

Aspects of η^2 binding by osmiumammines

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Abstract - Traditional coordination complexes such as the metalammines have not figured prominently in the field of organometallic chemistry. It therefore comes as something of a surprise that the organometallic chemistry of osmiumammines is proving to be very rich. The powerful tendency of osmium(II), when the auxiliary ligands are saturated, for back-bonding interactions account in large part for the stability of a large number of the new organometallic species based on this metal center, which have been prepared. In most cases, the one-electron oxidation of the osmium(II) complexes takes place at potentials of less than 1 V, and the resultant species have enough kinetic stability for the organometallic product to be characterizable. Because of the different requirements of osmium(II), with its tendency for electron donation to π acids, and osmium (III), which acts mainly as a σ acceptor, the oxidation is often accompanied by dramatic changes.

Among the specific topics to be dealt with are these: the interaction of osmium(II) with aromatic molecules, and the attending activation for hydrogenation, linkage isomerization accompanying oxidation, characterization of alkyne, allyl and dihydrogen complexes. The early work has been done with the pentaammine moiety; many new effects are being revealed in the studies with the cis-tetraammine complexes, now underway, and the highlights of this effort will be touched on.

Characteristic of the compositions and chemistry of traditional coordination complexes are the following features: the oxidation states lie in the range 2+ to 4+; the ligands are usually saturated, that is, their mode of interaction is limited to electron donation; water and similar solvents serve as reaction media. As to the first stipulation, oxidation states below 2+ are not common, and most complexes which feature them are labile (it must be kept in mind that the principles on which the subject rests were developed by taking advantage of the substitution inertia of robust complexes). In the oxidation states above 4+, an alien feature is introduced, namely that we now encounter ligands which are not capable of independent existence under ordinary conditions — thus contrast O_2^{2-} with OH^- or H_2O . The restrictions on oxidation states and nature of ligands are interdependent. Saturated, as compared to unsaturated, ligands stabilize the higher oxidation states. Among saturated ligands, NH_3 plays a special role. Its mode of interaction with the metal center is the simplest, and in qualitative discussion is viewed as involving only σ donation. Several properties combine to make it especially valuable as a co-ligand. Its steric demands are small; at least in acid solution, it is quite resistant to oxidation and reduction; it is less readily replaced than most other saturated ligands. The typically greater lability of water compared to ammonia as

ligand is an important advantage in that substitution can be limited to particular sites by using ammonia as a blocking group. The choice of water as reaction medium is of course a great convenience, but until recently, it has also been a matter of necessity, most of the compounds dealt with in the past being usefully soluble only in water or similar solvents.

By contrast, in the field of organometallic chemistry, low oxidation states are common — even negative ones are represented — and such states are accessible only because of the electron withdrawing capacity of π -acceptor ligands. Probably more for historical than for purely rational reasons, water is avoided as a solvent. While there is by now a fairly extensive chemistry of organometallic complexes in which the co-ligands are saturated, it represents only a very small portion of the subject. Macrocyclic ligands seem to endow the metal-carbon bond with special stability,¹ an effect which is probably largely kinetic as contrasted to thermodynamic, in origin. This stability is particularly marked for macrocyclic ligands such as porphyrins, which combine negative charge with bond conjugation, and the resulting chemistry is an important transition zone between traditional coordination chemistry and organometallic chemistry.²

In particular organometallic chemistry in which ammonia alone is the co-ligand is quite limited. It therefore comes as something of a surprise that the organometallic chemistry of the $[\text{Os}(\text{NH}_3)_5]^{2+}$ proves to be extensive. It is however not entirely a surprise, because it was foreshadowed by work with $\text{Ru}(\text{II})$ ammines which showed that the ethylene and acetylene complexes are quite stable.³ They owe their stability in large part to the fact that $[\text{Ru}(\text{NH}_3)_5]^{2+}$ has a strong tendency for back-bonding. Preparative work on the congener has suggested that the corresponding tendency for $[\text{Os}(\text{NH}_3)_5]$ is much greater; just how much greater is indicated by the following data. The values of pK_a for pyrazium ion^{4,5} when it is free, and when it is coordinated to $[\text{Ru}(\text{NH}_3)_5]^{2+}$ and $[\text{Os}(\text{NH}_3)_5]^{2+}$, are respectively 2.1, 2.4 and 7.5. Absent back-bonding the metal cations will cause a decrease in the value of pK_a — for example on attachment of the ligand to $[\text{Ru}(\text{NH}_3)_5]^{3+}$, pK_a becomes less than zero. The increase in the basicity of the remote nitrogen by more than a factor of 10^5 attending ligand attachment to $[\text{Os}(\text{NH}_3)_5]^{2+}$, calls for a large transfer of electron density from metal to ligand, all the more so because the effect is indirect — the proton adds to the nitrogen in a σ mode while electron density is transferred from the metal in a π mode. Analysis of the effect of protonation on the energy of the metal to ligand transition

in fact shows that the unperturbed π^* level of pyrazinium ion lies below the unperturbed π^* levels of Os(II). The enormous back-bonding propensity of $[\text{Os}(\text{NH}_3)_5]^{2+}$ as revealed in these and other studies suggested that an investigation of the organometallic chemistry of $[\text{Os}(\text{NH}_3)_5]^{2+}$ would prove to be rewarding though just what, in detail, would be uncovered was not at all clear.

W. Dean Harman, who joined my research group in 1984, and whose work mainly is described in this paper, took up the challenge of exploring the new field. Because the Os(III)/Os(II) couples for complexes containing only saturated ligands are reducing enough to liberate H_2 from water,⁶ Harman opted from the outset for preparative work in non-aqueous solvents, and of course in an anaerobic environment. It should be noted that despite the liberation of H_2 as a side reaction, Shepherd and coworkers⁷ have had considerable success in characterizing the complexes of $[\text{Os}(\text{NH}_3)_5]^{2+}$ with olefins and dienes as solution species prepared in water. Moreover, because the potential of the 3+/2+ couple is considerably raised by the η^2 binding, the species once prepared do persist in water.

Thanks to the special properties of CF_3SO_3^- — it is a weak nucleophile,⁸ it is resistant to reduction, and salts having it as a counter ion prove to be soluble in a variety of organic solvents⁹ — the preparative work was greatly facilitated. For many of the syntheses which underlie the results to be described, the solvent was dimethoxyethane (DME). In a typical procedure, the precursor compound $[\text{Os}(\text{NH}_3)_5(\text{SO}_3\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, dissolved in DME, is reduced by Mg. The solubility of the precursor can be increased by the addition of polar solutes such as dimethylacetamide, and, though this at first sight might seem surprising, also by NaSO_3CF_3 . The use of a reducing agent as powerful as Mg(0) is not mandatory for the success of the preparations, and in certain environments the weaker reducing agent Zn/Hg is in fact advantageous.

The compound $[\text{Os}(\text{NH}_3)_5(\text{C}_6\text{H}_6)](\text{CF}_3\text{SO}_3)_2$ (1) is readily prepared¹⁰ in good yield by the procedure outlined. The ^1H NMR spectrum taken on a solution in acetone- d_6 at -87°C shows three kinds of ring protons in equal numbers, as expected for η^2 -binding. At room temperature, the signals have coalesced into a single broad band, which becomes sharper as the temperature rises. Electron withdrawing groups and, as well, electron releasing groups reduce the rate of ring rotation.¹¹ For example a study, by ^1H NMR spectroscopy, of the dynamics of ring relocation for the anisole complex shows that at room temperature, the only motion observed is migration between 2,3

and 5,6 positions; even at 105°C, the proton signals do not coalesce. As expected, steric interference also impedes ring movement. In no case has stable η^2 binding for aromatic molecules been observed unless both carbons involved bear hydrogen atoms. This outcome does not necessarily mean that attachment across $-\overset{\text{H}}{\text{C}}\cdots\overset{\text{OH}}{\text{C}}-$ for example cannot take place, but may only show that binding across $-\overset{\text{H}}{\text{C}}\cdots\overset{\text{H}}{\text{C}}-$ is favored. As to the ammine protons: in our experience thus far, the signals for cis vs. trans are separated by more than 1.0 ppm; for σ binding, the separation is usually less than 0.5.¹²

Compound 1 appears to be indefinitely stable at room temperature in an anaerobic atmosphere, and survives at least brief contact with air without noticeable change. As already indicated, water does not cause rapid deterioration. It is the most stable complex of benzene thus far prepared, though there is no reason to believe that other combinations will not prove to be even more stable. For present purposes it is only important that it is stable enough so that the effect of η^2 coordination on the reactivity of benzene can easily be studied. The scope of compositions that lead to stable benzene complexes is, among other factors, limited by metal insertion into the CH bond.¹³ Oxidative addition leading to a product of coordination number 6 is hampered in our case by the substitution inertia of the Os-NH₃ bonds, and while oxidative addition leading to a product of coordination number 7 is in principle possible, this mode of decomposition is apparently slow, at any rate slower than others which will now be described.

When Compound 1 is dissolved in acetone the cation is converted to the η^2 -acetone complex, the half-life for the change being ca 8 hours. Other pentaammine derivatives can be prepared by simple substitution, though these reactions are also slow. In this connection it should be noted that the replacement of the η^2 bound derivative 1,2,3,4 - tetramethylbenzene from the complex is rapid enough¹⁴ so that this complex is a useful precursor to preparing other pentaammineosmium(II) species. When 1 is dissolved in the weakly coordinating solvent ethylacetate, the cation over a period of 24 hr. reorganizes according to the stoichiometry

$$2[\text{Os}(\text{NH}_3)_5(\eta^2\text{-C}_6\text{H}_6)]^{2+} = [(\text{Os}(\text{NH}_3)_5)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)]^{4+} + \text{C}_6\text{H}_6 \quad (1)$$

(a small amount of $[\text{Os}(\text{NH}_3)_5(\text{C}_2\text{H}_4)]^{2+}$ is also produced.) Reaction (1) is not measurably reversed by C₆H₆, and we are led to conclude that the affinity of benzene for $[\text{Os}(\text{NH}_3)_5]^{2+}$ is greatly enhanced by the addition of the first moiety, this in spite of the coulombic barrier faced in the second stage. The

principal factor responsible for the increase in affinity in the second stage is the loss, when the ring structure is disrupted, of the stabilization by electron delocalization characteristic of aromatic molecules. This is estimated as ca 34 kcal for benzene, but is at most 4 kcal for butadiene.¹⁵ A similar effect presumably operates to account for the fact that while $[\text{Ru}(\text{NH}_3)_5]^{2+}$ does not bind to benzene, it does to 1.^{16,17}

With the exception of the allylic species, $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_6\text{H}_9)]^{3+}$ (vide infra), all of the organometallic complexes which will be introduced show redox reactivity in the readily accessible range, $0 < E_{1/2} < -1.5$ V (for the allylic species, there is no signal in cyclic voltammetry within the range of the solvent window ± 1.5 V). For the benzene complex, at high enough scan rates, and in an appropriate solvent, the 3+/2+ couple approaches reversibility with $E_{1/2} = 0.18$ V vs NHE. At lower scan rates, the reducing wave diminishes in amplitude, and that of the solvento species begins to appear. The rate of loss of benzene from $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-C}_6\text{H}_6)]^{2+}$ is solvent dependent; in methylpyrrolidinone, k for the appearance of the solvento species is $3 \times 10^3 \text{sec}^{-1}$. In contrast, the $1e^-$ oxidation of the binuclear species results in a product which is much longer lived, so much so that the absorption spectrum of the mixed valence species can be taken without difficulty. The near infra red region is rich in transitions. The most prominent band, at $\lambda_{\text{max}} = 1.8 \times 10^3 \text{cm}^{-1}$, is ascribable to the mixed valence character of the species. The narrowness of this band, the stability of the complex to disproportionation ($K_{\text{com}} \sim 10^8$), and the kinetic stability to substitution compared to a mononuclear Os(III) species, all point to the conclusion that the species is valence delocalized. This is indicated also by the properties of the spin-orbit transitions, which lie at lower energy and have a much higher intensity than is characteristic of an orthodox Os(III) species. Electronic coupling mediated by the benzene ring is obviously very strong. Another point of interest is that the rate of loss of $[\text{Os}(\text{NH}_3)_5]^{3+}$ from the fully oxidized binuclear species is slower than it is from the mononuclear, thus indicating a cooperative effect in metal-to-ligand interaction in the 3+, as well as in the 2+ state of the metal atoms.

With suitably chosen ligands, redox changes are accompanied by linkage isomerization, several examples of which will be offered. A simple one is the behavior of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-acetone})]^{2+}$ in cyclovoltammetry. In acetone as solvent, on oxidation at a scan rate of 100mV/s^{-1} , a broad wave is observed at 0.25 V, but there is no complementary reduction wave; reduction takes place at -0.45 V, but there is no complementary

oxidation wave. The observed oxidation at $E_a=0.25$ V corresponds to producing the unstable η^2 form of the 3+ ion. This rearranges to the η^1 - form so rapidly that measurement of this rate is outside the scope of cyclic voltammetry. Reduction at $E_c=-0.45$ produces the unstable η^1 form of the 2+, which rearranges to the stable η^2 form at a rate which has been measured as $1.3 \pm 0.45s^{-1}$. The standard free energy associated with this change has been determined as -5.0 kcal/mol. In other cases, more dramatic rearrangements have been observed. The major product in the preparation of the benzophenone complex of Os(II) has the metal moiety attached to the 2,3 position of one of the benzene rings. When the ligand is modified by replacing one of the phenyl groups by the tertiary butyl, only the complex with the metal bound to the aromatic ring is formed and it is stable to rearrangement; when the metal is oxidized, a very rapid rearrangement to the molecule in which Os(III) is bound η^1 to the carbonyl takes place. On reduction, the corresponding form of the Os(II) species can be observed, now η^2 bound, which rapidly rearranges to the more stable ring-bound form.¹⁸ For the case of aniline and dimethyl aniline,¹⁹ the full energetics of the "square scheme" have been worked and the results are reproduced in Fig. 1. Of particular interest are the effects of the ligand modification on the dynamics of the linkage

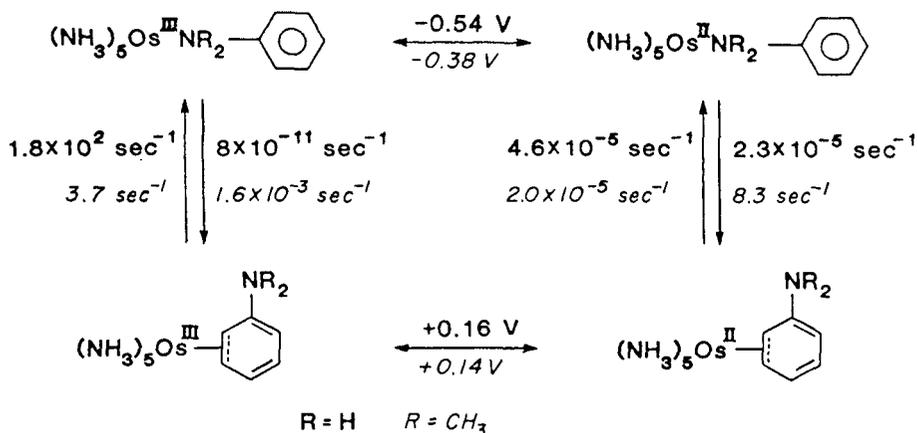
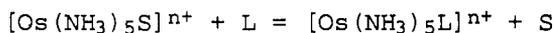


Figure 1. Summary of kinetic and thermodynamic parameters for redox-coupled linkage isomerizations with η^2 -coordinated anilines.

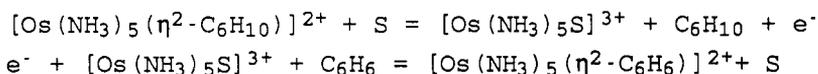
isomerization in each of the two states. For Os(II), K_{iso} ($=[\text{N-bound}]/[\eta^2\text{-form}]$) decreases from 2.0 to 4.1×10^{-6} from aniline to dimethylaniline, and for Os(III), from 2.4×10^{12} to 2.4×10^2 for the same change. To be noted is that the values of K_{iso} can provide access to the "absolute" values of the affinity of η^2 binding of these particular ligands to both $[Os(NH_3)_5]^{2+}$ and $[Os(NH_3)_5]^{3+}$. All that is needed is a single value of the

equilibrium quotient for a reaction of the type

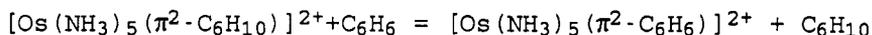


(where L represents ligand and S represents solvent, whether ring or N bound). The "absolute" values will of course depend on the choice of solvent; the values of K_{iso} however are not expected to be strongly dependent on the solvent, provided it is aprotic. As to the changes in rates, this is observed to be greater for the rearrangement of the N-bound to the ring bound forms than for the reverse changes, as would be expected if the activation processes involved mainly bond breaking. This is the likely outcome for linkage isomerization in a rigid system where the adjacent site of attachment cannot approach the site from which the metal leaves.

Many of the observations which have been made on the changes in reactivity which result from the association of $[\text{Os}(\text{NH}_3)_5]^{2+}$ with aromatic molecules involve hydrogenation in the presence of heterogeneous catalysts and those will now be outlined. When benzene dissolved in methanol is subjected at 30° to the action of H_2 at one atmosphere in the presence of Pd/C as catalyst, there is no noticeable reduction even after one hour. Under the same conditions, 1 is reduced essentially quantitatively to the cyclohexene complex,²⁰ a reaction which might have practical applications were it not for the fact that the product ligand is bound very tightly to the metal ion — for example heating the product in CH_3CN for one hour fails to remove the ligand. It is removable when the product is oxidized to the 3+ state, and when this is done in a weakly nucleophilic solvent such as DME, the benzene complex can be reconstituted after reduction, a cycle being thereby completed. But since the oxidation, as an irreversible process, takes place at ca 0.2 V, while the reduction, again as an irreversible process, takes place at ca -0.75 V, nearly one electron volt of energy is consumed for every mole of cyclohexene formed. This energy cost would be somewhat reduced could the redox changes be done reversibly — for example were the reduction and oxidation processes:



to occur at close to the corresponding values of E° . This is not easily realizable; moreover even under equilibrium conditions the energy cost would be that corresponding to the net change:



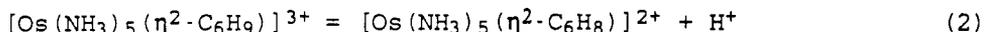
which is probably still very great.

When D_2 is used for the reduction,²¹ it is found to add to only one side of the ring, and for a derivative of benzene, by exploiting NOE, it was shown that it adds to the side opposite to that occupied by the metal moiety. Because of the bulk of the metal complex, covering as it does the face it occupies, any other outcome would be astonishing. It would require a ring flip; while this is not impossible in principle, it has not been observed in any of our work. The binuclear complex is not hydrogenated by the heterogeneous catalysts we have used, though Harman²² reports that, by using a homogeneous hydrogenation catalyst, some reduction to a μ -cyclohexadiene product is observed.

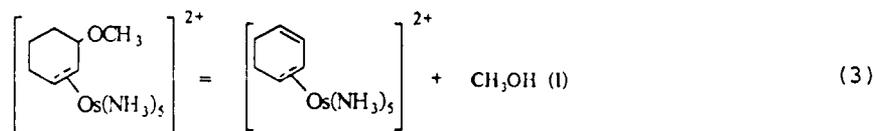
As has been mentioned, for many other aromatic molecules as ligands, ring rotation is frozen out at room temperature and thus it is no surprise to learn that hydrogenation under conditions as described is regio specific.²¹ With the naphthalene complex, the coordinated 3,4-dihydro product is formed in a ~95% yield, what appears to be the 1,4 isomer constituting the remainder. The metal free ring is left fully aromatic, and is not activated significantly by the osmium on the adjacent ring.

Reduction of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-}2,3\text{-anisole})]^{2+}$ leads to hydrogenation at the 4,5,6,1 positions, no other product being detectable. Similarly, for 1,4-dimethoxybenzene, $[\text{Os}(\text{NH}_3)_5]^{2+}$ attaches only at 2,3 and the remaining positions are hydrogenated. For these derivatives, hydrogenation of the complex with Pd/C catalyst is sluggish, and instead Rh/C was used. When the hydrogenation of the anisole complex is carried out in 1 M acid, and with the addition of a small amount of water, the conditions otherwise being kept the same, the product is $[(\text{NH}_3)_5\text{Os}(\eta^2\text{-}2,3\text{-hexen-1-one})]^{2+}$ in >80% recovered yield. The experiment shows that the 4,5 position is reduced first; the resulting allyl ether can add water across the 6,1 position, and on elimination of CH_3OH from the 6 position, the designated product is formed.

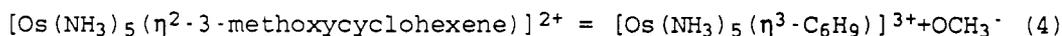
When $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-}2,3\text{-C}_6\text{H}_9\text{OCH}_3)]^{2+}$ in CH_3OH is treated with strong acid (1M HO_3SCF_3), CH_3OH is eliminated and a sparingly soluble salt forms which by analysis combined with ^1H NMR studies on solutions is shown to contain as cation the allyl complex $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_6\text{H}_9)]^{3+}$.²³ This species is found to be in measurable equilibrium with respect to the cyclohexadiene complex and H^+ , reaction (2):



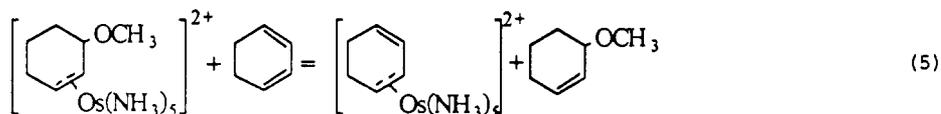
The equilibrium quotient, K_2 , for this reaction in methanol was determined as 0.31. It should be noted that equilibration is rather slow, requiring some hours at 20° C. We were interested in the equilibrium quotient for reaction (3), for reasons which will presently appear:



It can be calculated if in addition to K_2 , the equilibrium quotient for the self-dissociation of methanol, and the equilibrium quotient for the reaction:



The value of K_4 cannot be measured directly because deprotonation of the allyl complex takes precedence, so it was measured for $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_3\text{H}_5)]^{3+}$ and this value, 0.2, was taken as K_4 . These quantities lead to $K_3 = 2 \times 10^{15}$, a result not so interesting in itself, as it is when taken in combination with a similar value for the free ligand, which, by making use of group thermodynamic properties as compiled by Benson,²⁴ we estimated as 0.1. When this is combined with K_3 , we have for reaction (5):

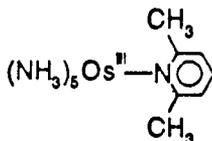


an equilibrium quotient of 2×10^{16} . Even after making generous allowance for uncertainties in the quantities on which it is based, the result testified to an enormous increase in the affinity of $[\text{Os}(\text{NH}_3)_5]^{2+}$ for a double bond in conjugation with another, over an isolated double bond. The two double bonds in conjugation gain little in stabilization by delocalization, but the energy of the LUMO lies considerably below that of an isolated double bond. The 3+/2+ redox potentials for the two complexes shown in equation (5) are virtually identical, and thus nearly the same equilibrium quotient applies to reaction (5) written as involving the 3+ species. There is evidence that Os(III), despite the higher oxidation state, still engages significantly in π donation.²⁵ Moreover, corresponding to the lowering of the energy of a π^* orbital for two double bonds in conjugation, the HOMO is raised, strengthening the σ component to the Os(III)-ligand interaction.

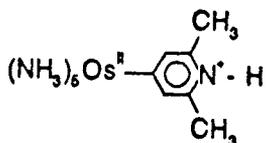
The foregoing shows that hydrogenation can lead to the conversion of the 3-methoxycyclohexene complex to that of cyclohexene; for the 1,4-dimethoxybenzene complex, it leads through identified intermediate stages to the benzene adduct.²³

In work done at the University of Virginia, Harman and Hipple²⁶ by the use of NMR measurements have uncovered some remarkable tautomerisms. They have shown that in a solution of the phenol adduct at equilibrium there exist measurable quantities of the keto forms in each of which a ring carbon now bears an extra proton. In fact for the ortho cresol and meta cresol complexes of $[\text{Os}(\text{NH}_3)_5]^{2+}$ the orthodox form is less abundant than is one of the two keto isomers possible in each case. In a related system, they have shown that when acid is added to the η^2 -3,4-dimethylaniline complex, in the major protonated component of the solution, the proton adds to the ring para to the nitrogen atom, rather than to nitrogen.

The chemistry dealt with thus far involves η^2 binding of the organic molecule to pentaammineosmium. No special effort has thus far been exerted to explore the chemistry of species in which the organic moiety is bound in an η^1 mode. Except in special circumstances, there is no reason to believe that such species would be especially interesting for the 2+ state of $[\text{Os}(\text{NH}_3)_5]$, being as it is an 18 e⁻ system, with all the positions cis to the organic fragments blocked by NH_3 ligands. The 3+ state would have at least the element of interest that studies with it might lead to instructive comparisons with the extensive literature²⁷ on the organometallic chemistry of $[\text{Cr}(\text{H}_2\text{O})_5]^{3+}$. I shall however describe one system in which we encountered a σ bound organic fragment in the course of following our interest in η^2 bound complexes.²⁸ When 2,6-lutidine is used as ligand, and the usual preparative procedure is followed, a complex forms in which $[\text{Os}(\text{NH}_3)_5]^{2+}$ is attached to the 3,4 position of the ligand. The blocking methyl groups are needed to prevent the attachment of the metal to the nitrogen atom. (Though not germane to the main thrust of this paragraph, it is of interest to note that 1e⁻ oxidation leads to the formation of:



in high yield; on reduction the η^2 form of Os(II) is regenerated.) When the η^2 form is kept in solution, over a period of 3 hrs. it rearranges to:

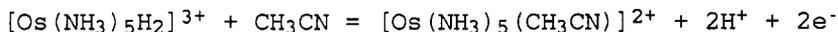


which shows metal to ligand charge transfer absorption not much

different from that of an orthodox pyridine complex. The facile scission of the C-H bond is of interest, as is the fact that a reversible 3+/2+ couple is observed for the complex ($E_{1/2} = -0.50$ V), the reversibility indicating that the complex in the higher oxidation state is also reasonably stable. It is remarkable that $E_{1/2}$ for the C-bound form is so little different from that of the orthodox N-bound species, which in the case of pyridine is measured as -0.45 V.

In the foregoing, examples of η^2 attachment of $[\text{Os}(\text{NH}_3)_5]$ to C=C, C...C, C=O have been dealt with. A radically different kind of η^2 binding has been recognized by Kubas,²⁹ namely to H_2 , and I shall now introduce an example of a complex which features this kind of binding and which we first encountered in our work on the $[\text{Os}(\text{NH}_3)_5]^{2+}$ moiety.³⁰ This in turn will serve to introduce a very brief account of the experience we have had with the tetraammine moiety, taken from work now in progress.³¹ When $[\text{Os}(\text{NH}_3)_5(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)_2$ dissolved in acidified CH_3OH is reduced by Zn/Hg, a solid of composition $[\text{Os}(\text{NH}_3)_5(\text{H}_2)](\text{O}_3\text{SCF}_3)_2$ (2) can be recovered in reasonably good yield (~50%). The cation is unchanged by acid or by base, at least at concentrations up to 1 M. Both reagents, however, bring about H-D exchange in CH_3OD as solvent. Measurements by ^1H NMR spectroscopy of the H-D coupling constant in the complex yields the value of 15.2 Hz which is in the low range shown by species in which H_2 is taken to be bound in the η^2 mode. It is on this basis mainly that we conclude that our species is of this kind, rather than being an osmium(IV) cis-dihydride of coordination #7. (The separation, 0.68 ppm, of the signals for the cis and trans ammine protons, it must be admitted, is the smallest we have encountered for an η^2 complex.)

Cyclovoltammetry of a solution of (2) in dry acetonitrile (or in 1 M aqueous acid) at high scan rates approaches reversible behavior, the 3+/2+ couple appearing at $E_{1/2} = 0.58$ (or 0.41 V). In both cases, a second, now irreversible, oxidation occurs, which, in the case of CH_3CN as solvent, is described by:



While the complex in the 2+ state is rather unreactive — no reaction with butyne even after 24 hr or with pyridine after several hours — the 3+ species was found to react extremely rapidly with acetone ($k > 1 \times 10^3 \text{M}^{-1}\text{s}^{-1}$). This was demonstrated by the complete disappearance of the second oxidation wave when even a trace of acetone is added to the solution of 2 in CH_3CN , and by the formation of the isopropyl alcohol complex of $[\text{Os}(\text{NH}_3)_5]^{3+}$ as the immediate product.

The investigation of the dihydrogen complexes has been extended also to the cis-tetraammine case.³¹ By following the procedure used in the preparation of compound 2, a salt containing the cation $[\text{Os}(\text{NH}_3)_4\text{H}_2]^{2+}$, 3, is produced which is an orthodox dihydride of Os(IV), analogous to cis $[\text{Os}(\text{NH}_3)_4\text{H}_2]^{2+}$. The latter was prepared and characterized almost two decades ago,³² but on the basis of the experiments done with it then we did not find it very interesting. In the light of experience to be described it has gained a great deal in interest. Cation 3 is found to react in CH_3CN or in pyridine to form in each case a μ -dihydrogen complex. That this is indeed the outcome is indicated by a shift of the ^1H NMR absorption from $\delta \sim 11$, the region of absorption for $[\text{Os}(\text{NH}_3)_4\text{H}_2]^{2+}$, to $\delta \sim 8$, the region of absorption for 2, by the value of the H-D coupling constant and by analysis of a solid obtained from the solution in CH_3CN which shows the cation to have the composition $[\text{Os}(\text{NH}_3)_4(\text{CH}_3\text{CN})\text{H}_2]^{2+}$. The species $[\text{Os}(\text{NH}_3)_4\text{H}_2]^{2+}$ undergoes a similar transformation in CH_3CN as solvent, but in this case, the reaction is only partially complete.

The species $[\text{Os}(\text{NH}_3)_4\text{H}_2]^{2+}$ is found to be quite reactive in other respects. With ethylene, $[\text{Os}(\text{NH}_3)_4(\text{C}_2\text{H}_4)_2]^{2+}$ is formed in good yield, but the fate of the metal bound "hydrogens" has not yet been established. With styrene, the olefin function is hydrogenated and with butadiene, polymerization ensues. A point which we find puzzling is that in the ^1H NMR spectrum of each of $[\text{Os}(\text{NH}_3)_4\text{H}_2]^{2+}$, $[\text{Os}(\text{NH}_3)_4(\text{CH}_3\text{CN})\text{H}_2]^{2+}$, $[\text{Os}(\text{NH}_3)_4(\text{C}_2\text{H}_4)_2]^{2+}$, there is only one signal for the ammine protons rather than two as would be expected for a cis arrangement. While in a single instance this could be ascribed to coincidence, to have observed it in at least three related cases suggests that some of the molecules do indeed have the trans structure. If this is the case for 3, in forming the CH_3CN derivative, there is a migration of hydrogens from a configuration in which they are mutually trans, to one in which they are adjacent.

A comparison of the effects observed for the tetraammine species taken in relation to those described for the pentaammine illustrates the point that when two labile positions are open, new reaction opportunities arise. These can come about because for a particular ligand, interaction at two adjacent sites is now possible, and also because juxtaposition in the coordination of two putative reactants is now possible. Moreover by using one of the labile positions to introduce a firmly bound π -acid ligand of choice, instructive comparisons with the pentaammine case are enabled. An obvious candidate for modifying reactivity is pyridine or CH_3CN , each of which is a π -acid, and is

therefore expected to moderate the back-bonding capacity of Os(II). These considerations are an incentive for continuation of work now in progress in the course of which a number of novel species or of effects have been observed, only one of which will be mentioned. The product of the interaction of $[\text{Os}(\text{NH}_3)_5]^{2+}$ with an aromatic molecule is kinetically stable at room temperature, and only after heating is decomposition to — or synthesis of — η^6 species³³ observed. By contrast, in the preparation of the tetraammine complex, with benzene, phenol or naphthalene as entering ligands, even at room temperature, only the η^6 products are recovered as solids. The reactions are stepwise, and in the case of naphthalene, ¹H NMR spectroscopy reveals an η^4 species as an intermediate. This ready access to η^6 products under mild conditions in ordinary environments provides additional opportunities for extending the chemistry.

By no means all of the organometallic chemistry that has been uncovered since the beginning of this work has been referred to, and there is no reason to suppose that discovery of qualitatively new effects is at an end. I believe that there are other good reasons for continuing the research. Ammonia is perhaps the simplest ligand to understand, and the approach to understanding the interaction of metal ions with organic ligands involving such simple compositions as we have dealt with provides a new perspective on the subject. By a systematic introduction of other co-ligands, as already suggested above, there is an opportunity to improve our understanding of the new chemistry at a basic level. Finally, the chemistry which is being uncovered serves an important didactic purpose. Organometallic and traditional coordination chemistry have developed with little in the way of cross reference, and this new chemistry, and other organometallic chemistry with mainly saturated co-ligands, serves to bridge the two areas and to unify the subject of coordination chemistry.

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REFERENCES

1. Endicott, J.P.; Balakrishnan, K.P.; Wong, C.-L., *J. Am. Chem. Soc.*, 1980, 102, 5519.
2. Brothers, P.J.; Collman, J.P., *Acc. Chem. Research*, 1986, 19, 209.
3. Lehman, H.; Schenk, K.G.; Chapius, G.; Ludi, A., *J. Am. Chem. Soc.*, 1979, 101, 6197.
4. Ford, P.; Gaunder, R.; Rudd, DeF. P.; Taube, H., *J. Am. Chem. Soc.*, 1968, 90, 1187.
5. Sen, J.; Taube, H., *Acta. Chem. Scand.*, 1979, A33, 125.
6. Gulens, J.; Page, J.A., Jr., *Electroanal. Chem.*, 1974, 55, 239; 1976, 67, 215.
7. Elliott, M.G.; Shepherd, R.E., *Inorg. Chem.*, 1988, 27, 3332.
8. Scott, A.; Taube, H., *Inorg. Chem.*, 1971, 10, 62.
9. Dixon, N.E.; Jackson, W.G.; Lancaster, M.J.; Lawrence, G.A.; Sargeson, A.M., *Inorg. Chem.*, 1981, 20, 470.
10. Harman, W.D.; Taube, H., *J. Am. Chem. Soc.*, 1987, 109, 1883.
11. Harman, W.D.; Sekine, M.; Taube, H., *J. Am. Chem. Soc.*, 1988, 110, 5725.
12. Harman, W.D., Ph.D. Thesis, Stanford Univ., 1987, p. 223.
13. Jones, W.D.; Feher, F.J., *J. Am. Chem. Soc.*, 1984, 106, 1650.
14. Harman, W.D.; Taube, H., *Inorg. Chem.*, 1987, 26, 3316.
15. March, J., *Advanced Organic Chemistry*, McGraw-Hill Book Co., 1977, p. 31 et seq.
16. Harman, W.D.; Taube, H., *J. Am. Chem. Soc.*, 1988, 110, 755.
17. The same number will be used as shorthand notation for the cation of interest, and for the salt containing it.
18. Harman, W.D.; Sekine, M.; Taube, H., *J. Am. Chem. Soc.*, 1988, 110, 2439.
19. Harman, W.D.; Taube, J., *J. Am. Chem. Soc.*, 1988, 110, 5725.
20. Harman, W.D.; Taube, H., *J. Am. Chem. Soc.*, 1988, 110, 7906.
21. Harman, W.D.; Schaefer, W.P.; Taube, H., *J. Am. Chem. Soc.*, 1990, 112, 2682.
22. Harman, W.D., Private Communication.
23. Harman, W.D.; Hasegawa, T.; Taube, H., accepted for publication, *J. Am. Chem. Soc.*
24. Benson, S.W., *Thermochemical Kinetics*, Second Edition, John Wiley & Sons, Inc., N.Y., 1976.
25. Johnson, A.; Taube, H., *J. Ind. Chem. Soc.*, 1989, 66, 503.
26. Harman, W.D.; Hipple, W.G., Submitted to *J. Am. Chem. Soc.*
27. Espenson, J.H., *Progress in Inorganic Chemistry*, (Lippard, S.J., Editor), John Wiley & Sons, 1983, p. 189 et seq.
- 28a. Cordone, R.; Taube, H., *J. Am. Chem. Soc.*, 1987, 109, 8101.
- 28b. Cordone, R.; Harman, W.D.; Taube, H., *ibid.*, 1989, 111, 2896.
29. Kudas, G.J., *J. Chem. Soc.*, Chem. Communication, 1980, 61.
30. Harman, W.D.; Taube, H., *J. Am. Chem. Soc.*, 1990, 112, 2261.
31. Research in progress by Zaiwei Li.
32. Malin, J.; Taube, H., *Inorg. Chem.*, 1971, 10, 2403.
33. Harman, W.D.; Gebhard, M.; Taube, H., *Inorg. Chem.*, 1990, 29, 567.
34. Li, Zaiwei; Harman, W.D.; Taube, H., in preparation for publication.