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Site Preference of the *tert*-Butyl Isocyanide Ligand in Pentaosmium Carbonyl Clusters. Crystal Structures of $Os_5(CO)_{18}(CNBu^t)$ and $Os_5(CO)_{15}(CNBu^t)$

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The cluster $Os_5(CO)_{18}(CNBu^t)$ (1) was prepared by the addition of $Os(CO)_4(CNBu^t)$ to $Os_4(CO)_{14}$ in CH_2Cl_2 at room temperature. The X-ray structure determination of 1 reveals a bow-tie arrangement of osmium atoms (the Os–Os lengths range from 2.839(1) to 2.940(1) Å); the isocyanide ligand occupies an axial site on an outer osmium atom. Pyrolysis of 1 in solution at 44–47 °C provided $Os_5(CO)_{17}(CNBu^t)$ (2) which by analogy to $Os_5(CO)_{18}$ and $Os_5(CO)_{17}(PMe_3)$ probably has a raft configuration of metal atoms. Pyrolysis of 2 in solution at 65–70 °C yielded $Os_5(CO)_{15}(CNBu^t)$ (3). The structure of 3 consists of a somewhat distorted trigonal bipyramidal configuration of osmium atoms with the Os–Os lengths in the range 2.748(1)–2.915(1) Å. The $CNBu^t$ ligand occupies the site that is believed to be the sterically most crowded site within the molecule, namely, coordinated to the osmium atom that has four terminal ligands and lying approximately in the equatorial Os_3 plane of the trigonal bipyramid. The site preference of the $CNBu^t$ ligand in these clusters is believed to be dictated by electronic rather than steric considerations. Crystallographic data for compound 1: space group $P\bar{1}$; a = 9.079(1) Å, b = 12.065(2) Å, c = 15.757(2) Å, α = 76.36(1)°, β = 76.63(1)°, γ = 77.86(1)°; R = 0.021, 3355 observed reflections. For compound 3: space group $P2_1/n$, a = 9.048(1) Å, b = 18.389(2) Å, c = 17.759(2) Å, β = 102.65(1)°; R = 0.025, 3240 observed reflections.

Introduction

Isocyanide (CNR)[1,2] and organophosphine (PR_3)[3] ligands are ubiquitous ligands in metal carbonyl chemistry. Although both classes of ligands are believed to be better σ-donors and poorer π-acceptors than carbonyl itself,[4–6] they have different site preferences in binuclear and trinuclear metal carbonyl complexes. In binuclear compounds phosphines are usually, but not always, found in the sites trans to the metal–metal bond (the axial sites).[7,8] Isocyanide ligands, on the other hand, invariably adopt sites that are cis to the metal–metal bonds (i.e., in radial or equatorial sites).[9,10] Similarly, in trinuclear metal carbonyl clusters phosphines occupy positions trans to the metal–metal bonds,[11] whereas isocyanides occupy positions cis to the metal–metal bonds.[12] The recent report of the structure of $Os_3(CO)_{10}(CNPr)(PPh_3)$ illustrates the latter observations.[13]

This difference in site preference can undoubtedly be attributed to the different steric requirements of the two classes of ligands. The sterically-undemanding isocyanide ligands[14] can enter electronically-preferred coordination sites that are inaccessible for steric reasons to bulky phosphine ligands.[15,16]

We have recently reported the synthesis of clusters of the formula $Os_5(CO)_n(PMe_3)$ (n = 18, 17, 15) and determined their structures by X-ray crystallography.[17] Two isomers of $Os_5(CO)_{15}(PMe_3)$ were characterized: one in which the phosphine ligand was coordinated to an apical osmium atom, and a second in which the phosphine ligand was coordinated to a sterically crowded site at an osmium

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atom in the equatorial plane of the trigonal bipyramid of the Os$_5$ skeleton. The unexpected stability of the second isomer appeared to indicate that electronic factors were overriding the normal steric requirements of the phosphine ligand. There are also a significantly larger number of chemically-different coordination sites in the pentanuclear binary carbonyls of osmium (i.e., Os$_5$(CO)$_{19}$,[18] Os$_5$(CO)$_{18}$,[19] Os$_5$(CO)$_{16}$[20]) than the two sites in Os$_3$(CO)$_{12}$.[21] It was therefore of interest to investigate the site preference of the CNBu^t ligand in clusters of the formula Os$_5$(CO)$_n$(CNBu^t) ($n = 18, 17, 15$). We report here the results of this study.

Experimental Section

Standard Schlenk techniques were employed in the syntheses; solvents were dried and stored under nitrogen before use. Literature procedures were used to prepare Os(CO)$_4$(CNBu^t)[10] and Os$_4$(CO)$_{14}$[22] (a detailed description of the preparation of Os$_4$(CO)$_{15}$ is given in ref 23). Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the NMR spectra, on a Bruker SY-100 spectrometer. Microanalyses were carried out by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of Os$_5$(CO)$_{18}$(CNBu^t) (1). A solution of Os$_4$(CO)$_{14}$ (26 mg, 0.023 mmol) and Os(CO)$_4$(CNBu^t) (9 mg, 0.02 mmol) in CH$_2$Cl$_2$ (25 mL) was stirred at room temperature for 24 h. The solvent was removed on the vacuum line and the remaining solid subjected to chromatography on a silica gel column. Elution with CH$_2$Cl$_2$/hexane (1/7) gave a red band from which red, air-stable crystals of 1 (26 mg, 78%) were obtained: IR (hexane), cm^{-1}: ν(CN) 2190 (w); ν(CO) 2116 (m), 2081 (s), 2066 (s), 2054 (m), 2034 (s), 2031 (sh), 2015 (m), 1977 (m), 1978 (vw), 1930 (vw). ^{1}H NMR (CDCl$_3$): δ 1.55 (s). Anal. Calcd for C$_{23}$H$_9$NO$_{18}$Os$_5$: C, 17.96; H, 0.59; N, 0.91. Found: C, 18.19; H, 0.63; N, 0.99.

Preparation of Os$_5$(CO)$_{17}$(CNBu^t) (2). A solution of 1 (30 mg, 0.020 mmol) in CH$_2$Cl$_2$ (35 mL) was placed in a round-bottom flask fitted with a Teflon valve. The vessel and contents were cooled to −196 °C, and the vessel was evacuated; the solution was degassed with three freeze–pump–thaw cycles. The flask was sealed under vacuum and heated at 44–47 °C for 3 days. Isolation by a similar procedure given for 1 gave a virtually quantitative yield of 2: IR (CH$_2$Cl$_2$), cm^{-1}: ν(CN) 2194 (w); ν(CO) 2116 (m), 2076 (s), 2061 (m), 2033 (vs), 2020 (sh), 1998 (sh), 1958 (sh), 1821 (w, br). ^{1}H NMR (CDCl$_3$): δ 1.71 (s). Anal. Calcd for C$_{22}$H$_9$NO$_{17}$Os$_5$: C, 17.50; H, 0.60; N, 0.93. Found: C, 17.69; H, 0.65; N, 1.10.

Preparation of Os$_5$(CO)$_{15}$(CNBu^t) (3). A solution of 2 (23 mg, 0.015 mmol) in CH$_2$Cl$_2$ (50 mL) was cooled to −196 °C and degassed with three freeze–pump–thaw cycles. The vessel containing the solution was sealed under vacuum and heated at 65–70 °C for 5 days. Chromatography in a manner similar to that described for 1 afforded unreacted 2 (2 mg) and, from the initial colored band, 3 (20 mg, 90%) as red, air-stable crystals. IR (CH$_2$Cl$_2$), cm^{-1}: ν(CN) 2189 (w, br); ν(CO) 2088 (m), 2055 (s), 2032 (s), 1981 (m), 1942 (sh). ^{1}H NMR (CDCl$_3$): δ 1.59 (s). Anal. Calcd for C$_{20}$H$_9$NO$_{15}$Os$_5$: C, 16.52; H, 0.62; N, 0.96. Found: C, 16.60; H, 0.61; N, 1.01.

Table 1. Summary of Crystal Data and Details of Intensity Collection for Os$_5$(CO)$_{18}$(CNBu^t) (1) and Os$_5$(CO)$_{15}$(CNBu^t) (3)

	1	3
fw	1538.3	1482.3
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	9.079(1)	9.048(1)
b, Å	12.065(2)	18.389(2)
c, Å	15.757(2)	17.759(2)
α, deg	76.36(1)	
β, deg	76.63(1)	102.65(1)
γ, deg	77.86(1)	
V, Å^3	1609.4	2883.1
2θ range of unit cell, deg	30–44	30–36
Z	2	4
D_{calc}, g cm^{-3}	3.174	3.350
μ(Mo, Kα), cm^{-1}	197.64	220.50
cryst size, mm	0.020 × 0.19 × 0.16	0.047 × 0.057 × 0.22
transm coeff range[a]	0.138–0.681	0.281–0.393
scan method	ω–2θ	ω–2θ
scan width (ω), deg	$0.9 + 0.35 \tan\theta$	$0.9 + 0.35 \tan\theta$
scan rate (ω), deg min^{-1}	0.82–5.5	0.82–5.5
2θ, range deg	4–45	4–48
no. of unique rflns	4173	4507
no. of obsd rflns[b]	3355	3240
no. of variables	330	291
R[c]	0.021	0.025
R_w[d]	0.025	0.025
k[d]	0.0001	0.0001
GOF[e]	1.2	1.6
extinction coeff		0.329(16)
F(000)	1355.44	2542.90

[a] Absorption corrections. [b] $I_o > 2.5(I_o)$. [c] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [d] $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = [\sigma^2(F_o) + k(F_o)^2]^{-1}$. [e] GOF $= (\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom}))^{1/2}$.

X-ray Analysis of 1 and 3. The following procedure was employed for the structure determinations of both 1 and 3. A crystal was mounted on an Enraf-Nonius diffractometer, and intensity data were collected with the use of graphite-monochromated Mo Kα radiation. Background measurements were made by extending the scan width by 25% on each side of the scan. Two intensity standards, measured every 1.5 h (1) and 3 h (3) of aquisition time, decreased 5% (1) and 6% (3) during the data collection process. The final unit cell was determined from 25 well-centered high-angle reflections that were widely scattered in reciprocal space. Absorption corrections by Gaussian integration (checked against Ψ-scan measurements) were applied to the measured intensity data. Data reduction included the small corrections for intensity scale variation and for Lorentz and polarization effects.

The positions of the Os atoms were determined by direct methods. Subsequent electron density difference synthesis revealed the remaining non-hydrogen atoms. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and initially given isotropic thermal parameters 10% larger than the thermal parameters of the attached carbon atoms. The coordinates of carbon atoms with attached hydrogen atoms were linked so that the coordinate shifts included contributions from derivatives from the appropriate atom sites. Unit weights were employed initially, but at the final stage of each refinement a weighting scheme, based on counting statistics, was adopted for which $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. Complex scattering factors for neutral atoms were used in the calculation of the structure factors.[24] The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium, oxygen, and nitrogen atoms and carbon atoms of the *tert*-butyl group, isotropic thermal parameters for the carbonyl carbon atoms, and one variable for the shifts of the thermal parameters of all

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Table 2. Fractional Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for $Os_5(CO)_{18}(CNBu^t)$ (1)

atom	*x*	*y*	*z*	*U*(iso)
Os(1)	−6029.8(4)	−2797.0(3)	−2572.3(2)	324^a
Os(2)	−7955.5(4)	−4604.7(3)	−1933.6(2)	406^a
Os(3)	−6954.6(4)	−1673.5(3)	−1023.2(2)	411^a
Os(4)	−5428.3(4)	−469.6(3)	−2652.1(2)	364^a
Os(5)	−5358.6(4)	−4861.8(3)	−3325.6(2)	380^a
O(11)	−8798(8)	−1605(5)	−3462(4)	556^a
O(12)	−3396(8)	−4021(5)	−1592(4)	604^a
O(13)	−3831(9)	−2144(5)	−4299(4)	601^a
O(21)	−10002(10)	−3848(7)	−3337(5)	809^a
O(22)	−5953(9)	−5383(6)	−496(4)	685^a
O(23)	−8603(10)	−7068(6)	−1610(6)	832^a
O(24)	−10668(8)	−3671(6)	−600(4)	669^a
O(31)	−10058(8)	−1005(7)	−1649(5)	640^a
O(32)	−3864(9)	−2187(7)	−395(5)	744^a
O(33)	−7941(12)	317(8)	−29(7)	1017^a
O(34)	−8180(9)	−3551(7)	471(5)	774^a
O(41)	−3903(9)	575(6)	−4528(5)	724^a
O(42)	−2242(8)	−1753(6)	−2355(5)	675^a
O(43)	−5249(10)	1465(6)	−1771(6)	787^a
O(51)	−7095(8)	−3241(5)	−4730(4)	583^a
O(52)	−3578(10)	−6390(6)	−1903(5)	741^a
O(53)	−2286(8)	−4663(6)	−4591(5)	714^a
O(54)	−5989(9)	−7034(6)	−3738(5)	673^a
N(1)	−8579(9)	862(6)	−3229(5)	501^a
C(11)	−7774(11)	−2066(7)	−3102(6)	433(22)
C(12)	−4406(11)	−3577(8)	−1931(6)	450(22)
C(13)	−4675(11)	−2325(7)	−3622(6)	458(22)
C(21)	−9180(13)	−4089(9)	−2852(7)	606(27)
C(22)	−6644(11)	−5055(8)	−1064(6)	492(23)
C(23)	−8398(12)	−6122(9)	−1721(7)	616(27)
C(24)	−9645(11)	−3992(8)	−1096(6)	474(23)
C(31)	−8894(12)	−1246(8)	−1455(6)	498(23)
C(32)	−4977(13)	−2020(9)	−645(7)	585(26)
C(33)	−7543(14)	−444(10)	−395(8)	755(32)
C(34)	−7719(12)	−2873(9)	−92(7)	577(26)
C(41)	−4510(11)	171(8)	−3839(6)	491(23)
C(42)	−3428(12)	−1282(8)	−2425(6)	485(23)
C(43)	−5340(11)	754(8)	−2116(6)	526(24)
C(51)	−6502(11)	−3828(8)	−4182(6)	457(22)
C(52)	−4265(12)	−5797(9)	−2399(7)	567(26)
C(53)	−3444(12)	−4705(8)	−4126(6)	528(24)
C(54)	−5737(11)	−6224(8)	−3586(6)	519(24)
C(1)	−7498(11)	338(7)	−2978(6)	439(22)
C(2)	−9882(11)	1562(8)	−3591(8)	573^a
C(3)	−9811(21)	1217(14)	−4479(10)	1279^a
C(4)	−11315(14)	1287(11)	−3005(11)	939^a
C(5)	−9720(16)	2797(10)	−3773(13)	1013^a

[a] The cube root of the product of the principal axes of the thermal ellipsoid.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Os_5(CO)_{18}(CNBu^t)$ (1)

Bond Lengths

Os(1)–Os(2)	2.929(1)	Os(4)–C(1)	2.05(1)
Os(1)–Os(3)	2.938(1)	(Os–C$_{ax}$)	1.91(1)–1.96(1)
Os(1)–Os(4)	2.940(1)	(Os–C$_{eq}$)	1.87(1)–1.92(1)
Os(1)–Os(5)	2.900(1)	(C–O)	1.12(2)–1.17(2)
Os(2)–Os(5)	2.844(1)		
Os(3)–Os(4)	2.839(1)		

Bond Angles

Os(3)–Os(1)–Os(2)	98.42(2)	Os(4)–Os(3)–Os(1)	61.16(2)
Os(4)–Os(1)–Os(3)	57.76(2)	Os(3)–Os(4)–Os(1)	61.09(2)
Os(5)–Os(1)–Os(2)	58.40(2)	Os(2)–Os(5)–Os(1)	61.32(2)
Os(5)–Os(1)–Os(4)	149.14(2)	N(1)–C(1)–Os(4)	173.2(8)
Os(5)–Os(2)–Os(1)	60.28(2)		

Table 4. Fractional Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for $Os_5(CO)_{15}(CNBu^t)$ (3)

atom	*x*	*y*	*z*	*U*(iso)
Os(1)	2911.4(4)	1673.8(2)	2277.4(2)	354^a
Os(2)	3165.4(5)	182.6(2)	2789.8(2)	388^a
Os(3)	5057.4(4)	659.4(2)	1869.6(2)	324^a
Os(4)	5546.1(5)	1131.7(2)	3372.1(2)	401^a
Os(5)	2025.5(4)	448.4(2)	1234.9(2)	357^a
O(11)	3886(11)	3042(5)	3236(5)	783^a
O(12)	125(9)	2235(4)	1119(5)	624^a
O(13)	863(10)	1399(6)	3417(5)	757^a
O(21)	3292(14)	76(7)	4520(5)	906^a
O(22)	−78(10)	−379(6)	2593(5)	783^a
O(23)	4338(11)	−1353(5)	2796(7)	866^a
O(31)	8084(8)	1447(5)	2111(5)	608^a
O(32)	4949(9)	802(5)	146(4)	617^a
O(33)	6546(10)	−801(4)	1851(6)	709^a
O(41)	7617(11)	2439(5)	3453(6)	787^a
O(42)	4877(12)	1574(6)	4913(5)	858^a
O(43)	8099(10)	92(5)	4038(5)	710^a
O(51)	1554(10)	1270(5)	−279(4)	671^a
O(52)	−1387(8)	307(5)	1005(4)	561^a
O(53)	2364(10)	−1067(4)	623(5)	653^a
N(1)	4749(10)	2502(5)	1213(5)	494^a
C(11)	3566(14)	2513(7)	2908(7)	622(32)
C(12)	1143(12)	2000(6)	1537(6)	448(26)
C(13)	1662(14)	1427(7)	2988(7)	590(31)
C(21)	3371(14)	150(7)	3886(7)	653(34)
C(22)	1138(14)	−145(7)	2622(7)	594(32)
C(23)	3907(15)	−773(8)	2797(7)	707(37)
C(31)	6959(12)	1145(6)	2071(6)	467(26)
C(32)	4874(12)	735(6)	774(6)	448(26)
C(33)	5989(13)	−262(6)	1861(6)	540(29)
C(41)	6805(13)	1953(7)	3421(7)	559(30)
C(42)	5107(14)	1412(7)	4339(8)	657(34)
C(43)	7122(13)	472(6)	3799(6)	481(27)
C(51)	1738(12)	959(6)	284(6)	489(28)
C(52)	−105(13)	375(6)	1109(6)	463(26)
C(53)	2241(12)	−489(6)	855(6)	420(25)
C(1)	4176(12)	2123(6)	1583(6)	456(26)
C(2)	5568(13)	2975(6)	798(7)	532^a
C(3)	6924(12)	3283(6)	1372(8)	618^a
C(4)	4478(15)	3583(7)	436(8)	721^a
C(5)	6113(17)	2521(8)	188(7)	825^a

[a] The cube root of the product of the principal axes of the thermal ellipsoid.

hydrogen atoms attached to carbon atoms. An extinction parameter was included in the refinement of 3. The programs used for data reduction, structure solution, and initial refinement were from the NRCVAX crystal structure system.[25] The program suite CRYSTALS was employed in the final refinement.[26] All computations were carried out on a Micro VAX-II computer. Crystallographic data are summarized in Table 1. Final fractional coordinates for the atoms of 1 and 3 are given in Tables 2 and 4, respectively, and bond length and angle data in Tables 3 and 5, respectively.

Results and Discussion

$Os_5(CO)_{18}(CNBu^t)$ (1). Cluster 1 was isolated in good yield by the addition of $Os(CO)_4(CNBu^t)$ to $Os_4(CO)_{14}$ in CH_2Cl_2 at room temperature (eq 1). The cluster was isolated after chromatography as red, air-stable crystals.

$$Os_4(CO)_{14} + Os(CO)_4(CNBu^t) \rightarrow \underset{1}{Os_5(CO)_{18}(CNBu^t)} \qquad (1)$$

The structure of 1 (Figure 1) has the so-called bow-tie arrangement of metal atoms, a skeletal arrangement previously found for the parent carbonyl $Os_5(CO)_{19}$[18] and $Os_5(CO)_{18}(PMe_3)$.[17] The patterns of the Os–Os lengths in the three compounds are similar: the two peripheral

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[25] Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L. *NRCVAX*—An Interactive Program System for Structure Analysis. *J. Appl. Crystallogr.* 1989, *22*, 384.

[26] Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1984.

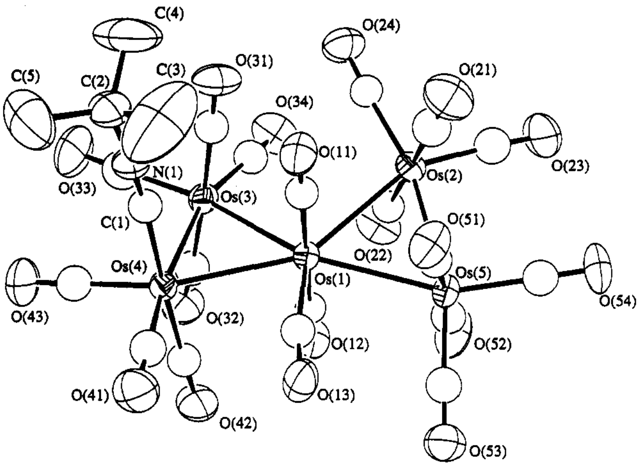

Figure 1. Molecular structure of $Os_5(CO)_{18}(CNBu^t)$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (3)

Bond Lengths			
Os(1)–Os(2)	2.882(1)	Os(2)–Os(4)	2.789(1)
Os(1)–Os(3)	2.897(1)	Os(2)–Os(5)	2.771(1)
Os(1)–Os(4)	2.903(1)	Os(3)–Os(4)	2.748(1)
Os(1)–Os(5)	2.915(1)	Os(3)–Os(5)	2.755(1)
Os(2)–Os(3)	2.756(1)	(Os–C)	1.88(1)–1.93(1)
Os(1)–C(1)	2.03(1)	(C–O)	1.13(2)–1.17(2)
Bond Angles			
Os(3)–Os(1)–Os(2)	56.96(1)	Os(5)–Os(2)–Os(4)	110.35(2)
Os(4)–Os(1)–Os(2)	57.65(1)	Os(4)–Os(3)–Os(1)	61.83(2)
Os(4)–Os(1)–Os(3)	56.57(1)	Os(4)–Os(3)–Os(2)	60.89(2)
Os(5)–Os(1)–Os(2)	57.11(1)	Os(5)–Os(3)–Os(1)	62.04(2)
Os(5)–Os(1)–Os(3)	56.60(1)	Os(5)–Os(3)–Os(2)	60.38(2)
Os(5)–Os(1)–Os(4)	103.36(2)	Os(5)–Os(3)–Os(4)	112.07(2)
Os(3)–Os(2)–Os(1)	61.78(1)	C(11)–Os(1)–Os(4)	77.4(4)
Os(4)–Os(2)–Os(1)	61.54(2)	C(12)–Os(1)–Os(5)	74.7(3)
Os(4)–Os(2)–Os(3)	59.42(2)	C(13)–Os(1)–Os(2)	65.5(4)
Os(5)–Os(2)–Os(1)	62.04(2)	C(1)–Os(1)–Os(3)	67.2(3)
Os(5)–Os(2)–Os(3)	59.80(2)		

metal–metal bonds are somewhat shorter than the average Os–Os length (2.877(3) Å) found for $Os_3(CO)_{12}$.[21] In 1 these distances are 2.839(1) and 2.844(1) Å. On the other hand, the Os–Os bonds that involve the central (Os(1)) atom are somewhat longer than 2.877 Å. In 1 these lengths range from 2.900(1) to 2.940(1) Å.

The isocyanide ligand in 1 occupies an axial site on an outer osmium atom (i.e., Os(4)). This is in contrast to $Os_5(CO)_{18}(PMe_3)$ where the phosphine ligand is in the equatorial site on Os(4) occupied by CO(43) in 1.[17] These observations are not unexpected, however, given the different site preferences, mentioned in the Introduction, of phosphorus-donor and isocyanide ligands in trinuclear metal carbonyl clusters.

In $Os_3(CO)_{12}$ the three axial sites are, of course, chemically equivalent, but in $Os_5(CO)_{19}$, if the Os_5 unit is planar, there are three chemically inequivalent axial sites. In other words, there are three possible isomers for $Os_5(CO)_{18}(L)$ if the ligand L adopts an axial position. (As a referee has pointed out, monoaxial or -equatorial carbonyl substitution on any of the osmium atoms except the central osmium atom of $Os_5(CO)_{19}$ produces a chiral molecule.) The single sharp resonance in the ^1H NMR spectrum of 1 in $CDCl_3$ at room temperature probably indicates there is only one isomer of 1 present in solution, although rapid exchange between two or more isomers cannot be completely ruled out.

The dimensions of the CNBu^t ligand in 1 (and 3, reported below) are similar to those found in other osmium carbonyl clusters with this ligand (e.g., the isomers of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$,[12c,27] $Os_4(CO)_{15}(CNBu^t)$,[23] and $Os_6(CO)_{16}(CNBu^t)_2$[28]). In 1 (and 3) the trans influence of the CNBu^t ligand is comparable to that of a carbonyl ligand (e.g., Os–C(42) = 1.94(1) Å, Os–C(52) = 1.95(1) Å).

$Os_5(CO)_{17}(CNBu^t)$ (2). Pyrolysis of 1 in CH_2Cl_2 at 44–47 °C (in an evacuated, sealed flask) for 3 days gave 2 in virtually quantitative yield (eq 2). Like 1, cluster 2 is an air-stable, red crystalline solid. Although several

$$1 \xrightarrow{44\text{–}47\ ^\circ C} \underset{2}{Os_5(CO)_{17}(CNBu^t)} \qquad (2)$$

attempts were made, crystals of 2 suitable for X-ray crystallography could not be obtained. It would be expected to have a planar, raftlike arrangement of metal atoms (i.e., similar to the arrangement of metal atoms in 1, but with a bond between Os(2) and Os(3)). Such a configuration of metal atoms was found for the parent carbonyl $Os_5(CO)_{18}$[19] and $Os_5(CO)_{17}(PMe_3)$.[17] By analogy to the structures of $Os_5(CO)_n(PMe_3)$ (n = 18, 17),[17] the isocyanide ligand in 2 remains in essentially the same position it adopts in 1. The weak band in the infrared spectrum of 2 at 1821 cm^{-1} is consistent with a bridging carbonyl ligand, as found for $Os_5(CO)_{17}(L)$ (L = CO, PMe_3).

$Os_5(CO)_{15}(CNBu^t)$ (3). This cluster was synthesized by the thermolysis of 2 in CH_2Cl_2 at 65–70 °C (in a sealed, evacuated vessel) over 5 days (eq 3); the yield was essentially quantitative. Like 1 and 2, 3 is also a red, air-stable crystalline solid.

$$2 \xrightarrow{65\text{–}70\ ^\circ C} \underset{3}{Os_5(CO)_{15}(CNBu^t)} \qquad (3)$$

In one synthesis, the reaction was monitored by infrared spectroscopy in the carbonyl stretching region. There was no evidence by this technique of an intermediate product in the conversion of 2 to 3; in other words, there was no evidence of $Os_5(CO)_{16}(CNBu^t)$. This observation is similar to that observed in the pyrolysis of $Os_5(CO)_{18}$ and $Os_5(CO)_{17}(PMe_3)$, to yield $Os_5(CO)_{16}$ and $Os_5(CO)_{15}(PMe_3)$, respectively.[17,19] Furthermore, there was no evidence for a second isomer of 3. (Two isomers of $Os_5(CO)_{15}(PMe_3)$ were isolated from the pyrolysis of $Os_5(CO)_{17}(PMe_3)$; both isomers were structurally characterized.[17])

The structure (Figure 2) of 3 reveals a trigonal bipyramidal arrangement of osmium atoms, and in this respect it resembles the structures of other clusters of the formula $Os_5(CO)_{15}(L)$ (L = CO,[20] PMe_3[17]). The patterns of Os–Os lengths in all these clusters are similar. The two longest Os–Os bonds involve the osmium atom in the equatorial plane that has four terminal ligands coordinated to it (i.e., Os(1)) and the apical Os atoms (Os(4), Os(5)). In 3, these lengths are 2.903(1) and 2.915(1) Å. The next two longest Os–Os lengths involve Os(1) and the remaining osmium atoms (Os(2), Os(3)) in the equatorial plane (for 3, these distances are 2.882(1) and 2.897(1) Å). The remaining five Os–Os vectors are all significantly shorter than 2.877(3) Å, the average Os–Os distance in $Os_3(CO)_{12}$. For 3, these vectors range in length from 2.748(1) to 2.789(1) Å. It is usually found that, compared to the Os–Os distance in $Os_3(CO)_{12}$, Os–Os bonds are somewhat shorter in more

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(27) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 1909.

(28) Orpen, A. G.; Sheldrick, G. M. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 1989.

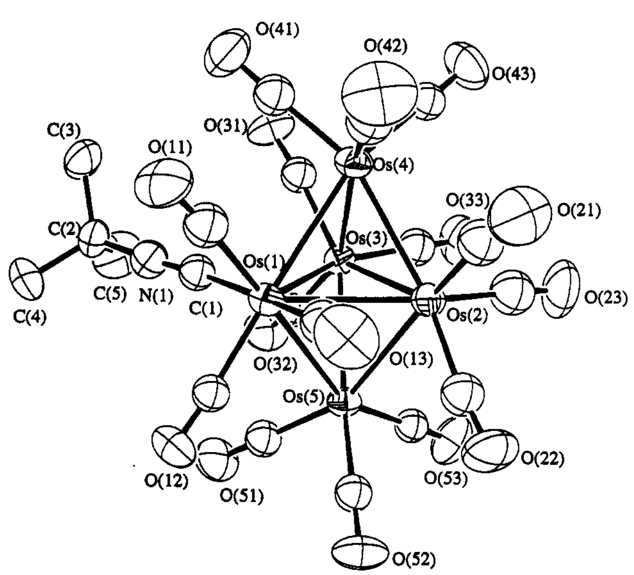

Figure 2. Molecular structure of $Os_5(CO)_{15}(CNBu^t)$.

condensed, higher nuclearity clusters of osmium.[29]

As can be seen from Figure 2, the isocyanide ligand in 3 occupies a site that is arguably the sterically most crowded site in the molecule: it is coordinated to the osmium that has four terminal ligands, and furthermore, it is adjacent to one of the shorter Os–Os bonds that involve this osmium atom. Given the known mobility of both carbonyl and isocyanide ligands in multinuclear complexes and the temperature at which 3 was synthesized, it is probable that the isomer observed for 3 is thermodynamically the most stable isomer.

For the PMe_3 analogue of 3, $Os_5(CO)_{15}(PMe_3)$, two isomers were characterized: the axial form (4a) in which the PMe_3 ligand is located in the site occupied by CO(43) in 3, and the equatorial form (4e) in which the PMe_3 is located in the position occupied by CO(11) in 3.[17] Three structural isomers of formula $Os_5(CO)_{15}(L)$ have, therefore, been prepared and characterized by X-ray crystallography. Infrared spectra in the carbonyl stretching region of 3, 4a, and 4e are shown in Figure 3. In order to distinguish the two equatorial isomers we have labeled 3 the *eq,eq* isomer and 4e the *eq,ax* isomer to denote the metal atom and the site within the coordination sphere of the metal atom, respectively, that the non-carbonyl ligand is coordinated to.

It was found that 4a was the kinetically-preferred isomer, but that 4e was somewhat more thermodynamically-preferred at temperatures above 100 °C at which the two isomers were in dynamic equilibrium.[17] The unexpected stability of the equatorial isomer, 4e, was rationalized by electronic arguments: the dative metal–metal bonds thought present in these clusters would be stabilized by having the better donor ligand coordinated to the osmium that has four terminal ligands.[17] This is shown in Chart 1. The isomer observed for 3 may be rationalized similarly.

The difference between the site of occupancy of the non-carbonyl ligand in 3 and 4e can be rationalized by using arguments previously used to explain the site preference of phosphine and isocyanide ligands in bi- and trinuclear metal carbonyl compounds. In Table 6 are listed the nearest nonbonded contacts for C(11) (in an *eq,ax* site) and C(13) (in an *eq,eq* site) of 3. As can be seen, the carbon–carbon nonbonded contacts for C(11) and C(13) that are less than ~3.5 Å are comparable. The carbon to neighboring osmium atom distances are, however, significantly different: C(11)···Os(4) = 3.11(2) Å whereas C(13)···Os(2) = 2.72(2) Å. For the carbonyl and isocyanide ligands these interactions with neighboring osmium atoms may be attractive interactions, but for the trimethylphosphine ligand this contact would almost certainly be repulsive. (In 3 the Os(4)Os(1)C(11) angle is 77.4(4)° whereas in 4e the corresponding Os(4)Os(1)P angle is 100.7(1)°.) For this reason, we believe that for a phosphine ligand the *eq,ax* positions in $Os_5(CO)_{15}(L)$ clusters are less hindered than the *eq,eq* positions, and that is why the bulky PMe_3 grouping is found in one of the former positions. On the other hand, it would be expected that the *eq,eq* sites would be the electronically-preferred sites for a ligand that is a poorer π-acceptor than the carbonyl

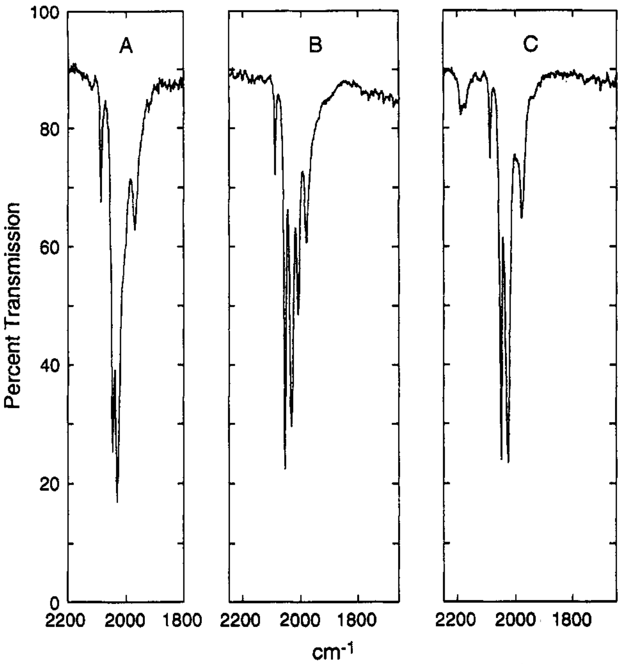

Figure 3. Infrared spectra (carbonyl stretching region, CH_2Cl_2 solution) for $Os_5(CO)_{15}(ax\text{-}PMe_3)$ (A), $Os_5(CO)_{15}(eq,ax\text{-}PMe_3)$ (B), and $Os_5(CO)_{15}(eq,eq\text{-}CNBu^t)$ (C).

Chart 1

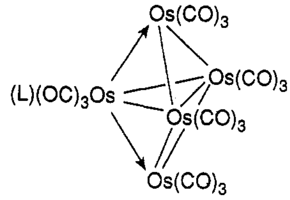

Table 6. Nearest Nonbonded Contacts (Å) for C(11) and C(13) in 3

	C···C Contacts		
C(11)···C(1)	2.63(2)	2.66(2)	C(13)···C(11)
C(11)···C(13)	2.66(2)	2.73(2)	C(13)···C(12)
C(11)···C(12)	3.05(2)	2.98(2)	C(13)···C(22)
C(11)···C(41)	3.05(2)	3.06(2)	C(13)···C(21)
C(11)···C(42)	3.31(2)	3.49(2)	C(13)···C(42)
		3.89(2)	C(13)···C(52)
	C···Os Contacts		
C(11)···Os(4)	3.11(2)	2.72(2)	C(13)···Os(2)
C(11)···Os(3)	4.23(2)	3.47(2)	C(13)···Os(4)
C(11)···Os(2)	4.30(2)	3.67(2)	C(13)···Os(5)

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(29) (a) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161. (b) Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437. (c) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.

ligand. This is because the resulting pseudo-*fac* configuration of the Os(CO)$_3$(L)(X)$_2$ (X = Os$_2$(CO)$_6$) unit avoids, as far as possible, the strong π-acceptor ligands competing for the same electron density on the central osmium atom.

The consequence of these different site preferences is that the CNBu^t ligand makes more acute angles with the Os–Os vectors of the Os$_5$ unit than does the PMe$_3$ ligand. In **3**, the C(1)Os(1)Os angles are in the range 67.2(3)–124.2(3)° whereas in **4e** the POs(1)Os angles are in the range 100.7(1)–154.4(1)°. In other words, the CNBu^t and PMe$_3$ groups are, as far as the geometry of the cluster allows, in cis and trans positions, respectively, to the metal–metal bonds in the cluster. In this respect the site preferences, therefore, resemble those observed in bi- and trinuclear carbonyl complexes.

In conclusion, the use of CNBu^t in place of phosphine as the non-carbonyl ligand, L, has provided new geometric isomers of the pentanuclear carbonyls of osmium of the formula Os$_5$(CO)$_n$(L) (n = 18, 17, 15). The different site preferences of the CNBu^t and PMe$_3$ ligands in the pentanuclear carbonyl clusters resemble those previously observed in trinuclear clusters. The difference in site preference is consistent with the view that the CNBu^t ligand adopts the site that is electronically-preferred, but the PMe$_3$ ligand adopts, for the most part, the site that is sterically-preferred in the clusters. An exception occurs for the Os$_5$(CO)$_{15}$(L) clusters where, remarkably, there is apparently a dominating electronic preference for the non-carbonyl ligand to coordinate to the most sterically crowded osmium atom in the cluster, namely, the osmium atom to which there are four terminal ligands attached.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for financial support.

Supplementary Material Available: Tables of fractional coordinates and isotropic temperature factors for the hydrogen atoms, additional bond lengths and angles, and anisotropic temperature factors for 1 and 3 (11 pages). Ordering information is given on any current masthead page.

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