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Iridium Carbonyl Clusters. 2.[1] Crystal Structure and Molecular Geometry of $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$, a Derivative of $Ir_4(CO)_{12}$ with No Bridging Carbonyl Ligands

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The title complex has been characterized structurally by means of a single-crystal X-ray diffraction study. It crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 13.503$ (2) Å, $b = 14.358$ (2) Å, $c = 12.421$ (2) Å, $\beta = 97.07$ (1)°, $V = 2389.8$ (6) Å^3, and ρ(calcd) = 3.22 g cm^{-3} for mol wt 1160.13 and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved by conventional Patterson, difference Fourier, and full-matrix least-squares refinement techniques. The resulting discrepancy indices were $R_F = 7.2\%$ and $R_{wF} = 4.7\%$ for all 3146 independent reflections ($3° < 2\theta < 45°$; Mo Kα radiation) and $R_F = 4.9\%$ and $R_{wF} = 4.3\%$ for those 2473 data with $I > 3\sigma(I)$. The four iridium atoms define a tetrahedron. The isocyanide ligand occupies a site on Ir(4), the Ir–CN(t-Bu) bond length being 1.976 (19) Å. Ir–CO distances range from 1.80 (3) to 1.92 (3) Å. There are slight variations in Ir–Ir distances within the tetrahedral cluster. Distances involving the unique Ir(4) average 2.681 [2] Å and are slightly shorter than the other $[(OC)_3Ir\text{–}Ir(CO)_3]$ bond lengths, which average 2.689 [2] Å.

Introduction

We recently reported[1] the results of an X-ray diffraction study of $Ir_4(CO)_{12}$ from which we had hoped (inter alia) to obtain an accurate (nonbridged) Ir–Ir bond length appropriate to tetrahedral cluster complexes. The disorder found in our study of $Ir_4(CO)_{12}$ thwarted this objective, although an average Ir–Ir distance at 2.693 Å was obtained.

All previously reported derivatives of $Ir_4(CO)_{12}$ (e.g., those in which one or more carbonyl ligands are replaced by a phosphine,[2,3] 1,5-cyclooctadiene,[4] or halide anion[5]) possess structures in which there are three mutually adjacent bridging carbonyl ligands. Recently, however, Shapley and Stuntz[6] have synthesized the species $Ir_4(CO)_{12-n}[CN(t\text{-}Bu)]_n$ (n = 1–4) and have shown, via infrared spectroscopy, that those species with n = 1–3 have no bridging carbonyl ligands. We have now undertaken a single-crystal X-ray structural study of the monosubstituted species $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$ with the expectation of determining accurate molecular dimensions for an *ordered*, nonbridged $Ir_4(CO)_{12}$ derivative. A preliminary account of the structural study has appeared previously in conjunction with a report of the variable temperature ^{13}C NMR spectra of this complex.[7]

Experimental Section

A. Collection of Diffraction Data. A crystalline sample of $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$ was kindly donated by Professor J. R. Shapley of the University of Illinois. The crystal selected for the structural study was a parallelepiped of approximate dimensions 0.11 × 0.10 × 0.20 mm. It was mounted along its extended direction on the top of a thin glass fiber which was fixed with beeswax into an aluminum pin and mounted in a eucentric goniometer. Visual inspection with a polarizing microscope and preliminary precession photographs indicated that the crystal was of good quality and belonged to the monoclinic system.

The crystal was transferred to a Syntex $P2_1$ four-circle diffractometer and was centered accurately. Determinations of preliminary cell parameters, orientation matrix, and crystal quality (the last via θ–2θ and ω scans along the principal reciprocal axes) were carried out as described previously.[8] A unique set of data in the shell defined by $25° < 2\theta < 30°$ was next collected at the maximum scan rate (29.3°/min). A careful survey led to the selection of 24 strong reflections, well dispersed in reciprocal space, from which *accurate* cell parameters could be obtained. Collection of intensity data (via the θ–2θ scan technique) was carried out as described previously.[8] Details appear in Table I. Data were corrected for absorption and for Lorentz and polarization effects. Redundant data were averaged.

B. Solution and Refinement of the Structure. All calculations were performed with a locally modified version of the Syntex XTL crystallographic program package on our in-house Data General NOVA 1200 computer with associated Diablo disk unit.[9] For structure factor calculations, we used the analytical scattering factors[10a] of neutral Ir, O, N, C, and H; both $\Delta f'$ and $\Delta f''$ contributions[10b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, and the "ignorance factor" used was $p = 0.015$.

Table I. Experimental Data for the X-ray Diffraction Study on Crystalline $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$

(A) Crystal Parameters[a] at 24 °C

cryst system: monoclinic
space group: $P2_1/c$ [C_{2h}^5; No. 14]
$a = 13.5032$ (22) Å
$b = 14.3578$ (19) Å
$c = 12.4211$ (16) Å
$\beta = 97.070$ (12)°
$V = 2389.8$ (6) Å^3
$Z = 4$
ρ(calcd) = 3.22 g cm^{-3}
mol wt: 1160.13

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710\ 73$ Å)
monochromator: highly oriented graphite
rflcns measd: $\pm h$, $+k$, $+l$
2θ range: 3–45°
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 2.0°/min (in 2θ)
scan width: from $[2\theta(K\alpha_1) - 0.7]°$ to $[2\theta(K\alpha_2) + 0.7]°$
bkgd measurement: stationary crystal and counter; at beginning and end of the 2θ scan–each for half the time taken for the 2θ scan
std rflcns: 3 measd every 47 rflcns [411, 004, $\bar{1}41$]; no significant changes in intensity were observed
rflcns collected: 3322 total, yielding 3146 independent rflcns; $R(I) = 3.8\%$ for 176 averaged pairs of rflcns
abs coeff: $\mu = 236.0$ cm^{-1}
abs cor: empirical, based on a series of χ scans; rflcns used, their 2θ values and max to min intensity ratios: {004}, 13.22°, 2.10:1; {006}, 19.88°, 2.13:1; $\{\bar{1}17\}$, 23.24°, 2.16:1

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of the reflections $\{\bar{8}04\}$, $\{\bar{8}50\}$, $\{\bar{4}56\}$, $\{\bar{3}37\}$, $\{\bar{2}28\}$, {183}, {292}–all with 2θ = 25–28°.

The positions of the four iridium atoms were determined from a Patterson map. Refinement of positional and anisotropic thermal parameters for these atoms led to $R_F = 11.5\%$. A difference Fourier synthesis now led to the location of all remaining nonhydrogen atoms. Refinement of positional parameters, anisotropic thermal parameters for iridium atoms, and isotropic thermal parameters for all other nonhydrogen atoms (and with all hydrogen atoms in idealized positions with d(C–H) = 0.95 Å[11] and in appropriate staggered tetrahedral locations about their carbon atoms) led to convergence ($\Delta/\sigma < 0.005$ for all parameters) with $R_F = 5.9\%$, $R_{wF} = 4.5\%$, and GOF = 1.30 for those 2798 data with $I > \sigma(I)$ which were included in the refinement. The data-to-parameter ratio is 2798:149 or approximately 18.8:1. [For comparison we note that the discrepancy indices for all 3146 data were $R_F = 7.2\%$ and $R_{wF} = 4.7\%$; for those 2473 data with $I > 3\sigma(I)$ the discrepancy indices were $R_F = 4.9\%$ and $R_{wF} = 4.3\%$.] Attempts to refine the lighter atoms anisotropically were not totally successful and were abandoned.

A final difference Fourier synthesis revealed no unexpected features, and the average value of the function $\sum w(|F_o| - |F_c|)^2$ showed no major

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Table II. Final Positional and Thermal Parameters for $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$

A. Positional and Isotropic Thermal Parameters[a]

atom	x	y	z	B, Å^2
Ir(1)	0.14547 (7)	0.52842 (5)	0.28696 (7)	
Ir(2)	0.17051 (7)	0.34916 (5)	0.34594 (7)	
Ir(3)	0.33036 (6)	0.46056 (6)	0.34367 (6)	
Ir(4)	0.22432 (6)	0.40740 (5)	0.15673 (6)	
O(11)	0.1122 (16)	0.6077 (14)	0.5078 (16)	8.9 (5)
O(12)	−0.0663 (17)	0.5149 (14)	0.1853 (16)	9.0 (5)
O(13)	0.2106 (13)	0.6960 (12)	0.1690 (13)	6.8 (4)
O(21)	−0.0312 (18)	0.2842 (14)	0.2448 (17)	9.4 (6)
O(22)	0.2846 (14)	0.1669 (12)	0.3506 (13)	7.1 (4)
O(23)	0.1369 (15)	0.3792 (13)	0.5830 (16)	8.2 (5)
O(31)	0.4402 (15)	0.6165 (13)	0.2475 (15)	8.0 (5)
O(32)	0.4818 (15)	0.3075 (13)	0.3496 (14)	7.8 (5)
O(33)	0.3501 (18)	0.5128 (15)	0.5824 (19)	10.6 (6)
O(41)	0.0350 (15)	0.3592 (12)	0.0164 (14)	7.4 (4)
O(42)	0.3514 (13)	0.2434 (11)	0.1143 (13)	6.4 (4)
C(11)	0.1261 (22)	0.5809 (18)	0.4247 (23)	7.1 (7)
C(12)	0.0179 (22)	0.5227 (18)	0.2249 (21)	6.7 (6)
C(13)	0.1829 (17)	0.6338 (16)	0.2168 (18)	5.1 (5)
C(21)	0.0429 (23)	0.3106 (18)	0.2900 (21)	6.7 (6)
C(22)	0.2372 (19)	0.2343 (16)	0.3498 (18)	5.4 (5)
C(23)	0.1505 (20)	0.3648 (18)	0.4937 (21)	6.4 (6)
C(31)	0.4018 (19)	0.5551 (16)	0.2856 (19)	5.7 (5)
C(32)	0.4273 (18)	0.3650 (15)	0.3520 (17)	4.8 (5)
C(33)	0.3455 (20)	0.4925 (17)	0.4901 (22)	6.4 (6)
C(41)	0.1090 (18)	0.3783 (15)	0.0733 (18)	4.9 (5)
C(42)	0.3036 (16)	0.3061 (14)	0.1284 (16)	4.3 (4)
C(5)	0.2762 (15)	0.4967 (13)	0.0563 (16)	3.8 (4)
C(1)	0.3393 (18)	0.6144 (15)	−0.0801 (18)	4.8 (5)
C(2)	0.3098 (30)	0.7112 (25)	−0.0560 (30)	11.6 (11)
C(3)	0.2973 (28)	0.5887 (23)	−0.1886 (29)	10.5 (9)
C(4)	0.4491 (38)	0.6181 (32)	−0.0605 (36)	15.2 (14)
N	0.3061 (13)	0.5495 (11)	−0.0014 (13)	4.3 (4)
H(21)	0.3338	0.7519	−0.1073	10.0
H(22)	0.3381	0.7286	0.0149	10.0
H(23)	0.2391	0.7160	−0.0616	10.0
H(31)	0.3182	0.6308	−0.2402	10.0
H(32)	0.2266	0.5896	−0.1924	10.0
H(33)	0.3188	0.5274	−0.2031	10.0
H(41)	0.4724	0.6594	−0.1114	10.0
H(42)	0.4761	0.5578	−0.0691	10.0
H(43)	0.4698	0.6400	0.0108	10.0

B. Anisotropic Thermal Parameters (Å^2) for the Iridium Atoms[b]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir(1)	3.80 (5)	3.24 (4)	4.45 (4)	0.42 (3)	1.47 (3)	−0.03 (3)
Ir(2)	4.06 (5)	3.47 (4)	3.74 (4)	−0.20 (3)	1.35 (3)	0.66 (3)
Ir(3)	3.43 (4)	3.89 (4)	3.47 (4)	−0.22 (3)	0.59 (3)	−0.49 (3)
Ir(4)	3.58 (4)	2.83 (3)	2.92 (3)	−0.31 (3)	0.81 (3)	−0.03 (3)

[a] Hydrogen atoms are in idealized positions (see text). [b] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme was thus deemed to be satisfactory and the structure complete.

Final positional and thermal parameters are collected in Table II.

Results and Discussion

The crystal consists of discrete molecular units of formula $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$; there are no abnormally close intermolecular contacts. The overall structure of the molecule and the scheme used for labeling atoms are illustrated in Figure 1. Interatomic distances and angles are collected in Tables III and IV. The molecule contains a tetrahedral Ir_4 core, which has idealized C_{3v} (rather than T_d) symmetry. Each iridium atom is linked to three other iridium atoms and to three terminal ligands. Atoms Ir(1), Ir(2), and Ir(3) are linked to three terminal carbonyl ligands, while Ir(4) is in a unique environment, being linked to two terminal carbonyl ligands and a terminal *tert*-butyl isocyanide ligand. Metal–metal distances involving the unique iridium atom (i.e., the $(OC)_3Ir–Ir(CO)_2[NC(t\text{-}Bu)]$ linkages) are Ir(1)–Ir(4) = 2.682 (1) Å, Ir(2)–Ir(4) = 2.678 (1) Å, and Ir(3)–Ir(4) = 2.684 (1) Å. The average value is 2.681 Å with σ(ext) = 0.003 Å and σ(av) = 0.002 Å.[11] In contrast to this, the remaining iridium–iridium distances (i.e., the $(OC)_3Ir–Ir(CO)_3$ linkages) are Ir(1)–Ir(2) = 2.686 (1) Å, Ir(1)–Ir(3) = 2.692 (1) Å and Ir(2)–Ir(3) = 2.689 (1) Å; the average value of 2.689 Å [σ(ext) = 0.003 Å, σ(av) = 0.002 Å] is slightly longer than for the other set. This presumably reflects the greater electron-withdrawing effect of a carbonyl vis a vis an isocyanide ligand.

Iridium–carbonyl linkages range from Ir(1)–C(12) = 1.800 (30) Å to Ir(1)–C(11) = 1.916 (28) Å; the average value is 1.863 Å [σ(ext) = 0.035 Å, σ(av) = 0.011 Å]. The carbon–oxygen distances range from C(32)–O(32) = 1.109 (30) Å to C(12)–O(12) = 1.188 (37) Å; the average value is 1.156 Å [σ(ext) = 0.023 Å, σ(av) = 0.007 Å]. The Ir–C–O systems are each close to linear, ranging from 172.1 (25) to 178.2 (20)°, with an average value of 176.0° [σ(ext) = 1.7°, σ(av) = 0.5°].

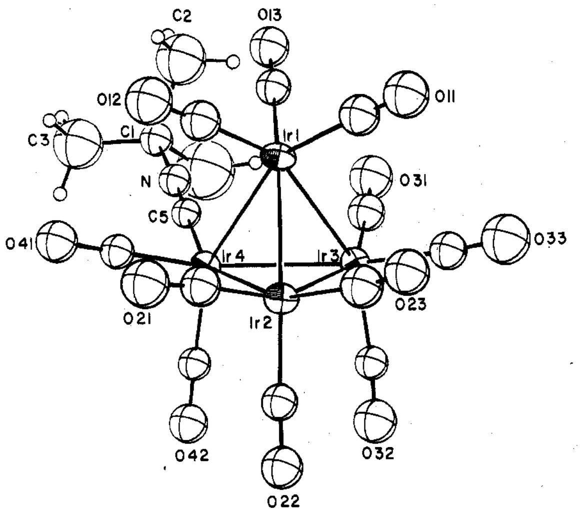

Figure 1. Stereochemistry of the $Ir_4(CO)_{11}[NC(t\text{-}Bu)]$ molecule (ORTEP-II diagram; 30% probability ellipsoids for all atoms other than hydrogen atoms, which are reduced in size for clarity).

Table III. Interatomic Distances (Å) for $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$

(A) Iridium–Iridium Bond Lengths			
Ir(1)–Ir(2)	2.686 (1)	Ir(1)–Ir(4)	2.682 (1)
Ir(1)–Ir(3)	2.692 (1)	Ir(2)–Ir(4)	2.678 (1)
Ir(2)–Ir(3)	2.689 (1)	Ir(3)–Ir(4)	2.684 (1)
(B) Iridium–Carbonyl and Carbon–Oxygen Distances			
Ir(1)–C(11)	1.916 (28)	C(11)–O(11)	1.139 (35)
Ir(1)–C(12)	1.800 (30)	C(12)–O(12)	1.188 (37)
Ir(1)–C(13)	1.847 (23)	C(13)–O(13)	1.160 (28)
Ir(2)–C(21)	1.861 (30)	C(21)–O(21)	1.150 (37)
Ir(2)–C(22)	1.877 (24)	C(22)–O(22)	1.160 (30)
Ir(2)–C(23)	1.901 (26)	C(23)–O(23)	1.164 (32)
Ir(3)–C(31)	1.861 (24)	C(31)–O(31)	1.154 (31)
Ir(3)–C(32)	1.890 (23)	C(32)–O(32)	1.109 (30)
Ir(3)–C(33)	1.863 (27)	C(33)–O(33)	1.177 (35)
Ir(4)–C(41)	1.809 (24)	C(41)–O(41)	1.184 (30)
Ir(4)–C(42)	1.865 (21)	C(42)–O(42)	1.133 (27)
(C) Distances within CN(*t*-Bu) Ligand			
Ir(4)–C(5)	1.976 (19)	C(1)–C(2)	1.486 (43)
C(5)–N	1.150 (25)	C(1)–C(3)	1.445 (42)
N–C(1)	1.461 (28)	C(1)–C(4)	1.474 (57)

Table IV. Interatomic Angles (deg) for $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$

(A) Angles between Metal Atoms			
Ir(2)–Ir(1)–Ir(3)	60.01 (3)	Ir(1)–Ir(2)–Ir(3)	60.10 (3)
Ir(2)–Ir(1)–Ir(4)	59.85 (3)	Ir(1)–Ir(2)–Ir(4)	60.01 (3)
Ir(3)–Ir(1)–Ir(4)	59.94 (3)	Ir(3)–Ir(2)–Ir(4)	60.02 (3)
Ir(1)–Ir(3)–Ir(2)	59.88 (3)	Ir(1)–Ir(4)–Ir(2)	60.15 (3)
Ir(1)–Ir(3)–Ir(4)	59.85 (3)	Ir(1)–Ir(4)–Ir(3)	60.21 (3)
Ir(2)–Ir(3)–Ir(4)	59.78 (3)	Ir(2)–Ir(4)–Ir(3)	60.21 (3)
(B) Ir–Ir–C Angles			
Ir(2)–Ir(1)–C(11)	99.2 (8)	Ir(2)–Ir(1)–C(12)	98.9 (9)
Ir(3)–Ir(1)–C(11)	97.6 (8)	Ir(3)–Ir(1)–C(12)	154.6 (9)
Ir(4)–Ir(1)–C(11)	154.3 (8)	Ir(4)–Ir(1)–C(12)	98.2 (9)
Ir(2)–Ir(1)–C(13)	151.7 (7)	Ir(1)–Ir(2)–C(21)	95.9 (8)
Ir(3)–Ir(1)–C(13)	96.9 (7)	Ir(3)–Ir(2)–C(21)	151.7 (8)
Ir(4)–Ir(1)–C(13)	95.4 (7)	Ir(4)–Ir(2)–C(21)	96.0 (8)
Ir(1)–Ir(2)–C(22)	153.2 (7)	Ir(1)–Ir(2)–C(23)	97.0 (8)
Ir(3)–Ir(2)–C(22)	98.0 (7)	Ir(3)–Ir(2)–C(23)	98.6 (8)
Ir(4)–Ir(2)–C(22)	96.6 (7)	Ir(4)–Ir(2)–C(23)	153.7 (8)
Ir(1)–Ir(3)–C(31)	98.2 (8)	Ir(1)–Ir(3)–C(32)	153.0 (7)
Ir(2)–Ir(3)–C(31)	153.2 (8)	Ir(2)–Ir(3)–C(32)	96.9 (7)
Ir(4)–Ir(3)–C(31)	96.8 (8)	Ir(4)–Ir(3)–C(32)	97.7 (7)
Ir(1)–Ir(3)–C(33)	98.8 (8)	Ir(1)–Ir(4)–C(41)	96.7 (7)
Ir(2)–Ir(3)–C(33)	97.4 (8)	Ir(2)–Ir(4)–C(41)	97.1 (7)
Ir(4)–Ir(3)–C(33)	153.8 (8)	Ir(3)–Ir(4)–C(41)	152.9 (7)
Ir(1)–Ir(4)–C(42)	154.0 (6)	Ir(1)–Ir(4)–C(5)	99.1 (6)
Ir(2)–Ir(4)–C(42)	98.4 (6)	Ir(2)–Ir(4)–C(5)	155.8 (6)
Ir(3)–Ir(4)–C(42)	97.3 (6)	Ir(3)–Ir(4)–C(5)	99.7 (6)
(C) Angles within the CN(*t*-Bu) Ligand			
Ir(4)–C(5)–N	179.2 (18)	C(5)–N–C(1)	176.3 (20)
N–C(1)–C(2)	110.5 (22)	N–C(1)–C(3)	110.1 (21)
N–C(1)–C(4)	107.3 (24)	C(2)–C(1)–C(3)	110.1 (25)
C(2)–C(1)–C(4)	102.8 (27)	C(3)–C(1)–C(4)	115.8 (28)
(D) C–Ir–C Angles			
C(11)–Ir(1)–C(12)	99.9 (12)	C(21)–Ir(2)–C(22)	99.7 (11)
C(11)–Ir(1)–C(13)	100.1 (11)	C(21)–Ir(2)–C(23)	99.2 (12)
C(12)–Ir(1)–C(13)	97.9 (11)	C(22)–Ir(2)–C(23)	101.8 (11)
C(31)–Ir(3)–C(32)	99.3 (10)	C(41)–Ir(4)–C(42)	100.7 (10)
C(31)–Ir(3)–C(33)	101.5 (11)	C(41)–Ir(4)–C(5)	97.8 (9)
C(32)–Ir(3)–C(33)	97.6 (11)	C(42)–Ir(4)–C(5)	97.5 (8)
(E) Ir–C–O Angles			
Ir(1)–C(11)–O(11)	176.3 (25)	Ir(2)–C(21)–O(21)	172.1 (25)
Ir(1)–C(12)–O(12)	177.1 (24)	Ir(2)–C(22)–O(22)	175.0 (21)
Ir(1)–C(13)–O(13)	175.3 (20)	Ir(2)–C(23)–O(23)	176.5 (23)
Ir(3)–C(31)–O(31)	175.5 (22)	Ir(4)–C(41)–O(41)	178.2 (20)
Ir(3)–C(32)–O(32)	175.1 (21)	Ir(4)–C(42)–O(42)	177.8 (19)
Ir(3)–C(33)–O(33)	176.7 (24)		

The Ir–Ir–CO angles break down into two distinct sets—those in the range 95.4 (7) to 99.2 (8)° and those between 151.7 (7) and 154.6 (9)°.

The isocyanide ligand occupies a normal terminal site on Ir(4). The Ir–C(5) distance is 1.976 (19) Å, with C(5)–N = 1.150 (25) Å and N–C(1) = 1.461 (28) Å; this is consistent with the expected valence bond structure $Ir{-}C{\equiv}N{-}CMe_3$. Angles within this system are close to linear: Ir–C(5)–N = 179.2 (18)° and C(5)–N–C(1) = 176.3 (20)°. The C(1)–C(methyl) distances [C(1)–C(2) = 1.486 (43) Å, C(1)–C(3) = 1.445 (42) Å, and C(1)–C(4) = 1.474 (57) Å] are shorter than the ideal $C(sp^3)–C(sp^3)$ distance of 1.54 Å, probably because of the substantial librational motion associated with the *tert*-butyl group.

The following additional points should also be noted. (1) The results from this structural study confirm our conclusions on the molecular parameters of $Ir_4(CO)_{12}$ as deduced from the highly disordered structure of the parent carbonyl (cf. ref 1). (2) The present structural study is the first on a nonbridged derivative of $Ir_4(CO)_{12}$. As such it provides accurate Ir–Ir and Ir–CO distances for these species. (3) Comparison of the structures of $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$ and $Ir_4(CO)_{12}$ with those of the carbonyl-bridged analogues, $Ir_4(CO)_{10}(PPh_3)_2$,[3] $Ir_4(CO)_9(PPh_3)_3$,[3] and $[Ir_4(CO)_{11}Br^-]$,[5] shows no clear distinction between bridged and nonbridged iridium–iridium distances. Further *accurate* work is necessary to clarify this unusual result. (Carbonyl-bridged metal–metal distances are usually shorter than the analogous nonbridged metal–metal distances.) (4) The present structure analysis of $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$ and that of $Ir_4(CO)_{12}$[1] are, to the best of our knowledge, the only two studies of tetrahedral metal carbonyl cluster complexes *of any metal* in which there are no bridging ligands (i.e., which are held together only by metal–metal bonds).

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Registry No. $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$, 70775-27-8.

Supplementary Material Available: A table of data processing formulas and a listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) The following reference should be considered to be Part 1 of this series: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.
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(9) This system has been described in detail previously: Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1978**, *17*, 1453.

(10) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV: (a) pp 99–101; (b) pp 149–150.

(11) σ(ext), an external estimate of the esd on each bond length, is given by $[\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where N is the number of equivalent bond lengths, d_i is the ith bond length, and $\bar{d}$ is the average bond length. σ(av), the esd of the average bond length, is given by $[\sum(d_i - \bar{d})^2/N(N-1)]^{1/2}$.

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Crystal Structure and Molecular Geometry of $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$, a Mononuclear Tungsten(VI) Complex with Metal–Alkylidyne, Metal–Alkylidene, and Metal–Alkyl Linkages

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[1,2-Bis(dimethylphosphino)ethane](neopentylidyne)(neopentylidene)(neopentyl)tungsten(VI), $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$, previously prepared by Clark and Schrock, has been investigated via a three-dimensional single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.784$ (3) Å, $b = 29.200$ (8) Å, $c = 9.859$ (2) Å, $\beta = 109.54$ (2)°, $V = 2654$ (1) Å^3, mol wt 544.4, $Z = 4$, and ρ(calcd) = 1.36 g cm^{-3}. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer using Mo Kα radiation and an ω-scan mode of collection. The structure was solved by conventional Patterson, difference Fourier, and full-matrix least-squares refinement techniques, the resulting discrepancy indices being $R_F = 3.9\%$ and $R_{wF} = 3.1\%$ for all 2475 symmetry-independent reflections with $4.5° < 2\theta < 40°$ ($R_F = 3.2\%$ and $R_{wF} = 3.1\%$ for those 2199 reflections with $I > 3\sigma(I)$). The tungsten atom is in a distorted square-pyramidal coordination environment, with the neopentylidyne ligand in the apical site and with the neopentylidene and neopentyl ligands in adjacent basal sites. The tungsten–neopentyl bond length is W–C(11) = 2.258 (9) Å (∠W–C(11)–C(12) = 124.5 (7)°), the tungsten–neopentylidene bond length is W–C(6) = 1.942 (9) Å (∠W–C(6)–C(7) = 150.4 (8)°), and the tungsten–neopentylidyne bond length is W–C(1) = 1.785 (8) Å (∠W–C(1)–C(2) = 175.3 (7)°).

Introduction

For the past year or two we have been interested in the bonding of small highly reactive organic fragments to transition metals, and we have reported the results of X-ray diffraction studies on a neopentylidene–tantalum complex $[Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl]$,[1] a benzylidyne–tantalum complex $[Ta(\eta^5\text{-}C_5Me_5)(\equiv CPh)(PMe_3)_2Cl]$,[2] a bis(neopentylidene)–tantalum complex $[Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2]$,[3] and a benzyne–tantalum complex $[Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$.[4]

A number of mixed isoskeletal[5] alkyl–alkylidene complexes have been investigated by others [cf. $Ta(\eta^5\text{-}C_5H_5)_2(=CH_2)(CH_3)$[6] and $Ta(\eta^5\text{-}C_5H_5)_2(=CHC_6H_5)(CH_2C_6H_5)$[7]], as has an isoskeletal alkyl–alkylidyne complex $[Ta(\equiv CCMe_3)(CH_2CMe_3)_3\cdot Li(dmp)]$.[8] However, X-ray and neutron diffraction studies show that transition-metal alkyls, alkylidenes, and alkylidynes have a number of unusual structural characteristics—(i) the M–C(α)–C(β) angles in alkyls are frequently as large as 120–125°; (ii) the M=C(α)—C(β) angles in alkylidenes vary widely (for the *neopentylidene* ligand, these angles are 168.9 (6) and 154.0 (6)° in $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$,[3a] 161.2 (1)° in $[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$,[9] and 150.4 (5)° in $Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl$[1a]); (iii) the M≡C($\alpha$)—C($\beta$) angles in alkylidynes appear to be deformed easily from linearity (an angle of 165 (1)° is found in $Ta(\equiv CCMe_3)(CH_2CMe_3)_3\cdot Li(dmp)$ and an angle of 171.8 (6)° is found in $Ta(\eta^5\text{-}C_5Me_5)(\equiv CPh)(PMe_3)_2Cl$[2]). It is due to these factors, we believe, that several mixed alkyl–alkylidene systems (e.g., $Nb(=CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$)[10] are subject to severe disorder in the solid state.

Recently, Clark and Schrock[11] reported the synthesis of the species $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2$ and $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$ (dmpe = $Me_2P(CH_2)_2PMe_2$), which are *rigid* on the NMR time scale and thus (hopefully) are likely to be *ordered* in the solid state. These species are unique in possessing metal–alkylidyne, metal–alkylidene and metal–alkyl linkages. Because of this and because of the interest in tungsten–alkylidenes as intermediates in the olefin metathesis reaction,[12] we have undertaken an X-ray diffraction study of $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$; a preliminary report has appeared previously.[13]

Experimental Section

A. Collection and Processing of the X-ray Diffraction Data. Red columnar crystals of $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$ were provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The material decomposes *rapidly* upon exposure to the air, melting and bubbling to form a thick, viscous liquid.

A well-formed crystal of approximate dimensions 0.3 × 0.3 × 0.5 mm was removed from the provided vial in an inert-atmosphere drybox and was carefully wedged into a 0.3-mm diameter thin-walled glass capillary, which was flame-sealed, fixed into an aluminum pin with beeswax, and mounted into an eucentric goniometer. (Preliminary photographs were not taken, since we were concerned about the potential for decomposition of the crystal.) The crystal was centered on our Syntex $P2_1$ automated diffractometer. Determinations of the crystal class, the orientation matrix, and accurate unit cell dimensions were carried out as described previously.[14] Both θ–2θ and ω scans were monitored graphically for selected reflections along (and adjacent to) each of the principal reciprocal axes. As a result of the rather long b axis (ca. 29.2 Å) and concomitantly short spacings of reflections along b^*, we elected to collect data via the "wandering ω-scan" technique,[15] rather than by the customary θ–2θ method. Details of the data collection appear in Table I. A survey of the complete data set revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/n$ is thereby strongly indicated.

All crystallographic computations were carried out on our in-house Syntex XTL system (NOVA 1200 computer; Diablo disk; Versatec printer/plotter), including the XTL interactive program package[16] as modified by our research group at SUNY—Buffalo.

Data were corrected for absorption ($\mu = 47.3$ cm^{-1}) by an empirical method, based upon a set of ψ scans of carefully selected reflections. Each of these reflections was collected at intervals of 10° about its diffraction vector from $\psi = 0$ to 350°; each was converted to a

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