Intramolecular Comparison of the π-Donor Capability of Oxo and Organoimido Ligands. X-ray Crystal Structures of *N*-1-Adamantylimidotrioxoosmium and Bis(*N*-*tert*-butylimido)dioxoosmium

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Abstract: The structures of the two title compounds have been determined and refined to final weighted *R* values of 0.029 and 0.039, respectively. The monoimido derivative shows a nearly linear [171.4 (4)°] Os–N–C arrangement, while the bisimido complex possesses both a linear [178.9 (9)°] and a bent [155.1 (8)°] organoimido ligand. In these molecules the Os–N bond lengths are on average 0.02–0.03 Å shorter than the Os–O bonds. In contrast, for isostructural organoimido and oxo complexes, intermolecular comparison of Os–N and Os–O finds the latter to be shorter on average by 0.05 Å. The results are explained in terms of differences in Os–O and Os–N bond orders consistent with the higher electronegativity of oxygen vs. nitrogen.

Introduction

Complexes in which a main-group element (carbon, nitrogen, or oxygen) is multiply bonded to a transition metal are currently the focus of considerable research activity.[1] Interest in this area reflects a growing recognition of the role played by such species in heterogeneous, homogeneous, and enzymatic catalysis. It is therefore of interest to delineate both the general principles underlying the chemistry of such tightly bonded ligands and also the differences between the various multiply bonded ligands. In the present paper structural studies will be utilized in the first intramolecular comparison of the π-donor capabilities of organoimido (NR) and oxo ligands.

Compounds of the type $OsO_3(NR)$ and $OsO_2(NR)_2$ utilized in this study are also of intrinsic interest because of the remarkable electrophilic reactivity of their organoimido ligands. Sharpless and co-workers[2] have demonstrated the addition of the imido nitrogen atoms in these compounds to olefins, a reaction of considerable synthetic utility. In contrast, we have recently prepared related d^0 four-coordinate organoimido derivatives of the group 4, 5, 6, and 7 transition metals,[3] but in no case have we observed analogous electrophilic reactivity.

Results

We have structurally characterized two osmium organoimido derivatives: *N*-1-adamantylimidotrioxoosmium (I) and bis(*N*-*tert*-butylimido)dioxoosmium (II). Both I and II were first prepared by Sharpless and co-workers.[2a,b] For the preparation of I we utilized the literature procedure[2a] involving direct reaction of 1-adamantylamine with OsO_4. However, as an alternative to the literature synthesis,[2b] II was prepared by reaction of OsO_4 with excess *tert*-butyltrimethylsilylamine. In this way the chromatographic workup required for the former (phosphinimine) route was avoided. Slow evaporation of the reaction mixture afforded crystals of II suitable for X-ray diffraction.

The structure of I is shown in Figure 1 and important bond distances and angles are summarized in Table I. The coordination around osmium is essentially tetrahedral. The C–C bond distances not given in Table I ranged from 1.520 (6) to 1.553 (7) Å and averaged 1.527 Å. As an internal standard these values indicate that the structure refined satisfactorily.

The organoimido ligand is nearly linear [Os–N–C(1) = 171.4 (4)°]. However, the small bend in Os–N–C(1) was confirmed by determining the dihedral angle between the plane containing O(1), O(2), and O(3) and that containing C(2), C(3), and C(4). The observed dihedral angle is 8.6°. This slight bend in the direction of C(4) may in fact reflect intermolecular forces. Both C(2) and C(3) have contacts with two oxygen atoms of neighboring molecules which are less than 3.5 Å while C(4) has no such contacts. It is also worthy of note that the oxo ligands and the adamantyl group are not staggered with respect to one another. Instead they adopt the nearly eclipsed geometry shown in Figure 2 in which the average C–C–Os–O dihedral angle is 10.6°.

Pertinent to the discussion to follow, the Os–N bond length in I is very short[24] at 1.697 (4) Å. In contrast, the average Os–O bond length is longer by ca. 0.02 Å at 1.715 (4) Å.

The structure of II is again approximately tetrahedral (Figure 3 and Table II). The molecule occupies a crystallographic mirror plane and possesses one nearly linear [Os–N–C = 178.9 (9)°] and one bent [Os–N–C = 155.1 (8)°] *tert*-butylimido ligand. The *tert*-butyl group of the bent ligand is disordered as indicated in Figure 3. Again the *tert*-butyl group of the linear organoimido ligand eclipses the other atoms attached to the osmium atom. The Os–N bond length for the linear ligand is ostensibly slightly shorter than for the bent ligand but the difference is not significant [1.710 (8) vs. 1.719 (8) Å].

Again particular attention is called to the Os–N and Os–O bond lengths. The average Os–N distance [1.714 (8) Å] is exceeded by Os–O [1.744 (6) Å], the difference in this case being 0.03 Å.

Discussion

The Os–O bond lengths in I do not differ greatly from those observed in osmium tetroxide itself[4,5] (1.711 Å) and in the OsO_4–quinuclidine complex[6] (1.706 Å). The near linearity of Os–N–C(1) in I is consistent with the observed linearity of most of the organoimido complexes which have been structurally characterized. Linearity has been interpreted to indicate triple-bond character in the metal–nitrogen bond.[1c] On the other hand, there is also precedent[7,8] for the observation of a bent NR ligand in compound II. Bending appears to occur when insufficient metal d orbitals are available for π bonding with two nitrogen p orbitals.[1c]

The unusual feature in these structures requiring special comment is the observation that the Os–N bond lengths in both are shorter than the corresponding Os–O bond length. The

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Table I. Selected Bond Distances (Å) and Angles (deg) for Compound I

	Bond Distances		
Os-O(1)	1.710 (3)	N-C(1)	1.448 (6)
Os-O(2)	1.714 (4)	C(1)-C(2)	1.534 (6)
Os-O(3)	1.720 (4)	C(1)-C(3)	1.542 (6)
Os-N	1.697 (4)	C(1)-C(4)	1.534 (7)
	Bond Angles		
O(1)-Os-O(2)	109.2 (2)	Os-N-C(1)	171.4 (4)
O(1)-Os-O(3)	109.0 (2)	N-C(1)-C(2)	109.3 (4)
O(1)-Os-N	109.9 (2)	N-C(1)-C(3)	108.7 (4)
O(2)-Os-O(3)	109.7 (2)	N-C(1)-C(4)	108.7 (4)
O(2)-Os-N	109.8 (2)	C(2)-C(1)-C(3)	110.1 (4)
O(3)-Os-N	109.2 (2)	C(2)-C(1)-C(4)	109.9 (4)
		C(3)-C(1)-C(4)	110.2 (4)
	Torsion Angles		
C(2)-C(1)-Os-O(1)	107.6	C(2)-N-Os-O(1)	97.4
C(3)-C(1)-Os-O(1)	−129.3	C(3)-N-Os-O(1)	−120.0
C(4)-C(1)-Os-O(1)	−10.6	C(4)-N-Os-O(1)	−9.9
C(2)-C(1)-Os-O(2)	−133.7	C(2)-N-Os-O(2)	−142.4
C(3)-C(1)-Os-O(2)	−10.5	C(3)-N-Os-O(2)	0.2
C(4)-C(1)-Os-O(2)	108.1	C(4)-N-Os-O(2)	110.3
C(2)-C(1)-Os-O(3)	−10.8	C(2)-N-Os-O(3)	−22.2
C(3)-C(1)-Os-O(3)	112.3	C(3)-N-Os-O(3)	120.5
C(4)-C(1)-Os-O(3)	−129.0	C(4)-N-Os-O(3)	−129.4

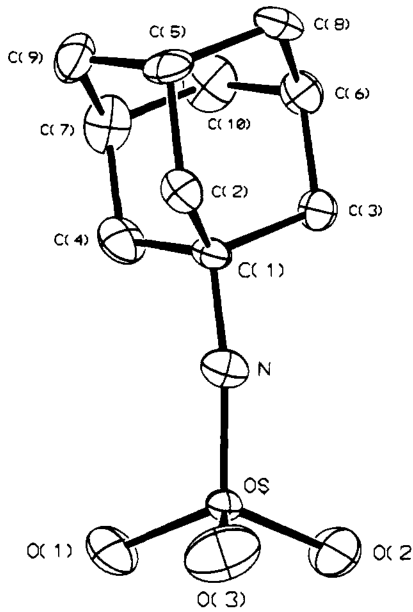

Figure 1. The structure of *N*-1-adamantylimidotrioxoosmium.

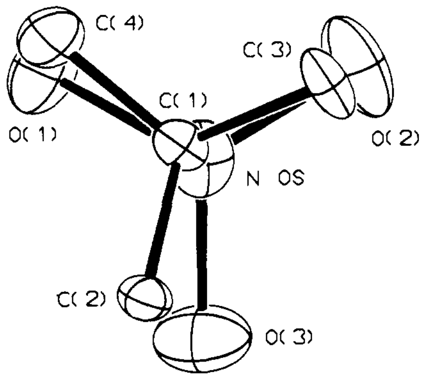

Figure 2. View of I along Os-N axis showing eclipsed relationship of adamantyl carbons with oxo ligands.

relative length of the bonds from a given element to oxygen and to nitrogen can be approached from the standpoint of the covalent radii of N and O. When the bond order to oxygen is the same as the bond order to nitrogen, the bond to nitrogen is generally 0.05 Å longer than that to oxygen.[9] This relationship is maintained for all states of hybridization.

Table III examines the applicability of this principle to transition metal oxo and organoimido derivatives. In it we compare six pairs of isostructural M=O and M=NR complexes. In fact the average difference in bond length for the six pairs is 0.05 Å but there is considerable variation from this mean. However, a consistent trend is evident in that the M-N bond is in each case longer than the corresponding M-O bond.

In view of the above, the observation of Os-N < Os-O in I and II suggests that the bond order to nitrogen is higher than that to oxygen in these complexes. This situation can be rationalized in terms of a competition for empty metal d orbitals between the filled p orbitals of oxygen and nitrogen.

In tetrahedral transition metal complexes the symmetry of the nine metal orbitals available for bonding will allow formation of four σ bonds and five π bonds. In species such as OsO_4 this might in principle be achieved by the combination of one triple-bonded oxo ligand and three double-bonded oxo ligands. However, the apparent equivalence of the Os-O bond lengths[4] suggests that the molecule instead contains identical bonds of order 2.25.[26]

In compounds I and II the competition for osmium d orbitals now involves p orbitals on unlike atoms. The nitrogen-containing ligand is expected to be the better donor by virtue of the lower electronegativity of nitrogen vs. oxygen. As a result of the greater π-donor capability of nitrogen, the bond orders of the organoimido ligands are higher than those of the corresponding oxo ligands and consequently the Os-N bonds are shorter than the corresponding Os-O bonds.

Finally, one may question whether the structure of II, containing one bent and one linear organoimido ligand, is electronically optimum (as compared with two bent organoimido ligands) or whether this aspect is dominated by intra- or intermolecular steric factors (e.g., crystal packing). Modified extended Hückel calculations[19] carried out on $[(CH_3N)_2OsO_2]$ and $[(t\text{-BuN})_2OsO_2]$ suggest that there is a very shallow potential well[20] (<1 kcal/mol) for Os-N-C angle defor-

Table II. Selected Bond Distances (Å) and Angles (deg) for Compound II

	Bond Distances		
Os-O	1.744 (6)	C(1)-C(3)	1.55 (1)
Os-N(1)	1.710 (8)	C(4)-C(5)	1.55 (3)
Os-N(2)	1.719 (8)	C(4)-C(5)P	1.66 (3)
N(1)-C(1)	1.43 (1)	C(4)-C(6)	1.56 (2)
N(2)-C(4)	1.45 (1)	C(4)-C(6)P	1.48 (2)
C(1)-C(2)			
	Bond Angles		
O-Os-O′	109.9 (4)	N(1)-C(1)-C(3)	106.3 (7)
O-Os-N(1)	109.7 (2)	C(2)-C(1)-C(3)	111.3 (7)
O-Os-N(2)	108.0 (2)	C(3)-C(1)-C(3)′	113.5 (11)
N(1)-Os-N(2)	111.5 (4)	N(2)-C(4)-C(5)	108.3 (12)
Os-N91)-C(1)	178.9 (9)	N(2)-C(4)-C(5)P	100.9 (14)
Os-N(2)-C(4)	155.1 (8)	N(2)-C(4)-C(6)	108.9 (10)
N(1)-C(1)-C(2)	107.8 (10)	N(2)-C(4)-C(6)P	108.7 (9)
	Torsion Angles		
O-Os-C(1)-C(2)	−119.8	O-Os-C(4)-C(5)	116.8
O-Os-C(1)-C(3)	−0.2	O-Os-C(4)-C(5)P	−63.2
		O-Os-C(4)-C(6)	1.7
		O-Os-C(4)-C(6)P	53.2

Table III. Structural Comparison of Oxo and Imido Complexes[a]

complexes	M-N, Å	M-O, Å	difference, Å	ref
$Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$ $NbO(S_2CNEt_2)_3$	1.76 (1)	1.74 (1)	0.02	10 11
$Ta(N\text{-}t\text{-}Bu)(NMe_3)_3$ $TaO(N\text{-}i\text{-}Pr_2)_3$	1.77 (2)	1.725 (7)	0.04	3a 12
$Mo_2(N\text{-}t\text{-}Bu)_2Cp_2S_2$ $Mo_2O_2Cp_2S_2$	1.733 (4)	1.679 (4)	0.05	13 14
$Mo(NPH)_2(S_2CNEt_2)_2$ $MoO_2(S_2CN\text{-}n\text{-}Pr_2)_2$	1.772 (av)	1.696 (av)	0.08	8 15
$MoCl_2(NPh)(S_2CNEt_2)_2$ $MoOCl_2(S_2CNEt_2)_2$	1.734 (4)	1.701 (4)	0.03	10 16
$ReCl_3(p\text{-}NC_6H_4COCH_3)(PEt_2Ph)_2$ $ReOCl_3(PEt_2Ph)_2$	1.690 (5)	1.60 (2)	0.09	17 18

[a] Abbreviations: Me = CH_3, Et = C_2H_5, *n*-Pr = $CH_2CH_2CH_3$, *t*-Bu = $C(CH_3)_2$, *i*-Pr = $CH(CH_3)_2$, Ph = C_6H_5.

mation (separately or in concert) and that a maximum occurs when both are linear. Consistent with this point, in toluene solution both the ^1H and ^{13}C NMR of II show the *tert*-butyl groups to be equivalent. In the methyl model, there is a very slight preference for both imido groups being bent toward[25] each other (161 and 167°); however, in the *tert*-butyl case the optimum calculated geometry contains one bent and one linear imido group (163 and 177°, respectively). As the linear imido group bends toward the other, a steric interaction between *tert*-butyl groups begins to appear. It therefore seems probable that intramolecular steric factors control this aspect of the structure.

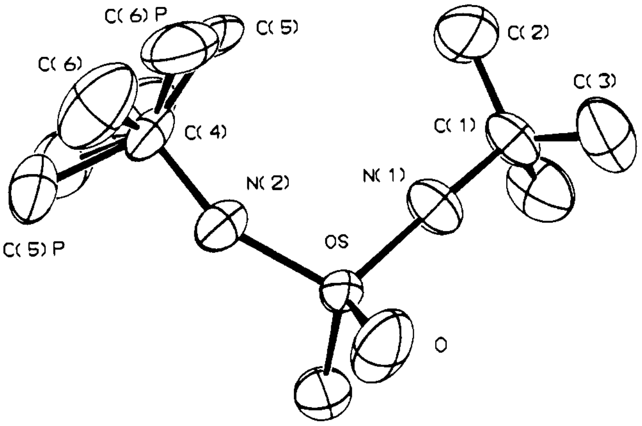

Figure 3. The structure of bis(*N*-*tert*-butylimido)dioxoosmium.

Experimental Section

Preparation of Complexes. Compound I was prepared by the literature procedure[2a] from osmium tetroxide and 1-adamantylamine in hexane. Slow evaporation (under N_2) of a solution containing 0.2 g of I in 1.0 mL of octane and 2.5 mL of methylene chloride afforded crystals suitable for X-ray diffraction. Crystals of compound II were prepared by allowing a solution of 1.0 g of osmium tetroxide, 4.57 g of *tert*-butyltrimethylsilylamine, and 15 mL of hexane to evaporate to dryness.

NMR Spectra of II. ^1H and ^{13}C spectra were recorded on a solution of 0.5 M II in toluene-d_8 vs. 1% tetramethylsilane as internal standard. The ^1H spectrum was a singlet at δ 1.18 while the ^{13}C spectrum consisted of singlets at δ 29.63 (methyl C) and 75.13 (quaternary C). For comparison the ^{13}C spectrum of *N*-*tert*-butylimidotrioxoosmium was also determined and contained singlets at δ 27.49 (methyl C) and 82.73 (quaternary C). Its ^1H spectrum consists of a single resonance at δ 0.90. NMR tubes were sealed with plastic caps.

Structural Details. Crystals of both compounds were mounted on glass fibers and placed on a Syntex P3 diffractometer (graphite monochromator, Mo Kα radiation, λ = 0.710 69 Å). The crystal system, space group, and approximate unit-cell dimensions of each crystal were determined during a preliminary investigation. The

Table IV. Summary of the Crystal Data for the Two Crystallographic Studies

molecular formula	$O_3OsNC_{10}H_{15}$	$O_2Os[NC(CH_3)_3]_2$
mol wt	387.4	364.4
crystal dimensions, mm	0.25 × 0.17 × 0.25	0.10 × 0.17 × 0.20
crystal temp, °C	−70	25
crystal system	trigonal	orthorhombic
space group	$R\bar{3}$ (no. 148)	*Pnma* (no. 62)
unit cell	$a = 23.125\ (10)$ Å	$a = 11.805\ (2)$ Å
	$c = 10.860\ (2)$ Å	$b = 10.046\ (2)$ Å
		$c = 10.530\ (2)$ Å
	$V = 5030$ Å^3	$V = 1249$ Å^3
Z	18	4
calcd density, g cm^{-3}	2.302	1.938
absorption coeff, cm^{-1}	121.2	108.3

Table V. Summary of the Refinement of the Two Structures

	I	II
no. of reflections with $I > 2\sigma(I)$	2207	975
no. of variables	137	85
hydrogen atoms	calcd; not refined	not included
extinction parameter	3.28×10^{-7}	no
R^a	0.028	0.041
$R_w{}^a$	0.029	0.039
peaks in final difference Fourier	all less than 0.31 e Å^{-3}	~0.9 e Å^{-3} near Os

^{a} $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

quality of both crystals was found to be adequate on the basis of ω scans which showed the peak width at half-height to be ca. 0.25°. The unit-cell dimensions were subsequently refined from the Bragg angles of 50 computer-centered reflections. A summary of the crystal data is given in Table IV.

Intensity data were collected using the ω-scan technique ($4° < 2\theta < 55°$; scan width of 1.0°, variable scan rate of 2.0–5.0° min^{-1}; background measurements at both ends of the scan; total background time equal to scan time). For II, 1515 reflections were recorded with the crystal at ambient temperature; for I, 2561 reflections, with the crystal cooled to −70 °C. The intensities of four standard reflections were monitored periodically; only statistical fluctuations were noted. The intensities of several reflections were measured in 10° increments about the diffraction vector; as a result, empirical corrections for absorption were applied (factors ranged from 0.61 to 1.00 for II and from 0.53 to 1.00 for I).

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the programs supplied by the Enraf-Nonius Corp.[21] The atomic scattering factors were taken from the tabulations of Cromer and Waber;[22a] anomalous dispersion corrections were by Cromer.[22b] In the least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $1/\sigma^2(F_o)$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor", p, of 0.02.[23]

Both structures were solved by heavy-atom techniques and refined by the full-matrix least-squares method. The methyl groups of one of the *tert*-butyl moieties in compound II was found to be disordered in a 1:1 ratio (see Figure 3); the occupation factors were adjusted accordingly. All of the nonhydrogen atoms in both structures were refined with anisotropic thermal parameters. The results are summarized in Table V.

Supplementary Material Available: Final positional parameters (as fractional coordinates), tables of thermal parameters, and structure factor amplitudes (observed and calculated) (28 pages). Ordering information is given on any current masthead page.

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(24) The sum of the covalent radii for Os and N is 2.01 Å. Cf. also typical metal–nitrogen triple bonds in Table III.

(25) The calculations reproduce the observed preference of the imido ligands for bending toward one another instead of toward the (presumably sterically smaller) oxo ligands. An analysis of the differences in orbital energies between these two configurations has failed to uncover any single overriding factor which is responsible for this preference.

(26) NOTE ADDED IN PROOF: It has recently been pointed out, based on PMO theory, that while the total number of π bonds in tetrahedral molecules such as OsO$_4$ is five, bonding to the t$_2$ orbitals is only ca. ⅓ as effective as that with the e orbitals. Based on this model, it would be more appropriate to consider the total π bond order in OsO$_4$ to be 3 rather than 5. This should not affect the qualitative arguments in the present paper. See K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, **18**, 984 (1979).