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Structural Studies of Triazenido Complexes. 1. Crystal and Molecular Structure of *trans*-Bis(triphenylphosphine)carbonyl(1,3-di-*p*-tolyltriazenido)hydridoruthenium(II), *trans*-$[Ru(H)(CH_3C_6H_4N_3C_6H_4CH_3)(CO)(P(C_6H_5)_3)_2]$

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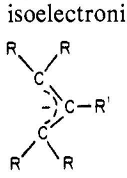
The structure of *trans*-bis(triphenylphosphine)carbonyl(1,3-di-*p*-tolyltriazenido)hydridoruthenium(II) has been determined from three-dimensional x-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with two molecules in the unit cell of dimensions $a = 14.074$ (2) Å, $b = 15.264$ (3) Å, $c = 12.195$ (2) Å, $\alpha = 109.78$ (1)°, $\beta = 111.74$ (1)°, $\gamma = 65.03$ (1)°, and $V = 2154$ Å^3; $\rho_{calcd} = 1.35$ and $\rho_{obsd} = 1.34$ g cm^{-3}. A full-matrix least-squares refinement of the structure by standard procedures resulted in an R index of 0.038 for the 5847 independent data for which $F_o^2 > 3\sigma(F_o^2)$. The coordination about the ruthenium atom is approximately octahedral. The triazenido ligand is coordinated to the metal atom in a bidentate mode with a N(1)–Ru–N(3) angle of 57.7 (1)° and a N(1)–N(2)–N(3) angle of 105.2 (3)°. The Ru–N(3) bond length is 2.179 (3) Å compared with the Ru–N(1) distance of 2.149 (3) Å. The N–N bond lengths within the triazenido moiety are equal with N(1)–N(2) and N(2)–N(3) distances of 1.318 (4) and 1.310 (4) Å, respectively. The entire ruthenium–triazenido system is essentially planar, indicative of π delocalization over the whole system.

Introduction

The study of transition metal complexes containing triazenido ligands has increased greatly in the last few years. Although isoelectronic with allyl (I), carboxylato (II), and amidino (III), the triazenido ligand (IV) had not received much interest compared with the former ligands. Owing to the fact that each of these anions is potentially either a two- or four-electron donor, much research has centered on the preferred bonding arrangement of the ligand in a given system.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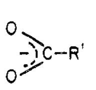
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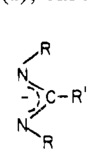
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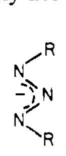
IV

As early as 1941, Dwyer and Mellor[1] proposed that 1,3-diphenyltriazenido (dpt) complexes of nickel contained bidentate triazenido ligands, resulting in a strained four-membered chelate ring. This formulation was later disputed[2] and ultimately shown to be incorrect. Structural studies of $[Ni(dpt)_2]_2$,[3,4] $[Cu(dpt)_2]_2$,[4] $[Pd(dpt)_2]_2$,[4] and $[Cu(dpt)]_2$[5] confirmed that the triazenide ligand actually bridges the metal centers in these compounds. The first compound to be shown to have a bidentate triazenide coordinated to a single metal atom was $Co(dpt)_3$.[6] The structures of two different crystalline forms have been reported (the first with toluene solvate[6,7] and the other unsolvated[8]), and both confirm the presence of the four-membered $\overline{\text{M–N–N–N}}$ ring. Very recently, synthetic work has been reported on organometallic complexes of second- and third-row transition metals containing triazenido ligands.[9-17] These workers have deduced both bridging and bidentate bonding modes for the triazenido ligand in these complexes. We present here the structure of one such complex, *trans*-$Ru(H)(dtt)(CO)(PPh_3)_2$[9a] (dtt = 1,3-di-*p*-tolyltriazenido, Ph = C_6H_5) in which the dtt ligand is coordinated to the metal in a bidentate fashion.[18]

Table I. Crystal Data for *trans*-$[Ru(H)(dtt)(CO)(PPh_3)_2]$

Mol formula	$C_{51}H_{45}N_3OP_2Ru$
Mol wt	878.96 amu
Cell constants[a]	$a = 14.074$ (2) Å $b = 15.264$ (3) Å $c = 12.195$ (2) Å $\alpha = 109.78$ (1)° $\beta = 111.74$ (1)° $\gamma = 65.03$ (1)° $V = 2154$ Å^3
Space group	C_i^1-$P\bar{1}$
Z	2
Density	1.35 (calcd), 1.34 (exptl) g cm^{-3}
Crystal dimensions	0.521 × 0.452 × 0.173 mm
Crystal vol	1.16×10^{-2} mm^3
Absorption coeff, μ[a]	40.29 cm^{-1}

[a] Cu Kα_1 (λ 1.540 562 Å) at 22 °C ambient temperature.

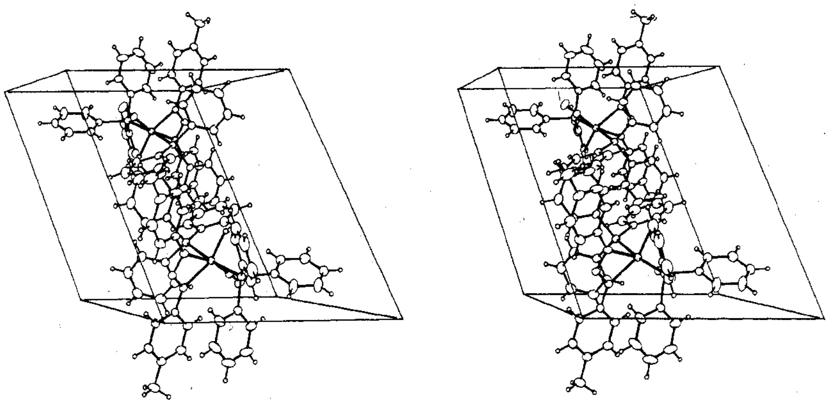

Figure 1. Stereoscopic drawing of the unit cell of *trans*-[Ru(H)(dtt)(CO)$(PPh_3)_2$]. The *x* axis is perpendicular to the plane of the paper going away from the reader; the *y* axis is vertical, and the *z* axis is horizontal and to the right. For the sake of clarity the hydrogen atoms have been assigned an arbitrarily small thermal motion of 1 Å^2. The thermal ellipsoids are drawn at the 20% probability level.

Experimental Section

Orange crystals of *trans*-Ru(H)(dtt)(CO)$(PPh_3)_2$ were obtained by recrystallization from a benzene–methanol solution of material kindly supplied by Dr. S. D. Robinson. An examination of the crystals by precession methods established that they belong to the triclinic system. The space group is C_i^1-$P\bar{1}$, as ultimately confirmed by the structure solution. The crystal used for intensity measurements was mounted on a glass fiber approximately along the crystallographic *b* axis. The 12 faces of the crystal were identified as belonging to {001}, {110}, {11$\bar{1}$}, {011}, {10$\bar{1}$}, and {010}. The lattice constants were determined by a least-squares analysis[19] of the angle settings of 18 hand-centered reflections on a Picker FACS-I diffractometer (λ(Cu Kα_1) 1.540 562 Å) in the range 55° > 2θ > 45°. The refined, reduced cell constants and other relevant crystal data are given in Table I.

Intensity data were measured in the θ–2θ scan mode on the Picker FACS-I using Ni-filtered Cu Kα radiation at a takeoff angle of 3.8°. The counter was positioned 32 cm from the crystal with an aperture 4.3 mm high and 4.3 mm wide. The reflections were scanned at 2°/min from 0.8° below the Kα_1 peak to 0.8° 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. Intensity data for $\pm h,-k,\pm l$ were collected out to 2θ = 120°. Past this point only about 5% of the data appeared to be above background. During the data collection the intensities of six standard reflections were measured after every 100 reflections. These standards showed no significant variations throughout the data collection.

The intensity data were processed as described previously[19] with the parameter *p* chosen as 0.04. Of the 6664 unique data collected, 5847 independent reflections were found with significant intensity ($I_o > 3\sigma(I_o)$) and were used in the subsequent solution and refinement of the structure.

The ruthenium atom and both phosphorus atoms were located from a Patterson synthesis. A least-squares refinement[20] of these three atoms followed by a difference Fourier synthesis located an additional fifteen atoms. The remainder of the nonhydrogen atoms were located in a subsequent difference Fourier map. 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 $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors and the anomalous dispersion terms were taken from the well-known sources.[21] The carbon atoms of the eight phenyl rings in the structure were refined as rigid groups[22] initially with individual isotropic thermal parameters (D_{6h} symmetry, C–C = 1.395 Å). With all of the nonhydrogen atoms included with isotropic thermal parameters, the structure refined to $R = 0.118$ and $R_w = 0.171$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$.

Before proceeding any further an absorption correction was applied to the intensity data. The transmission factors ranged from 0.375 to 0.671 (μ = 40.3 cm^{-1} for Cu Kα radiation). In the subsequent least-squares cycle the nongroup atoms were refined anisotropically. In the resulting Fourier map all of the phenyl and methyl hydrogen atoms were located. At the position of the hydrido ligand, however, two weak peaks were found that suggested a slight positional disorder between the hydrido and carbonyl ligands. In the difference Fourier map the electron density of the peak closer to the ruthenium atom was greater (0.83 e Å^{-3}) than the further peak (0.66 e Å^{-3}). This observation is consistent with a significant contribution of the hydrido ligand to the nearer peak. In the next least-squares cycle the total occupancy of the carbonyl ligand was constrained[23] to be 1.0 between the two ligand positions resulting in a 20% carbonyl for the two weak peaks (isotropic thermal motion) and an 80% carbonyl (anisotropic thermal motion) at its established position. Owing to the significant electron density of the hydrido ligand when compared with that of the 20% carbonyl group and also because of the expectation that the Ru–H vector is near to but not necessarily coincident with the Ru–C(2) vector, no further embellishments of the model of disorder were deemed fruitful. All of the hydrogen atoms were included in the final calculations as a fixed contribution. The positions of the phenyl hydrogens were uniquely determined from the phenyl carbon positions assuming ideal geometry and a C–H distance of 0.95 Å. The six methyl hydrogen atoms were ideally located by a least-squares fit based on the positions of the peaks found in the difference Fourier map. Each of the 44 hydrogen atoms was assigned an isotropic thermal parameter 1 Å^2 greater than the carbon atom to which it is attached. After an additional anisotropic least-squares cycle with the hydrogen contribution, agreement indices of $R = 0.066$ and $R_w = 0.101$ were obtained. On the difference Fourier map virtually all of the significant residual peaks (average peak height ~0.9 e Å^{-3}) were associated with the phenyl ring carbon atoms. Apparently some of the rings had significant librational motion not accounted for by the isotropic model. To remedy this problem the rigid-group atoms were allowed to refine with individual anisotropic thermal parameters.[20] The final full-matrix refinement (5847 independent observation, 436 variables) resulted in $R = 0.038$ and $R_w = 0.060$. The error in an observation of unit weight is 2.28 electrons. The largest peaks in the final difference Fourier synthesis were approximately 0.3 e Å^{-3} (equivalent to less than 10% of a carbon atom). Of the 577 unobserved reflections 13 were found to have $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$.

It is important to note that inclusion of anisotropic thermal motion for the carbon atoms of the phenyl groups, while improving the agreement indices and lowering the estimated standard deviations with concomitant increase in computing time, did not result in any significant shifts in the atoms of the inner coordination sphere. We conclude, therefore, that use of this more elaborate model is not generally justified.

The final positional and thermal parameters for the nonhydrogen atoms along with their estimated standard deviations are given in Table II. Table III lists the positional and orientation parameters for the eight rigid groups. The root-mean-square amplitudes of vibration for the anisotropic atoms are given in Table IV.[24] Table V gives the idealized positions of the hydrogen atoms.[24] A listing of the observed and calculated structure amplitudes is also available.[24]

Description of the Structure and Discussion

The crystal structure consists of discrete monomeric units of the ruthenium complex with no molecules of solvation. A stereoview of the contents of the triclinic unit cell is given in Figure 1. The geometry of the six-coordinate *trans*-

Table II. Positional and Thermal Parameters for the Nonhydrogen Atoms of trans-[$Ru(H)(CH_3C_6H_5N_3C_6H_5CH_3)(CO)(P(C_6H_5)_3)_2$]

ATOM	X[A]	Y	Z	B11[B] OR B, A^2	B22	B33	B12	B13	B23
RU	0.217394(21)	0.216205(19)	0.393247(23)	64.71(25)	49.78(21)	70.41(29)	-28.01(16)	16.91(18)	6.51(16)
P(1)	0.320697(73)	0.285726(67)	0.358331(80)	61.44(66)	50.32(56)	71.40(78)	-25.52(49)	10.55(57)	14.83(52)
P(2)	0.116532(77)	0.157648(69)	0.450879(83)	69.38(70)	51.46(56)	73.40(80)	-27.69(51)	17.99(59)	9.25(53)
N(1)	0.09097(24)	0.25221(22)	0.23289(28)	65.1(23)	46.4(18)	86.9(29)	-19.7(17)	21.8(21)	7.6(19)
N(2)	0.11933(24)	0.16694(21)	0.15659(27)	67.5(23)	48.2(18)	75.8(26)	-19.3(17)	17.9(20)	11.6(18)
N(3)	0.20819(23)	0.11098(21)	0.21969(26)	61.0(22)	49.1(18)	75.0(26)	-19.5(17)	16.5(20)	15.6(18)
C(1)	0.33976(39)	0.15412(35)	0.50513(43)	74.2(37)	58.5(30)	83.3(43)	-36.3(28)	16.6(33)	14.4(30)
O(1)	0.41672(30)	0.11394(32)	0.57264(37)	75.1(30)	107.7(34)	123.3(43)	-30.1(26)	-21.1(29)	70.1(33)
C(2)	0.1702(15)	0.3354(14)	0.4887(17)	3.99(38)					
O(2)	0.1374(17)	0.4150(16)	0.5470(20)	8.63(54)					
C(3)	-0.30633(43)	0.54963(44)	0.05701(66)	82.2(40)	103.2(43)	244.2(95)	-1.1(33)	32.7(50)	85.5(54)
C(4)	0.39257(45)	-0.29355(35)	-0.00703(51)	122.7(47)	61.7(30)	150.7(60)	-14.6(30)	51.3(44)	-1.5(34)
PH1C1[C]	-0.00592(17)	0.32441(15)	0.18573(23)	62.8(28)	50.3(23)	100.7(38)	-18.8(21)	24.2(26)	17.0(24)
PH1C2	-0.08090(22)	0.29977(16)	0.07845(23)	82.6(34)	67.5(28)	107.1(43)	-13.7(26)	11.7(31)	9.9(28)
PH1C3	-0.17800(21)	0.37271(23)	0.03713(23)	87.9(39)	99.2(40)	110.1(47)	-15.1(32)	0.8(34)	33.3(35)
PH1C4	-0.20012(18)	0.47029(19)	0.10309(29)	76.0(33)	72.9(31)	178.1(60)	-7.4(26)	40.2(37)	56.4(36)
PH1C5	-0.12514(23)	0.49494(13)	0.21038(28)	87.5(38)	50.2(25)	188.4(62)	-16.1(25)	45.1(40)	27.6(32)
PH1C6	-0.02804(20)	0.42200(18)	0.25170(22)	68.7(29)	50.4(24)	145.3(49)	-19.8(22)	23.2(30)	19.1(27)
PH2C1	0.25247(19)	0.01273(13)	0.15864(19)	60.7(26)	53.0(22)	74.1(31)	-18.8(20)	22.2(23)	14.5(21)
PH2C2	0.34315(19)	-0.04991(18)	0.22624(16)	68.7(29)	60.4(25)	90.2(36)	-24.0(22)	5.1(26)	15.7(25)
PH2C3	0.38842(17)	-0.14897(16)	0.17263(23)	68.9(30)	59.1(26)	122.8(46)	-13.5(23)	16.4(30)	23.9(28)
PH2C4	0.34302(21)	-0.18540(13)	0.05144(23)	79.6(32)	55.6(25)	115.1(43)	-14.3(23)	40.0(31)	14.5(27)
PH2C5	0.25234(22)	-0.12276(18)	-0.01616(16)	100.9(37)	69.6(29)	82.8(37)	-16.4(27)	27.6(30)	9.8(27)
PH2C6	0.20707(18)	-0.02370(17)	0.03744(19)	86.9(32)	60.7(25)	68.3(32)	-9.3(23)	15.8(26)	15.8(23)
PH3C1	0.41122(20)	0.33887(20)	0.49176(19)	67.2(27)	51.5(22)	82.0(34)	-28.2(21)	-2.4(24)	23.1(22)
PH3C2	0.49559(23)	0.35511(23)	0.47673(22)	90.0(35)	86.5(32)	120.5(48)	-51.7(29)	13.8(32)	13.9(32)
PH3C3	0.56103(21)	0.40127(25)	0.57543(30)	95.7(39)	99.5(38)	170.2(64)	-66.2(33)	-6.6(39)	24.2(40)
PH3C4	0.54208(25)	0.43119(25)	0.68917(24)	116.7(43)	93.9(38)	133.8(53)	-67.1(35)	-28.8(38)	32.2(36)
PH3C5	0.45770(29)	0.41495(27)	0.70421(18)	180.3(60)	133.9(47)	79.9(39)	-99.8(46)	-17.4(38)	22.0(34)
PH3C6	0.39227(22)	0.36878(24)	0.60550(22)	116.3(41)	100.2(36)	84.0(38)	-68.0(33)	-3.0(31)	20.3(30)
PH4C1	0.41669(19)	0.20063(17)	0.26769(23)	61.9(26)	61.3(24)	89.7(35)	-27.7(21)	17.4(24)	14.6(24)
PH4C2	0.47824(24)	0.10843(19)	0.29742(24)	96.4(36)	60.1(26)	123.8(46)	-22.5(25)	43.3(34)	14.9(28)
PH4C3	0.55362(24)	0.03939(17)	0.23403(31)	100.9(42)	71.9(32)	154.4(58)	-16.1(30)	51.7(41)	14.2(35)
PH4C4	0.56744(24)	0.06255(22)	0.14090(29)	93.5(41)	96.6(39)	136.5(56)	-28.8(33)	49.3(40)	-3.9(37)
PH4C5	0.50589(27)	0.15476(26)	0.11117(26)	101.0(42)	130.1(46)	131.8(52)	-23.2(36)	56.5(39)	41.1(40)
PH4C6	0.43051(23)	0.22380(19)	0.17457(27)	86.9(36)	96.5(35)	128.7(49)	-22.4(29)	39.5(35)	42.2(35)
PH5C1	0.24102(19)	8.39046(15)	0.28395(20)	59.7(26)	56.7(23)	79.3(32)	-24.3(20)	9.9(23)	23.2(22)
PH5C2	0.19294(22)	0.37350(16)	0.15962(19)	74.5(31)	80.1(29)	80.0(35)	-28.6(25)	13.9(26)	21.3(26)
PH5C3	0.12857(23)	0.45323(23)	0.10336(18)	86.1(36)	115.3(42)	97.5(41)	-29.6(32)	7.4(31)	48.3(35)
PH5C4	0.11228(23)	0.54991(19)	0.17144(28)	88.9(38)	91.8(36)	169.0(61)	-21.2(30)	5.3(38)	73.2(41)
PH5C5	0.16036(24)	0.56686(14)	0.29578(27)	92.9(38)	60.8(28)	159.4(57)	-26.3(27)	4.1(37)	44.0(33)
PH5C6	0.22473(22)	0.48714(18)	0.35204(18)	80.9(32)	60.4(26)	113.3(42)	-31.5(24)	4.0(29)	27.3(27)
PH6C1	-0.03221(15)	0.21223(19)	0.40807(25)	72.9(29)	75.2(28)	74.2(33)	-26.9(24)	22.7(25)	15.2(25)
PH6C2	-0.07670(23)	0.31145(19)	0.40042(28)	86.8(35)	83.8(32)	112.7(44)	-10.9(27)	42.5(32)	23.3(31)
PH6C3	-0.18932(25)	0.35777(20)	0.36918(31)	96.8(43)	114.7(43)	139.9(54)	6.0(35)	54.9(40)	53.8(40)
PH6C4	-0.25745(16)	0.30488(30)	0.34558(30)	79.8(39)	177.6(59)	119.5(51)	-18.4(40)	33.9(36)	54.0(46)
PH6C5	-0.21297(22)	0.20566(29)	0.35322(30)	84.2(39)	172.5(57)	123.0(53)	-65.7(40)	18.9(36)	30.8(44)
PH6C6	-0.10035(23)	0.15934(19)	0.38447(28)	82.9(34)	115.2(39)	106.5(44)	-54.6(31)	15.0(30)	27.6(33)
PH7C1	0.14341(24)	0.16588(23)	0.61287(17)	80.9(30)	57.7(24)	81.1(35)	-25.0(23)	17.1(26)	11.9(23)
PH7C2	0.21140(26)	0.21606(23)	0.70000(24)	156.9(49)	73.0(30)	85.4(39)	-62.4(33)	22.5(35)	5.3(27)
PH7C3	0.23346(30)	0.21841(26)	0.82212(21)	213.1(65)	95.0(37)	78.1(40)	-87.6(42)	2.9(40)	-1.7(31)
PH7C4	0.18754(32)	0.17060(28)	0.85711(18)	183.1(60)	89.3(36)	77.1(36)	-49.0(40)	39.5(38)	8.6(29)
PH7C5	0.11955(31)	0.12042(29)	0.76999(27)	160.1(58)	175.5(59)	104.6(49)	-93.6(50)	25.7(43)	48.8(45)
PH7C6	0.09748(27)	0.11806(27)	0.64786(23)	144.9(50)	182.3(55)	99.1(44)	-112.4(46)	3.0(37)	43.9(40)
PH8C1	0.14332(24)	0.02617(15)	0.38842(24)	103.3(36)	57.7(24)	94.7(37)	-44.5(25)	43.2(30)	0.9(24)
PH8C2	0.22543(27)	-0.04239(24)	0.45486(26)	155.9(54)	58.6(27)	162.1(63)	-27.0(32)	62.4(48)	25.0(34)
PH8C3	0.25360(31)	-0.14329(20)	0.40211(42)	213.2(78)	57.6(33)	268.(10)	-16.8(41)	124.2(76)	34.9(49)
PH8C4	0.19966(38)	-0.17563(17)	0.28292(43)	284.5(92)	71.5(36)	308.(11)	-83.3(49)	216.8(88)	-44.1(49)
PH8C5	0.11755(34)	-0.10707(27)	0.21648(28)	220.7(74)	116.0(48)	178.9(64)	-117.5(52)	122.1(58)	-68.1(46)
PH8C6	0.08938(24)	-0.00618(24)	0.26923(24)	134.6(47)	92.5(33)	116.0(45)	-69.2(34)	61.6(38)	-22.9(32)

[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. [C] THIS ATOM AND THOSE THAT FOLLOW ARE THE CARBON ATOMS OF THE ANISOTROPIC RIGID GROUPS. THE POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS ARE DERIVED FROM THE RIGID GROUP PARAMETERS GIVEN IN TABLE III.

$RuH(dtt)(CO)(PPh_3)_2$ molecule (shown in Figure 2) is approximately octahedral with the triazenido ligand coordinated in a bidentate fashion. The two trans triphenylphosphine ligands show a P(1)–Ru–P(2) angle of 173.44 (3)°. The Ru–P(1) and Ru–P(2) distances of 2.343 (1) and 2.354 (1) Å, respectively, are typical in such Ru(II) complexes.[25,26] (The apparently significant difference in the two Ru–P distances may result from an underestimation of the standard deviations by a factor of 2 or 3 as judged by the agreement among the six P–C distances.) The equatorial plane consists of the hydrido, carbonyl, and triazenido ligands. The angles between these ligands are very distorted from ideal octahedral geometry. This distortion is caused primarily by the small bite of the triazenido moiety resulting in a N(1)–Ru–N(3) angle of 57.7 (1)°. A view of the inner coordination geometry about the ruthenium atom makes this fact clear (see Figure 3). A listing of relevant bond distances and angles is given in Table VI.

Table III. Rigid-Group Parameters of *trans*-[$Ru(H)(CH_3C_6H_5N_3C_6H_5CH_3)(CO)(P(C_6H_5)_3)_2$]

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
PH1	-0.10302(15)	0.39735(14)	0.14441(18)	-0.4176(22)	-2.2960(20)	0.1559(24)
PH2	0.29775(13)	-0.08633(12)	0.10504(15)	1.3528(23)	2.3593(15)	0.8906(23)
PH3	0.47665(16)	0.38503(15)	0.59047(18)	2.2060(32)	-2.2826(15)	-1.6246(32)
PH4	0.49207(15)	0.13159(15)	0.20430(18)	0.2875(22)	2.5991(18)	2.1738(22)
PH5	0.17665(14)	0.47018(14)	0.22770(17)	-0.3331(32)	2.0883(17)	0.6662(33)
PH6	-0.14483(15)	0.25855(19)	0.37682(17)	3.0209(18)	-3.1841(19)	3.1594(18)
PH7	0.16547(18)	0.16824(16)	0.73499(17)	2.5205(24)	3.0544(17)	-1.2675(21)
PH8	0.17149(22)	-0.07473(15)	0.33567(25)	1.2747(29)	2.3802(22)	0.7676(27)

[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).

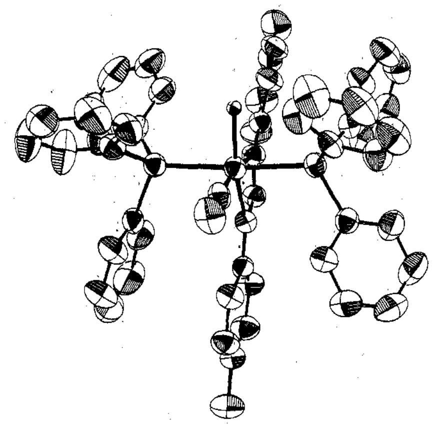

Figure 2. Overall view of the *trans*-[Ru(H)(dtt)(CO)(PPh_3)$_2$] complex. In this and the following drawing the 20% disordered carbonyl is not shown for clarity but the H atom is placed at the position of C(2). Both figures show the atoms at the 50% probability contour of thermal motion.

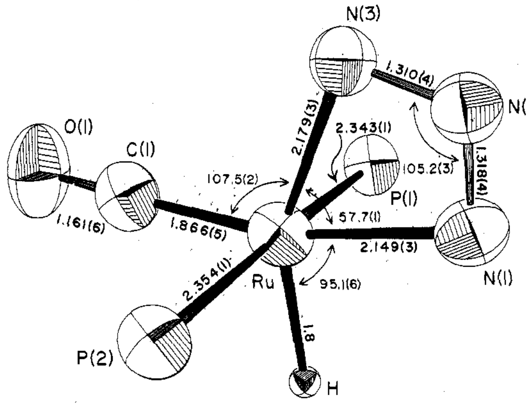

Figure 3. View of the coordination geometry about the ruthenium atom.

Table VI. Interatomic Distances (Å) and Angles (deg) in *trans*-[RuH(dtt)(CO)(PPh_3)$_2$]

Bonding Distances			
Ru–P(1)	2.343 (1)	P(2)–PH7C1	1.838 (3)
Ru–P(2)	2.354 (1)	P(2)–PH8C1	1.814 (2)
Ru–N(1)	2.149 (3)	N(1)–PH1C1	1.408 (3)
Ru–N(3)	2.179 (3)	N(3)–PH2C1	1.411 (3)
Ru–C(1)	1.866 (5)	N(1)–N(2)	1.318 (4)
Ru–C(2)[a]	1.80 (2)	N(2)–N(3)	1.310 (4)
P(1)–PH3C1	1.836 (3)	C(1)–O(1)	1.161 (6)
P(1)–PH4C1	1.840 (3)	C(2)–O(2)[a]	1.18 (3)
P(1)–PH5C1	1.830 (3)	C(3)–PH1C4	1.525 (6)
P(2)–PH6C1	1.833 (2)	C(4)–PH2C4	1.523 (5)
Nonbonding Distances			
Ru–N(2)	2.694 (3)	Ru–O(2)	2.97 (2)
Ru–O(1)	3.026 (4)	N(1)–N(3)	2.087 (4)
Bond Angles			
P(1)–Ru–P(2)	173.44 (3)	PH3C1–P(1)–PH4C1	100.9 (1)
P(1)–Ru–N(1)	90.87 (8)	PH3C1–P(1)–PH5C1	101.3 (1)
P(1)–Ru–N(3)	94.35 (8)	PH4C1–P(1)–PH5C1	104.9 (1)
P(1)–Ru–C(1)	89.8 (1)	Ru–P(2)–PH6C1	118.6 (1)
P(1)–Ru–C(2)	84.5 (6)	Ru–P(2)–PH7C1	118.0 (1)
P(2)–Ru–N(1)	93.23 (8)	Ru–P(2)–PH8C1	111.0 (1)
P(2)–Ru–N(3)	92.17 (8)	PH6C1–P(2)–PH7C1	100.7 (1)
P(2)–Ru–C(1)	87.6 (1)	PH6C1–P(2)–PH8C1	104.2 (1)
P(2)–Ru–C(2)	90.0 (6)	PH7C1–P(2)–PH8C1	102.3 (2)
N(1)–Ru–N(3)	57.7 (1)	Ru–N(1)–N(2)	99.2 (2)
N(1)–Ru–C(1)	165.2 (2)	Ru–N(1)–Ph1C1	145.1 (2)
N(1)–Ru–C(2)	95.1 (6)	PH1C1–N(1)–N(2)	115.5 (2)
N(3)–Ru–C(1)	107.5 (2)	N(1)–N(2)–N(3)	105.2 (3)
N(3)–Ru–C(2)	152.7 (6)	Ru–N(3)–N(2)	98.0 (2)
C(1)–Ru–C(2)	99.7 (6)	Ru–N(3)–PH2C1	145.6 (2)
Ru–P(1)–PH3C1	116.9 (1)	PH2C1–N(3)–N(2)	116.1 (2)
Ru–P(1)–PH4C1	115.9 (1)	Ru–C(1)–O(1)	178.5 (5)
Ru–P(1)–PH5C1	114.8 (1)	Ru–C(2)–O(2)	177 (2)

[a] C(2) and O(2) are the minor components of the disordered carbonyl group.

The minor positional disorder in the structure, as mentioned in the previous section, consists of a partial carbonyl occupancy in the hydride position. As determined from the least-squares refinement the occupancy factor is 0.198 (5) for C(2)–O(2) and 0.802 (5) for C(1)–O(1). The contribution of the hydrido ligand was not taken into account, but the electron density distribution suggests that the hydride position is very close to that of atom C(2). Accordingly, we display the H ligand at the position of C(2) and omit C(2) and O(2) from the drawings. The bond distances and angles of C(2)–O(2), as shown in Table VI, are acceptable for a carbonyl group when the relatively large standard deviations are taken into account. The type of disorder observed in this structure is not unusual as a number of structures showing a positional disorder between a halide and carbonyl have been reported.[27-29] A 50%–50% (i.e., statistical) disorder is not always found as shown in the structure reported here and in at least one other structure.[29]

The most interesting feature of the present structure involves the ruthenium–triazenido system. There is a small, possibly significant, difference in the Ru–N(1) and Ru–N(3) bond lengths (2.149 (3) and 2.179 (3) Å, respectively) owing perhaps to the trans influence of the hydrido ligand which is mainly opposite to atom N(3). The N(1)–N(2)–N(3) angle of 105.2 (3)° is much smaller than the typical 117° angle observed in structures having a triazenido ligand bridging two metal centers.[3-5] That there is extensive π delocalization over the ruthenium–triazenido system is apparent from the equivalence of the two N–N bond lengths (average of 1.314 (4) Å, intermediate between a single- and a double-bond distance) and from the near planarity of the entire system. This planarity can readily be seen in Figure 2 and from the data of Table VII, where various least-squares planes are presented. The angle between the two tolyl rings is 15.4°, whereas the angles between the planar $\overline{\text{Ru–N(1)–N(2)–N(3)}}$ ring and each of the two tolyl rings PH1 and PH2 are 18.1 and 5.6°, re-

Table VII. Selected Weighted Least-Squares Planes

Coefficients of the Plane Equation $Ax + By + Cz = D^a$

Plane	*A*	*B*	*C*	*D*
1	12.560	11.164	−7.474	2.205
2	12.571	10.971	−7.669	2.096
3	12.464	10.981	−7.866	2.006
4	12.504	10.994	−7.780	2.039
5	12.559	11.129	−7.519	2.185
6[b]	11.302	9.354	−10.048	1.102
7[c]	12.848	10.122	−7.856	2.127

Deviations (Å) of Various Atoms from the Planes

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
Ru	−0.0006 (4)[d]	−0.0074 (4)	−0.0159 (4)	−0.0028 (4)	−0.0054 (4)
N(1)	0.012 (1)	0.028 (1)	0.065 (1)	0.060 (1)	0.013 (1)
N(2)	−0.013 (1)	0.034 (1)	0.083 (1)	0.071 (1)	−0.006 (1)
N(3)	0.006 (1)	0.054 (1)	0.079 (1)	0.076 (1)	0.013 (1)
C(1)				−0.026 (1)	−0.001 (1)
O(1)				−0.031 (1)	0.011 (1)
C(2)				−0.025 (1)	0.011 (1)
O(2)				−0.013 (4)	0.047 (4)
C(3)	−0.343	−0.354 (4)	−0.237 (4)	−0.270 (4)	
C(4)	−0.500	−0.328 (4)	−0.281 (4)	−0.302 (4)	
PH1C1	−0.046	−0.036	0.021 (4)	0.009 (4)	
PH1C2	−0.461	−0.426	−0.340 (4)	−0.365 (4)	
PH1C3	−0.558	−0.530	−0.424 (3)	−0.456 (3)	
PH1C4	−0.239	−0.243	−0.147 (4)	−0.173 (4)	
PH1C5	0.176	0.147	0.214 (4)	0.201 (4)	
PH1C6	0.272	0.251	0.298 (3)	0.292 (3)	
PH2C1	−0.078	0.000	0.033 (7)	0.024 (7)	
PH2C2	−0.144	−0.065	−0.057 (7)	−0.057 (7)	
PH2C3	−0.280	−0.172	−0.159 (6)	−0.163 (6)	
PH2C4	−0.352	−0.213	−0.171 (6)	−0.188 (6)	
PH2C5	−0.286	−0.147	−0.082 (6)	−0.107 (6)	
PH2C6	−0.149	−0.041	0.020 (5)	−0.001 (5)	

Dihedral Angles between Planes

Plane A	Plane B	Angle, deg	Plane A	Plane B	Angle, deg
1	2	1.43	3	4	0.54
1	3	2.42	3	5	2.14
1	4	1.92	3	6	15.72
1	5	0.30	3	7	4.57
1	6	18.14	4	5	1.63
1	7	5.62	4	6	16.23
2	3	1.25	4	7	4.55
2	4	0.73	5	6	17.85
2	5	1.13	5	7	5.38
2	6	16.84	6	7	15.38
2	7	4.42			

[a] The plane is in crystal coordinates. [b] Plane of phenyl 1. [c] Plane of phenyl 2. [d] Numbers with estimated standard deviations given in parentheses indicate the atoms which determined each of the least-squares planes.

spectively. In the structures of $Co(dpt)_3$, these interplanar angles range from 5.2 to 31.1° for the unsolvated form[8] and are approximately 20° in the toluene solvated form.[6]

The structures of two ruthenium complexes containing bidentate acetate and formate ligands (isoelectronic with triazenido) merit comparison with the ruthenium triazenido complex reported here. These compounds are $RuH(O_2CMe)(PPh_3)_3$[25] and $RuH(O_2CH)(PPh_3)_3$.[30] The carboxylate groups in both of these structures have equivalent C–O bond lengths indicative of the expected π-delocalized system. The small O–Ru–O bite angles of 57.6 (4) and 55.0 (13)° for the acetate and formate structures, respectively, agree very well with the N(1)–Ru–N(3) angle of 57.7 (1)° found in the triazenide. The O–C–O angles in the acetate and formate complexes are larger (114.8 and 114.2°, respectively) than the 105.2° triazenide N(1)–N(2)–N(3) angle. This difference reflects the longer Ru–O and the shorter C–O bond distances (ca. 2.20 and 1.25 Å, respectively) in the carboxylate structures compared with the Ru–N and N–N bonds in the triazenide. Within the rather large standard deviations in both the acetate and formate structures the trans influence of the hydrido ligand was not detected. Skapski and Stephens[25] indicated that the $RuH(O_2CMe)(PPh_3)_3$ complex may be considered to be pseudo five-coordinate with the center of the bidentate group taken as a fifth coordination site. In this context the present ruthenium triazenide structure is a pseudo trigonal bipyramid with the trans triphenylphosphine groups in the axial positions and with equatorial angles N(2)–Ru–C(1) = 136.3 (2)°, N(2)–Ru–C(2) = 123.9 (6)°, and C(1)–Ru–C(2) = 99.7 (6)°. This type of geometric interpretation has also been discussed elsewhere.[26]

Very recently, the structure of another bidentate triazenido complex, $Mo(dfpt)(C_5H_5)(CO)_2$ (dfpt = 1,3-bis(3,5-bis(trifluoromethyl)phenyl)triazenido), was reported.[31] The important distances and angles found in this Mo triazenide structure, the two $Co(dpt)_3$ structures,[7,8] and the ruthenium triazenide structure reported here are compared in Table VIII. The N–N and N–C distances agree very well for all four structures. The small N–N–N angles are evidence of the strain in the four-membered M–N–N–N ring. Among these angles, there is very close agreement between the two $Co(dpt)_3$

Table VIII. Structural Parameters for Reported Bidentate Triazenido Complexes

	$[Co(dpt)_3]\cdot C_6H_4CH_3$ [a]	$Co(dpt)_3$ [b]	$[Mo(dfpt)(C_5H_5)(CO)_2]$ [c]	*trans*-$[RuH(dtt)(CO)(PPh_3)_2]$ [d]
M-N, Å	1.93 (1)	1.919 (5)	2.120 (9)	2.149 (3) 2.179 (3)
N-N, Å	1.32 (1)	1.311 (7)	1.31 (1)	1.314 (4)
N-N-N, deg	103.6 (7)	103.2 (7)	100.8 (7)	105.2 (3)
N-M-N, deg	65.5 (5)	64.8 (3)	56.8 (3)	57.7 (1)
M-N-N, deg	95.5 (6)	96.0 (4)		98.6 (2)
N-C, Å	1.40 (1)	1.407 (7)	1.423 (13)	1.410 (3)
M-N-C, deg	144.9 (6)			145.4 (2)
N-N-C, deg	118.4 (6)	118.9 (5)	116.5 (8)	115.8 (2)

[a] Reference 7. [b] Reference 8. [c] Reference 31. [d] This work.

structures; their average value is about 2° less than in the Ru structure. This difference can be accounted for by the smaller size of the Co compared with the Ru atom. In the Mo structure, however, this N–N–N angle is further reduced to 100.8 (7)°, almost 5° less than for the Ru complex. Since the Mo(II) bonding radius is comparable with that of Ru(II), the change in N–N–N angle must result from the vastly different ligand environments of the two complexes. The N–M–N angles in the Mo and Ru complexes (56.8 (3) and 57.7 (1)°, respectively) are much smaller than that of about 65° in the $Co(dpt)_3$ complexes. This is expected upon consideration of the longer metal–nitrogen distance in the Mo and Ru complexes. Based upon a simple geometric relation ($\sin[(N–M–N)/2] \propto$ M–N distance) and the given M–N distances, a N(1)–Ru–N(3) angle of 57° results from the N–Co–N angle of 65°.

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Registry No. *trans*-Ru(H)(dtt)(CO)(PPh_3)$_2$, 54206-37-0.

Supplementary Material Available: Table IV, the root-mean-square amplitudes of vibration, Table V, a listing of the idealized positions of the hydrogen atoms, and a listing of observed and calculated structure amplitudes (43 pages). Ordering information is given on any current masthead page.

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