and the other band to a Rh–Rh $\pi^* \rightarrow$ Rh–O σ^* transition. The basic differences in the visible spectra of $Rh_2(ONHCCF_3)_4L_2$ and $Rh_2(OOCCH_3)_4L_2$ with a given axial ligand, L, are an ~40 and ~70 nm shift to higher energy of the lower and higher energy bands, respectively, for $Rh_2(ONHCCF_3)_4L_2$. Even though theoretical and experimental studies are needed, it is attractive to assign the lower energy band of $Rh_2(ONHCCF_3)_4$ to the $\pi^* \rightarrow \sigma^*$ transition and the band at ~380 nm to some type of $\pi^* \rightarrow$ Rh–O or Rh–N σ^* transition.

In conclusion, the molecular weight of the complexes (shown in Figure 2) in bands 1–3 are the same, and thus all three are probably geometric isomers. The complex in band 1 can be tentatively identified from the ^{19}F NMR spectrum as the isomer with three N atoms and one O atom on one rhodium and the reverse combination on the other. This complex shows three CF_3 resonances, which is consistent with such an isomer. The complex in band 2 is known from the structure determination reported in this paper. Band 3 is one of the remaining two possible isomers. We are presently working on several other amide systems, and preliminary results indicate that for a few systems relatively large amounts of all four isomers can be produced and isolated.

Acknowledgment. We would like to acknowledge Dr. Marvin Vestal for his assistance in obtaining the mass spectra of our samples. We also thank the Robert A. Welch Foundation (I.B. and J.D.K., Grant E-594; J.L.B. and A.M.D., Grant E-918) for operational support.

Supplementary Material Available: Tables of observed and calculated structure factors and atomic coordinates and thermal parameters (8 pages). Ordering information is given on any current masthead page.

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Geometric Isomerism in Seven-Coordinate Tungsten(II) Mixed Carbonyl–Iodide–*tert*-Butyl Isocyanide Complexes[1,2]

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Received October 22, 1982

The crystal and molecular structures of two monoclinic forms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$ (**1** and **2**) and of $W(CO)I_2(t\text{-}C_4H_9NC)_4 \cdot CHCl_3$ (**3**) have been determined. The coordination geometries of **1** and **2** are similar, approximating that of a 4:3 C_s piano stool. Two iodine atoms and a *tert*-butyl isocyanide carbon atom constitute the triangular cap, and the remaining four ligands constitute the tetragonal base. This isomer differs from that found in the previously studied orthorhombic form (**4**), in which one of the carbonyl ligands and the two iodine atoms form the triangular cap. Apart from their common 4:3 piano-stool structures, molecules in the three different crystalline forms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$ all have *cis*-WI_2 (W–I = 2.861 (2)–2.878 (1) Å; I–W–I = 85–88°) and *cis*-$W(CO)_2$ units (W–C = 1.87 (2)–2.00 (1) Å and C–W–C ~ 66–73°). The tungsten coordination geometry in **3** may be described as capped octahedral with the carbonyl group as the capping ligand (W–C = 1.93 (3) Å) and the two iodide atoms on the uncapped face (W–I = 2.876 (2) and 2.897 (2) Å; I–W–I = 87.9 (1)°). The W–CNR distances in the three structures range from 2.04 (3) to 2.19 (2) Å. Crystal data: for **1**, a = 9.362 (4) Å, b = 13.705 (2) Å, c = 19.797 (6) Å, β = 100.19 (3)°, space group $P2_1/n$, Z = 4, final R factor 0.037; for **2**, a = 9.773 (2) Å, b = 23.387 (6) Å, c = 11.918 (4) Å, β = 102.68 (2)°, space group $P2_1/n$, Z = 4, final R factor 0.065; for **3**, a = 9.763 (14) Å, b = 34.196 (10) Å, c = 11.484 (5) Å, β = 113.25 (6)°, space group $P2_1/n$, Z = 4, final R factor 0.050.

Introduction

Recently we have been studying the reductive coupling of coordinated alkyl isocyanide ligands in seven-coordinated d^4 molybdenum(II) and tungsten(II) complexes.[4] Although electronic effects are undoubtedly important in promoting this reaction,[2,4,5] the close nonbonded contacts between carbon atoms in a higher coordinate molecule having mostly linear ligands may also be a contributing factor. Since higher coordinated complexes of this kind are usually fluxional, it is difficult to probe their solution stereochemistries by conventional methods such as nuclear magnetic resonance spectroscopy. We have therefore undertaken an extensive and systematic X-ray crystallographic investigation of seven-coordinate group 6B metal isocyanide complexes in order to identify the solid-state structural patterns that might ultimately prove useful in designing reductive coupling reactions in solution.[6]

In the present paper we report the structures of two monoclinic crystalline forms (**1** and **2**) of $W(CO)_2I_2(tert\text{-}C_4H_9NC)_3$. An orthorhombic form (**4**) of this compound was previously shown to have the 4:3 tetragonal base–trigonal cap piano-stool geometry.[7] Preliminary work on a third monoclinic form (**5**) revealed a disordered structure that could not be refined. The low calculated density (1.565 g/cm^3 vs. 1.87–1.97 g/cm^3 for **1**, **2**, and **4**) of this crystal caused us to doubt whether it was characteristic of the bulk material in the sample, the analysis of which indicated it to be $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$.[7] We have thus far been unable to obtain form **5** again, but attempts to do so have led reproducibly to **1**, **2**, and **4**. Forms **1** and **2** are shown here to be geometric isomers

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(1) Part 19 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 18 see ref 2.

(2) Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860.

(3) To whom correspondence should be addressed at the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

(4) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263.

(5) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.

(6) (a) Dewan, J. C.; Mialki, W. S.; Walton, R. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 133. (b) Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069. (c) Szalda, D. J.; Dewan, J. C.; Lippard, S. J. *Ibid.* **1981**, *20*, 3851. (d) Dewan, J. C.; Lippard, S. J. *Ibid.* **1982**, *21*, 1682. (e) Dewan, J. C.; Wood, T. E.; Walton, R. A.; Lippard, S. J. *Ibid.* **1982**, *21*, 1854.

(7) Dreyer, E. B.; Lam, C. T.; Lippard, S. J. *Inorg. Chem.* **1979**, *18*, 1904.

(8) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142.

0020-1669/83/1322-1529$01.50/0

of **4**, a rare but not unprecedented phenomenon in seven-coordination chemistry.[9,10] We also describe the structure of $W(CO)I_2(t\text{-}C_4H_9NC)_4\cdot CHCl_3$, the synthesis of which was reported previously.[8] Of the ten $M(CO)_xI_y(CNR)_z^{(2-y)+}$ complexes involved in the synthesis and interconversion reactions of seven-coordinate Mo(II) and W(II) halo-carbonyl–isocyanide complexes,[8] five have now been structurally characterized.

Experimental Section

Collection and Reduction of X-ray Data. Dicarbonyldiiodotris(*tert*-butyl isocyanide)tungsten(II), $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, Form 1. The synthesis and crystallization of this molecule in the orthorhombic form (**4**) have been described previously,[7] with a full structural determination. Vapor diffusion of pentane into a chloroform solution of the compound under nitrogen gave, in our hands, crystals of monoclinic form **1**. The yellow crystal used in the diffraction study had approximate dimensions 0.43 mm × 0.28 mm × 0.56 mm and was sealed in a capillary. Its quality was checked on the diffractometer by taking open-counter ω scans of several strong low-angle reflections. The average peak widths at half-height were 0.13°, which was considered to be acceptable. The crystal system was shown to be monoclinic. Further details of the data collection and reduction appear in Table I and ref 11.

Dicarbonyldiiodotris(*tert*-butyl isocyanide)tungsten(II), $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, Form 2. Crystals of this form were obtained from diffusion of pentane into a THF solution of the compound. A second crop from the same solution gave the orthorhombic modification (**4**) as well.

The yellow crystal used for the diffraction study had approximate dimensions 0.33 mm × 0.33 mm × 0.47 mm and was sealed in a capillary. Study on the diffractometer showed that the crystal belonged to the monoclinic crystal system. The average half-height width of the ω scans was 0.12°. Table I and ref 11 further summarize the data collection and reduction procedures.

Carbonyldiiodotetrakis(*tert*-butyl isocyanide)tungsten(II)–Chloroform, $W(CO)I_2(t\text{-}C_4H_9NC)_4\cdot CHCl_3$ (3). The synthesis of **3** has been described previously.[8] Yellow crystals were grown from chloroform/pentane. The crystal selected for the diffraction study, 0.50 mm × 0.05 mm × 0.13 mm, was shown to be monoclinic. Its quality was checked on the diffractometer by taking open-counter ω scans. The average width of the peaks at half-height was rather broad (0.2°). Other details of the data collection and reduction appear in Table I and ref 11.

Determination and Refinement of the Structures. $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, Form 1. The diffractometer output revealed the systematic absences to be $h0l$ when $h + l \neq 2n$ and $0k0$ when $k \neq 2n$, indicating the space group to be $P2_1/n$.[12]

The structure was solved by using standard Patterson, Fourier, and least-squares refinement methods. Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were obtained from ref 13. All non-hydrogen atoms were refined anisotropically. In the final stages of refinement, methyl hydrogen atoms were set up and refined as rigid groups (C–H = 0.95 Å; H–C–H = 109.5°) pivoting on their respective carbon atoms. A common isotropic temperature factor for all these hydrogen atoms converged at U = 0.181 Å^2. In the final cycles of refinement these methyl hydrogen atoms were included as invariants with all parameters fixed at the values obtained in the last cycle of rigid-group refinement.

Using SHELX-76,[14] least-squares refinement was carried out on 227 variable parameters. These were used to fit 4255 data having $F_o > 4\sigma(F_o)$. The final residual indices[15] were $R_1 = 0.037$ and $R_2 = 0.044$. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.3187/[\sigma^2(F_o) + 0.000400F_o^2]$. In the final cycles of refinement, no parameter shifted by more than 0.003 of its estimated standard deviation and the largest peak on the final difference Fourier map was 1.78 e Å^{-3}, in the vicinity of the tungsten atom. All remaining peaks were <0.97 e Å^{-3}.

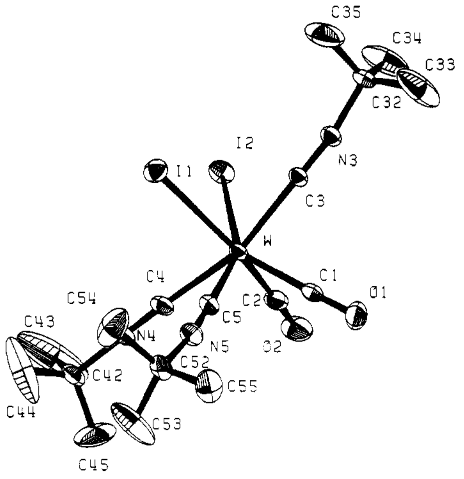

Figure 1. Structure of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, form **1**, showing the 20% probability thermal ellipsoids and the atom-labeling scheme. The atoms used to prepare this figure have been transformed ($-x$, $-y$, $-z$) from the coordinates listed in Table II in order to facilitate comparison with Figure 2.

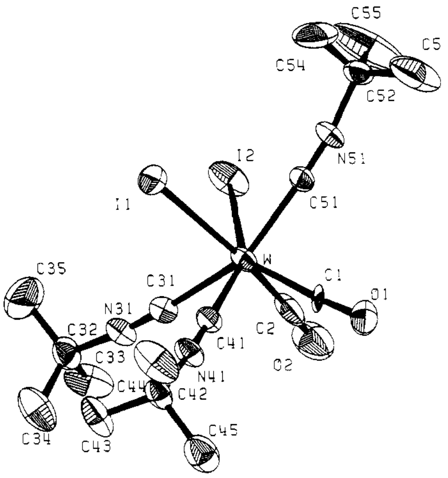

Figure 2. Structure of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, form **2**, showing the 20% probability thermal ellipsoids and the atom-labeling scheme.

Final non-hydrogen atom positional parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and angles, with estimated standard deviations, are given in Table V. Listings of final observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available in Tables S1, S4, and S7, supplied as supplementary material. Figure 1 shows the molecular geometry along with the atom-labeling scheme.

$W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, Form 2. Except as indicated below, the details of the structure analysis for form **2** are the same as those for **1**. The common isotropic temperature factor for the methyl hydrogen atoms coverged at U = 0.142 Å^2.

Using SHELX-76,[14] least-squares refinement was carried out on 227 variable parameters. These were used to fit 2734 data having $F_o > 4\sigma(F_o)$. The final residual indices[15] were $R_1 = 0.065$ and $R_2 = 0.068$. The weighting scheme was $w = 2.0785/[\sigma^2(F_o) + 0.000400F_o^2]$. The largest parameter shift in the final cycles of least-squares refinement was 0.002 of its estimated standard deviation, and the largest peaks on the final difference Fourier map were ~3.6 e Å^{-3}, lying along the b axis ±1.2 Å from the tungsten atom. All remaining peaks were <1.20 e Å^{-3}.

Tables III and VI list final non-hydrogen atom positional parameters and interatomic distances and angles. Final observed and calculated

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(9) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc. Dalton Trans.* **1977**, 557.

(10) For an excellent review see: Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.

(11) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

(12) A nonstandard setting of space group $P2_1/c$ (C_{2h}^5, No. 14): "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1973; Vol. I, p 99.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(14) Sheldrick, G. M. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C. Eds.; Delft University Press: Delft, 1978; p 34.

(15) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table I. Experimental Details of the X-ray Diffraction Studies of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$ (**1** and **2**) and $W(CO)I_2(t\text{-}C_4H_9NC)_4 \cdot CHCl_3$ (**3**)

	1	**2**	**3**
(A) Crystal Parameters[a] at 26 °C			
a, Å	9.362 (4)	9.773 (2)	9.763 (14)
b, Å	13.705 (2)	23.387 (6)	34.196 (10)
c, Å	19.797 (6)	11.918 (4)	11.484 (5)
β, deg	100.19 (3)	102.68 (2)	113.25 (6)
V, Å^3	2500.0	2657.6	3522.6
mol wt	743.1	743.1	917.6
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$[b]	$P2_1/n$[b]	$P2_1/n$[b]
Z	4	4	4
ρ(calcd), g cm^{-3}	1.97	1.86	1.73
(B) Measurement of Intensity Data[c]			
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized		
scan width, deg, variable, $\Delta\omega$	0.7 + 0.35 tan θ	0.7 + 0.35 tan θ	0.9 + 0.35 tan θ
scan rate, deg min^{-1} (in ω)	1.06–6.71	1.56–6.71	1.5–20
scan range	$3° \leqslant 2\theta \leqslant 55°$	$3° \leqslant 2\theta \leqslant 55°$	$3° \leqslant 2\theta < 45°$
bkgd measurements	moving crystal–moving detector, 25% added to scan width at both ends of each scan		
standards	three reflections measured every 3600 s of X-ray exposure time showed 30% decay for **3** but none for **1** or **2**		
	(400), (040), ($\bar{4}$00)	(200), (040), ($\bar{2}$00)	(5$\bar{7}\bar{1}$), ($\bar{1}$,12,4), ($\bar{5}$71)
no. of reflcns coll	6349	6599	6019
non space group extinguished	$3° \leqslant 2\theta \leqslant 25°$ $(-h,-k,\pm l)$; $3° \leqslant 2\theta \leqslant 55°$ $(+h,+k,\pm l)$	$3° \leqslant 2\theta \leqslant 55°$ $(+h,+k,\pm l)$	$2° \leqslant 2\theta \leqslant 20°$ $(-h,-k,\pm l)$; $3° \leqslant 2\theta \leqslant 45°$ $(+h,+k,\pm l)$
(C) Treatment of Intensity Data			
reduction to F_o and $\sigma(F_o)$	correction for background, attenuator, and Lorentz-polarization effects of monochromatized X radiation as described previously[c]		
μ, cm^{-1}	71.8	67.5	53.3
transmission factor range[d]	0.14–0.35	0.12–0.28	0.50–0.77
averaging, R_{av}[c]	0.028	0.090	0.020
no. of reflcns after averaging	5746	6081	3323
obsd unique data $[F_o > 4\sigma(F_o)]$	4255	2734	1888

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30°$. [b] Reference 12. See ref 11 for additional details about the data collection procedures used in our laboratory. [c] Reference 11. [d] Absorption corrections were performed with the Wehe-Busing-Levy ORABS program.

Table II. Final Positional Parameters for the Non-Hydrogen Atoms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, Form **1**[a,b]

atom	x	y	z
W	0.22304 (3)	0.29622 (2)	0.86853 (1)
I(1)	0.01402 (6)	0.20192 (4)	0.76499 (3)
I(2)	0.10516 (6)	0.18273 (4)	0.96738 (2)
C(1)	0.2846 (8)	0.4324 (6)	0.8686 (4)
O(1)	0.3187 (8)	0.5131 (5)	0.8690 (4)
C(2)	0.3657 (8)	0.3159 (6)	0.9537 (4)
O(2)	0.4508 (6)	0.3250 (6)	1.0031 (3)
C(3)	0.0333 (7)	0.3747 (5)	0.8785 (3)
N(3)	−0.0687 (6)	0.4166 (4)	0.8858 (3)
C(32)	−0.2080 (7)	0.4526 (6)	0.8985 (4)
C(33)	−0.2175 (18)	0.5575 (11)	0.8841 (10)
C(34)	−0.2150 (13)	0.4362 (13)	0.9716 (6)
C(35)	−0.3218 (12)	0.4080 (16)	0.8462 (9)
C(4)	0.3746 (7)	0.1795 (6)	0.8637 (4)
N(4)	0.4583 (6)	0.1201 (5)	0.8633 (3)
C(42)	0.5691 (8)	0.0448 (6)	0.8611 (5)
C(43)	0.563 (3)	−0.027 (2)	0.9096 (14)
C(44)	0.542 (3)	−0.0001 (14)	0.7949 (8)
C(45)	0.7041 (13)	0.0879 (13)	0.873 (2)
C(5)	0.3034 (8)	0.3182 (5)	0.7777 (4)
N(5)	0.3497 (7)	0.3275 (5)	0.7275 (3)
C(52)	0.4012 (9)	0.3258 (6)	0.6627 (3)
C(53)	0.5490 (17)	0.2812 (12)	0.6760 (6)
C(54)	0.3022 (17)	0.2639 (11)	0.6152 (6)
C(55)	0.4097 (14)	0.4286 (7)	0.6392 (6)

[a] Atoms are labeled as shown in Figure 1. [b] Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

Table III. Final Positional Parameters for the Non-Hydrogen Atoms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$, Form **2**[a]

atom	x	y	z
W	0.26801 (7)	0.40757 (3)	0.68222 (5)
I(1)	0.35819 (15)	0.29122 (6)	0.67001 (12)
I(2)	0.18294 (16)	0.37799 (9)	0.88965 (11)
C(1)	0.354 (3)	0.4741 (8)	0.6419 (17)
O(1)	0.4280 (18)	0.5120 (8)	0.6156 (13)
C(2)	0.171 (2)	0.4749 (11)	0.6987 (19)
O(2)	0.099 (2)	0.5137 (10)	0.7109 (17)
C(3)	0.0549 (19)	0.3789 (8)	0.6032 (14)
N(3)	−0.0546 (16)	0.3621 (7)	0.5688 (12)
C(32)	−0.191 (2)	0.3377 (11)	0.5385 (20)
C(33)	−0.296 (3)	0.3781 (14)	0.577 (2)
C(34)	−0.230 (2)	0.3347 (14)	0.404 (2)
C(35)	−0.184 (4)	0.2816 (16)	0.594 (3)
C(4)	0.2650 (16)	0.3972 (8)	0.5080 (14)
N(4)	0.2615 (15)	0.3913 (7)	0.4123 (11)
C(42)	0.2478 (19)	0.3798 (10)	0.2910 (13)
C(43)	0.108 (2)	0.3496 (11)	0.2501 (17)
C(44)	0.373 (3)	0.3523 (13)	0.2750 (20)
C(45)	0.232 (3)	0.4385 (13)	0.232 (2)
C(5)	0.4604 (18)	0.4088 (8)	0.8073 (13)
N(5)	0.5606 (15)	0.4069 (7)	0.8747 (11)
C(52)	0.675 (2)	0.3979 (11)	0.9728 (17)
C(53)	0.793 (3)	0.4339 (18)	0.970 (3)
C(54)	0.726 (7)	0.3420 (16)	0.961 (5)
C(55)	0.621 (4)	0.405 (3)	1.074 (3)

[a] Atoms are labeled as shown in Figure 2. See footnote *b*, Table II.

structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available as supplementary material in Tables S2, S5, and S8. Figure 2 shows the molecular geometry along with the atom-labeling scheme.

$W(CO)I_2(t\text{-}C_4H_9NC)_4 \cdot CHCl_3$ (3). Except as indicated below, the details of the structure analysis for **3** are the same as those for **1** and **2**. The *tert*-butyl groups were refined as rigid bodies (C–C = 1.541 Å; C–C–C = 109.5°; H–C–H = 109.5°; C–H = 0.95 Å) pivoting on the central carbon atoms. The common isotropic temperature factor for the hydrogen atoms converged at U = 0.374 Å^2.

Least-squares refinement fit 1888 data having $F_o > 4\sigma(F_o)$ to 275 variable parameters. The final residuals[15] were R_1 = 0.050 and R_2 = 0.054. The weighting scheme was $w = 1.8660/[\sigma^2(F_o) + 0.000625F_o^2]$. The largest parameter shift in the final cycles of the least-squares refinement was 0.73 of its estimated standard deviation, and the largest peak on the final difference Fourier map was 0.8 e Å^{-3}, near the tungsten atom.

Tables IV and VII list final non-hydrogen atom positional parameters and interatomic distances and angles. Final observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available as supplementary material in Tables S3, S6, and S9. Figure 3 shows the molecular geometry along with the atom-labeling scheme.

Discussion

$W(CO)_2I_2(t\text{-}C_4H_9NC)_3$. This molecule has now been obtained in at least three different crystalline forms. Recrystallization from chloroform/pentane gave both the orthorhombic (**4**)[7] and one of the monoclinic (**1**, this work) modifications. Use of the tetrahydrofuran/pentane solvent system first deposited crystals of the second monoclinic form (**2**), followed by orthorhombic **4**. In all three forms the coordi-

Table IV. Final Positional Parameters for the Non-Hydrogen Atoms of $W(CO)I_2(\textit{t}-C_4H_9NC)_4\cdot CHCl_3$ (**3**)[a]

atom	x	y	z
W	0.29340 (12)	0.10411 (3)	0.23330 (8)
I(1)	0.4023 (2)	0.10586 (6)	0.03433 (15)
I(2)	0.5721 (2)	0.13965 (5)	0.39783 (15)
C	0.207 (3)	0.3199 (8)	0.651 (2)
Cl(1)	0.1442 (10)	0.3033 (3)	0.4937 (7)
Cl(2)	0.3608 (10)	0.3506 (3)	0.6769 (8)
Cl(3)	0.2670 (10)	0.2802 (3)	0.7511 (7)
C(1)	0.170 (3)	0.0656 (8)	0.267 (2)
O(1)	0.108 (3)	0.0417 (6)	0.2959 (19)
C(2)	0.100 (3)	0.0930 (7)	0.070 (2)
N(2)	−0.003 (2)	0.0882 (6)	−0.0215 (20)
C(22)	−0.116 (3)	0.0795 (10)	−0.1290 (17)
C(23)	−0.061 (3)	0.0583 (10)	−0.2212 (17)
C(24)	−0.196 (3)	0.1177 (10)	−0.1904 (17)
C(25)	−0.224 (3)	0.0529 (10)	−0.0983 (17)
C(3)	0.217 (3)	0.1606 (9)	0.173 (2)
N(3)	0.197 (2)	0.1938 (7)	0.1413 (19)
C(32)	0.174 (2)	0.2324 (4)	0.0926 (15)
C(33)	0.044 (2)	0.2308 (4)	−0.0390 (15)
C(34)	0.315 (2)	0.2480 (4)	0.0794 (15)
C(35)	0.131 (2)	0.2598 (4)	0.1798 (15)
C(4)	0.433 (3)	0.0559 (8)	0.280 (2)
N(4)	0.521 (3)	0.0321 (7)	0.298 (2)
C(42)	0.644 (2)	0.0085 (7)	0.324 (2)
C(43)	0.788 (2)	0.0314 (7)	0.399 (2)
C(44)	0.633 (2)	−0.0272 (7)	0.403 (2)
C(45)	0.646 (2)	−0.0055 (7)	0.198 (2)
C(5)	0.249 (3)	0.1245 (7)	0.382 (2)
N(5)	0.229 (2)	0.1352 (7)	0.467 (2)
C(52)	0.201 (2)	0.1511 (6)	0.5657 (16)
C(53)	0.343 (2)	0.1499 (6)	0.6883 (16)
C(54)	0.074 (2)	0.1293 (6)	0.5870 (16)
C(55)	0.154 (2)	0.1939 (6)	0.5294 (16)

[a] Atoms are labeled as shown in Figure 3. See footnote *b*, Table II.

Table V. Interatomic Distances (Å) and Angles (deg) for $W(CO)_2I_2(\textit{t}-C_4H_9NC)_3$, Form **1**

Coordination Sphere

W-I(1)	2.878 (1)	W-C(3)	2.116 (6)
W-I(2)	2.869 (1)	W-C(4)	2.151 (7)
W-C(1)	1.953 (8)	W-C(5)	2.089 (7)
W-C(2)	1.976 (8)		
I(1)-W-I(2)	87.0 (0)	C(1)-W-C(2)	73.4 (4)
I(1)-W-C(1)	126.4 (3)	C(1)-W-C(3)	76.5 (3)
I(1)-W-C(2)	160.2 (3)	C(1)-W-C(4)	120.9 (3)
I(1)-W-C(3)	79.6 (2)	C(1)-W-C(5)	73.2 (3)
I(1)-W-C(4)	90.3 (2)	C(2)-W-C(3)	107.6 (3)
I(1)-W-C(5)	75.8 (2)	C(2)-W-C(4)	77.7 (3)
I(2)-W-C(1)	131.8 (2)	C(2)-W-C(5)	115.0 (3)
I(2)-W-C(2)	77.0 (2)	C(3)-W-C(4)	162.5 (3)
I(2)-W-C(3)	77.4 (2)	C(3)-W-C(5)	116.3 (2)
I(2)-W-C(4)	87.9 (2)	C(4)-W-C(5)	74.2 (3)
I(2)-W-C(5)	154.9 (2)		

Ligand Geometry

C(1)-O(1)	1.151 (9)	N(4)-C(42)	1.470 (9)
C(2)-O(2)	1.154 (9)	C(5)-N(5)	1.160 (8)
C(3)-N(3)	1.145 (7)	N(5)-C(52)	1.448 (8)
N(3)-C(32)	1.458 (8)	mean C-C(methyl)	1.452 (5)
C(4)-N(4)	1.131 (8)	range C-C(methyl)	1.38-1.49
W-C(1)-O(1)	178.8 (6)	C(5)-N(5)-C(52)	172.4 (7)
W-C(2)-O(2)	178.1 (7)	mean N-C-C(methyl)	108.4 (3)
W-C(3)-N(3)	178.1 (6)	range N-C-C(methyl)	107-112
C(3)-N(3)-C(32)	169.6 (7)	mean C(methyl)-C-C(methyl)	110.5 (5)
W-C(4)-N(4)	177.1 (6)		
C(4)-N(4)-C(42)	178.1 (7)	range C(methyl)-C-C(methyl)	105-114
W-C(5)-N(5)	177.9 (7)		

Table VI. Interatomic Distances (Å) and Angles (deg) for $W(CO)_2I_2(\textit{t}-C_4H_9NC)_3$, Form **2**

Coordination Sphere

W-I(1)	2.874 (2)	W-C(31)	2.193 (18)
W-I(2)	2.861 (2)	W-C(41)	2.084 (17)
W-C(1)	1.880 (24)	W-C(51)	2.128 (16)
W-C(2)	1.870 (25)		
I(1)-W-I(2)	88.0 (1)	C(1)-W-C(2)	66.1 (12)
I(1)-W-C(1)	127.6 (9)	C(1)-W-C(31)	125.4 (8)
I(1)-W-C(2)	166.1 (8)	C(1)-W-C(41)	75.6 (8)
I(1)-W-C(31)	87.8 (5)	C(1)-W-C(51)	78.0 (8)
I(1)-W-C(41)	77.1 (5)	C(2)-W-C(31)	81.2 (8)
I(1)-W-C(51)	79.3 (5)	C(2)-W-C(41)	107.8 (9)
I(2)-W-C(1)	130.7 (7)	C(2)-W-C(51)	107.7 (7)
I(2)-W-C(2)	82.1 (9)	C(31)-W-C(41)	74.5 (6)
I(2)-W-C(31)	82.5 (4)	C(31)-W-C(51)	156.1 (6)
I(2)-W-C(41)	152.8 (4)	C(41)-W-C(51)	121.1 (6)
I(2)-W-C(51)	77.1 (4)		

Ligand Geometry

C(1)-O(1)	1.227 (25)	N(41)-C(42)	1.447 (19)
C(2)-O(2)	1.181 (24)	C(51)-N(51)	1.123 (18)
C(31)-N(31)	1.130 (19)	N(51)-C(52)	1.445 (21)
N(31)-C(32)	1.420 (22)	mean C-C(methyl)	1.482 (11)
C(41)-N(41)	1.141 (18)	range C-C(methyl)	1.42-1.57
W-C(1)-O(1)	170.0 (26)	C(51)-N(51)-C(52)	169.4 (19)
W-C(2)-O(2)	172.9 (27)	mean N-C-C(methyl)	107.8 (6)
W-C(31)-N(31)	175.4 (16)	range N-C-C(methyl)	106-112
C(31)-N(31)-C(32)	173.3 (20)	mean C(methyl)-C-C(methyl)	110.0 (9)
W-C(41)-N(41)	179.0 (15)		
C(41)-N(41)-C(42)	174.9 (18)	range C(methyl)-C-C(methyl)	104-119
W-C(51)-N(51)	176.8 (17)		

Table VII. Interatomic Distances (Å) and Angles (deg) for $W(CO)I_2(\textit{t}-C_4H_9NC)_4\cdot CHCl_3$ (**3**)

Coordination Sphere

W-I(1)	2.876 (2)	W-C(3)	2.090 (32)
W-I(2)	2.897 (2)	W-C(4)	2.073 (30)
W-C(1)	1.925 (32)	W-C(5)	2.044 (29)
W-C(2)	2.108 (28)		
I(1)-W-I(2)	87.9 (1)	C(1)-W-C(2)	69.1 (10)
I(1)-W-C(1)	129.1 (8)	C(1)-W-C(3)	121.9 (10)
I(1)-W-C(2)	77.1 (7)	C(1)-W-C(4)	78.7 (9)
I(1)-W-C(3)	85.0 (7)	C(1)-W-C(5)	73.1 (10)
I(1)-W-C(4)	79.1 (7)	C(2)-W-C(3)	78.1 (9)
I(1)-W-C(5)	157.5 (7)	C(2)-W-C(4)	110.8 (9)
I(2)-W-C(1)	131.2 (7)	C(2)-W-C(5)	113.2 (9)
I(2)-W-C(2)	159.7 (7)	C(3)-W-C(4)	159.2 (10)
I(2)-W-C(3)	87.1 (6)	C(3)-W-C(5)	78.2 (9)
I(2)-W-C(4)	79.1 (6)	C(4)-W-C(5)	113.0 (9)
I(2)-W-C(5)	76.6 (7)		

Ligand Geometry

C(1)-O(1)	1.145 (27)	C(4)-N(4)	1.141 (27)
C(2)-N(2)	1.141 (26)	N(4)-C(42)	1.372 (25)
N(2)-C(22)	1.323 (23)	C(5)-N(5)	1.122 (26)
C(3)-N(3)	1.182 (28)	N(5)-C(52)	1.385 (24)
N(3)-C(32)	1.419 (23)		
W-C(1)-O(1)	173.8 (24)	W-C(4)-N(4)	170.4 (25)
W-C(2)-N(2)	177.1 (24)	C(4)-N(4)-C(42)	170.4 (28)
C(2)-N(2)-C(22)	174.1 (29)	W-C(5)-N(5)	177.3 (23)
W-C(3)-N(3)	169.2 (25)	C(5)-N(5)-C(52)	175.5 (27)
C(3)-N(3)-C(32)	174.7 (25)	mean N-C-C(methyl)	109.6 (4)
		range N-C-C(methyl)	106-112

Solvate Geometry

C-Cl(1)	1.762 (23)	C-Cl(3)	1.723 (26)
C-Cl(2)	1.762 (24)		
Cl(1)-C-Cl(2)	106.8 (13)	Cl(2)-C-Cl(3)	108.2 (13)
Cl(1)-C-Cl(3)	108.5 (15)		

nation geometry about the tungsten atom resembles that of the C_s 4:3 tetragonal base–trigonal cap piano-stool structure. This judgement is made most readily by comparison of the interbond angles at the tungsten atom with those of the idealized stereochemistries (Table VIII), as discussed previously.[6c,7] In form **4** the trigonal cap is comprised of the two iodine atoms and one of the carbonyl ligands. Forms **1** and **2**, however, have an isocyanide ligand in place of the carbonyl group in the trigonal cap (Figures 1 and 2) and are thus both

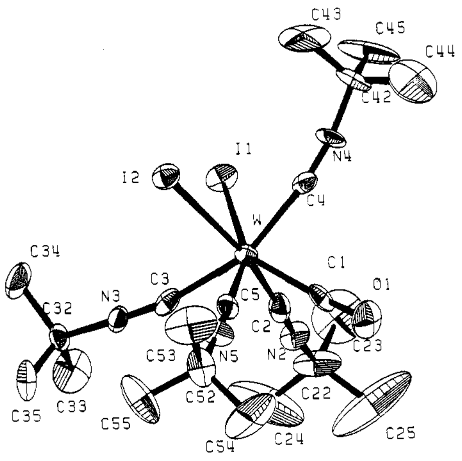

Figure 3. Structure of $W(CO)I_2(t\text{-}C_4H_9NC)_4$ (**3**), showing the 20% probability thermal ellipsoids and the atom-labeling scheme; the chloroform molecule of solvation is not depicted.

Table VIII. Summary of Interbond Angles (deg) for Seven-Coordinate Structures[a]

angle no.	PB (D_{5h})	CO (C_{3v})[b]	CTP (C_{2v})[c]	4:3 (C_s)[b]	1[d]	2[d]	3[d]	4[e]
1	180.0	160.0	164.0	170.0	162.5	166.1	159.7	165.8
2	144.0	160.0	164.0	153.6	160.2	156.1	159.2	155.1
3	144.0	160.0	144.2	153.6	154.9	152.8	157.5	154.4
4	144.0	130.0	144.2	130.8	131.8	130.7	131.2	132.0
5	144.0	130.0	119.0	130.8	126.4	127.6	129.1	131.5
6	144.0	130.0	119.0	120.0	120.9	125.4	121.9	119.7
7	90.0	108.9	118.8	120.0	116.3	121.1	113.2	117.5
8	90.0	108.9	118.8	108.8	115.0	107.8	113.0	110.5
9	90.0	108.9	99.0	108.8	107.6	107.7	110.8	109.2
10	90.0	83.1	99.0	89.4	90.3	88.0	87.9	89.5
11	90.0	83.1	83.7	89.4	87.9	87.8	87.1	87.9
12	90.0	83.1	83.7	83.1	87.0	82.5	85.0	84.7
13	90.0	82.0	80.3	83.1	79.6	82.1	79.1	81.1
14	90.0	82.0	80.3	83.1	77.7	81.2	79.1	80.8
15	90.0	82.0	78.8	75.5	77.4	79.3	78.7	77.1
16	90.0	82.0	78.6	75.5	77.0	78.0	78.2	76.6
17	72.0	82.0	75.2	75.5	76.5	77.1	78.1	75.6
18	72.0	82.0	75.2	75.5	75.8	77.1	77.1	75.1
19	72.0	70.0	75.0	73.3	74.2	75.6	76.6	74.7
20	72.0	70.0	75.0	73.3	73.4	74.5	73.1	74.1
21	72.0	70.0	71.5	70.0	73.2	66.1	69.1	72.9

[a] Angles are listed by decreasing size. Abbreviations: PB, pentagonal bipyramid; CO, capped octahedron; CTP, capped trigonal prism; 4:3, the 4:3 "piano-stool" structure. [b] The internal angles of these reference geometries are calculated from the corresponding optimized geometries for d^4 complexes (Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* 1977, *16*, 511). [c] The structure of $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ (the reference geometry was taken from: Lewis, D. L.; Lippard, S. J. *J. Am. Chem. Soc.* 1975, *97*, 2697). [d] This work. [e] Reference 7.

the same geometric isomer of the structure found in **4**.

A study of Figures 1 and 2 as well as Tables V and VI reveals that the coordination geometries of **1** and **2** are closely similar. The two compounds differ mainly in their unit cell packing, the comparable W–I, W–CO, and W–CNR bond lengths and interbond angles being statistically equivalent. Only the W–CO bond lengths in **2** seem a bit shorter than those in **1**, but in view of the large esd's this difference cannot be given any significance. In all three compounds **1**, **2**, and **4** the longest W–CNR bond involves an isocyanide ligand in the tetragonal base adjacent to the WI_2 unit on the trigonal cap and opposite the carbonyl group in the base. In the alternate description of these molecules as a C_{3v} capped octahedron,[7,10] this isocyanide ligand is the only one in the uncapped face. Other similar features in the three structures are the existence of both *cis*-WI_2 and *cis*-$W(CO)_2$ fragments. Since crystal packing forces are a prime factor in determining the choice of solid-state stereochemistry for seven-coordinate complexes of this kind,[6] the occurrence of these structural features in three crystalline forms strongly suggests that they will persist in solution. This information could be useful for interpreting the reaction chemistry of $W(CO)_2I_2(CNR)_3$ complexes.

$W(CO)I_2(t\text{-}C_4H_9NC)_4 \cdot CHCl_3$. Examination of the interbond angles for this molecule shows it to be marginally closer to the C_{3v} capped-octahedral than the C_s 4:3 structure (Table VIII). In this reference geometry the carbonyl group is the capping ligand, three *tert*-butyl isocyanide groups comprise the capped face, and the remaining *tert*-butyl isocyanide and two iodide ligands form the uncapped face. The similarity between the C_{3v} capped-octahedral and C_s 4:3 piano-stool structures has been discussed previously.[7,10] In this regard it is noteworthy that a description of all three forms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$ in terms of the C_{3v} capped-octahedral reference geometry would have a carbonyl ligand in the capping position and two iodine atoms and the most weakly (vide supra) bonded *t*-BuNC ligand on the uncapped face. This structural pattern also occurs in numerous seven-coordinate Mo(II) and W(II) mixed carbonyl–halide complexes having bidentate chelating phosphine or arsine ligands (cf. Table X, ref 10). Other features of the geometry of **3** are comparable to those of **1**, **2**, and other *tert*-butyl isocyanide–halide complexes of Mo(II) and W(II).[6,7] The structure of the chloroform molecule agrees with a literature report.[16]

Acknowledgment. We are grateful to the National Science Foundation for support of this work under NSF Grant CHE 81-09390.

Supplementary Material Available: Tables S1–S3 reporting the final observed and calculated structure factor amplitudes, Tables S4–S6 listing the final anisotropic thermal parameters, and Tables S7–S9 giving the final hydrogen atom positional parameters for **1**, **2**, and **3** (44 pages). Ordering information is given on any current masthead page.

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[16] *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*, M60S.