Very low yields of a $[(C_6H_5NH)P(S)NC_6H_5]_2$, II, which may be a different isomer from I, are obtained from the thermolysis products of the α-$P_4S_3I_2$–$C_6H_5NH_2$ reaction. Because the compound appears less stable than I and only low yields were obtained, adequate crystals for X-ray analysis or sufficiently large samples for NMR spectral analysis were not obtained.

The formation of I in the β-$P_4S_3I_2$–aniline reaction represents a novel source of it. I undoubtedly forms as a result of a complex series of reactions. However, by examination of ^{31}P NMR and mass spectra of samples collected from β-$P_4S_3I_2$–$C_6H_5NH_2$ reactions in toluene solvent, which were carried out for varying time and temperature conditions, some information about the sequence of events that occurs can be obtained. β-$P_4S_3I_2$ and $C_6H_5NH_2$ react immediately upon combination, below room temperature. Precipitation of $C_6H_5NH_3I$ occurs, and P_4S_3 forms along with a complex mixture of (phenylamino)- and/or (phenylimido)phosphorus sulfide materials. After the reaction mixture was heated at 80–90 °C for 3–4 h, small quantities of what can be characterized tentatively in the mixture as $(C_6H_5NH)_3PS$, along with traces of I and β-P_4S_4, are evident. Further heating results in increased formation of I and traces of P_4S_5. Attempts to identify other materials have so far been unsuccessful. However, studies of the reaction products and the mechanism of formation of I are being pursued, currently.

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Registry No. I, 70160-66-6; II, 55935-79-0; β-$P_4S_3I_2$, 34330-76-2; $C_6H_5NH_2$, 62-53-3; α-$P_4S_3I_2$, 19257-89-7; $(C_6H_5NH)_3PS$, 4743-38-8.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(15) $\mathrm{RLP} = 1/Lp = (2.0 \sin\theta \cos\theta)/\{0.5[(\cos^2 2\theta_m + \cos^2 2\theta)/(1 + \cos^2 2\theta_m)] + 0.5[(\cos 2\theta_m + \cos^2 2\theta)/(1 + \cos 2\theta m)]\}$, where θ and θ_m are the Bragg angles for the crystal and the monochromator ($2\theta_m = 26.6°$). The fractional mosaicity of the monochromator is assumed to be 0.5.

(16) A reflection was taken as significant when $F_o^2 > 3.0\sigma(F_o^2)$. $\sigma(F_o^2) = \mathrm{RLP}\{\mathrm{TSC} + \mathrm{BACK} + [P(\mathrm{TSC} - \mathrm{BACK})]^2\}^{1/2}$, where TSC is the total number of counts accumulated during the measurement scan, BACK is the total number of counts accumulated during the background measurement, and RLP is defined above; P, a damping factor, was given a value of 0.04 [W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957); P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967)].

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Synthesis and Structure of Diiododicarbonyltris(*tert*-butyl isocyanide)tungsten(II), an Example of the 4:3 Piano Stool Seven-Coordinate Geometry[1]

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The synthesis of diiododicarbonyltris(*tert*-butyl isocyanide)tungsten(II) from $(t\text{-}C_4H_9NC)_3W(CO)_3$ and elemental iodine is described. The compound crystallizes in polymorphic forms, depending upon the choice of solvent. The structure of an orthorhombic modification, space group *Pbca*, was revealed in a single-crystal X-ray diffraction study. The crystal parameters are $a = 18.297$ (5) Å, $b = 20.632$ (6) Å, and $c = 13.550$ (4) Å. With eight molecules per unit cell the calculated density is 1.930 g/cm^3, comparable to the observed value of 1.92 (3) g/cm^3. The structure was solved and refined on F to a final value of 0.045 for the discrepancy index R_1 by using 2832 unique observed reflections. The tungsten atom is coordinated to two iodine atoms with W–I bond lengths of 2.863 (1) and 2.865 (1) Å, two carbonyl groups, W–C = 1.997 (13) and 1.959 (15) Å, and three isocyanide ligands, W–C = 2.093 (13), 2.100 (13), and 2.145 (13) Å. A detailed analysis of the geometry reveals the coordination polyhedron of the tungsten to be that of a 4:3 square base–trigonal cap piano stool. Criteria for choosing this structure are discussed.

Introduction

The geometries of most seven-coordinate complexes can be described in terms of one of three idealized structures, the 1:5:1 D_{5h} pentagonal bipyramid, the 1:4:2 C_{2v} capped trigonal prism, and the 1:3:3 C_{3v} capped octahedron.[3-9] It was therefore unexpected when the structure of $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$, prepared in the course of studies of the chemistry of higher coordinate isocyanide complexes,[2] could not clearly be assigned

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to any of these polyhedral forms. Rather, as described in the present report, the geometry closely approximates that of a 4:3 square base–trigonal cap "piano stool". This polyhedral form has been reported for polymeric structures, such as those of ZrO_2[10] and $YbCl_2$[11] (but see below), and is usually included in discussions of seven-coordinate geometries. It has been stated, however, that the 4:3 geometry is not sufficiently different from those of the capped trigonal prism and capped octahedron to deserve separate mention.[9] While no polyhedron occupies a uniquely stable minimum on the seven-coordinate potential energy surface and the barriers to interconversion are not high,[8] the 4:3 structure should probably not be excluded. The complex $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$ is an authentic example of a mononuclear complex having this geometry and, as will be shown, there are other compounds in the literature that have the same structure. Moreover, the 4:3 piano stool geometry is a logical intermediate for dissociative reactions of square-antiprismatic eight-coordinate molecules. It is therefore a useful idealization to retain.

Experimental Procedure and Results

Preparation of Compounds. Tris(*tert*-butyl isocyanide)tricarbonyltungsten(0), $(t\text{-}C_4H_9NC)_3W(CO)_3$. A solution containing 1.8 g of $W(CO)_6$ in 15 g of degassed *tert*-butyl isocyanide was refluxed under nitrogen for 4 days. Excess isocyanide was distilled off in vacuo. The resultant yellow powder was purified by silica gel chromatography with chloroform as the solvent. Recrystallization by slow evaporation from a chloroform/heptane mixture gave pure product in 70–80% yield. Anal. Calcd for $C_{18}H_{27}N_3O_3W$: C, 41.79; H, 5.26; N, 8.12; W, 35.54. Found: C, 41.71; H, 5.41; N, 8.08; W, 35.40. IR (Nujol mull): 2160 (m), 2110 (s), 1935 (sh), 1918 (s), 1850 (s), 1235 (w), 1210 (m), 598 (w), 595 (w), 582 (m), 547 (w), 428 (m) cm^{-1}.

Diiododicarbonyltris(*tert*-butyl isocyanide)tungsten(II), $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$. A solution containing 1.70 g (3.3 mmol) of $(t\text{-}C_4H_9NC)_3W(CO)_3$ and 0.74 g (2.9 mmol) of iodine in 100 mL of degassed 1:1 benzene–diethyl ether was stirred under nitrogen at room temperature for 3 h. The solvent was removed from the brown solution under reduced pressure. The resultant orange-yellow powder was purified by silica gel chromatography with either (A) chloroform or (B) benzene to elute the column. Material from A was crystallized by vapor diffusion of pentane into the chloroform solution to yield 0.98 g (45%) of orange needles. Vapor diffusion of pentane into the benzene solution from B yielded the orange-yellow crystalline product (80%). Anal. Calcd for $C_{17}H_{27}N_3O_2I_2W$: C, 27.48; H, 3.66; N, 5.65; I, 34.16. Found (A, B, B): C, 27.48, 27.99, 28.09; H, 3.78, 3.72, 3.89; N, 5.58, 6.07, 4.90; I, 33.72, 33.68, 34.14. The two compounds had virtually identical IR spectra (Nujol mulls): 2210 (s), 2175 (s), 2150 (s), 1978 (s), 1915 (s), 1242 (m), 1208 (s), 578 (sh, w), 571 (m), 528 (m), 488 (m), 450 (w), 432 (w), 412 (w), 384 (vw), 335 (vw), 302 (vw) cm^{-1}.

X-ray Structural Work on $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$. A crystal grown from benzene–pentane of approximate dimensions 0.05 mm × 0.05 mm × 0.25 was mounted in a 0.1-mm diameter capillary under a nitrogen atmosphere. Preliminary study on precession and Weissenberg cameras revealed the Laue symmetry to be *mmm* and the following extinctions: $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$, consistent with space group *Pbca* (D_{2h}^{15}, No. 61).[12a] The crystal was then transferred to a four-circle automated diffractometer for precise determination of the unit cell parameters and data collection. Details are given in Table I.

The structure was solved by using standard Patterson, Fourier, and least-squares refinement methods. Hydrogen atoms of the *tert*-butyl groups were located on Fourier sections plotted for planes expected to contain these atoms. The hydrogen isotropic thermal parameters were assigned values one greater than the isotropic *B*'s of the corresponding methyl carbon atoms. Positional and thermal parameters of the hydrogen atoms were fixed during the refinement. All nonhydrogen atoms were refined with anisotropic temperature factors. Full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$, converged at final values of 0.045 and 0.055 for the residuals $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, respectively. A total of 226 variable parameters were used to fit 2832 data having $F_o^2 > 3\sigma(F_o^2)$. In the final refinement cycle no parameter shifted by more than 0.017 times its estimated standard deviation. Atomic scattering factors and anomalous dispersion contributions for tungsten and iodine were taken from ref 13. The standard deviation of an observation of unit weight was 1.520 and average values of the function $w\Delta^2$ showed no unusual variations for data sectioned

Table I. Experimental Details of the X-ray Diffraction Studies of $[(t\text{-}C_4H_9NC)_3W(CO)_2I_2]$

(A) Crystal Parameters at 23 °C

$a = 18.297\ (5)$ Å[a]	$a = 14.502\ (13)$ Å[b]
$b = 20.632\ (6)$ Å	$b = 9.559\ (7)$ Å
$c = 13.550\ (4)$ Å	$c = 22.762\ (18)$ Å
$V = 5115.1$ Å^3	$\beta = 91.85\ (1)°$
mol wt = 743.08	$V = 3153.7$ Å^3
$Z = 8$	mol wt = 743.08
ρ(calcd) = 1.930 g/cm^3	$Z = 4$
ρ(obsd) = 1.92 (3) g/cm^3 [c]	ρ(calcd) = 1.565 g/cm^3
space group *Pbca*	ρ(obsd) = 1.59 (5) g/cm^3 [d]
	space group $P2_1/c$

(B) Measurement of Intensity Data

instrument: Picker FACS-I-DOS diffractometer
radiation: graphite-monochromatized Mo Kα (λ_{α_1} 0.709 30 Å)
attenuator: Al foil attenuators used for counts >10 kHz
takeoff angle: 1.85°
detector aperature: 6.3 × 6.3 mm
crystal–detector distance: 33 cm
scan mode: coupled θ(crystal)–2θ(counter)
scan rate: 1°/min
scan range: 1.75°; symmetric, plus K_{α_1}–K_{α_2} dispersion
maximum 2θ: 50°
background measurements: stationary crystal, stationary counter, 20 s at each end of 2θ scan range
standards: 3 reflections (293), $(\bar{4}74)$, $(6\bar{6}4)$ measured after every 47 data reflections
no. of reflections measured: 5772

(C) Treatment of Intensity Data[e]

reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attentuators and Lorentz–polarization of monochromatized radiation in the usual manner; $\epsilon = 0.05$[f,g]
correction for crystal decomposition:[h] data scaled for approximately 10% anisotropic decay
absorption correction:[i] $\mu = 70.2\ cm^{-1}$; transmission factors ranged from 0.282 to 0.382
averaging: 12 doublets and 1 triplet averaged, $R_{av} = 0.013$[j]
scaling: Wilson's method, $\bar{B} = 4.13$ Å^2 [k]
observed data: 2832 unique reflections for which $F_o^2 > 3\sigma(F_o^2)$

[a] From a least-squares fit to the setting angles of 22 reflections; these crystals were obtained from benzene–pentane. [b] From a least-squares fit to the setting angles of 12 reflections; these crystals were obtained from chloroform–pentane. [c] By flotation in an aqueous solution of zinc bromide. [d] The markedly lower density of this form might be the result of ligand disorder (see text). [e] Programs for an IBM 360/91 computer used in this work are described in J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, **15**, 1155 (1976). [f] B. G. Segal and S. J. Lippard, *ibid.*, **13**, 822 (1974). [g] J. T. Gill and S. J. Lippard, *ibid.*, **14**, 751 (1975). [h] Anisotropic scaling method is described in E. I. Lerner and S. J. Lippard, *ibid.*, **16**, 6 (1977). [i] Absorption corrections were carried out by using a local version of **ORABS**, the Wehe–Busing–Levy program, adapted to the Picker FACS geometry. [j] Using **AVERAGE** by J. T. Gill, $R_{av} = \Sigma_{i=1}^{N}\Sigma_{j=1}^{N}|\bar{F}_o^2 - F_{ij}^2|/\Sigma_{i=1}^{N}F_i^2$. [k] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

Table II. Final Positional and Thermal Parameters of the Nonhydrogen Atoms[a-c]

ATOM	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.06596(3)	0.17390(2)	0.21917(3)	2.907(16)	1.833(11)	5.20(3)	0.032(13)	0.23(2)	0.241(14)
I1	0.07083(6)	0.24173(5)	0.40342(7)	6.83(5)	3.33(3)	5.38(6)	−0.35(3)	0.27(5)	−0.50(3)
I2	0.15551(7)	0.08006(5)	0.31743(8)	6.04(5)	3.46(3)	8.30(7)	1.29(3)	−0.95(5)	1.48(4)
C1	−0.0118(8)	0.1250(6)	0.2909(10)	4.0(5)	2.5(3)	7.4(9)	0.0(4)	2.4(6)	0.4(5)
O1	−0.0564(6)	0.0955(5)	0.3285(10)	6.3(5)	3.4(3)	14.1(11)	−1.5(3)	3.5(6)	0.4(5)
C2	−0.0113(8)	0.1643(6)	0.1201(11)	3.3(5)	2.4(4)	9.8(11)	−0.4(4)	−0.3(6)	−0.3(5)
O2	−0.0572(6)	0.1587(5)	0.0654(9)	5.1(4)	3.7(3)	13.3(10)	−0.6(3)	−2.9(6)	−0.0(5)
C3	0.1081(7)	0.1158(6)	0.1061(10)	4.2(5)	2.0(3)	6.4(9)	0.4(3)	0.6(6)	−0.7(4)
N3	0.1349(6)	0.0859(5)	0.0467(9)	4.7(5)	2.5(3)	8.2(9)	0.3(3)	0.6(5)	−0.4(4)
C32	0.1779(8)	0.0432(7)	−0.0173(11)	5.0(6)	3.4(4)	7.9(10)	1.4(4)	−0.1(7)	−2.0(6)
C4	0.1645(7)	0.2221(6)	0.1749(10)	2.7(4)	2.0(3)	8.3(10)	−0.2(3)	−0.1(5)	−0.5(4)
N4	0.2179(6)	0.2460(5)	0.1535(8)	3.8(4)	2.8(3)	7.9(8)	−0.3(3)	1.0(5)	0.4(4)
C42	0.2891(9)	0.2717(8)	0.1222(15)	3.7(6)	3.3(4)	13.5(15)	−1.1(4)	1.6(8)	−0.5(7)
C5	0.0300(6)	0.2682(6)	0.1872(9)	2.7(4)	2.7(4)	5.2(8)	−0.1(3)	−1.1(5)	−0.8(4)
N5	0.0124(6)	0.3206(5)	0.1707(7)	4.3(4)	1.9(2)	6.5(7)	0.5(3)	−0.7(5)	−0.7(4)
C52	−0.0020(8)	0.3886(5)	0.1589(10)	4.8(6)	1.7(3)	7.5(10)	0.1(3)	0.6(6)	0.3(4)
C33	0.2032(11)	0.0820(9)	−0.1048(12)	8.6(10)	5.3(6)	7.8(11)	2.1(7)	3.4(9)	−0.2(7)
C34	0.2413(11)	0.0220(9)	0.0443(15)	8.3(10)	5.6(7)	12.1(16)	3.4(7)	1.4(11)	−1.0(9)
C35	0.1305(11)	−0.0111(9)	−0.0454(16)	8.5(10)	3.8(5)	15.5(19)	−1.0(6)	2.6(12)	−2.9(9)
C43	0.2823(12)	0.3386(9)	0.106(2)	7.4(10)	3.5(6)	34(4)	−1.3(6)	6.2(16)	2.7(12)
C44	0.3395(12)	0.2573(16)	0.200(3)	4.5(8)	10.2(14)	37(5)	−2.2(10)	−3.4(17)	6(2)
C45	0.3097(18)	0.2337(18)	0.036(3)	16(2)	17(2)	41(5)	−12.5(19)	20(3)	−19(3)
C53	−0.0192(11)	0.4156(7)	0.2595(14)	7.8(9)	2.7(4)	11.1(13)	0.5(5)	1.9(9)	−1.9(6)
C54	0.0649(12)	0.4156(7)	0.1180(15)	10.3(12)	2.3(4)	12.6(16)	0.4(6)	2.6(11)	−0.5(6)
C55	−0.0640(12)	0.3961(9)	0.0894(16)	9.6(11)	3.8(5)	14.9(19)	2.9(7)	−4.6(12)	−0.9(8)

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic thermal ellipsoids is $\exp[-(\beta_{11}h^2 + \beta_{22}h^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are ×10³.

Table III. Molecular Geometry of $[(t\text{-}C_4H_9NC)_3W(CO)_2I_2]$[a,b]

(A) Coordination Sphere			
W–I1	2.863 (1)	W–C3	2.092 (13)
W–I2	2.865 (1)	W–C4	2.145 (13)
W–C1	1.997 (13)	W–C5	2.099 (13)
W–C2	1.959 (15)		
I1–W–I2	84.68 (4)	C1–W–C2	76.6 (6)
I1–W–C1	81.1 (4)	C1–W–C3	109.2 (5)
I1–W–C2	132.0 (4)	C1–W–C4	165.8 (6)
I1–W–C3	155.1 (4)	C1–W–C5	110.2 (5)
I1–W–C4	89.5 (3)	C2–W–C3	72.9 (6)
I1–W–C5	74.7 (3)	C2–W–C4	117.5 (6)
I2–W–C1	80.8 (4)	C2–W–C5	74.1 (5)
I2–W–C2	131.5 (4)	C3–W–C4	75.6 (5)
I2–W–C3	75.1 (4)	C3–W–C5	119.7 (5)
I2–W–C4	87.9 (3)	C4–W–C5	77.1 (5)
I2–W–C5	154.4 (3)		
(B) Ligand Geometry			
C1–O1	1.139 (14)	C42–C43	1.402 (23)
C2–O2	1.126 (15)	C42–C44	1.434 (32)
C3–N3	1.127 (15)	C42–C45	1.457 (30)
N3–C32	1.464 (16)	C5–N5	1.150 (13)
C32–C33	1.502 (22)	N5–C52	1.437 (14)
C32–C34	1.495 (22)	C52–C53	1.506 (21)
C32–C35	1.467 (21)	C52–C54	1.456 (21)
C4–N4	1.133 (14)	C52–C55	1.481 (22)
N4–C42	1.468 (18)		
W–C1–O1	177.2 (1.3)	N4–C42–C44	106.4 (1.7)
W–C2–O2	177.9 (1.4)	N4–C42–C45	105.5 (1.5)
W–C3–N3	175.8 (1.2)	C43–C42–C44	111.9 (2.2)
C3–N3–C32	170.4 (1.4)	C43–C42–C45	115.4 (2.5)
N3–C32–C33	108.2 (1.2)	C44–C42–C45	108.3 (2.6)
N3–C32–C34	105.2 (1.2)	W–C5–N5	177.8 (1.0)
N3–C32–C35	107.2 (1.3)	C5–N5–C52	172.5 (1.3)
C33–C32–C34	111.0 (1.5)	N5–C52–C53	107.4 (1.1)
C33–C32–C35	112.6 (1.5)	N5–C52–C54	105.1 (1.2)
C34–C32–C35	112.3 (1.6)	N5–C52–C55	108.3 (1.2)
W–C4–N4	177.5 (1.1)	C53–C52–C54	112.2 (1.3)
C4–N4–C42	175.1 (1.3)	C53–C52–C55	112.2 (1.4)
N4–C42–C43	108.7 (1.5)	C54–C52–C55	111.2 (1.5)

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each value. No corrections were made for thermal motion.

according to $|F_o|$ or $(\sin\theta)/\lambda$. A final difference Fourier map showed peaks ~0.9 Å from the tungsten atom with electron density about 0.4 times that of a carbon atom and was free of unusual features elsewhere.

Nonhydrogen atomic positional and thermal parameters, together with their standard deviations as derived from the inverse matrix of the final least-squares refinement cycle, are given in Table II. Corresponding hydrogen parameters are available as Table S1.[14] Interatomic distances and angles are summarized in Table III and, for hydrogen atoms, in Table S2. A listing of observed and calculated structure factor amplitudes and the root-mean-square amplitudes of thermal vibration are given as Tables S3 and S4, respectively.[14] The molecular geometry and atom-labeling scheme are shown in Figure 1. The coordination geometry is depicted in Figure 2.

Crystals from chloroform–pentane grow as parallelepipeds of approximate dimensions 0.05 mm × 0.05 mm × 0.15 mm. Preliminary precession and Weissenberg photographs using nickel-filtered copper Kα radiation revealed $2/m$ Laue symmetry and the systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. The space group was therefore determined to be $P2_1/c$.[12b] The lattice parameters are given in Table I. An attempt was made to collect data and solve the structure of this form. After approximately 1400 reflections had been collected, the intensities of the standard reflections had fallen to 75% of their initial values and data collection was terminated. While a structure could be solved and refined by using these data, the standard deviations were high and the carbonyl and *tert*-butyl groups appeared to be disordered in the coordination sphere. Two subsequent attempts to grow crystals from chloroform/pentane were unsuccessful. Further studies were therefore continued by using the orthorhombic modification obtained from benzene/pentane as reported above. It is not known whether decomposition of the monoclinic crystal was a result of reaction with air, the effect of X radiation, or both. Additional work on this form is planned if suitable crystals can be obtained.

Discussion

When tungsten hexacarbonyl is refluxed in *tert*-butyl isocyanide, chemical analysis shows the major product isolated to be $(t\text{-}C_4H_9NC)_3W(CO)_3$. Oxidative addition of iodine to this compound, with loss of one carbonyl ligand, affords the title compound in reasonable yields. There is considerable precedent in the literature for oxidative addition of halogen to zerovalent, hexacoordinate group 6 transition metals to form divalent heptacoordinate complexes.[2,9,15]

A stereoscopic view of the structure of $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$ is shown in Figure 1. Visual inspection of this and other stereo drawings and study of an accurate model of the compound suggested that the geometry might be classified as either a capped trigonal prism, with I1 or I2 as the capping

Table IV. Dihedral Angle Calculations[a] for Seven-Coordinate Molecules in Various Trial Geometries

		dihedral angle values, deg	
compound	trial geometry	dihedral angles	idealized values[b]
$(t\text{-BuNC})_3W(CO)_2I_2$, this work	capped octahedron C2 capping	21.2, 20.8, 2.3	16.2, 16.2, 16.2
	capped trigonal prism I1 capping	37.7, 2.3, 21.2	41.5, 0, 0
	capped trigonal prism I2 capping	37.2, 20.8, 2.3	41.5, 0, 0
	4:3 piano stool	4.8, 2.3	0, 0
polymeric ZrO_2, ref 10	capped octahedron O2D capping	19.8, 1.3, 28.8	16.2, 16.2, 16.2
	capped trigonal prism O1A capping	36.6, 1.3, 28.8	41.5, 0, 0
	4:3 piano stool	9.3, 1.4	0, 0
polymeric $YbCl_2$, ref 11	capped octahedron Cl2 capping	42.4, 1.7, 2.0	16.2, 16.2, 16.2
	capped trigonal prism Cl1″ capping	42.5, 2.0, 1.7	41.5, 0, 0
	4:3 piano stool	12.9, 1.7	0, 0
$MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2$, ref 17	capped octahedron C1 capping	1.7, 21.8, 25.1	16.2, 16.2, 16.2
	capped trigonal prism Br1 (or As2) capping	39.3, 1.7, 25.1 (or 40.3, 1.7, 21.8)	41.5, 0, 0
	4:3 piano stool	9.3, 1.7	0, 0
$MoI_2(CO)_3[rac\text{-}o\text{-}C_6H_4(AsMePh)_2]$, ref 18	capped octahedron C2 capping	24.6, 2.1, 17.3	16.2, 16.2, 16.2
	capped trigonal prism I1 (or As1) capping	41.6, 2.1, 17.3 (or 35.9, 2.1, 24.6)	41.5, 0, 0
	4:3 piano stool	5.1, 2.1	0, 0

[a] The published coordinates were used to project the structure onto a sphere[7] after which the usual dihedral angles (δ') between planes[6] were calculated. [b] These are taken from ref 6. For the 4:3 piano stool, the first angle refers to the dihedral angle between the trigonal plane and the best plane through the four atoms comprising the quadrilateral face; the second angle is taken across the diagonal of the quadrilateral face.

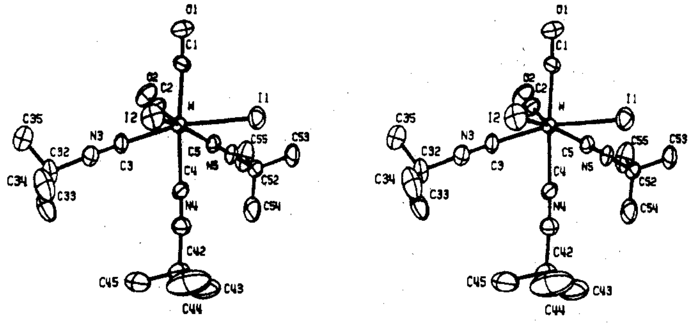

Figure 1. Stereoview of the geometry of diiododicarbonyltris(*tert*-butyl isocyanide)tungsten(II) in the orthorhombic crystal form. The 30% probability thermal ellipsoids and atom labeling scheme are displayed. Hydrogen atoms are omitted for clarity.

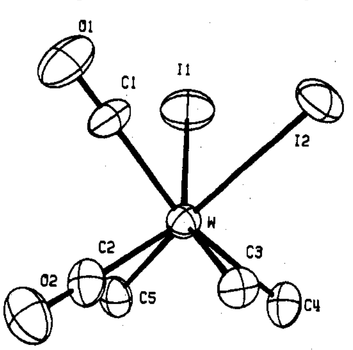

Figure 2. Coordination geometry of $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$ oriented to show the 4:3 piano stool structure. Only the coordinated carbon atoms of the *tert*-butyl isocyanide ligands are shown.

ligand, or a capped octahedron with C2 capping. As shown in Table IV, however, dihedral angle calculations using the "points on a unit sphere" method[5-7] reveal significant departures from the ideal values. The two capped trigonal-prismatic trial geometries are inferior to that of the capped octahedron. The latter has a 2.3° dihedral angle between planes defined by atoms C2, C3, and C5 and atoms C3, C4, and C5, compared with the ideal value of 16.2°. The fact that atoms C2, C3, C4, and C5 were nearly coplanar led us to explore the 4:3 piano stool configuration. As may be seen from Table IV and Figure 2, the geometry of $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$ agrees rather well with such a description. The angle between the two planes defined by I1, I2, and C1 and C2, C3, C4, and C5 is 4.8° while the dihedral angles across the diagonals of the quadrilateral face are 2.3°. The ideal values are all 0°. Thus the structure more closely approximates the 4:3 geometry than any of the usual alternatives.

Similar calculations were made for a number of other known heptacoordinate molecules. The results are included in Table IV. As reported,[10] the zirconium dioxide polymer is best described as a 4:3 structure. Polymeric $YbCl_2$ on the other hand, while previously assigned a 4:3 geometry,[11] is in fact better described as a capped trigonal prism. The molecule $MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2$[16,17] is well described as a 4:3 structure, as is $MoI_2(CO)_3[rac\text{-}o\text{-}C_6H_4(AsMePh)_2]$.[18] These calculations demonstrate that the 4:3 geometry can sometimes be a better idealized structure for a given molecule than either the C_{2v} capped trigonal prism or the C_{3v} capped octahedron.

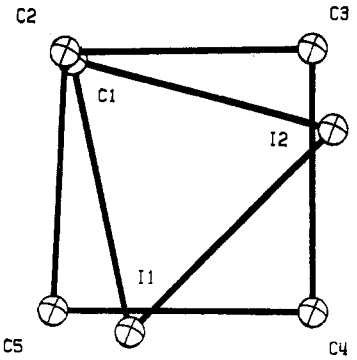

Figure 3. Projection of the quadrilateral plane onto the trigonal plane of coordinated atoms (transformed to a unit sphere) in (t-$C_4H_9NC)_3W(CO)_2I_2$. Lines joining the atoms are drawn to define the planes. The tungsten atom is omitted.

It may represent a shallow minimum on the potential energy surface connecting these heptacoordinate stereochemistries. From Table IV it is apparent that the 4:3 piano stool should be tried whenever one and only one of the δ' dihedral angles in a capped octahedral or capped trigonal-prismatic test geometry is near 0°.

Figure 3 displays the projection of the quadrilateral plane onto that of the triangle. The distances of the tungsten atom from these planes are 1.06 and 1.60 Å, respectively. The geometry adopted by (t-$C_4H_9NC)_3W(CO)_2I_2$, one of many possible conformations related by twisting the trigonal face relative to the quadrilateral one,[4] has nearly perfect mirror symmetry with respect to the mean plane passing through atoms W, C1, C2, and C4 (Figure 3). The bond length pairs W–C3, W–C5, and W–I1, W–I2 are identical (Table III). The angles subtended by the vector joining the center of the triangular face and the tungsten atom with the W–I1, W–I2, and W–Cl bond vectors are 47.1, 46.9, and 55.0°, respectively, averaging to 49.7°. Similar angles for the quadrilateral face range from 119.4 to 121.9° and average 120.7°. These averages are notably close to the θ values of 50 and 120°, respectively, calculated for d^4 ML_7 molecules having a trigonal base–tetragonal base structure.[8]

Other features of the geometry, summarized in Table III, are unexceptional. The W–I and W–CO bond lengths agree with values reported for related seven-coordinate compounds.[19] Bond distances to the three isocyanide carbon atoms are within the range found for analogous seven-coordinate molybdenum(II) complexes.[1,2] The W–C4 distance is slightly longer than the other two because of the trans influence of the carbonyl groups (Figure 3). The internal geometry of the ligands is normal.

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Registry No. (t-$C_4H_9NC)_3W(CO)_2I_2$, 70046-78-5; (t-$C_4H_9NC)_3W(CO)_3$, 70095-01-1; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Tables S1–S4 listing respectively final positional and thermal parameters of the hydrogen atoms, interatomic distances and angles involving hydrogen atoms, observed and calculated structure factor amplitudes, and root-mean-square amplitudes of thermal vibration (21 pages). Ordering information is given on any current masthead page.

References and Notes

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