

# Crystallographic disorder of carbonyl, propyl isocyanide and acetonitrile groups in the structures of $\text{Os}_3(\text{CO})_{10}(\text{CNR})(\text{NCMe})$

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(Received December 15, 1993; in revised form March 2, 1994)

## Abstract

Crystallographic disorder between structurally inequivalent groups in complexes  $\text{Os}_3(\text{CO})_{10}(\text{CNR})(\text{NCMe})$  (**1a**, R = Ph; **1b**, R = Pr) has been investigated by X-ray structure analysis. The disorder between NCMe and CO in **1a** is caused by a crystallographic mirror symmetry whereas the disorder between NCMe and CNPr in **1b** is caused by a crystallographic two-fold symmetry. Crystal data: **1a**:  $P2_1/m$ ;  $a = 8.047(2)$ ,  $b = 12.125(3)$ ,  $c = 12.549(2)$  Å;  $\beta = 106.50(2)^\circ$ ,  $V = 1174.0(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.037$ ,  $R_w = 0.029$ . **1b**:  $Pbcn$ ;  $a = 13.292(1)$ ,  $b = 12.655(2)$ ,  $c = 14.926(2)$  Å;  $V = 2510.6(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.045$ ,  $R_w = 0.046$ .

**Key words:** Osmium; Acetonitrile; Carbonyl; Crystallography; Disorder; Isocyanide

## 1. Introduction

Crystallographic disorder between structurally inequivalent groups is well known [1]. Many examples have been observed of disorder between carbonyl and other ligand [2], N<sub>2</sub> and Cl [3], methyl (CH<sub>3</sub>) and ethylidyne (C≡CH<sub>3</sub>) [4] in metal complexes, however, disorder between coordinated NCMe and other groups is less thoroughly explored. In the course of previous attempts to learn the effect of isocyanide-carbonyl replacement on the reactivity of the metal carbonyl cluster, we studied the preparation and reactivity of the "lightly stabilized" complexes  $\text{Os}_3(\text{CO})_{10}(\text{CNR})(\text{NCMe})$  [5]. Here we report our findings on the characterization and comparison of molecular structures of  $\text{Os}_3(\text{CO})_{10}(\text{CNR})(\text{NCMe})$  (**1a**, R = Ph; **1b**, R = Pr). The NCMe ligand is disordered with CO in complex **1a**; whereas NCMe is disordered with CNPr group in **1b**. These observations provided examples of disordered

crystal structure between the NCMe, CO and CNR ligands, differing in both composition and structure.

## 2. Results and discussion

### 2.1. Crystal structure of $\text{Os}_3(\text{CO})_{10}(\text{CNPh})(\text{NCMe})$

The molecular structure and atomic labelling scheme of  $\text{Os}_3(\text{CO})_{10}(\text{CNPh})(\text{NCMe})$  (**1a**) are shown in Fig. 1. The three Os atoms define an isosceles triangle. The CNPh ligand occupies an axial coordination site on Os(1). The NCMe ligand is coordinated at the axial site of Os(2) but disordered with the axial CO ligand [C(6)O(6)] as required by crystallographic mirror symmetry. Both the NCMe and C(6)O(6) ligands are *anti* to the CNPh ligand with respect to a plane defined by three Os atoms. The NCMe group and the [C(6)O(6)] group have been successfully and independently refined. The bond length of Os(2)–C(6) [1.73(3) Å] is shorter than the other axial bond lengths of Os(2)–C [1.87(2), 1.86(1) Å] and that of C(6)–O(6) [1.29(4) Å] is longer than other carbonyls [average C–O = 1.16(2) Å] in the molecule, whereas the Os–N(2) [2.16(1) Å] is

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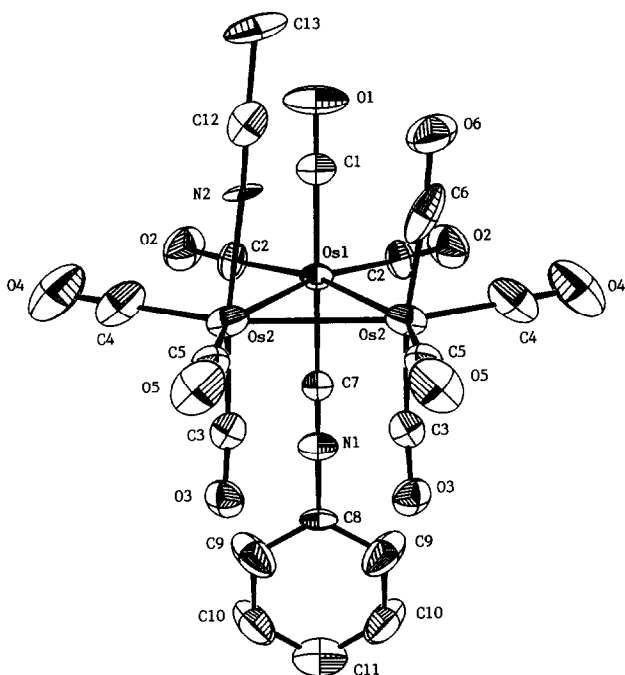


Fig. 1. ORTEP diagram of  $Os_3(CO)_{10}(CNPh)(NCMe)$  (**1a**). Only one site for the NCMe ligand and C(6)O(6) group is shown.

longer than that of the related acetonitrile complexes  $Os_3(CO)_{11}(NCMe)$  [2.07(2) Å] and  $Os_3(CO)_{10}(NCMe)_2$  [2.13(2), 2.13(1) Å] [6]. These structural parameters are only known with limited accuracy, resulting from incomplete separation of electron density peaks into N(2) and C(6), together with poorly defined anisotropic thermal parameters. The axial Os–C distances are apparently shorter than the equatorial Os–C lengths. The vectors of Os(2)–NCMe and Os(2)–C(6)O(6) are not truly coincident [N(2)–Os(2)–C(6) = 19(1)°].

## 2.2. Crystal structure of $Os_3(CO)_{10}(CNPr)(NCMe)$

Replacing CNPh by a less symmetric CNPr ligand, X-ray crystal structure analysis of complex  $Os_3(CO)_{10}(CNPr)(NCMe)$  (**1b**) was undertaken in order to see to what extent the removal of the (disorder-causing) crystallographic mirror perpendicular to the  $Os_3$  plane would affect the crystal structure. An ORTEP drawing of **1b** is shown in Fig. 2. Interestingly, its crystal structure also possesses a disorder problem yet in a different pattern. Three Os atoms define a triangle skeleton with similar Os–Os bond lengths. Os(1) is coordinated by four CO groups. The CNPr and NCMe ligands are coordinated at the axial site of the other two Os atoms, respectively, and *anti* to each other with respect to the

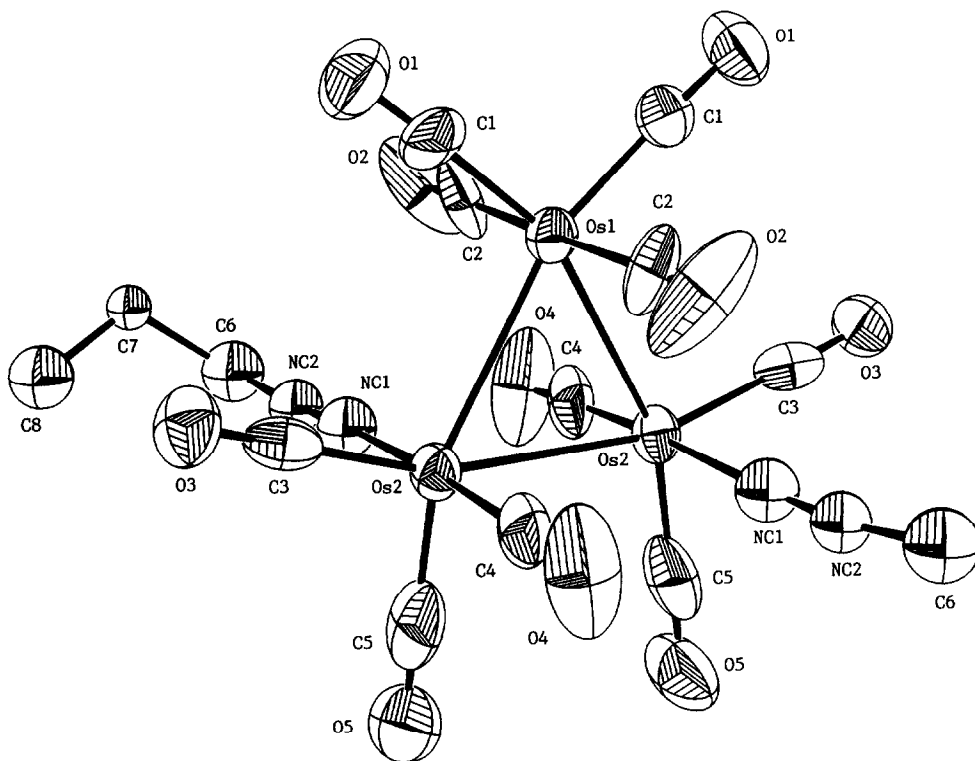


Fig. 2. ORTEP diagram of  $Os_3(CO)_{10}(CNPr)(NCMe)$  (**1b**).

TABLE 1. Crystal and intensity collection data for Os<sub>3</sub>(CO)<sub>10</sub>-(CNPPh)(NCMe) (1a) and Os<sub>3</sub>(CO)<sub>10</sub>(CNPPr)(NCMe) (1b)

	1a	1b
formula	C <sub>18</sub> H <sub>8</sub> N <sub>2</sub> O <sub>10</sub> Os <sub>3</sub>	C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> O <sub>10</sub> Os <sub>3</sub>
fw	985.89	914.87
space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>Pbcn</i>
<i>a</i> , Å	8.047(2)	13.292(1)
<i>b</i> , Å	12.125(3)	12.655(2)
<i>c</i> , Å	12.549(2)	14.926(2)
$\beta$ , deg	106.50(2)	
<i>V</i> , Å <sup>3</sup>	1174.0(5)	2510.6(5)
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	2.789	2.420
<i>Z</i>	2	4
cryst dimension, mm	0.32 × 0.32 × 0.40	0.20 × 0.20 × 0.20
abs coeff $\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	16.27	15.21
temp	room temperature	room temperature
radiation	Mo K $\alpha$	Mo K $\alpha$
2 $\theta$ (max)	49.9°	49.8°
scan type	$\theta$ / 2 $\theta$	$\theta$ / 2 $\theta$
total no. of reflectn	2329	2231
no. of observed reflectn	1629	1073
<i>F</i> <sub>o</sub> > 2 $\sigma$ ( <i>F</i> <sub>o</sub> )		
observed variables	188	121
<i>R</i>	0.037	0.045
<i>R</i> <sub>w</sub>	0.029	0.046
$\Delta(\rho)$ , e Å <sup>-3</sup>	1.290	1.290
$\Delta / \sigma_{\max}$	0.062	0.035
GOF	2.50	2.59

TABLE 2. Atomic coordinates and isotropic thermal parameters (Å<sup>2</sup>) for Os<sub>3</sub>(CO)<sub>10</sub>(CNPPh)(NCMe) (1a)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> <sup>a</sup>
Os1	0.50259(9)	1/4	0.37024(6)	3.14(3)
Os2	0.23018(7)	0.13214(5)	0.21566(4)	4.55(3)
N1	0.3029(17)	1/4	0.5514(10)	4.3(8)
N2	0.3597(21)	0.1552(15)	0.0884(13)	3.4(9)
C1	0.6289(20)	1/4	0.2660(12)	3.7(9)
C2	0.6284(17)	0.1282(10)	0.4460(9)	4.6(7)
C3	0.1056(14)	0.1299(10)	0.3203(9)	3.9(6)
C4	0.3109(16)	-0.0142(13)	0.2523(11)	7.0(9)
C5	0.0139(16)	0.1160(11)	0.0976(11)	5.3(8)
C6	0.361(4)	0.1080(23)	0.1297(22)	6.9(16)
C7	0.3712(19)	1/4	0.4802(11)	2.9(8)
C8	0.2172(20)	1/4	0.6354(13)	3.9(10)
C9	0.1750(23)	0.3464(13)	0.6752(12)	10.0(13)
C10	0.0946(23)	0.3476(13)	0.7592(12)	9.4(12)
C11	0.0456(30)	0.2500	0.7977(16)	8.4(17)
C12	0.4239(29)	0.1628(21)	0.0189(20)	5.0(13)
C13	0.5166(36)	0.1751(25)	-0.0692(20)	7.6(20)
O1	0.7152(16)	0.2500	0.2046(9)	7.5(10)
O2	0.7107(13)	0.0541(8)	0.4901(8)	8.1(7)
O3	0.0237(10)	0.1232(7)	0.3838(6)	5.1(5)
O4	0.3634(15)	-0.1032(10)	0.2762(9)	11.3(9)
O5	-0.1082(12)	0.1054(9)	0.0278(7)	7.7(6)
O6	0.4485(28)	0.0995(17)	0.0582(16)	8.7(15)

<sup>a</sup> *B*<sub>iso</sub> is the mean of the principal axes of the thermal ellipsoid.TABLE 3. Selected bond distances and angles for Os<sub>3</sub>(CO)<sub>10</sub>-(CNPPh)(NCMe) (1a)

Bond Distances (Å)			
Os(1)–Os(2)	2.8627(10)	N(2)–O(6)	1.12(3)
Os(1)–Os(2)	2.8627(10)	C(1)–O(1)	1.175(19)
Os(1)–C(1)	1.870(16)	C(2)–O(2)	1.159(16)
Os(1)–C(2)	1.888(12)	C(3)–O(3)	1.173(14)
Os(1)–C(2)	1.888(12)	C(4)–O(4)	1.166(20)
Os(1)–C(7)	1.962(15)	C(5)–O(5)	1.123(16)
Os(2)–Os(2)	2.8579(15)	C(6)–C(12)	1.74(4)
Os(2)–N(2)	2.158(14)	C(6)–O(6)	1.29(4)
Os(2)–C(3)	1.864(11)	C(8)–C(9)	1.351(17)
Os(2)–C(4)	1.900(16)	C(8)–C(9)	1.351(17)
Os(2)–C(5)	1.949(13)	C(9)–C(10)	1.385(19)
Os(2)–C(6)	1.73(3)	C(10)–C(11)	1.378(20)
N(1)–C(7)	1.175(20)	C(11)–C(10)	1.378(20)
N(1)–C(8)	1.414(20)	C(12)–C(13)	1.51(3)
N(2)–C(6)	0.77(3)	C(12)–O(6)	0.90(3)
N(2)–C(12)	1.14(3)	C(13)–C(13)	1.82(6)
Bond Angles (deg)			
Os(2)–Os(1)–Os(2)	59.89(3)	C(7)–N(1)–C(8)	178.8(15)
Os(2)–Os(1)–C(1)	89.4(4)	Os(2)–N(2)–C(6)	47(3)
Os(2)–Os(1)–C(2)	98.5(4)	Os(2)–N(2)–C(12)	176.7(17)
Os(2)–Os(1)–C(2)	158.4(4)	Os(2)–N(2)–O(6)	131.2(17)
Os(2)–Os(1)–C(7)	90.8(4)	C(6)–N(2)–C(12)	131(3)
Os(2)–Os(1)–C(1)	89.4(4)	C(6)–N(2)–O(6)	83(3)
Os(2)–Os(1)–C(2)	158.4(4)	C(12)–N(2)–O(6)	47.1(17)
Os(2)–Os(1)–C(2)	98.5(4)	Os(1)–C(1)–O(1)	176.9(13)
Os(2)–Os(1)–C(7)	90.8(4)	Os(1)–C(2)–O(2)	177.1(11)
C(1)–Os(1)–C(2)	91.8(5)	Os(2)–C(3)–O(3)	176.5(10)
C(1)–Os(1)–C(2)	91.8(5)	Os(2)–C(4)–O(4)	178.7(12)
C(1)–Os(1)–C(7)	179.7(6)	Os(2)–C(5)–O(5)	178.1(11)
C(2)–Os(1)–C(2)	103.0(5)	Os(2)–C(6)–N(2)	113(3)
C(2)–Os(1)–C(7)	88.0(4)	Os(2)–C(6)–C(12)	143.0(20)
C(2)–Os(1)–C(7)	88.0(4)	Os(2)–C(6)–O(6)	173.1(20)
Os(1)–Os(2)–Os(2)	60.056(20)	N(2)–C(6)–C(12)	29.5(21)
Os(1)–Os(2)–N(2)	89.9(4)	N(2)–C(6)–O(6)	59.7(25)
Os(1)–Os(2)–C(3)	89.5(3)	C(12)–C(6)–O(6)	30.3(14)
Os(1)–Os(2)–C(4)	99.1(4)	Os(1)–C(7)–N(1)	175.6(13)
Os(1)–Os(2)–C(5)	155.8(4)	N(1)–C(8)–C(9)	120.2(8)
Os(1)–Os(2)–C(6)	91.3(8)	N(1)–C(8)–C(9)	120.2(8)
Os(2)–Os(2)–N(2)	82.6(5)	C(9)–C(8)–C(9)	119.6(14)
Os(2)–Os(2)–C(3)	90.9(4)	C(8)–C(9)–C(10)	120.8(14)
Os(2)–Os(2)–C(4)	159.0(4)	C(9)–C(10)–C(11)	120.0(15)
Os(2)–Os(2)–C(5)	95.8(4)	C(10)–C(11)–C(10)	118.4(17)
Os(2)–Os(2)–C(6)	99.8(9)	N(2)–C(12)–C(6)	19.5(15)
N(2)–Os(2)–C(3)	172.7(6)	N(2)–C(12)–C(13)	177.3(24)
N(2)–Os(2)–C(4)	95.5(7)	N(2)–C(12)–O(6)	65.8(22)
N(2)–Os(2)–C(5)	88.0(6)	C(6)–C(12)–C(13)	160.2(23)
N(2)–Os(2)–C(6)	19.1(10)	C(6)–C(12)–O(6)	46.3(19)
C(3)–Os(2)–C(4)	91.8(6)	C(13)–C(12)–O(6)	114(3)
C(3)–Os(2)–C(5)	89.5(5)	C(12)–C(13)–C(13)	95.7(17)
C(3)–Os(2)–C(6)	168.2(10)	N(2)–O(6)–C(6)	36.3(16)
C(4)–Os(2)–C(5)	105.1(5)	N(2)–O(6)–C(12)	67.2(23)
C(4)–Os(2)–C(6)	76.5(10)	C(6)–O(6)–C(12)	103(3)
C(5)–Os(2)–C(6)	94.5(9)		

Os<sub>3</sub> plane. The CNPr and NCMe ligands are disordered with each other as related by a crystallographic two-fold axis.

If there are sufficient voids, a less-symmetric molecule can be packed more freely in lattice to behave on average like a more-symmetric moiety as observed by X-ray crystal structure analysis. For example, an octahedral  $\text{PF}_6^-$  anion usually behaves like a sphere in the analysis, such that the F atoms are characterized with large thermal ellipsoids and often with more than one orientation [7]. In the present study, **1a** and **1b** have a  $C_1$  molecular symmetry and occupy, respectively, crystallographic special positions of mirror and two-fold. Concerning the molecular volumes,  $\text{Os}_3(\text{CO})_{12}$  has a volume of  $427.6 \text{ \AA}^3$  as calculated [8] from its crystallographic cell volume/ $Z$ ;  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})$   $476.7 \text{ \AA}^3$ ; and  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$   $516.6 \text{ \AA}^3$  [6]. For **1a**, the molecular volume is  $587.0 \text{ \AA}^3$  within reasonable expansion from the above parent compounds, taking a  $15\text{--}35 \text{ \AA}^3$  increase in volume for each additional non-H atom. For **1b**, the molecular volume is  $627.8 \text{ \AA}^3$  which is too big for **1b** to be packed efficiently in the solid state.

A Ph skeleton is generally more dominating towards the crystal packing than a Pr skeleton because the Ph group is much more rigid due to its planar hexagonal shape. As **1a** has a CNPh ligand and **1b** has a CNPr ligand, a more efficient packing would be expected for **1a** in which CO and NCMe do not affect much of the crystallization process, resulting in the mirror imposed disorder. For **1b**, the packing is determined partly by the  $\text{Os}_3(\text{CO})_{10}$  skeleton (23 non-H atoms) which occupies less than *ca.*  $370 \text{ \AA}^3$ , (estimated from  $427.6 \text{ \AA}^3$  less

TABLE 4. Atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) for  $\text{Os}_3(\text{CO})_{10}(\text{CNPr})(\text{NCMe})$  (**1b**)

Atom	x	y	z	$B_{\text{iso}}^a$
Os1	0	0.53910(14)	1/4	5.11(9)
Os2	0.08960(9)	0.34206(11)	0.19659(8)	4.94(6)
C1	0.0917(21)	0.6335(24)	0.1938(22)	8.2(20)
C2	-0.0874(21)	0.5415(26)	0.1388(20)	8.1(21)
C3	0.2039(22)	0.3879(21)	0.1309(17)	6.1(18)
C4	0.0072(22)	0.3345(25)	0.0904(20)	7.8(19)
C5	0.1060(22)	0.2035(28)	0.1919(21)	9.5(23)
C6	0.3123(23)	0.3454(28)	0.4423(20)	7.9(9)
C7	0.4004(37)	0.4179(38)	0.4083(30)	4.1(11)
C8	0.4654	0.3665	0.3475	7.9
NC1	0.1832(18)	0.3378(21)	0.3144(16)	6.5(7)
NC2	0.2402(18)	0.3352(20)	0.3747(15)	5.7(6)
O1	0.1492(15)	0.6890(18)	0.1598(15)	9.6(15)
O2	-0.1276(19)	0.5394(23)	0.0785(13)	14.6(20)
O3	0.2702(16)	0.4156(17)	0.0880(12)	7.9(13)
O4	-0.0427(17)	0.3274(29)	0.0281(14)	14.9(23)
O5	0.1157(17)	0.1105(19)	0.1911(17)	11.8(17)

<sup>a</sup>  $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.

TABLE 5. Selected bond distances and angles for  $\text{Os}_3(\text{CO})_{10}(\text{CNPr})(\text{NCMe})$  (**1b**)

Bond Distances ( $\text{\AA}$ )			
Os(1)–Os(2)	2.8761(11)	Os(2)–N(C1)	2.154(24)
Os(1)–Os(2)	2.8761(11)	C(1)–O(1)	1.16(4)
Os(1)–C(1)	1.90(3)	C(2)–O(2)	1.05(4)
Os(1)–C(1)	1.90(3)	C(3)–O(3)	1.14(3)
Os(1)–C(2)	2.03(3)	C(4)–O(4)	1.14(4)
Os(1)–C(2)	2.03(3)	C(5)–O(5)	1.18(4)
Os(2)–Os(2)	2.8662(23)	C(6)–C(7)	1.57(6)
Os(2)–C(3)	1.90(3)	C(6)–N(C2)	1.40(4)
Os(2)–C(4)	1.93(3)	C(7)–C(8)	1.41(5)
Os(2)–C(5)	1.77(4)	N(C1)–N(C2)	1.18(3)
Bond Angles (deg)			
Os(2)–Os(1)–Os(2)	59.77(5)	Os(2)–Os(2)–C(3)	162.2(8)
Os(2)–Os(1)–C(1)	99.0(9)	Os(2)–Os(2)–C(4)	89.2(8)
Os(2)–Os(1)–C(1)	158.8(9)	Os(2)–Os(2)–C(5)	97.2(9)
Os(2)–Os(1)–C(2)	91.3(10)	Os(2)–Os(2)–N(C1)	91.5(6)
Os(2)–Os(1)–C(2)	90.1(8)	C(3)–Os(2)–C(4)	92.6(11)
Os(2)–Os(1)–C(1)	158.8(9)	C(3)–Os(2)–C(5)	100.6(12)
Os(2)–Os(1)–C(1)	99.0(9)	C(3)–Os(2)–N(C1)	88.1(10)
Os(2)–Os(1)–C(2)	90.1(8)	C(4)–Os(2)–C(5)	89.3(14)
Os(2)–Os(1)–C(2)	91.3(10)	C(4)–Os(2)–N(C1)	175.7(12)
C(1)–Os(1)–C(1)	102.1(13)	C(5)–Os(2)–N(C1)	86.4(13)
C(1)–Os(1)–C(2)	89.8(12)	Os(1)–C(1)–O(1)	178 (3)
C(1)–Os(1)–C(2)	89.1(13)	Os(1)–C(2)–O(2)	175 (3)
C(1)–Os(1)–C(2)	89.1(13)	Os(2)–C(3)–O(3)	176.9(23)
C(1)–Os(1)–C(2)	89.8(12)	Os(2)–C(4)–O(4)	178 (3)
C(2)–Os(1)–C(2)	178.3(13)	Os(2)–C(5)–O(5)	178 (3)
Os(1)–Os(2)–Os(2)	60.11(4)	C(7)–C(6)–N(C2)	109 (3)
Os(1)–Os(2)–C(3)	102.1(8)	C(6)–C(7)–C(8)	113 (3)
Os(1)–Os(2)–C(4)	92.0(9)	Os(2)–N(C1)–N(C2)	175.2(21)
Os(1)–Os(2)–C(5)	157.2(9)	C(6)–N(C2)–N(C1)	172 (3)
Os(1)–Os(2)–N(C1)	92.0(7)		

$4 \times 15 \text{ \AA}^3$ ) leaving a large space available for the totally disordered CNPr and NCMe (8 non-H atoms total).

### 3. Experimental section

#### 3.1. Crystallographic structure determination

The synthesis of  $\text{Os}_3(\text{CO})_{10}(\text{CNPh})(\text{NCMe})$  and  $\text{Os}_3(\text{CO})_{10}(\text{CNPr})(\text{NCMe})$  follows the reaction of  $\text{Os}_3(\text{CO})_{12}$  with phosphine imides, then oxidative decarbonylation by  $\text{Me}_3\text{NO}$  in the presence of MeCN as detailed elsewhere [5]. Crystals of both  $\text{Os}_3(\text{CO})_{10}(\text{CNPh})(\text{NCMe})$  (**1a**) and  $\text{Os}_3(\text{CO})_{10}(\text{CNPr})(\text{NCMe})$  (**1b**) were obtained from slow evaporation of hexane/ $\text{CH}_2\text{Cl}_2$ /MeCN solutions at  $-5^\circ\text{C}$ . Specimens of suitable quality were mounted in a glass capillary for precise determination of cell constants and intensity data collection was made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.70930 \text{ \AA}$ ) with  $\theta$ - $2\theta$  scan mode. Unit cells were determined and refined using 25 randomly

selected reflections obtained using the CAD-4 automatic search, centre, index and least-squares routines. Space groups were determined from the systematic absences observed during data collection. Systematic absences in the diffraction data of **1a** and **1b** unambiguously established the space groups as  $P2_1/m$  and  $Pbcn$ , respectively. An empirical absorption correction based on azimuthal scans of three reflections was applied to each of the data sets. The structures were solved by a combination of heavy-atom methods and difference syntheses, and was refined by a full-matrix least-squares procedure in which the function  $\sum \omega \Delta^2$  was minimized where  $\Delta = \|F_o\| - \|F_c\|$  and  $\omega$  is the counting statistical weight applied to each reflection. Refinement of **1a**: The NCMe group and C(6)O(6) ligand were disordered across a mirror plane, the disorder being 50/50 as required crystallographically. The atoms of C(6), O(6), N(2), C(12), and C(13) could be clearly resolved and independently refined anisotropically. Refinement of the disordered model led to convergence with  $R = 0.037$ ,  $R_w = 0.029$  and GOF = 2.50 for data with  $|F_o| > 2\sigma(|F_o|)$ . Removal of the crystallographic mirror, *i.e.*, using space group  $P2_1$  instead of  $P2_1/m$  led to singularity such that the attempted refinement was not possible. Refinement of **1b**: The molecule sits on a crystallographic two-fold axis such that the ligands NCMe and CNPr are symmetrically related in equivalent occupancy. The two donating atoms of ligands NCMe and CNPr were accordingly refined with one common set of atomic coordinates and isotropic thermal parameters, with 50N/50C composite scattering factor. The extending chain—C(6), C(7), and C(8)—of NCMe and CNPr were quite resistive to the analysis, too. The atoms of C(6) and C(7) were refined isotropically. The atom of C(8) was located and isotropically fixed. The reduction from  $Pbcn$  to lower symmetric space groups produced poorer results. Crystallographic data for **1a** and **1b** are shown in Table 1. Final atomic coordinates, isotropic thermal parameters, and selected bond distances and bond angles for the two complexes are listed in Tables 2–5. All the data processing was carried out on a Microvax 3600 using the NRCC SDP program [9].

## Acknowledgment

We thank the National Science Council of Taiwan for financial support.

## Supplementary material

Tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, bond lengths and angles (8 pages), and tables of structure factors (16 pages) are available from the authors.

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