Table I. Chemical Shifts, Isotropic Shifts, Geometric Factors, and Calculated Isotropic Shifts for Eu(dpm)₃(3-pic)₂ at −115°

Assignment	$\dfrac{3\cos^2\theta - 1}{r^3}$	$\dfrac{\sin^2\theta\cos 2\Omega}{r^3}$	Chem shift, ppm	$\left(\dfrac{\Delta\nu}{\nu_0}\right)_{\mathrm{obsd}}$[a]	$\left(\dfrac{\Delta\nu}{\nu_0}\right)_{\mathrm{calcd}}$[d]	$\left(\dfrac{\Delta\nu}{\nu_0}\right)_{\mathrm{calcd}}$[e]
Methine	+0.0090	−0.0028	+29.2	+35.0[b]	+37.6	37.5
tert-Butyl	+0.0030	−0.0005	+10.1	+11.3[b]	+10.8	12.5
Methyl (1)	−0.0009	+0.0022	−15.7	−13.4	−11.3	−3.8
Methyl (2)	−0.0037	+0.0008	−18.5	−16.2	−14.1	−15.4
Meta (1)	−0.0017	+0.0038	−28.1	−20.9	−20.0	−7.1
Meta (2)	−0.0047	+0.0024	−29.4	−22.2	−23.3	−19.6
Ortho (1)	−0.0089	+0.0089	−69.5	−61.1	−61.2	−37.0
Ortho (2)	−0.0246	+0.0014	−87.2	−78.8	−78.1	−102.4
Para	−0.0015	+0.0029	c	c	−15.4	−4.52
					R = 0.038	R = 0.337

[a] The diamagnetic references for the 3-picoline protons were taken from free 3-picoline and for the dpm⁻ chelate they were taken as CH₃ = −116 Hz and CH = −575 Hz as found for Lu(dpm)₃.[22] [b] Both the tert-butyl and methine peaks of the dpm⁻ chelate are found upfield of Me₄Si and can be assigned by their relative areas, 18:1, respectively. [c] Unobserved, see text. [d] Calculated using eq 2. [e] Calculated using eq 1.

experiments with pyridine and 4-methylpyridine and similar low-temperature results are obtained. These results show that for a system of this type *the lanthanide-induced shifts cannot be explained by eq 1 where the magnetic axis passes through the nitrogen atom of the substrate.*

For complexes of twofold symmetry the LIS should be governed by an equation of the form

$$\frac{\Delta\nu_i}{\nu_0} = D_1\left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle + D_2 \times \left\langle\frac{\sin^2\theta_i\cos 2\Omega_i}{r_i^3}\right\rangle \quad (2)$$

where $\Delta\nu_i$, ν_0, θ_i, and r_i have been previously defined, Ω_i is the angle which the projection of the *i*th vector into the *x*–*y* plane makes with the *x* magnetic axis, and the parameters D_1 and D_2 are related to magnetic anisotropy.[23]

The results of the X-ray crystal structure of Eu(dpm)₃-(py)₂[18,19] were used to calculate the two geometric factors in eq 2 and these are listed in Table I. The magnetic *z* axis was defined as the C₂ axis passing through the methine carbon of the unique dpm⁻ chelate. The *x* magnetic axis was refined by rotation about the *z* magnetic axis and the best fit was obtained when the *x* axis was rotated 8°, in the direction away from the center of the square face of the coordination polyhedron,[18,19] from a line which passes through the Eu ion and is parallel to the internitrogen vector. The methyl coordinates on the 3-picoline were calculated assuming tetrahedral angles and the methyl group was considered to be freely rotating. A better fit was obtained when the tert-butyl groups were considered to be nonrotating. A least-squares fit of the data using eq 2 yielded $D_1 = 2950 \pm 25$ VVk/mol and $D_2 = -3930 \pm 180$ VVk/mol (1 VVk = 10^{-6} cgsu). A comparison of calculated and observed isotropic shifts ($\Delta\nu/\nu_0$), using both eq 1 and 2, is given in Table I, along with the agreement factor R[24] defined by Willcott. While the para proton was not located, its calculated chemical shift using the results from eq 2 is −23.0 ppm, which would place it under the first downfield side band of

(22) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 87, 5254 (1965).
(23) W. DeW. Horrocks, Jr., and E. S. Greenberg, *Inorg. Chem.*, 10, 2190 (1971).
(24) M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, 94, 1744 (1972).

the *tert*-butyl protons thus rendering it unobservable. The single peak for the para position is confirmed in experiments with 4-picoline which shows only a single coordinated 4-methyl peak at −9.48 ppm at −115°.

In conclusion we feel that this represents conclusive experimental evidence that the principal axis of symmetry does not lie along the line defined by the metal ion and the donor nitrogen, as has been assumed,[1–14] at least for complexes of this type. Finally, the much better fit, found by using eq 2 rather than eq 1 for calculating isotropic shifts, indicates that the single term equation often assumed[1–14] is too simple and that lanthanide shifts can be reproduced using the theoretically correct equation.[25]

(25) NOTE ADDED IN PROOF. W. DeW. Horrocks, Jr., and J. P. Sipe III, *Science*, 177, 994 (1972), has reported the single-crystal magnetic anisotropies for the entire series of Ln(dpm)₃(4-pic)₂ complexes. Those results show large values for both D_1 and D_2 and that the location of the magnetic axes is in agreement with our results.

Roger E. Cramer,* Ronald Dubois
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822
Received September 21, 1972

Stereochemistry of Octadecacarbonylhexaosmium(0). A Novel Hexanuclear Complex Based on a Bicapped Tetrahedron of Metal Atoms

Sir:

The pyrolysis of dodecacarbonyltriosmium(0) provides[1] polynuclear complexes based on four, five, six, seven, and eight osmium atoms. The infrared spectra of Os₄(CO)₁₃, Os₅(CO)₁₆, Os₆(CO)₁₈, Os₇(CO)₂₁, Os₈-(CO)₂₃, and Os₅(CO)₁₅C are similar in that no bands assignable to bridging carbonyl groups are observed. It is reasonable to assign an octahedral arrangement of metal atoms in Os₆(CO)₁₈ with three terminal carbonyl groups per osmium, since such a stereochemistry would reflect an effective "rare-gas" electronic configuration about each metal. An X-ray analysis of Os₆(CO)₁₈, summarized here, fails to support this prediction.

The crystals (toluene–hexane) are triclinic with $a =$

(1) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, 37, C39 (1972).

11,369 (1), $b = 12.520$ (1), $c = 9.682$ (1) Å; $\alpha = 96.54$ (1), $\beta = 94.96$ (1), $\gamma = 85.56$ (1)°;[2] $D_{obsd} = 3.19$ g cm^{-3}; $Z = 2$; space group $P\bar{1}$ (structure analysis and refinement). Independent reflections (4316) with $F_o{}^2$ ⩾ 3.0σ $(F_o{}^2)$ and having $4° \leqslant 2\theta \leqslant 53°$ were observed by four-circle automatic diffractometry (Mo Kα graphite monochromator, $\omega-2\theta$ scan routine). Raw X-ray intensities were corrected for the usual geometrical factors and for absorption ($\mu = 297.5$ cm^{-1}; crystal dimensions $0.093 \times 0.062 \times 0.310$ mm). The structure analysis was straightforward and refinement, by full-matrix least-squares methods, of atomic positional parameters, of anisotropic thermal parameters for the osmium atoms and of isotropic thermal factors for the carbon and oxygen atoms, has converged to an un-weighted discrepancy index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.039. More important bond lengths are shown in Figure 1 which also illustrates the overall stereochemistry of the complex and atom labeling.

The structure can be imagined to be based on a central tetrahedron described by the atoms Os$_1$, Os$_3$, Os$_4$, and Os$_6$; Os$_2$ bridges the Os$_1$–Os$_3$–Os$_4$ face and Os$_5$ is bonded in an essentially symmetrical manner to Os$_3$ Os$_4$, and Os$_6$. Each osmium atom has three terminal carbonyl ligands, the mean Os–C and C–O bond lengths being 1.89 and 1.14 Å, respectively. The bond lengths in the central tetrahedron are seen to vary from 2.731 (1) to 2.807 (1) Å with a mean value of 2.782 Å. The average bond length of Os$_2$ to its three neighbors is 2.813 Å, that of Os$_5$ being 2.808 Å.

The individual metal–metal bond lengths show variations which reflect the coordination number (and formal oxidation state) of each metal atom. Metal atoms Os$_3$ and Os$_4$, each having five short metal–metal contacts and, therefore, a formal oxidation state of $+1$, are separated by 2.757 Å, a value close to the bond length of 2.731 Å for Os$_1$–Os$_6$ (four metal–metal bonds per atom; formal oxidation state of each is 0). The bond lengths between metals in different formal oxidation states are larger; the mean value of the lengths separating atoms in their 0 and $+$I oxidation states (Os$_1$, Os$_6$, Os$_3$, and Os$_4$) is 2.801 Å, that between atoms in 0 and $-$I states being 2.793 Å (Os$_1$–Os$_2$ and Os$_5$–Os$_6$) while that between atoms in $+$I and $-$I states averages 2.820 Å (Os$_2$–Os$_4$, Os$_2$–Os$_3$, Os$_3$–Os$_5$, and Os$_4$–Os$_5$).

Two separate but complementary views on the bonding in cluster complexes are useful in rationalizing the observed stereochemistry. The first is based on the observation that isogeometric boranes and transition metal clusters have the same number of skeletal electron pairs if it is assumed that each B–H and metal carbonyl fragment contribute only three hybrid orbitals for skeletal bonding and that the latter obeys the inert gas rule.[3,4] On this basis one would recognize that each Os(CO)$_3$ fragment contributes one bonding electron pair to the polyhedral-skeletal molecular orbitals; thus in Os$_6$(CO)$_{18}$, the six skeletal electron pairs will favor a tetrahedral geometry with two Os(CO)$_3$ moieties being envisaged as face-bonded bridging groups. This argument is derived from the molecular orbital calcula-
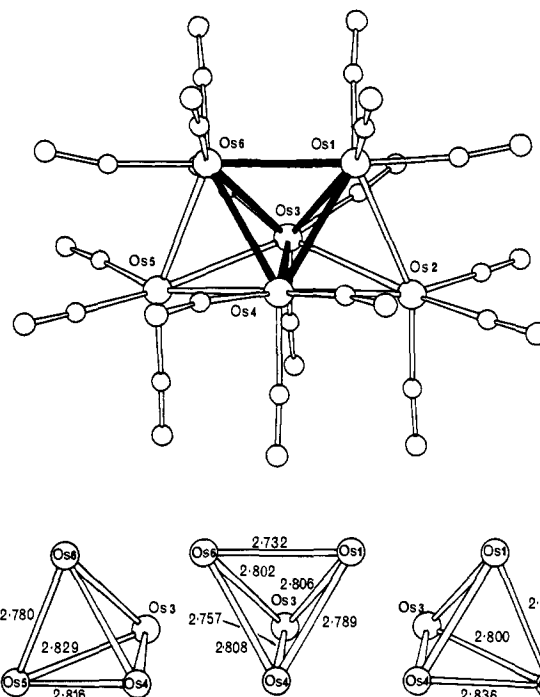

Figure 1

tions of Hoffmann and Lipscomb[5] on polyhedral boranes which show that the following capped and un-capped polyhedra have the same number of bonding skeletal molecular orbitals: tetrahedron (6 edges), monocapped tetrahedron (trigonal bipyramid), six skeletal MO's; trigonal prism (9 edges), bicapped trigonal prism (D_{3h}), nine skeletal MO's; cube (12 edges), bicapped cube (D_{4h}), 12 skeletal MO's. A regular octahedral geometry would, in contrast, be associated with seven skeletal electron pairs by analogy with B$_6$H$_6{}^{2-}$, e.g., Os$_6$(CO)$_{18}{}^{2-}$.

The second view recognizes the stability of 86 valence electrons in the octahedral cluster compounds Rh$_6$-(CO)$_{16}$,[6] Co$_6$(CO)$_{15}{}^{2-}$,[7] and H$_2$Ru$_6$(CO)$_{18}$[8] which do not conform to the inert gas rule. A semiempirical molecular orbital calculation for Co$_6$(CO)$_{14}{}^{4-}$ [9] has shown that the 86 valence electrons occupy 43 bonding and weakly antibonding molecular orbitals. The remaining 11 skeletal molecular orbitals are strongly antibonding, have predominantly cobalt 4s and 4p character, and have the same symmetries as the 11 antibonding skeletal molecular orbitals in the octahedral B$_6$H$_6{}^{2-}$ anion. This calculation consequently establishes the suggested link[3] between carbonyl metal cluster compounds and the borane polyhedra. The molecular orbital model naturally suggests that octahedral clusters with more than 86 valence electrons will be relatively unstable but gives no direct indication of the geometric consequences of occupation of antibonding orbitals by electrons. We note, with retrospective wisdom, that the trigonal prismatic arrangement of metals in the

(2) Here as elsewhere, the figures in parentheses refer to the standard deviation of the accompanying observation. The unit cell parameters were determined from a least-squares analysis of the angular settings of 12 reflections distributed widely in reciprocal space.

(3) K. Wade, Chem. Commun., 792 (1971).

(4) D. M. P. Mingos, Nature (London), Phys. Sci., 236, 99 (1972).

(5) R. Hoffmann and W. N. Lipscomb, J. Chem. Phys., 36, 2179 (1962).

(6) E. R. Corey, L. F. Dahl, and W. Beck, J. Amer. Chem. Soc., 85, 1202 (1963).

(7) V. Albano, P. Chini, and V. Scatturin, J. Organometal. Chem., 15, 423 (1968).

(8) M. R. Churchill and J. Wormald, J. Amer. Chem. Soc., 93, 5670 (1971).

(9) D. M. P. Mingos, private communication, 1972.

carbidopentadecacarbonylhexarhodate dianion $(Rh_6\text{-}(CO)_{15}C)^{2-}$ [10] with 90 valence electrons and therefore nine skeletal electron pairs could have been anticipated (see above) on the basis of the polyhedron skeletal electron pair theory (PSEPT).

The polyhedron skeletal electron pair theory allows a clear prediction of the stereochemistries of the several remaining osmium cluster complexes isolated by Eady, et al.[1] $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ each have seven skeletal electron pairs and therefore are consistent with capped octahedral geometries.[11]

Acknowledgment. We are grateful to the Science Research Council for their support of these studies.

(10) V. G. Albano, M. Sansori, and P. Chini, Abstract VI-12, International Union of Crystallography Congress, Kyoto, Japan, 1972.

(11) Note Added in Proof. After much experimental difficulty, Professor Lewis provided us with one suitable crystal of $Os_7(CO)_{21}$. As predicted above, an X-ray analysis shows the seven osmium atoms in a capped octahedral arrangement.

R. Mason,* K. M. Thomas

School of Molecular Sciences, University of Sussex
*Brighton, England*

D. M. P. Mingos

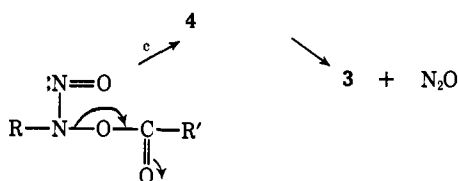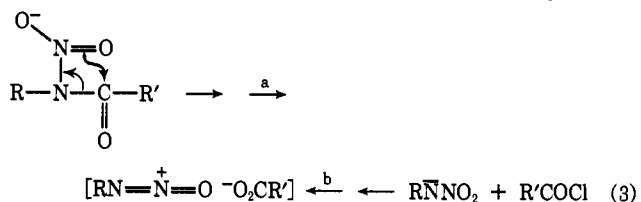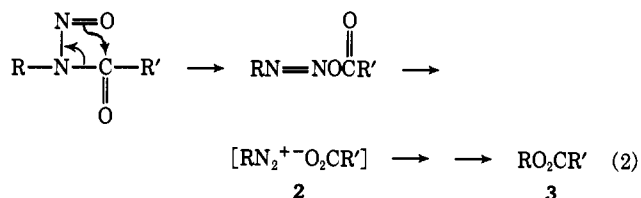*Department of Chemistry, Queen Mary College*
London, England

A Comparison of Intermediates from the Deamination of N-Nitrosohydroxylamines and the Reaction of Alkyl Azides with Nitrosonium Tetrafluoroborate

Sir:

In the nitrous acid deamination of aliphatic amines, alkyl diazonium ions **1** can be written, formally, as reaction intermediates
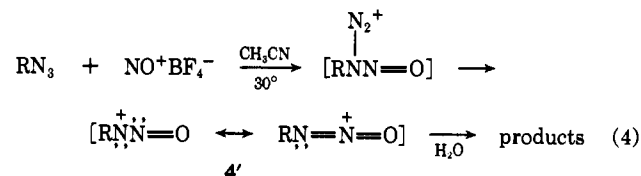
$$RNH_2 \longrightarrow [RNH] \longrightarrow [RN=NOH] \xrightarrow{HX}$$
$$[RN_2^+X^-] \longrightarrow R^+X^- \longrightarrow RX \quad (1)$$
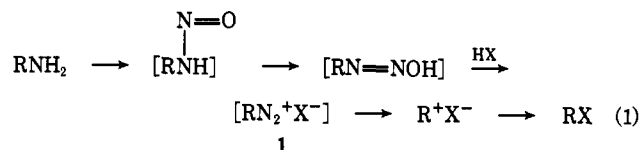
Similar species (**2** and **4**) can be written for the decomposition of N-nitrosoamides (eq 2), N-nitroamides

$$[RN_2^{+-}O_2CR'] \longrightarrow \longrightarrow RO_2CR' \quad (2)$$

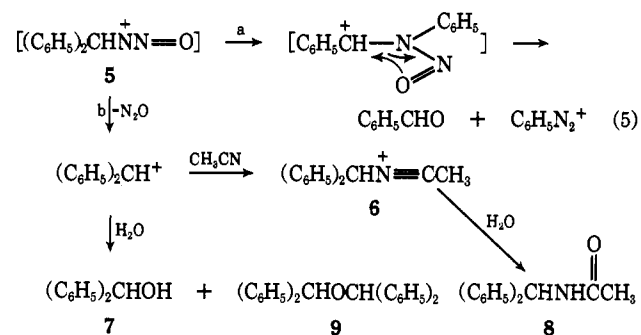$$[RN=N=O\ ^-O_2CR'] \xleftarrow{b} \longleftarrow R\bar{N}NO_2 + R'COCl \quad (3)$$

$$3 + N_2O$$

(eq 3, path a), and N-nitrosohydroxylamines (eq 3, path c). Species **4** is relatively unstable since infrared spectra of reactions 3, path b, and 3, path c, at Dry Ice temperature gave no evidence for its presence, but showed instead the instantaneous formation of nitrous oxide.[1] No reaction of **4** other than loss of nitrous oxide has ever been detected in our studies.[2]

The same cation, **4′**, has been proposed recently as an interceptible intermediate in the reaction of alkyl azides with nitrosonium tetrafluoroborate (eq 4).[3]

$$RN_3 + NO^+BF_4^- \xrightarrow[30°]{CH_3CN} [RNN=O] \longrightarrow$$
$$[R\ddot{N}\ddot{N}=O \longleftrightarrow R\ddot{N}=\overset{+}{N}=O] \xrightarrow{H_2O} products \quad (4)$$

For R = benzhydryl, it was reported that benzaldehyde, a phenyl diazonium compound, and benzophenone were formed in addition to the major products, benzhydrol **7** and N-(benzhydryl)acetamide (**8**), the latter being formed, presumably, during the quenching of the reaction with water. The authors proposed that the first two of the minor products originated in a 1,2-phenyl migration in species **5** = **4′** (eq 5). Such a

$$[(C_6H_5)_2CH\overset{+}{N}N=O] \xrightarrow{a} [C_6H_5\overset{+}{C}H\text{—}N\overset{C_6H_5}{\underset{O}{\overset{N}{\diagdown}}}] \longrightarrow$$
$$C_6H_5CHO + C_6H_5N_2^+ \quad (5)$$

$$(C_6H_5)_2CH^+ \xrightarrow{CH_3CN} (C_6H_5)_2CH\overset{+}{N}=CCH_3$$

$$(C_6H_5)_2CHOH + (C_6H_5)_2CHOCH(C_6H_5)_2 \quad (C_6H_5)_2CHNH\overset{O}{\overset{\|}{C}}CH_3$$

migration, in principle, could lead to information concerning the lifetime of **4** and related ions. We now report investigations of the azide reaction (eq 4 and 5) which show that the minor products are not formed by reaction 5, but by a pathway related to the Schmidt reaction of azides.[4]

We first treated N-benzhydryl-O-benzoylhydroxylamine with NO$^+$BF$_4^-$ in acetonitrile under the same conditions used by Doyle and Wierenga for reaction 4. The intermediate N-nitroso compound **10** decomposed spontaneously to cleanly yield benzhydryl benzoate (**11**, 20%), benzoyl fluoride (**12**, 20%), and N-benzhydrylacetamide (**8**, 60%) in 91% overall yield, but no benzaldehyde (<0.5%), one of the expected products if reaction 5a were operating.[5] Reactions 4 and 6 have

(1) (a) E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, 90, 4734 (1968); (b) E. H. White, M. J. Todd, M. Ribi, T. J. Ryan, A. A. F. Sieber, R. E. Dickerson, and J. Bordner, *Tetrahedron Lett.*, 4467 (1970).

(2) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483.

(3) M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, 92, 4999 (1970); 94, 3896 3901 (1972).

(4) For examples, see P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 457.

(5) The products were identified by their ir and nmr spectra and glpc retention times on 3% SE-30 and 5% QF-1 columns. Authentic samples were either commercially available or they were synthesized by well-established procedures.