35)	0.16836(13)	0.47879(16)	3.26(9)
PH4C5	0.94340(41)	0.39924(18)	0.35180(14)	5.34(14)	PH10C2	0.48515(38)	0.13172(17)	0.52890(14)	4.24(11)
PH4C6	0.89305(39)	0.35522(13)	0.38711(17)	4.16(11)	PH10C3	0.43642(43)	0.07533(16)	0.52624(16)	5.77(15)
PH5C1	0.55508(40)	0.29297(17)	0.71259(15)	3.51(10)	PH10C4	0.37874(43)	0.05558(13)	0.47348(20)	5.64(15)
PH5C2	0.60315(44)	0.34577(14)	0.73312(18)	5.05(13)	PH10C5	0.36580(40)	0.09222(17)	0.42336(16)	5.36(14)
PH5C3	0.64634(47)	0.35117(15)	0.79293(20)	6.37(17)	PH10C6	0.41253(38)	0.14861(16)	0.42602(14)	4.09(11)
PH5C4	0.64146(49)	0.30378(20)	0.83219(15)	6.01(16)	PH11C1	0.92332(65)	-0.00325(44)	0.30507(47)	13.36(42)
PH5C5	0.59339(54)	0.25099(16)	0.81166(19)	4.88(16)	PH11C2	0.91466(72)	0.03069(44)	0.35724(43)	12.08(38)
PH5C6	0.55020(48)	0.24558(13)	0.75185(20)	4.70(15)	PH11C3	0.7989(10)	0.04816(37)	0.37750(32)	13.32(41)
PH6C1	0.47551(38)	0.36331(13)	0.61603(19)	3.96(11)	PH11C4	0.69170(66)	0.03168(40)	0.34560(44)	12.06(36)
PH6C2	0.37803(35)	0.39237(19)	0.64407(19)	5.14(14)	PH11C5	0.70036(71)	-0.00226(39)	0.29344(41)	10.33(31)
PH6C3	0.36268(38)	0.45189(19)	0.63521(21)	6.22(17)	PH11C6	0.8162(10)	-0.01973(36)	0.27317(33)	12.65(38)

RIGID GROUP PARAMETERS

GROUP	X$_C^A$	Y$_C$	Z$_C$	DELTA^B	EPSILON	ETA
PH1	0.93208(26)	0.34267(12)	0.67994(13)	-2.7926(55)	-2.0365(26)	-0.5992(56)
PH2	0.72701(30)	0.06656(15)	0.74236(15)	2.2287(40)	2.4706(31)	-0.7974(40)
PH3	0.94463(26)	0.13189(12)	0.51576(12)	2.0968(28)	-2.4623(27)	-0.0484(31)
PH4	0.89475(24)	0.41222(12)	0.40841(12)	-2.8370(36)	2.3458(23)	0.9400(37)
PH5	0.59827(28)	0.29838(12)	0.77239(14)	2.8989(33)	-2.9654(24)	-1.2630(29)
PH6	0.46016(27)	0.42283(13)	0.60776(13)	-1.5541(30)	2.5024(28)	0.1725(33)
PH7	0.25445(30)	0.21390(13)	0.63394(14)	0.5961(25)	2.8699(31)	-0.0357(32)
PH8	0.66325(27)	0.24566(12)	0.35138(14)	0.5556(29)	2.8849(23)	1.9627(31)
PH9	0.30089(25)	0.32927(11)	0.46919(11)	-0.7082(20)	3.0559(26)	0.0721(25)
PH10	0.42547(24)	0.11197(12)	0.47613(12)	2.7713(25)	-3.1767(22)	1.9399(27)
PH11	0.80751(53)	0.01422(24)	0.32534(25)	2.401(10)	2.2809(57)	-2.598(9)

[A] X$_C$, Y$_C$, AND Z$_C$ ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

With the correct formulation of the compound definitely established, the intensity data were corrected for absorption. The average transmission factor for the data was 0.228 with individual values ranging from 0.080 to 0.318 (μ = 57.44 cm^{-1} for Cu Kα radiation). The nine nongroup atoms were refined with anisotropic thermal parameters in the subsequent least-squares cycle. Before proceeding with the final calculations, the fixed contribution of the hydrogen atoms was calculated. The positions of the phenyl hydrogen atoms were determined from the corresponding positions of the carbon atoms assuming D_{6h} symmetry and a C–H bond distance of 0.95 Å. Each of the 56 hydrogen atoms was given a fixed isotropic thermal parameter 1 Å^2 greater than the carbon atom to which it is attached. During

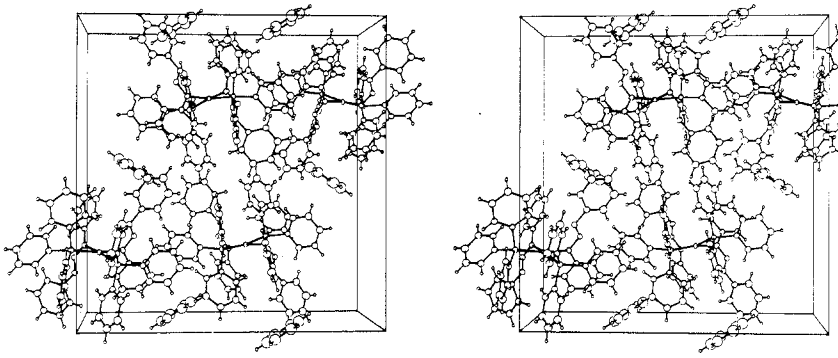


Figure 1. Stereoview of the unit cell of *cis*-[Pt(dpt)$_2$(PPh$_3$)$_2$]·C$_6$H$_6$. The *x* axis is perpendicular to the plane of the paper going away from the reader, the *y* axis is vertical, and the *z* axis is horizontal and to the right. The atoms are drawn at 20% probability contours of thermal motion. For clarity the hydrogen atoms have been arbitrarily assigned a small thermal parameter of 1 Å^2.

Table VI. Interatomic Distances (Å) and Angles (deg) in *cis*-Pt(dpt)$_2$(PPh$_3$)$_2$

Bonding Distances			
Pt-P(1)	2.286 (1)	P(2)-PH10C1	1.821 (3)
Pt-P(2)	2.304 (2)	N(1)-PH1C1	1.413 (6)
Pt-N(1)	2.089 (6)	N(3)-PH2C1	1.427 (6)
Pt-N(4)	2.088 (5)	N(4)-PH3C1	1.417 (6)
P(1)-PH5C1	1.840 (4)	N(6)-PH4C1	1.434 (6)
P(1)-PH6C1	1.822 (3)	N(1)-N(2)	1.333 (6)
P(1)-PH7C1	1.816 (4)	N(4)-N(5)	1.339 (6)
P(2)-PH8C1	1.848 (4)	N(2)-N(3)	1.282 (6)
P(2)-PH9C1	1.826 (4)	N(5)-N(6)	1.274 (6)
Nonbonding Distances			
Pt-N(2)	3.006 (4)	Pt-N(6)	2.932 (4)
Pt-N(3)	3.016 (5)	N(1)-N(3)	2.199 (6)
Pt-N(5)	2.980 (4)	N(4)-N(6)	2.181 (6)
Bond Angles			
P(1)-Pt-P(2)	98.26 (5)	PH6C1-P(1)-PH7C1	109.1 (2)
P(1)-Pt-N(1)	87.3 (2)	PH8C1-P(2)-PH9C1	103.5 (2)
P(1)-Pt-N(4)	170.0 (1)	PH8C1-P(2)-PH10C1	99.0 (2)
P(2)-Pt-N(1)	171.5 (1)	PH9C1-P(2)-PH10C1	106.4 (2)
P(2)-Pt-N(4)	87.7 (1)	Pt-N(1)-N(2)	121.3 (4)
N(1)-Pt-N(4)	87.8 (2)	Pt-N(4)-N(5)	119.2 (3)
Pt-P(1)-PH5C1	115.4 (1)	Pt-N(1)-PH1C1	125.5 (3)
Pt-P(1)-PH6C1	110.1 (1)	Pt-N(4)-PH3C1	126.9 (3)
Pt-P(1)-PH7C1	116.6 (1)	PH1C1-N(1)-N(2)	113.1 (5)
Pt-P(2)-PH8C1	118.9 (1)	PH3C1-N(4)-N(5)	113.8 (4)
Pt-P(2)-PH9C1	116.8 (1)	N(1)-N(2)-N(3)	114.5 (5)
Pt-P(2)-PH10C1	110.2 (1)	N(4)-N(5)-N(6)	113.2 (4)
PH5C1-P(1)-PH6C1	99.1 (2)	N(2)-N(3)-PH2C1	111.3 (4)
PH5C1-P(1)-PH7C1	104.9 (2)	N(5)-N(6)-PH4C1	110.8 (4)

Table VII. Selected Weighted Least-Squares Planes in *cis*-Pt(dpt)$_2$(PPh$_3$)$_2$

$Ax + By + Cz = D^a$

Plane	*A*	*B*	*C*	*D*
1	2.226	21.707	−5.936	3.586
2	7.565	−10.072	−12.717	−4.821
3	6.475	6.606	16.210	15.134

Distances (Å) of Various Atoms from the Planes

Atom	Plane 1	Plane 2	Plane 3
Pt	0.002 (2)	0.0000 (2)	0.0000 (2)
P(1)	0.022 (1)		
P(2)	−0.011 (1)		
N(1)	−0.229 (4)	−0.026 (6)	
N(2)		0.018 (5)	
N(3)		−0.010 (5)	
N(4)	0.274 (5)		−0.0008 (48)
N(5)			0.0009 (44)
N(6)			−0.0005 (45)

Dihedral Angles between Planes

plane 1-plane 2 = 96.7°
plane 1-plane 3 = 78.8°
plane 2-plane 3 = 97.3°

[a] Monoclinic coordinates.

the final cycle of least-squares refinement, an isotropic extinction parameter was varied. This extinction parameter refined to 2.28 (15) × 10^{-6} e^{-2}. The agreement indices after the final least-squares refinement (7923 independent observations, 215 variables) are R = 0.045 and R_w = 0.078. On the final difference Fourier map the 25 highest peaks (ranging from 0.57 to 1.07 e/Å^3) are associated with the carbon atoms of the phenyl rings. A typical carbon atom had a height of 4.5 e/Å^3. The error in an observation of unit weight is 3.14 electrons. Of the 1116 unobserved reflections, 47 have $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$; of these, 14 have $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$.

The final positional and thermal parameters for the nongroup atoms along with their estimated standard deviations are given in Table II. Table III lists the positional and orientation parameters for the eleven rigid groups. The root-mean-square amplitudes of vibration for the anisotropic atoms are given in Table IV.[23] The idealized positions of the hydrogen atoms are given in Table V.[23] A listing of the observed and calculated structure amplitudes is also available.[23]

Description of the Structure and Discussion

The unit cell contains four discrete *cis*-Pt(dpt)$_2$(PPh$_3$)$_2$ molecules and four benzene molecules of solvation. A stereoscopic view of the molecular packing is shown in Figure 1. The four-coordinate platinum complex has a square-planar geometry with both of the adjacent dpt ligands bound to the metal through only one nitrogen atom. An overall view of the complex is depicted in Figure 2. The two triazenido ligands take up the sterically favored positions above and below the PtP$_2$N$_2$ plane. This is best illustrated in the view of the inner coordination geometry (Figure 3). Interatomic distances and angles, along with standard deviations as estimated from the inverse matrix, are listed in Table VI.

The distances and angles found in the two cis triphenylphosphine ligands are typical for platinum(II) square-planar complexes.[24-26] The two Pt-P distances of 2.286 (1) and 2.304 (2) Å appear to be significantly different. On the basis of the observed variation in the P-C distances, however, these standard deviations may be somewhat underestimated. On the other hand, there is excellent agreement among the chemically equivalent bond distances in the two dpt ligands, as described below.

The monodentate configuration of both of the dpt ligands is observed for the first time in the structure reported here. The corresponding bond distances and angles for the two crystallographically independent dpt ligands agree very well. The Pt-N(1) and Pt-N(4) bond lengths average 2.089 (6) Å. The two nitrogen atoms not coordinated to the platinum atom have equal Pt-N nonbonded distances in the first dpt ligand (3.006 (4) and 3.016 (5) Å) and have nearly equal values in the second dpt ligand (2.980 (4) and 2.932 (4) Å). In addition, both Pt-N-N-N moieties are essentially planar. The parameters for the weighted least-squares planes are given in Table VII. Of particular interest are the N-N bond lengths

Table VIII. Reported Structures of Triazenido Complexes

Compd[a]	Bonding mode	N-N, Å	N-N-N, deg	M-N, Å	Ref
$Cu_2(dpt)_2$	Bridging	1.30 (3)	115.8 (20)	1.92 (2)	2
$[Cu(dmt)]_4$	Bridging	1.29 (4)	116.0 (3)	1.87 (3)	3
$Ni_2(dpt)_4$	Bridging	1.313 (16)	116.5 (9)	1.916 (25)	4, 5
$Pd_2(dpt)_4$	Bridging	1.313 (5)	117.6 (5)	2.041 (18)	5
$Cu_2(dpt)_4$	Bridging	1.296 (4)	117.1 (7)	2.02	5
$Zn_4O(dpt)_6$	Bridging	1.310 (18)	117.0 (15)	2.040 (13)	6
$[Pd(dtt)(allyl)]_2$	Bridging	1.300 (7)	116.8 (6)	2.109 (6)	7
$RhCuCl(dmt)(CO)(PPh_3)_2$	Bridging	1.26 (2)	119 (2)	2.14 (1), 1.91 (2)	8
$[Pd(dmt)(methallyl)]_2$	Bridging	1.343 (9) 1.281 (8)	118.3 (6)	2.116 (6)	9
$[Co(dpt)_3]\cdot C_6H_5CH_3$	Bidentate	1.32 (1)	103.6 (7)	1.93 (1)	10, 11
$Co(dpt)_3$	Bidentate	1.311 (7)	103.2 (7)	1.919 (5)	12
$Mo(dfpt)(C_5H_5)(CO)_2$	Bidentate	1.31 (1)	100.8 (7)	2.120 (9)	13
trans-$RuH(dtt)(CO)(PPh_3)_2$	Bidentate	1.314 (4)	105.2 (3)	2.149 (3) 2.179 (3)	1
cis-$[Pt(dpt)_2(PPh_3)_2]\cdot C_6H_6$	Monodentate	1.336 (6) 1.278 (6)	113.9 (5)	2.089 (6)	This work

[a] dpt = 1,3-diphenyltriazenido, dtt = 1,3-di-*p*-tolyltriazenido, dmt = 1,3-dimethyltriazenido, dfpt = 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-triazenido

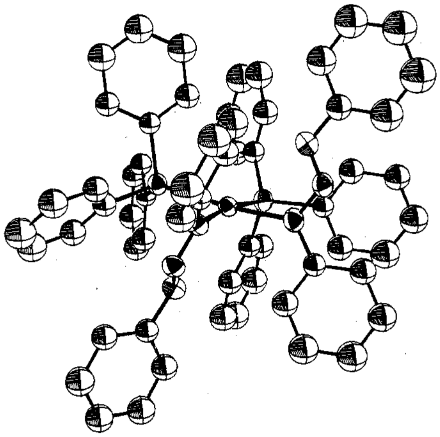


Figure 2. Overall view of the *cis*-$[Pt(dpt)_2(PPh_3)_2]$ complex. The thermal ellipsoids in this and the following figure are drawn at the 50% probability level.

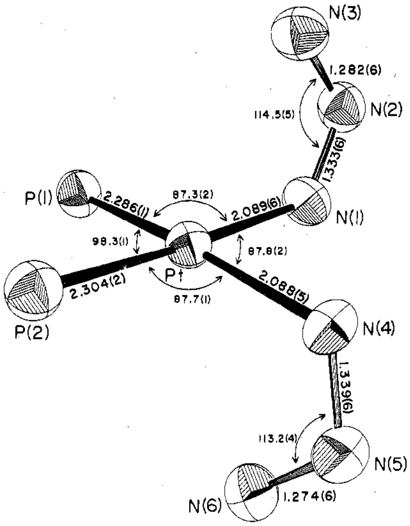


Figure 3. View of the inner coordination geometry about the platinum atom.

in the triazenido groups. The bond adjacent to the metal in both ligands is significantly longer (1.336 (6) Å, average) than the N–N bond away from the metal (1.278 (6) Å, average). The lower bond order in the adjacent N–N bond is consistent with a sizable contribution of the canonical "single–double bond" model (see structure III) to the delocalized triazenido bonding system.

In bidentate triazenido complexes the entire ligand is nearly planar with dihedral angles between the planes of the rings ranging from 5 to as much as 30°.[1,10,12] In the platinum triazenido complex the phenyl rings of the two monomeric dpt ligands are in different conformations. In the first ligand the planes of the two phenyl rings differ by 15.3°. In the second dpt ligand the phenyl ring attached to the uncoordinated nitrogen atom is twisted 43.2° with respect to the other ring (the dihedral angle between the Ru–N–N–N moiety and the ring bound to the coordinated nitrogen atom is 7.1°). The monodentate bonding mode allows a greater freedom in the conformation of the phenyl rings; the energy differences between these conformations must be small.

Selected parameters for all reported structures of triazenido complexes are presented in Table VIII. The majority of these compounds have the triazenido ligand bridging two metal centers. The structural change in the triazenido moiety for the three different modes of bonding is best illustrated by the change in the N–N–N angle. Whereas this angle averages 117° in the bridging mode, values of 105° or less are reported for the bidentate mode in which a strained four-membered $\overline{M{-}N{-}N{-}N}$ ring is present. For the monodentate triazenido complex reported here, the average N–N–N angle of 113.9 (5)° is significantly different from that found in either of the other bonding modes. In the bidentate mode this angle is greatly reduced to enable chelation to a single metal atom. In the bridging mode the N–N–N angle is opened slightly to accommodate the coordination to two different metal atoms. The intermediate value of the angle found for the monodentate mode, as expected, is comparable with that reported for the free 1,3-diphenyltriazene molecule.[27]

Since in the present compound not all of the bonding capabilities of the triazenido ligand are utilized, one might expect interesting reaction chemistry with suitable coordinatively unsaturated metal systems. Moreover, it is clear that the triazenido ligand, in common with its isoelectronic counterparts, must take part in a varied reaction and structural chemistry that has been investigated only modestly to date.

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Registry No. *cis*-$[Pt(dpt)_2(PPh_3)_2]\cdot C_6H_6$, 60251-47-0.

Supplementary Material Available: Table IV, the root-mean-square amplitudes of vibration, Table V, the idealized positions of the hydrogen atoms, and a listing of the observed and calculated structure amplitudes (56 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201,
and the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Studies on the Reactions of Carbon Dioxide with Transition Metal Complexes. Preparation and Structure of μ-Carbonato-pentakis(triphenylphosphine)dirhodium–Benzene

STEPHEN KROGSRUD,[1a] SANSHIRO KOMIYA,[1b] TAKASHI ITO,[1b] JAMES A. IBERS,*[1a]
and AKIO YAMAMOTO*[1b]

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The rhodium–hydrido complex $RhH(PPh_3)_4$ (Ph = C_6H_5) in toluene reacts with carbon dioxide at room temperature to give, on crystallization from benzene, red crystals of $Rh_2(CO_3)(PPh_3)_5 \cdot C_6H_6$, as characterized by diffraction methods. One mole of CO_2 per mole of the complex is evolved on thermolysis and acidolysis of the complex and by treatment with methyl iodide and triphenyl phosphite. The compound crystallizes in space group C_i^1-$P\bar{1}$ with four formula units in the cell. The unit cell has dimensions of $a = 22.518$ (9) Å, $b = 28.051$ (12) Å, $c = 12.841$ (7) Å, $\alpha = 96.12$ (3)°, $\beta = 97.91$ (3)°, $\gamma = 92.66$ (3)°, and $V = 7972$ Å^3. The observed density of 1.39 (1) g cm^{-3} is in good agreement with that of 1.38 g cm^{-3} calculated for four $Rh_2(CO_3)(PPh_3)_5 \cdot C_6H_6$ formula units per cell. There are thus two independent dimeric molecules in the cell. Refinement by full-matrix least-squares methods using 12330 observations for which $F_o^2 \geq 3\sigma(F_o^2)$ yielded a conventional agreement index of 0.079. Each independent molecule of the compound was found to consist of two Rh atoms, both having square-planar coordination and linked by a planar carbonato ligand. Two oxygen atoms of the carbonate group are coordinated to one Rh atom while the remaining carbonato oxygen atom is bound to the second Rh atom. Triphenylphosphine ligands fill out the four-coordinate geometry of each Rh atom. The bidentate coordination of the carbonato group to the metal atom creates a four-membered ring. The average O–C–O angle involved in this ring is 115.9°, a slight decrease from the 120° value found in the free carbonate ion. The O–Rh–O angle of the four-membered ring averages 62.6°. No trend in the carbonato group C–O bond lengths is evident, the average value being 1.29 Å. The $^{31}P\{^1H\}$ NMR spectrum of the complex in benzene is compatible with the unsymmetrical binuclear structure consisting of two rhodium(I) nuclei coordinated respectively with two and three triphenylphosphine ligands, as found in the solid state.

Introduction

Recently much attention has been focused on the interaction of carbon dioxide with transition metal compounds as a step toward an efficient catalytic system of carbon dioxide fixation. For example, insertions of CO_2 into metal–hydrogen,[2–7] –carbon,[8–13] –nitrogen,[14] and –oxygen[15–17] bonds are known as well as the formation of CO_2-coordinated complexes.[10–12,18–23] Reactions of carbon dioxide with some rhodium complexes have been reported to produce CO_2-coordinated complexes, e.g., $Rh_2Cl_2(CO_2)(PPh_3)_5$[18] (Ph = C_6H_5), $Rh_2(CO_2)(CO)_2(PPh_3)_3$,[19] and $Rh(OH)(CO_2)(CO)(PPh_3)_2$.[20] Previously, we reported that the reaction of $RhH(PPh_3)_4$ with carbon dioxide afforded a red crystalline compound, to which, on the basis of its ir and Raman spectra and chemical behavior, a formula of $Rh_2H_2(CO_2)(PPh_3)_6$ was assigned.[5] By x-ray analysis, however, we now show that the compound in question contains not carbon dioxide but the carbonate moiety, as in the earlier case of two other suspected carbon dioxide complexes.[23–25] The crystallographic evidence indicates that the compound is in fact $Rh_2(CO_3)(PPh_3)_5 \cdot C_6H_6$. The present paper reports the preparation, characterization, and structure of this carbonato complex.

Experimental Section

All manipulations were carried out under deoxygenated dinitrogen or under a vacuum. Solvents were dried in the usual manner, distilled, and stored under a dinitrogen atmosphere.