in the high- and the low-spin forms. In the present case, x_0 can be as large as 0.2 Å for the P and N(3) donor atoms taking into account bond-distance and -angle variations. This effect does not appear evident from the data of Table V. The ratio of the values at room and low temperature appears to be normal. Also the root-mean-square displacements for the two room-temperature structures appear to be quite similar. The only exception is that of the parameters for the Co and N(2) atoms which appear to be larger for the intermediate-spin complex. However, these differences can be hardly rationalized as the Co–N(2) bond distance does not change on cooling.

Finally, although the interpretation of the X-ray diffraction data still leaves some problems open, IR and ESR data are in favor of the hypothesis of a disordered spin state.

Registry No. Co(NCS)$_2$(nnp), 29993-37-1.

Supplementary Material Available: A listing of calculated and observed structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Iridium(I) and Rhodium(I) Complexes of Benzotriazole. Structure of Bis(triphenylphosphine)carbonyl(benzotriazenido)iridium(I)

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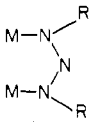
Thallium benzotriazenide has been prepared from benzotriazole, thallium(I) acetate, and triethylamine in ethanol. The compound serves as a convenient starting material for the synthesis of organometallic benzotriazenides. It reacts with [Ir(CO)(acetone)(PPh$_3$)$_2$][PF$_6$] to yield the tetramer [Ir(BTA)(CO)(PPh$_3$)]$_4$, where Ph = phenyl and BTA = benzotriazenido. A similar reaction with RhCl(CO)(PPh$_3$)$_2$ yields the hexamer [Rh(BTA)(CO)(PPh$_3$)]$_6$. Direct reaction of Tl(BTA) with IrCl(CO)(PPh$_3$)$_2$ yields Ir(BTA)$_2$(CO)(PPh$_3$)Tl·C$_6$H$_6$. A methanol solution of this material rapidly changes color from violet to yellow and from this solution the compound Ir(BTA)(CO)(PPh$_3$)$_2$ is obtained. On the basis of an X-ray crystal structure, the Ir atom in Ir(BTA)(CO)(PPh$_3$)$_2$ is coordinated by trans P atoms, the CO ligand, and the BTA ligand in nearly a square-planar arrangement. Despite the symmetric nature of the N$_3$ portion of the BTA ligand, the ligand is coordinated to the Ir atom through atom N(1). The ligand makes an angle of approximately 78° with the Ir(CO)P$_2$ plane. The compound crystallizes with four molecules in space group C_{2h}^5-$P2_1/n$ of the monoclinic system in a cell of dimensions a = 13.508 (3) Å, b = 20.225 (4) Å, c = 13.372 (3) Å, and β = 103.36 (1)°. The structure has been refined by full-matrix least-squares methods to a final R index of 0.035 for 199 variables, based on 6321 observations.

Introduction

Structure and bonding in transition-metal triazenido complexes have attracted much interest in recent years. The triazenido ligand may function as a bridging group between two metal centers (I), a bidentate, three-electron donor (II), or a monodentate, one-electron donor (III). Reported structures of triazenido complexes have been summarized.[2,3] The conjugate base of benzotriazole, **1**, is a particularly interesting triazenido ligand **2**, because of the conformational rigidity imposed by the fused benzene ring and the anticipated delocalization energy associated with the cyclic C$_2$N$_3$$^-$ system **2**. This paper reports the synthesis of rhodium(I) and iridium(I) derivatives of **2** and the structure of bis(triphenylphosphine)carbonyl(benzotriazenido)iridium(I), Ir(BTA)(CO)(PPh$_3$)$_2$, where BTA = benzotriazenido.



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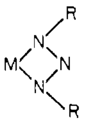

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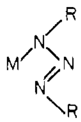

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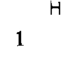

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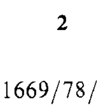

2

Experimental Section

All analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The method used for the analysis of Ir is that of Ayres and Quick.[4] Molecular weights were determined by vapor pressure osmometry.

Syntheses. Thallium Benzotriazenide [Tl(BTA)]. Thallium(I) acetate, 5.26 g (20 mmol), was dissolved in 100 mL of hot absolute ethanol. The solution was filtered and to it was added 2.24 g (20 mmol) of benzotriazole and 20 mmol of triethylamine in 15 mL of absolute ethanol. After the solution was cooled for 2 h in an ice bath, the thin flakes of thallium benzotriazenide were collected on a filter, washed with cold ethanol, and vacuum dried; yield 4.1 g (63%). The product is sufficiently pure at this point for synthetic purposes. An analytical sample was obtained as blades from hot water. Anal. Calcd for C$_6$H$_4$N$_3$Tl: C, 22.35; H, 1.24; N, 13.04; Tl, 63.35. Found: C, 22.28; H, 1.22; N, 13.44; Tl, 63.50. IR (Nujol): 1475 (m), 1270

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(w), 1250 (w), 1150 (w), 1125 (m), 1085 (s), 900 (m), 775 (m), 730 (s), 680 (w), 625 (m), 540 (w) cm^{-1}. The Raman spectrum in water shows a strong band at 1023 cm^{-1} (5145-Å excitation) which we attribute to the N–N stretching vibration. Electronic spectrum (CH_3OH): λ_{max} 274 (log $\epsilon = 3.98$).

$Ir(BTA)_2(PPh_3)Tl\cdot C_6H_6$. A mixture of 0.38 g of $IrCl(CO)(PPh_3)_2$ (0.5 mmol) and 0.17 g (0.53 mmol) of Tl(BTA) in 20 mL of deoxygenated 1:1 benzene–acetone was refluxed and stirred under dinitrogen for 20 h. The reaction mixture was filtered in a drybox and the filtrate slowly diluted with *n*-hexane to precipitate the product as violet microcrystals. The crystals were washed with *n*-hexane and vacuum dried; yield 0.30 g (60%). Anal. Calcd for $C_{37}H_{29}IrN_6OPTl$: C, 44.40; H, 2.90; Cl, 0.00; Ir, 19.20; N, 8.40; P, 3.10; Tl, 20.40; mol wt, 1000. Found: C, 44.22; H, 3.31; Cl, <1.0, Ir, 20.33; N, 8.00; P, 2.61; Tl, 20.34; mol wt (C_6H_6), 1122. IR (toluene): 1980 cm^{-1}. IR (Nujol): 3040 (w), 1980 (s), 1475 (m), 1435 (m), 1090 (m), 775 (w), 740 (s), 690 (s), 535 (m), 515 (s) cm^{-1}. ^{31}P NMR (toluene): δ −21.9. Electronic spectrum (Nujol): λ_{max} at 525, 405 (sh) nm. The acetone–benzene insoluble phase was identified as thallium(I) chloride from its X-ray powder pattern.

$[Ir(BTA)(CO)(PPh_3)]_4$. A mixture of 0.76 g of $IrCl(CO)(PPh_3)_2$ (1 mmol), 0.25 g of $AgPF_6$ (1 mmol), 15 mL of toluene, and 50 mL of acetone was stirred for 15 min under dinitrogen. Then 0.32 g of Tl(BTA) (1 mmol) was added and stirring was continued for 20 h. During this period, the color of the mixture turned from orange to purple to orange again. The reaction mixture was filtered in air through Celite, and the solvents were removed from the filtrate under vacuum. The residue was dissolved in methylene chloride and chromatographed on a 10 in. × 0.5 in. silica gel column, eluting with the same solvent to remove a yellow band. The material thus obtained was twice recrystallized by slow evaporation of an acetone–cyclohexane solution. The yellow crystals weighed 0.36 g (60%) after vacuum drying. Anal. Calcd for $[C_{25}H_{19}IrN_3OP]_4$: C, 50.00; H, 3.16; Cl, 0.00; Ir, 32.00; N, 7.00; P, 5.17; Tl, 0.00; mol wt 2402. Found: C, 49.55; H, 3.17; Cl, <0.4; N, 6.69; Ir, 30.81; P, 6.29; Tl, <0.2; mol wt 2200 ($CHCl_3$). IR ($CHCl_3$): 1973 cm^{-1}. IR (Nujol): 3040 (w), 1980 (s), 1510 (w), 1580 (w), 1475 (m), 1435 (s), 1180 (s), 1090 (s), 990 (w), 835 (s), 780 (m), 740 (s), 690 (s), 600 (w), 555 (m), 530 (s), 515 (m), 500 (w) cm^{-1}. Mp > 240 °C dec. ^{31}P NMR (CH_2Cl_2): δ −17.2. Electronic spectrum (1,2-$C_2H_4Cl_2$): λ_{max} 448 (2.61), 387 (3.15), 340 (3.42), 272 (3.90) nm. Crystal data: $a = 16.98$, $b = 17.46$, $c = 16.60$ Å; $\alpha = 97.5$, $\beta = 111.0$, $\gamma = 77.0°$; $\rho_{obsd} = 1.79$, $\rho_{calcd} = 1.784$ g/cm^3 for two tetramers in the triclinic cell.

$[Rh(BTA)(CO)(PPh_3)]_6$ was prepared in a similar manner but the chromatography step was omitted. The yield of yellow microcrystals from acetone–toluene was 0.4 g (78%). Anal. Calcd for $[C_{25}H_{19}N_3OPRh]_6$: C, 58.71; H, 3.72; Cl, 0.00; N, 8.22; P, 6.07; Rh, 20.16; Tl. 0.00; mol wt 3068. Found: C, 58.31; H, 4.08; Cl, <0.2; N, 7.63; P, 6.59; Rh, 20.59; Tl, <0.2; mol wt 3070 ($CHCl_3$). Mp >240 °C dec (vacuum). IR ($CHCl_3$): 1990 cm^{-1}. IR (Nujol): 3040 (w), 1985 (s), 1575 (w), 1475 (m), 1435 (m), 1305 (w), 1175 (s), 1140 (m), 1090 (s), 1020 (w), 990 (w), 885 (s), 780 (m), 740 (s), 690 (s), 585 (w), 570 (m), 545 (m), 530 (s), 510 (s) cm^{-1}. ^{31}P NMR (CH_2Cl_2): δ −43.5, $J_{Rh-P} = 153$ Hz. Electronic spectrum (1,2-$C_2H_4Cl_2$): λ_{max} 364 (3.31), 315 (sh), 274 (4.11), 268 (4.09) nm.

$Ir(BTA)(CO)(PPh_3)_2$. To 0.30 g (0.3 mmol) of $Ir(BTA)_2(CO)(PPh_3)Tl\cdot C_6H_6$ in 10 mL of methanol sufficient toluene was added to give a clear solution. Triphenylphosphine, 0.1 g, was added. The solution was warmed gently and stirred in air as the color turned from purple to yellow. The solution was filtered and taken to dryness under reduced pressure. The residue was twice recrystallized by slow evaporation of a methylene chloride–methanol solution to give 0.15 g of bright yellow rods; mp 235–237 °C (vacuum). Anal. Calcd for $C_{43}H_{34}IrNOP_2$: C, 59.86; H, 3.94; Ir, 22.27; N, 4.87; P, 7.19; mol wt 863. Found: C, 60.02; H, 4.04; Ir, 24.00; N, 4.53; P, 6.85; mol wt 928 (C_6H_6). IR ($CHCl_3$): 1974 cm^{-1}. IR (Nujol): 3045 (w), 1970 (s), 1480 (m), 1435 (s), 1305 (w), 1180 (m), 1095 (s), 995 (w), 775 (w), 740 (s), 690 (s), 605 (w), 520 (s), 510 (s) cm^{-1}. ^{31}P NMR (CH_2Cl_2): δ −24.6. ^1H NMR ($CDCl_3$): complex multiplet centered at δ −7.6. Electronic spectrum (1,2-$C_2H_4Cl_2$): λ_{max} 450 (3.00), 390 (2.19), 280 (4.38) nm.

X-ray Diffraction Determination of the Structure of $Ir(BTA)(CO)(PPh_3)_2$. On the basis of preliminary Weissenberg and precession photographs $Ir(BTA)(CO)(PPh_3)_2$ was assigned to space group C_{2h}^5-$P2_1/n$ of the monoclinic system. Unit cell parameters, obtained from angular data on 15 reflections hand-centered on a Picker FACS-I diffractometer, are given in Table I. Intensity data were collected by methods standard in this laboratory,[5] and important details are also given in Table I.

Table I. Crystal Data and Data Collection for $Ir(BTA)(CO)(PPh_3)_2$

compound	$Ir(N_3C_6H_4)(CO)(P(C_6H_5)_3)_2$	*a*, Å	13.508 (3)
formula	$C_{43}H_{34}IrN_3OP_2$	*b*, Å	20.225 (4)
mol wt	862.92	*c*, Å	13.372 (3)
space group	C_{2h}-$P2_1/n$	β, deg	103.36 (1)
ρ_{obsd}, g/cm^3	1.58 (2)	*V*, Å^3	3554
ρ_{calcd}, g/cm^3	1.612		

crystal shape	complex, of approximately equant habit with bounding faces $\{10\bar{1}\}$, $\{110\}$, $\{021\}$, (011), $(0\bar{1}\bar{1})$, $(02\bar{5})$, $(0\bar{2}5)$
crystal vol, mm^3	0.104
μ, cm^{-1}	38.82
transmission factors	0.184 to 0.270
radiation	Mo Kα (λ(Mo Kα_1) = 0.709 30 Å) monochromatized from mosaic graphite
takeoff angle, deg	2.7
aperture	3.9 mm wide by 4.9 mm high, 32 cm from crystal
scan range	0.8° in 2 θ below Kα_1 to 0.8° in 2 θ above Kα_2
scan speed	2°/min in 2 θ
background counts	10 s with rescan option
2 θ limits	3.5 to 54.0°
reflcts obsd	± *h*,*k*,*l*
No. obsd	8369
unique data with $F_o^2 > 3\sigma(F_o^2)$	6321

The structure was solved from a three-dimensional, origin-removed, sharpened Patterson function and was refined by methods and with computer programs standard in this laboratory.[5] The six phenyl rings were refined as rigid groups, with each carbon atom being assigned its own variable isotropic thermal parameter. The other heavy atoms were refined anisotropically. The positions of the four hydrogen atoms on the BTA ligand and the 30 hydrogen atoms on the phenyl rings were idealized (C–H = 0.95 Å, $B(H) = B(C) + 1.0$ Å^2) and the contributions of these atoms were held fixed in the final cycle of full-matrix, least-squares refinement. This refinement of 199 variables converged to conventional and weighted *R* indices on F_o of 0.035 and 0.043, respectively, and to an error in an observation of unit weight of 1.44 electrons for the 6321 observations. A final difference Fourier map displayed electron density as high as 2.1 (1) e/Å^3 in the vicinity of phenyl ring 2 and somewhat less density near other carbon atoms of the phenyl rings. Such density presumably arises from the limitations of the isotropic model for vibration of these atoms. Of the 1756 F_o values omitted from the refinement because $F_o^2 < 3\sigma(F_o^2)$ only 8 have $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices displays no unexpected trends.

Table II presents the final parameters for the nongroup atoms, along with their estimated standard deviations. Parameters for the phenyl groups are presented in Table III. Table IV[6] presents the values of $10|F_o|$ vs. $10|F_c|$ for the reflections used in the refinement.

Results and Discussion

The thallium salt of **2**, Tl(BTA), is a convenient starting material for the synthesis of organometallic benzotriazenides. It is readily prepared from benzotriazole, thallium(I) acetate, and triethylamine in ethanol. This salt is indefinitely stable in air and, indeed, may be recrystallized from hot water. A strong band in the infrared spectrum at 1085 cm^{-1} (Nujol mull) and in the Raman spectrum at 1023 cm^{-1} (aqueous solution) is attributed to an N–N stretching mode. This absorption is at lower energy than the 1205-cm^{-1} absorption in **1** attributed[7] to $\nu_{N=N}$, since structure **2** implies an averaging of N=N and N—N bond lengths.

Reaction of Tl(BTA) with $[Ir(CO)(acetone)(PPh_3)_2][PF_6]$, prepared from $IrCl(CO)(PPh_3)_2$ and $AgPF_6$ in acetone, yields $[Ir(BTA)(CO)(PPh_3)]_4$ (**3**). The molecularity of **3**, established by vapor pressure osmometry on a chloroform solution, is consistent with the fact that the unit cell accommodates two

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $Ir(BTA)(CO)(PPh_3)_2$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
IR	0.238948(13)	0.066022(9)	0.404752(13)	29.62(12)	13.99(5)	32.32(12)	0.25(6)	7.03(8)	-1.89(6)
P(1)	0.32395(9)	0.11715(6)	0.55514(9)	32.6(7)	17.8(3)	32.3(7)	0.1(4)	8.5(6)	-3.1(4)
P(2)	0.16590(9)	0.03046(6)	0.23847(9)	34.8(7)	13.9(3)	34.2(7)	-1.9(4)	8.5(6)	-2.2(4)
O(1)	0.4045(4)	-0.03337(25)	0.4266(4)	75.(3)	43.6(16)	73.(4)	37.0(20)	-5.5(29)	-9.7(20)
N(1)	0.12194(29)	0.13412(20)	0.3923(3)	38.2(24)	13.7(10)	36.4(24)	1.7(13)	10.8(19)	-0.8(13)
N(2)	0.1135(3)	0.18662(22)	0.3293(3)	64.(3)	16.8(13)	42.7(27)	-0.9(16)	12.7(23)	4.6(15)
N(3)	0.0276(4)	0.21957(23)	0.3281(3)	65.(3)	19.7(13)	59.(3)	7.3(17)	14.5(26)	9.1(16)
C(1)	0.3396(4)	0.00459(29)	0.4172(4)	44.(4)	25.9(16)	46.(4)	7.0(20)	3.(3)	-9.0(20)
C(2)	0.0384(4)	0.13320(24)	0.4336(4)	34.5(28)	14.6(12)	39.(3)	0.0(15)	8.2(24)	-3.2(16)
C(3)	-0.0213(4)	0.18606(25)	0.3904(4)	42.(3)	14.9(13)	57.(4)	6.0(17)	6.7(27)	-1.1(17)
C(4)	-0.1172(5)	0.1968(3)	0.4136(5)	53.(4)	26.6(19)	89.(5)	16.4(24)	16.(4)	-1.4(26)
C(5)	-0.1463(5)	0.1526(4)	0.4796(6)	45.(4)	37.9(24)	106.(6)	9.4(27)	29.(4)	-5.(3)
C(6)	-0.0853(5)	0.0999(4)	0.5221(5)	54.(4)	33.0(23)	70.(4)	-0.1(26)	24.(4)	4.2(27)
C(7)	0.0078(4)	0.0888(3)	0.5007(5)	45.(4)	21.7(16)	52.(4)	3.2(20)	12.(3)	4.0(20)

[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 $Ir(BTA)(CO)(PPh_3)_2$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
C(11)	0.42932(21)	0.16671(16)	0.53170(25)	2.59(8)	C(41)	0.17566(26)	-0.05754(13)	0.21087(29)	2.62(8)
C(12)	0.47125(25)	0.15047(16)	0.44885(23)	3.14(10)	C(42)	0.27215(21)	-0.08351(17)	0.2147(3)	3.79(11)
C(13)	0.55705(26)	0.18396(19)	0.43424(24)	3.70(11)	C(43)	0.28402(23)	-0.15111(18)	0.2004(3)	4.22(12)
C(14)	0.60100(23)	0.23369(18)	0.50248(28)	3.79(11)	C(44)	0.1994(3)	-0.19274(13)	0.1822(3)	4.26(13)
C(15)	0.55907(26)	0.24993(16)	0.58533(25)	3.93(11)	C(45)	0.10292(25)	-0.16678(17)	0.1783(3)	4.93(16)
C(16)	0.47323(26)	0.21644(17)	0.59994(22)	3.24(10)	C(46)	0.09105(20)	-0.09917(18)	0.1927(3)	3.87(11)
C(21)	0.38021(29)	0.06512(18)	0.66461(25)	3.04(9)	C(51)	0.22705(27)	0.07104(17)	0.14709(25)	2.88(9)
C(22)	0.3581(3)	-0.00233(19)	0.66116(28)	4.35(13)	C(52)	0.27916(29)	0.13015(17)	0.17565(22)	3.23(10)
C(23)	0.4008(4)	-0.04270(15)	0.7445(4)	5.72(17)	C(53)	0.3277(3)	0.16195(16)	0.1076(3)	4.44(12)
C(24)	0.4657(4)	-0.01563(21)	0.8314(3)	5.72(15)	C(54)	0.3241(3)	0.13464(20)	0.01108(27)	4.69(14)
C(25)	0.4879(3)	0.05182(22)	0.83483(26)	5.82(16)	C(55)	0.2720(3)	0.07553(21)	-0.01749(23)	5.15(13)
C(26)	0.4451(3)	0.09220(15)	0.7514(3)	4.70(13)	C(56)	0.2235(3)	0.04374(16)	0.05052(29)	4.69(13)
C(31)	0.24823(25)	0.17528(15)	0.60981(27)	2.87(9)	C(61)	0.03149(20)	0.04928(18)	0.19544(26)	2.70(9)
C(32)	0.2089(3)	0.15656(16)	0.69330(28)	4.16(13)	C(62)	-0.03134(27)	0.02854(18)	0.25880(23)	3.43(10)
C(33)	0.1393(3)	0.19732(22)	0.72610(28)	5.54(15)	C(63)	-0.13443(25)	0.04496(21)	0.23428(29)	4.38(12)
C(34)	0.1091(3)	0.25681(21)	0.6754(3)	5.74(16)	C(64)	-0.17470(21)	0.08211(22)	0.1464(3)	4.91(14)
C(35)	0.1484(3)	0.27553(16)	0.5919(3)	5.03(13)	C(65)	-0.11187(29)	0.10285(20)	0.08304(26)	4.73(13)
C(36)	0.2180(3)	0.23476(18)	0.55910(25)	3.97(11)	C(66)	-0.00878(27)	0.08643(19)	0.10756(25)	3.87(11)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
RING 1	0.51516(17)	0.20020(11)	0.51709(17)	-0.019(4)	-2.1560(21)	2.497(4)
RING 2	0.42296(21)	0.02475(15)	0.74800(22)	-0.5392(28)	-2.7440(25)	-2.2734(28)
RING 3	0.17864(19)	0.21604(14)	0.64260(20)	-0.075(4)	2.2869(24)	-0.798(4)
RING 4	0.18753(19)	-0.12514(13)	0.19653(18)	1.7032(20)	-3.0294(25)	0.1658(24)
RING 5	0.27560(19)	0.10284(13)	0.07908(20)	2.745(3)	2.4721(20)	1.324(3)
RING 6	-0.07161(20)	0.06570(12)	0.17092(19)	-0.248(4)	2.0942(25)	0.009(4)

[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).

tetramers. The aggregation observed in **3** most probably results from the benzotriazenido unit bridging two iridium atoms. There is precedence for this.[8] The use of infrared spectroscopy to infer structural features in metal triazenides has been a source of controversy[9,10] which this work does not resolve. However, a comparison of the infrared spectra of **3**, $IrCl(CO)(PPh_3)_2$, benzotriazole, and Tl(BTA) indicates a unique band of medium intensity at 1185 cm^{-1} in **3** which may be assigned to an N—N stretching mode.

A similar reaction starting with $RhCl(CO)(PPh_3)_2$ produces the rhodium analogue of **3**, $[Rh(BTA)(CO)(PPh_3)]_6$ (**4**). While the Ir complex is tetrameric, the solution molecular weight on the Rh analogue, as determined by vapor-phase osmometry, is consistent with its being hexameric. In the infrared spectrum, ν_{CO} at 1990 cm^{-1} and an N–N stretching band at 1140 cm^{-1} are observed. The $^{31}P\{^1H\}$ NMR spectrum is a doublet: δ −43.5 (vs. H_3PO_4) with $J_{^{31}P-^{103}Rh}$ = 153 Hz (cf. $RhCl(CO)(PPh_3)_2$, δ −20.1, $J_{^{31}P-^{103}Rh}$ = 124 Hz).[11] These data are consistent with a square-planar rhodium(I) center and bridging benzotriazenido ligands.

The direct reaction of Tl(BTA) and $IrCl(CO)(PPh_3)_2$ in benzene–acetone, without prior removal of the chloro ligand, affords, after addition of hexane to the filtered reaction mixture, $Ir(BTA)_2(CO)(PPh_3)Tl{\cdot}C_6H_6$ (**5**) as violet microcrystals. A toluene solution of **5**, in which solvent the compound is monomeric, exhibits ν_{CO} at 1980 cm^{-1} and a band at 1185 cm^{-1} which we assign to an N–N stretching mode. The structure of **5** is not obvious from spectroscopic data. We may consider an ionic formulation **5a**, with tight ion pairing to account for the observed molecular weight and solubility in hydrocarbons, or covalent formulation **5b**, with an iridium–thallium bond. Precedent for the latter structure may be

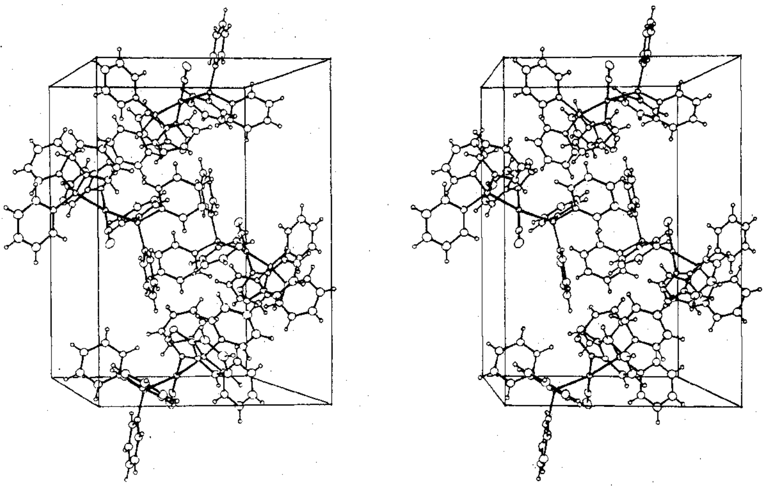


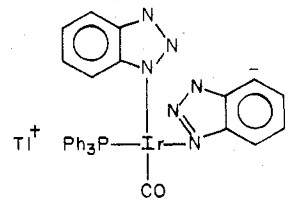
Figure 1. A stereoview of the unit cell of $Ir(BTA)(CO)(PPh_3)_2$. The 20% probability ellipsoids are shown, except those for hydrogen atoms which have been drawn artificially small.

Table V. Selected Bond Distances (Å) and Angles (deg) in $Ir(BTA)(CO)(PPh_3)_2$

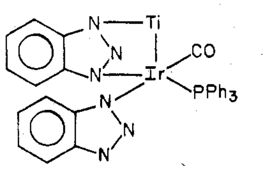
Ir-P(1)	2.316 (1)	P(1)-C(21)	1.820 (4)
Ir-P(2)	2.328 (1)	P(1)-C(31)	1.819 (4)
Ir-C(1)	1.821 (6)	P(2)-C(41)	1.829 (3)
Ir-N(1)	2.074 (4)	P(2)-C(51)	1.821 (4)
C(1)-O(1)	1.150 (7)	P(2)-C(61)	1.814 (3)
P(1)-C(11)	1.826 (3)		

Ir-C(1)-O(1)	178.6 (5)	C(21)-P(1)-C(31)	102.7 (2)
C(1)-Ir-P(1)	90.9 (2)	C(41)-P(2)-C(51)	103.8 (2)
C(1)-Ir-N(1)	178.4 (2)	C(41)-P(2)-C(61)	104.7 (2)
C(1)-Ir-P(2)	91.1 (2)	C(51)-P(2)-C(61)	105.6 (2)
P(1)-Ir-N(1)	89.4 (1)	Ir-N(1)-N(2)	121.8 (3)
P(1)-Ir-P(2)	169.3 (1)	Ir-N(1)-C(2)	130.1 (3)
N(1)-Ir-P(2)	89.0 (1)	C(7)-C(2)-N(1)	131.5 (5)
C(11)-P(1)-C(21)	105.0 (2)	N(3)-C(3)-C(4)	131.1 (5)
C(11)-P(1)-C(31)	104.3 (2)		

found in the work of Kuyper et al.[12] and, indeed, the long-wavelength absorption in the electronic spectrum of **5** appears inconsistent with a simple $IrX_2(CO)(PPh_3)^-$ salt.



5a



5b

In the solid state, the thallium compound **5** is stable to air. However, solutions quickly turn from purple to yellow, whether or not PPh_3 is added. The yellow product was identified as *trans*-$Ir(BTA)(CO)(PPh_3)_2$ (**6**) on the basis of elemental analyses and spectroscopic properties. Carbonyl stretching frequencies have been tabulated for a large series of compounds of the type *trans*-$IrX(CO)(PPh_3)_2$. The ν_{CO} band in **6** at 1974 cm^{-1} ($CHCl_3$), which may be compared with 1976 cm^{-1} for X = NCS, 1971 cm^{-1} for X = ONO_2, and 1965–1966 cm^{-1} for X = Cl, Br, I, and N_3, indicates that benzotriazenide (as an η^1 ligand, see below) is a moderately strong π acceptor. It has been reported[14] that strong π-acceptor ligands stabilize the π_{b_1} level in *trans*-$MX(CO)(PPh_3)_2$ (M = Rh, Ir) complexes, lowering the energy of the long-wavelength transition. This transition in **6** occurs at 450 nm, also consistent with π-acceptor behavior of benzotriazenide. In order to confirm the proposed structure of **6** and to explore further the bonding in transition metal triazenido complexes, the structure determination of this material has been carried out.

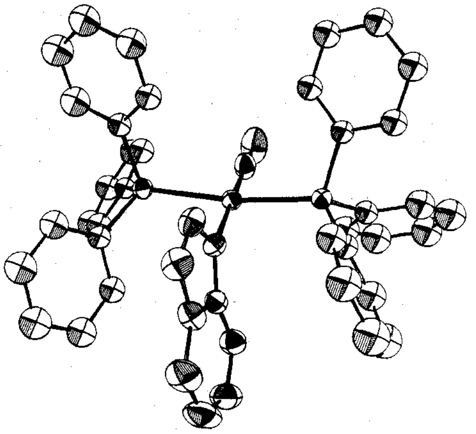


Figure 2. An overall view of the $Ir(BTA)(CO)(PPh_3)_2$ molecule. Hydrogen atoms are omitted for clarity. The 50% probability ellipsoids are shown.

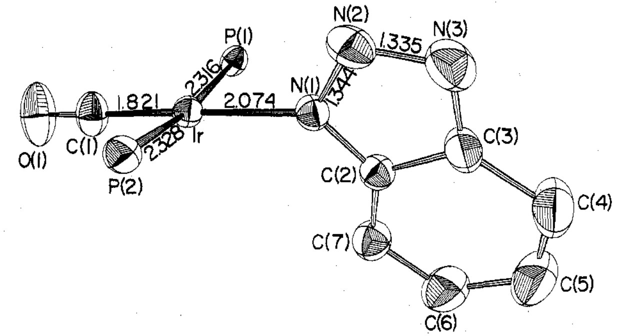


Figure 3. The inner-coordination sphere of $Ir(BTA)(CO)(PPh_3)_2$. The labeling scheme and principal bond distances are shown. The 50% probability ellipsoids are shown.

The crystal structure of $Ir(BTA)(CO)(PPh_3)_2$ consists of well-separated molecular units (Figure 1), with the shortest H···H contact being 2.38 Å. The overall molecular structure is shown in Figure 2, while Figure 3 displays the inner-coordination sphere, the labeling scheme, and some of the bond distances. Tables V and VI give bond distances and angles.

The Ir center is essentially in a square-planar environment, although deviations from this geometry are significant. Thus, the P(1)–Ir–P(2) angle is 169.5 (4)°. In other terms, the best, weighted, least-squares plane through atoms Ir, P(1), P(2), C(1), O(1), and N(1) has the equation $8.683x + 12.676y -$

Table VI. Comparison of the BTA Ligand in $Ir(BTA)(CO)(PPh_3)_2$ with Benzotriazole

distance, Å, or angle, deg	$Ir(BTA)(CO)(PPh_3)_2$ [a]	Benzotriazole [b]
N(1)-N(2)	1.344 (6)	1.346 (10) [c]
N(2)-N(3)	1.335 (6)	1.310 (7)
N(3)-C(3)	1.358 (7)	1.362 (35)
C(3)-C(2)	1.383 (7)	1.389 (10)
C(2)-N(1)	1.366 (6)	1.366 (14)
C(3)-C(4)	1.416 (8)	1.409 (9)
C(4)-C(5)	1.376 (9)	1.368 (10)
C(5)-C(6)	1.387 (9)	1.405 (10)
C(6)-C(7)	1.370 (8)	1.367 (5)
C(7)-C(2)	1.398 (7)	1.404 (8)
C(2)-N(1)-N(2)	107.8 (4)	110.3 (1.3)
N(1)-N(2)-N(3)	110.4 (4)	108.8 (8)
N(2)-N(3)-C(3)	106.8 (4)	108.2 (4)
N(3)-C(3)-C(2)	108.8 (5)	108.4 (3)
C(3)-C(2)-N(1)	106.1 (4)	104.2 (8)
C(3)-C(4)-C(5)	116.9 (6)	116.2 (7)
C(4)-C(5)-C(6)	122.0 (6)	122.2 (4)
C(5)-C(6)-C(7)	121.9 (7)	122.7 (1)
C(6)-C(7)-C(2)	116.8 (6)	115.3 (5)
C(7)-C(2)-C(3)	122.3 (5)	122.7 (7)
C(2)-C(3)-C(4)	120.1 (5)	121.5 (5)

[a] Present work. [b] Reference 15. [c] In benzotriazole the H atom is attached to atom N(1). A given standard deviation of a single observation for benzotriazole is obtained from the agreement among the four independent molecules in the asymmetric unit.

$7.716z = -0.204$, and the deviations from this plane are −0.0080 (2), 0.218 (1), 0.190 (1), −0.009 (6), 0.000 (6), and −0.065 (4) Å, respectively.

The BTA ligand is nearly planar. The least-squares plane through the nine atoms of the plane has the equation $3.847x + 11.520y + 9.151z = 5.619$ and the deviations from this plane are the following: N(1), −0.014 (4); N(2), −0.019 (4); N(3), 0.020 (5); C(2), 0.032 (5); C(3), 0.016 (5); C(4), −0.018 (7); C(5), −0.035 (8); C(6), −0.018 (7); C(7), 0.016 (6) Å. The Ir atom is −0.235 Å from this plane. The BTA plane makes an angle of 78.4° with the Ir basal plane described above.

The metrical details of the BTA ligand in the present complex are compared with those of benzotriazole[15] in Table VI. Except for the N(2), N(3) region, the agreement is very good. Even the possibly significant alternation of bond lengths in the six-membered ring persists in the complex. Thus, substitution of $(Ph_3P)_2(CO)Ir$ for H appears to affect mainly the N_3 portion of the triazenido moiety. In a formal sense the present ligand, in view of the equivalence of the N—N bond lengths, may be thought of as Ir—N$\overset{-}{\cdots}$N$\overset{-}{\cdots}$N, whereas in benzotriazole itself the formal representation is H—N—N═N.

The only other example of the η^1 coordination of a triazenido ligand to a transition metal is in *cis*-$Pt(PhNNNPh)_2(PPh_3)_2$.[3] Here the Pt–N(1) distance is 2.089 (6) Å and the N(1)–N(2) distance is 1.336 (6) Å, values which do not differ significantly from their counterparts in the present structure. However, in the unconstrained PhNNNPh ligand, the N(2)–N(3) distance is 1.278 (6) Å, significantly shorter than that of 1.335 (6) Å found here.

The η^2 coordination of the benzotriazenido ligand has been found in the structure of hexakis(benzotriazolyl)hexakis(allylamine)trinickel(II),[16] where the ligand bridges two Ni atoms through atoms N(1) and N(2). Curiously, the N–N distances of 1.333 (7) and 1.328 (7) Å do not differ from one another nor from those found in the present structure. On the other hand, in the compound (1-*N*-allylbenzotriazole)tricarbonyliron[17] the N(1)–N(2) distance of 1.35 (1) Å possibly differs from the N(2)–N(3) distance of 1.30 (1) Å. In this compound the Fe atom is bonded to atom N(2), while the allyl group on atom N(1) also coordinates to the Fe atom.

In the two known cases of benzotriazenido ligation to transition metals, the N—N distances remain equivalent and consistent with the formulation N$\overset{-}{\cdots}$N$\overset{-}{\cdots}$N. In neither the Ni structure[16] nor the present one does there appear to be sufficient room to enable the benzotriazenido ligand to interact with the metal in a π fashion, reminiscent of π-allyl. In fact, no such bonding mode for any triazenido ligand has been observed. Nevertheless, on the basis of the present results it would appear that the benzotriazenido ligand might be capable of such π coordination in a sterically acceptable environment.

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Registry No. **3**, 67328-65-8; **4**, 67328-66-9; **6**, 67328-67-0; $Ir(BTA)(CO)(PPh_3)Tl$, 67328-68-1; $Ir(BTA)_2(PPh_3)Tl$, 67328-69-2; $IrCl(CO)(PPh_3)_2$, 14871-41-1; Tl(BTA), 67350-99-6.

Supplementary Material Available: Table IV, the listing of structure amplitudes (×10) (43 pages). Ordering information is given on any current masthead page.

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