Inorg. Chem. 1992, 31, 4499–4502

Isomerization, Photoreaction, and Structure Studies of Osmium Complexes Containing Carboxamido and Halide Ligands

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Received April 16, 1992

Reactions of the hydrido(carboxamido)triosmium cluster (μ-H)$Os_3(CO)_{10}$(μ-OCNHCHMe$_2$) (**1**) with bromine and iodine have been studied. The reactions yield in the first stage dinuclear compounds (μ-X)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)X_2 (X = Br, **2a**-cis; X = I, **2b**-cis) with two halogen atoms in the cis form. Compound **2**-cis is a kinetic product and in solution slowly transforms to a trans isomer (**2**-trans). The rate of transformation depends on the polarity of the solvent, and the rate for **2a**-cis is faster than that of **2b**-cis. Kinetic studies show that the transformation of **2a**-cis to **2a**-trans follows the first-order rate law. The rate constants of this transformation in CD_3COCD_3 are 1.66×10^{-3} min^{-1}, 5.24×10^{-3} min^{-1}, and 2.02×10^{-2} min^{-1}, at 21, 30, and 40 °C, respectively, and the activation energy thus obtained is 24.2 kcal/mol. In $CDCl_3$, the rate of isomerization is slower with an activation energy of 24.7 kcal/mol. Photolysis of complex **2**-cis with UV irradiation results in loss of a CO ligand and yields (μ-X)$_2Os_2(CO)_5$(μ-OCNHCHMe$_2$)X (X = Br, **3a**; X = I, **3b**) in moderate yield. Complex **3b** has been crystallographically characterized: space group $P2_1/c$, a = 10.043 (3) Å, b = 14.510 (9) Å, c = 12.973 (3) Å, β = 91.53 (2)°; and Z = 4. The structure was refined to R = 0.0384 and R_w = 0.0348 for 2728 reflections. The structure consists of two osmium metal centers, bridged by one μ-η^2-carboxamido and two iodide ligands. The two osmium metal centers are separated by 3.628 (2) Å, indicating no metal–metal bond.

Introduction

Hydridotriosmium clusters containing carboxamido ligands could be readily prepared from the reactions of $Os_3(CO)_{12}$ with a variety of amines. However, their chemical reactivities were not extensively explored, probably due to their thermal stability. Only under high-temperature thermolysis can the carboxamido cluster be converted to nitrene complexes where the metal skeleton still remains.[1,2] In our previous paper,[3] we reported that the reactions of the (μ-carboxamido)osmium cluster with iodine and bromine gave several di- or mononuclear osmium complexes in a stepwise mode. Careful observation of these reactions shows that all Os–Os bonds of the trinuclear cluster were cleaved by halogens, first in a regiospecific manner, and finally the reactions yielded the dinuclear (carboxamido)osmium complexes (μ-X)-$Os_2(CO)_6$(μ-OCNHCHMe$_2$)X_2 (X = Br, **2a**-cis; X = I, **2b**-cis) with no M–M bond.[4] Since halides, especially iodide, have been widely employed as promoters in many catalytic[5-7] as well as stoichiometric reactions,[8,9] it is essential to have more insights into those reactions that occur on metal complexes containing halide ligands. These might lead to a better understanding of the role of halides in those catalytic systems. Therefore, we synthesized these kinds of complexes and subsequently explored their chemical reactivities. In this paper, we describe the isomerization and photodecarbonylation reactions of these osmium complexes as well as the proposed intermediates for these transformations.

Results and Discussion

Isomerization of (μ-X)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)X_2 (X = Br, 2a-cis; X = I, 2b-cis). Reaction of the (carboxamido)-hydridotriosmium cluster (μ-H)$Os_3(CO)_{10}$(μ-OCNHCHMe$_2$) (**1**) with 2 equiv of bromine at room temperature causes the rupture of all three Os–Os bonds and yields mainly a dinuclear osmium complex. The dinuclear product was characterized as (μ-Br)-$Os_2(CO)_6$(μ-OCNHCHMe$_2$)Br_2 (**2a**-cis) by spectroscopic methods. The molecular structure of the iodide analogue **2b**-cis was confirmed previously by a single-crystal X-ray diffraction study.[3] The structure shows that the two terminal iodine atoms are disposed on the same side of the plane that contains the two osmium metal centers and the bridging iodine atom.

Complexes **2a**-cis and **2b**-cis are kinetic products derived from the regioselective cleavage of the M–M bond of **1** by a halogen.[4] These complexes are stable in the solid state but slowly isomerize in solution to yield thermodynamic products **2a**-trans and **2b**-trans (eq 1).

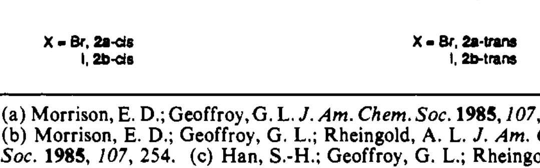

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Table I. Rate Constants and Associated Energy Parameters for Isomerization of *cis*-(μ-Br)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)Br_2 to Its Trans Form in CD_3COCD_3 and $CDCl_3$

solvent	temp (K)	k (min^{-1})	energy params
CD_3COCD_3	294	1.66×10^{-3}	
	303	5.24×10^{-3}	
	313	2.02×10^{-2}	
			$E_a = 24.2$ kcal/mol $\Delta H^{*} = 23.6$ kcal/mol $\Delta S^{*} = 1.1$ cal/(deg K mol)
$CDCl_3$	295	2.00×10^{-4}	
	315	2.51×10^{-3}	
	324	9.25×10^{-3}	
			$E_a = 24.7$ kcal/mol $\Delta H^{*} = 24.2$ kcal/mol $\Delta S^{*} = -1.7$ cal/(deg K mol)

The structure of complex **2a**-trans was previously determined by X-ray crystallography.[10] The spectroscopic data are consistent with its formulation. This structure showed that the two terminal bromine atoms are disposed in a trans mode with respect to the plane containing two Os atoms and the bridging Br atom. The ^1H NMR spectra for complexes **2a**-trans and **2b**-trans showed the characteristic resonances of the isopropyl group of the carboxamido ligand, and the ^{13}C NMR spectra showed all six terminal CO peaks for each complex. The rate of isomerization of bromide complex **2a**-cis is faster than that of the iodide analogue **2b**-cis. The rate also depends on the polarity of the solvent. In chloroform, **2a**-cis isomerizes to **2a**-trans in 1 week at room temperature; however, **2b**-cis transforms at a slower rate (within 1 month) to complete the reaction. A polar solvent such as acetone promotes the process of isomerization more efficiently than the less polar solvent $CHCl_3$.[11]

Kinetic Study. The rate of isomerization of bromide complex **2a**-cis is faster than that of the iodide analogue **2b**-cis. Complex **2a**-cis was thus chosen as a model to study the kinetic behavior. The kinetic studies were carried out in two different solvents, CD_3COCD_3 and $CDCl_3$, at three different temperatures. ^1H NMR spectra were chosen to monitor the concentration change of **2**-cis to **2**-trans, since the HN absorption peaks of the two isomers were well separated for the measurement of the integrated area. By contrast, the absorption peaks of IR spectra in the CO stretching region of these two isomers show extensive overlap and do not provide a good means of concentration measurements. Isomerization is not observed when **2**-cis is stored at room temperature as a solid or in solution below 0 °C for 1 month. At temperatures above 0 °C, **2**-cis slowly isomerizes to **2**-trans in solution. This transformation is irreversible. The rates of isomerization obey a first-order rate law, and linear least-squares fits were used to obtain the rate constants at three different temperatures. The rate constants, obtained from the ratios of the area of the HN peaks at each of the three temperatures, are listed in Table I. The temperature dependence of ln k is shown in Figure 1.

The first-order rate constants for the isomerization of **2a**-cis and **2b**-cis in $CDCl_3$ at 295 K are 2.00×10^{-4} min^{-1} and 2.25×10^{-5} min^{-1}, respectively. The rate of isomerization of the iodide-containing complex **2b**-cis is about 1 order of magnitude slower than that of **2a**-cis. The activation energies calculated from the kinetic data are 24.2 and 24.7 kcal/mol in acetone-d_6 and $CDCl_3$, respectively, for **2a**-cis. ΔS^{*} for **2a**-cis isomerization is close to zero both in acetone and in chloroform.

Proposed Mechanism of Isomerization. The kinetic study shows that the rate of isomerization of the bromide complex, **2a**-cis, is faster than that of the iodide analogue, **2b**-cis, and both rates are increased in polar solvent. The activation energy for the isomerization of **2a**-cis in acetone-d_6 is 24.2 kcal/mol. This is close to that of the irreversible isomerization of *cis*-[$Co(en)_2Cl_2$]$^+$ in methanol to the corresponding trans cation.[12] On the basis of the activation energy of 23.7 kcal/mol for the Co complex, the isomerization of the *cis*-[$Co(en)_2Cl_2$]$^+$ was proposed to proceed via the dissociation of Cl^-. Because the activation energies of these two systems are close, we suggest that the mechanism of isomerization of **2**-cis may proceed through rupture of the M–X bond. The solvent effect also supports the postulation of an ionic dissociation mechanism.[13] Since the value of ΔS^{*} is close to zero, the bond fission seems to occur through an intramolecular rather than an intermolecular process; i.e., the dissociation of Os(2)–X(3) is more plausible than the fission of Os(1)–X(1). It is noteworthy that dissociation of the M–X bond does not result in more randomness of the system, thus keeping ΔS^{*} close to zero. One feasible intermediate for this transformation could be the solvent-bound complex **2i** shown in eq 2. In complex **2i**, the X(3) ligand also remains attached on the dinuclear complex. Therefore, a pseudo turnstile-like mechanism[14] also shown in eq 2 is proposed to account for the observed data.

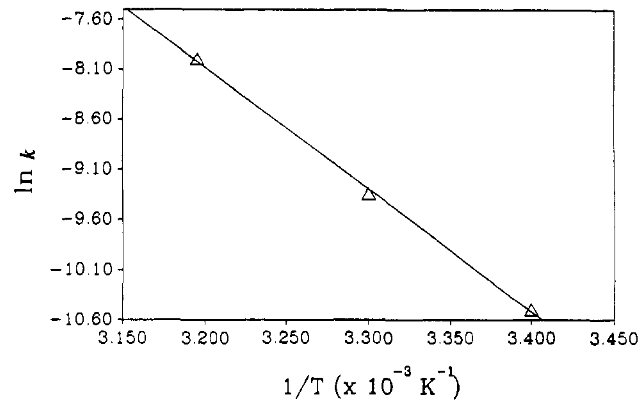
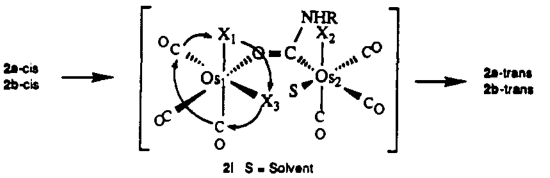
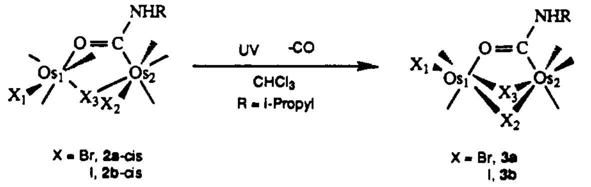


Figure 1. Plot of ln k vs $1/T$ for the isomerization of **2a**-cis to yield **2a**-trans.



2i S = Solvent (2)

Photochemical Reaction. Photolysis of complexes **2a**-cis and **2b**-cis in $CHCl_3$ with UV irradiation from a medium-pressure mercury lamp gives decarbonylation products (μ-X)$_2$Os$_2$(μ-OCNHCHMe$_2$)(CO)$_5$X (X = Br, **3a**; X = I, **3b**). Complexes **3a,b** are formed by removal of one of the labile CO ligands on Os(1) (eq 3) and transformation of the terminal ligand X(2) on Os(2) to a bridged form.



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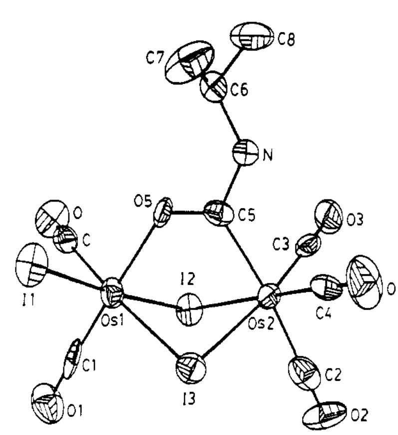
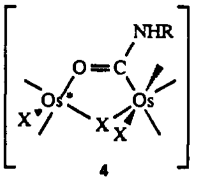


Figure 2. ORTEP drawing of **3b** with thermal ellipsoids shown at the 50% probability level.

Complexes **3a,b** were isolated as microcrystalline solids and spectroscopically characterized. Complex **3b** has also been crystallographically characterized, and the spectroscopic data are consistent with its formulation. An ORTEP drawing of complex **3b** is shown in Figure 2. The ^{13}C NMR spectrum of complex **3b** shows five terminal CO resonances at δ 175.22, 168.67, 168.57, 165.18, and 164.02 and, in addition, a characteristic carboxamido carbon peak at δ 197.15. From the photochemical transformation, it is worth noting that the more labile CO ligand in complex **2** is located at the Os(1) atom, which is bonded to the oxygen atom of the carboxamido ligand. We suggest that the photochemical reaction might proceed through an intermediate **4** shown as follows:



4

• : vacant site
R = i-Propyl

It is known that the oxygen ligands in transition metal complexes possess the ability to cause cis-labilizing effects.[15] Darensburg has noted that metal carbonyl complexes containing phosphine oxides and formate ligands[16] show strong CO labilization by the vicinal cis-oxygen donor ligands. Previously we[4] found a similar labilizing effect in the study of the addition of iodine to the metal–metal bond of the (carboxamido)triosmium cluster **1**. Recently Lu[17] also observed the facile replacement of a CO ligand cis to the oxygen end of the carboxamido ligand in the complex $Os_3(CO)_{10}(\mu\text{-OCNHR}')(\mu\text{-C=NHR})$ at ambient temperature. On the basis of these observations, the carboxamido ligand is likely also to possess the same ability for CO labilization.

Crystal Structure of 3b. An ORTEP drawing of **3b** is shown in Figure 2. The structure consists of two osmium metal centers triply-bridged by one μ-η^2-carboxamido and two iodide ligands. In addition, Os(1) and Os(2) are bound to two and three terminal CO ligands, respectively, and the terminal iodide is attached to Os(1). Two osmium metal centers, both with pseudooctahedral geometry, are separated by 3.628 (2) Å, indicating no metal–metal interaction. This is expected according to the EAN rule. The Os(1)–I(2)–Os(2) and Os(1)–I(3)–Os(2) angles are 83.16 (4) and 82.17 (4)°, respectively; these angles are much smaller than that in those complexes with only one bridging halide. For example, the Os(1)–X–Os(2) angles are 95.77 (2) and 101.0 (1)° for **2b**-cis[3] and **2a**-trans,[10] respectively. The bond length of Os(1)–C (2.04 (1) Å) is relatively long and the corresponding C–O (0.82 (1) Å) distance is relatively short for complex **3b**. This could possibly be due to the disorder of this CO and the terminal iodide ligand. Similar results were also observed previously.[4] Both C=O (1.26 (1) Å) and CN (1.37 (1) Å) bonds of the carboxamido ligand show partial double-bond character, similar to that of many other carboxamido complexes of the same type.[3,10]

Experimental Section

General Procedures. The complex $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCNHMe}_2)$ (**1**),[1] $(\mu\text{-Br})Os_2(\mu\text{-OCNHCHMe}_2)(CO)_6Br_2$ (**2a**-cis), and $(\mu\text{-I})Os_2(\mu\text{-OCNHCHMe}_2)(CO)_6I_2$ (**2b**-cis)[3] were prepared according to literature methods. Other reagents were purchased from commercial sources and were used as received. Solvents were purified by standard methods.[18] Although the cluster complexes were generally air stable, reactions and filtrations were routinely carried out under nitrogen atmosphere using Schlenkware techniques or in an inert-atmosphere box. Chromatographic separations and handling of neutral complexes can be done in air if exposure is limited to a few hours. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer using a liquid cell equipped with CaF_2 windows. NMR spectra were recorded on a Bruker AM-300WB spectrometer. Mass spectra were obtained on a JEOL-JMS D300 mass spectrometer at the Taipei Regional Center for Instrumentation located at National Taiwan Normal University. Elemental analyses were performed using a Perkin-Elmer 240C at the Department of Chemistry, National Taiwan University.

Isomerization of 2a-cis. The white powder of complex **2a**-cis is stable in the solid state, but it transformed to a yellow compound in chloroform over a 1-week period. The structure of the yellow compound was assigned as $(\mu\text{-Br})Os_2(\mu\text{-OCNHCHMe}_2)(CO)_6Br_2$ (**2a**-trans). Anal. Calcd for $Os_2C_{10}H_8Br_3NO_7$: C, 13.73; H, 0.91. Found: C, 13.80; H, 0.87. IR (CH_2Cl_2) (cm^{-1}): 3678 (w), 3440 (w), 2969 (w); 2119 (s, br), 2052 (vs, br), 2016 (m), 1978 (w), terminal CO absorption; 1603 (w), 1501 (m), 1440 (s), amide absorption. ^{1}H NMR ($CDCl_3$): δ 6.19 (d, br, 1 H, NH), 4.25 (m, 1 H, CH), 1.27 (d, 3 H, Me), 1.23 (d, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 214.09 (carboxamido carbon), 169.06, 167.58, 166.18, 164.56, 162.61, 162.49 (six terminal carbonyls), 44.91 (CH), 22.60 (Me), 22.22 (Me). MS (EI): m/z 874 (M^+). The crystal structure of **2a**-trans has been previously determined.[10]

Isomerization of 2b-cis. Similar to **2a**-cis, complex **2b**-cis isomerized to **2b**-trans but with a slower rate. The colorless complex **2b**-cis transformed to a yellow compound in chloroform over a 1-month period. The structure of the yellow compound was assigned as $(\mu\text{-I})Os_2(\mu\text{-OCNHCHMe}_2)(CO)_6I_2$ (**2b**-trans). Anal. Calcd for $Os_2C_{10}H_8I_3NO_7$: C, 11.82; H, 0.79. Found: C, 11.76; H, 0.73. IR (CH_2Cl_2) (cm^{-1}): 3679 (w), 3599 (w), 2111 (s, br), 2047 (vs, br), 2015 (m) [2118 (m), 2109 (s), 2046 (vs), 2036 (s), 2013 (s), 1981 (w), in n-hexane], terminal CO absorption: 1604 (w), 1499 (m), 1418 (s), amide absorption. ^{1}H NMR ($CDCl_3$): δ 6.19 (d, br, 1 H, NH), 4.22 (m, 1 H, CH), 1.27 (d, 3 H, Me), 1.21 (d, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 211.01 (carboxamido carbon), 166.96, 166.89, 166.56, 163.42, 162.56, 161.28 (six terminal carbonyls), 44.86 (CH), 22.88 (Me), 22.12 (Me).

Kinetic Study of Isomerization. The rate of transformation of **2a**-cis is faster than that of **2b**-cis; therefore, **2a**-cis was chosen for exploration. The processes were carried out in CD_3COCD_3 or $CDCl_3$ and monitored by ^{1}H NMR spectra. At temperatures above 0 °C, isomerization of **2a**-cis in solution slowly affords **2a**-trans. The relative concentrations of **2a**-cis and **2a**-trans were determined by measuring the relative areas under the HN peaks (broad doublet). Rates were measured at three different temperatures. The rate constants k obtained from the area ratios of the HN peaks are listed in Table I. The temperature dependence of ln k is shown in Figure 1. This is found to be linear as expected. The slope was calculated by a linear least-squares fit program with equal weight for all data.

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Photodecarbonylation of Complex (μ-I)Os$_2$(CO)$_6$(μ-OCNHCHMe$_2$)I$_2$ (2b-cis). A CHCl$_3$ solution of **2b**-cis (32 mg, 0.03 mmol) was equally divided into five NMR tubes and then photolyzed with UV irradiation. The solution turned yellow in 1 h, and the product was purified by column chromatography on silica gel to give complex (μ-I)$_2$Os$_2$(CO)$_5$(μ-OCHNCHMe$_2$)I (**3b**) (20 mg, 0.02 mmol, 64%). Anal. Calcd for Os$_2$C$_9$H$_8$I$_3$NO$_6$: C, 10.95; H, 0.81. Found: C, 10.83; H, 0.75. IR (CH$_2$Cl$_2$) (cm^{-1}): 3680 (w), NH absorption; 2117 (s), 2054 (s), 2044 (vs), 2026 (s), 1973 (m), terminal CO absorption; 1600 (w), 1479 (w), amide absorption. ^{1}H NMR (CDCl$_3$): δ 6.02 (d, br, 1 H, NH), 4.38 (m, 1 H, CH), 1.30 (d, 3 H, Me), 1.26 (d, 3 H, Me). ^{13}C NMR (CDCl$_3$): δ 197.15 (carboxamido carbon), 175.22, 168.67, 168.57, 165.18, 164.02 (five terminal carbonyls), 45.07 (CH), 22.73 (Me), 22.48 (Me). MS (EI): *m/z* 991 (M$^+$).

Photodecarbonylation of Complex (μ-Br)Os$_2$(CO)$_6$(μ-OCNHCHMe$_2$)Br$_2$ (2a-cis). The procedure was carried out in the same manner described in the case of **2b**-cis, except for the reaction time (1.5 h). The complex (μ-Br)$_2$Os$_2$(CO)$_5$(μ-OCNHCHMe$_2$)Br (**3a**) was obtained in 40–50% yield. IR (CH$_2$Cl$_2$) (cm^{-1}): 2126 (m), 2054 (vs), 2027 (s), 1979 (m), terminal CO absorption; 1600 (w), 1479 (w), amide absorption. ^{1}H NMR (CDCl$_3$): δ 6.08 (d, br, 1 H, NH), 4.48 (m, 1 H, CH), 1.31 (d, 3 H, Me), 1.29 (d, 3 H, Me). MS (EI): *m/z* 850 (M$^+$).

X-ray Crystallography. Air-stable single crystals of **3b** were grown from CH$_2$Cl$_2$–hexane at room temperature by the liquid diffusion method, and a yellow crystal was mounted on a glass fiber in air. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. PDP 11/23 computer by using the computing programs of the NRCC SDP PDP-11 package.[19] An empirical absorption correction based on azimuthal rotation from three reflections was made on the data. Transmission factors were between 0.78 and 1.00. The structure was solved by locating the Os atom in a Patterson map followed by locating the remaining non-hydrogen atoms in subsequent different maps. Positional parameters of all hydrogen were calculated and were not refined. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$; $\sigma(F_o)$ is from counting statistics. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Atomic scattering factors and anomalous dispersion terms were obtained from ref 20. Selected bond lengths and bond angles are listed in Table II. Complete listings of fractional atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths, and bond angles are included in the supplementary material.

Table II. Selected Bond Distances (Å) and Angles (deg) for (μ-I)$_2$Os$_2$(CO)$_5$(μ-OCNHCHMe$_2$)I (**3b**)

(a) Selected Bond Distances			
Os1–I1	2.698 (1)	Os1–I2	2.714 (1)
Os1–I3	2.778 (1)	Os1–C1	1.77 (1)
Os1–C	2.04 (1)	Os1–O5	2.094 (9)
Os2–I2	2.752 (1)	Os2–I3	2.743 (1)
Os2–C2	1.99 (1)	Os2–C3	1.88 (1)
Os2–C4	1.88 (1)	Os2–C5	2.13 (1)
I1–I3	3.920 (2)	I2–I3	3.683 (1)
C1–O1	1.20 (2)	C2–O2	1.13 (2)
C3–O3	1.15 (2)	C4–O4	1.16 (1)
C5–O5	1.26 (1)	C5–N	1.37 (1)
C6–C7	1.47 (2)	C6–C8	1.48 (2)
C6–N	1.47 (1)	C–O	0.82 (1)
(b) Selected Bond Angles			
I1–Os1–I2	172.11 (4)	I1–Os1–I3	91.42 (4)
I1–Os1–C1	92.0 (4)	I1–Os1–C	89.5 (4)
I1–Os1–O5	87.7 (2)	I2–Os1–I3	84.22 (4)
I2–Os1–C1	94.9 (4)	I2–Os1–C	94.4 (4)
I2–Os1–O5	85.4 (2)	I3–Os1–C1	93.7 (5)
I3–Os1–C	176.5 (3)	I3–Os1–O5	85.1 (2)
C1–Os1–C	89.7 (6)	C1–Os1–O5	178.7 (5)
C–Os1–O5	91.5 (4)	I2–Os2–I3	84.17 (4)
I2–Os2–C2	89.9 (4)	I2–Os2–C3	90.9 (4)
I2–Os2–C4	173.4 (4)	I2–Os2–C5	84.2 (3)
I3–Os2–C2	91.5 (4)	I3–Os2–C3	172.3 (4)
I3–Os2–C4	89.6 (4)	I3–Os2–C5	84.7 (3)
C2–Os2–C3	94.4 (6)	C2–Os2–C4	92.5 (6)
C2–Os2–C5	173.3 (6)	C3–Os2–C4	95.0 (6)
C3–Os2–C5	89.0 (5)	C4–Os2–C5	93.0 (6)
Os1–I1–I3	45.10 (2)	Os1–I2–Os2	83.16 (4)
Os1–C1–O1	178 (1)	Os2–C2–O2	179 (1)
Os2–C3–O3	178 (1)	Os2–C4–O4	177 (1)
Os2–C5–O5	124.0 (9)	Os2–C5–N	120 (1)
O5–C5–N	115 (1)	C7–C6–C8	114 (1)
C7–C6–N	110 (1)	C8–C6–N	110 (1)
Os1–C–O	170 (1)	Os1–O5–C5	124.1 (8)
C5–N–C6	124 (1)		

Acknowledgment. This work was supported by the National Science Council, Taiwan, Republic of China. We also thank Professor G. L. Geoffroy for valuable discussion.

Supplementary Material Available: Tables listing crystal and intensity collection data, positional parameters, thermal parameters, bond distances, and bond angles of complex **3b** and figures showing IR spectra of **3b** and **2b** in the CO stretching region (7 pages). Ordering information is given on any current masthead page.

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