via the σ system. This ground-state σ stabilization effect would not be observable in the spectral measurements, however, because the energy of the excited state is lowered as well, the photochemically formed Ru(III) having slightly more appropriate bond lengths than would otherwise be the case since the Franck–Condon principle applies. To the contrary, this difficulty should not arise with the equilibrium measurements, since the Ru(III) is formed in this case with its equilibrium metal–ligand bond lengths. Whether or not this added σ interaction plays an important role, the back-bonding values calculated from the two kinds of data are gratifyingly consistent and demonstrate the validity of our model for the Ru(II) back-bonding interaction and spectra for this class of compounds.

Acknowledgment.—Financial support for this research by the National Institutes of Health, both for Grant No. GM 13638-04 and for fellowships for Mrs. Creutz from 1967 to the present, is gratefully acknowledged. We are also grateful for many helpful discussions with Professor Henry Taube.

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The Relative Importance of σ and π Bonding of Molecular Nitrogen and Carbonyl in Osmium(II) Complexes as Determined by Infrared Intensities of the Molecular Nitrogen and Carbonyl Stretching Vibrations

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Integrated infrared intensity data are presented here for a series of complexes of the type $Os(N_2)X_2[PR_2C_6H_5]_3$ as well as for their carbonyl analogs. Dipole moment derivatives were calculated which involve both OsN or OsC and NN or CO stretching motions. The effective group dipole moment derivatives were found to be substantially larger for the carbonyl compounds as compared to the molecular nitrogen analogs and to vary within the dinitrogen series systematically with the nature of the phosphine and halide bound to the osmium. It is concluded on the basis of these results that CO is a better σ-donor and π-acceptor ligand than N_2.

Introduction

Along with the progress in synthetic routes to novel molecular nitrogen–transition metal complexes much interest in recent years has developed in the electronic and structural properties of the metal–nitrogen bond. In particular the question of the π-acceptor and σ-donor abilities of molecular nitrogen as compared with the isoelectronic carbon monoxide ligand has stimulated much discussion.

Answers to this question of the relative σ-donor and π-acceptor abilities of N_2 and CO have been put forth based on infrared frequency studies,[1-3] Mössbauer measurements,[4,5] rates of molecular nitrogen substitution reactions,[6] and comprehensive molecular orbital calculations.[7,8] These methods generally conclude CO to be an appreciably better σ donor and/or π acceptor than N_2. However, the most commonly employed technique of infrared frequency shifts has led to some conclusions which are disputable.

As part of a continuing study of the properties of metal–molecular nitrogen and metal–carbon monoxide bonds we have attempted to answer this question *via* infrared intensity measurements. Previously we demonstrated the utility of integrated infrared intensity measurements of ν_{N_2} and ν_{CO} vibrations in assessing π-electronic delocalization in transition metal–molecular nitrogen and –carbon monoxide compounds.[9-12] In order to obtain accurate intensity measurements it is necessary to have available pure, stable molecular nitrogen complexes. It would also be advantageous to have a series of complexes in which systematic changes in the metal's electronic character, as determined by the other affixed ligands, is also present. Such a series of complexes of the type $Os(N_2)X_2[PR_2C_6H_5]_3$ has recently been reported by Chatt, Leigh, and Richards[13] and by Maples, Basolo, and Pearson.[6] In addition the latter researchers have prepared several of their carbonyl analogs.

The purpose of the present study was to determine in more detail the usefulness of infrared intensity measurements by studying the variations in the intensity of the dinitrogen stretching frequency as the nature of the other ligands attached to the metal is varied. It is then

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possible to relate these variations in intensity with the accepted σ-donor and π-acceptor properties of the phosphine and halide ligands and their expected effect on the metal–nitrogen bond. In addition, intensities of the ν_{CO} vibration in isoelectronic osmium carbonyl analogs were also investigated for comparisons of the relative π-electronic delocalization in the M–N–N and M–C–O groupings.

Experimental Section

Materials.—Osmium tetroxide was obtained commercially from Stevens Metallurgical Corp., New York, N. Y., and was used as received. Dimethylphenylphosphine and diethylphenylphosphine were purchased from Strem Chemicals, Danvers, Mass. THF was refluxed over and distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. All reactions were performed under an atmosphere of nitrogen.

$OsCl_3(P(C_2H_5)_2C_6H_5)_3$ and $OsCl_3(P(CH_3)_2C_6H_5)_3$ were prepared by the method described in the literature.[14] $Os(N_2)Cl_2(P(C_2H_5)_2C_6H_5)_3$ and $Os(N_2)Cl_2(P(CH_3)_2C_6H_5)_3$ were synthesized and purified by the method of Chatt and coworkers.[13]

Anal. Calcd for $Os(N_2)Cl_2(P(C_2H_5)_2C_6H_5)_3$: C, 45.7; H, 5.80; N, 3.60. Found: C, 45.73; H, 5.93; N, 3.90 (mp 159–161° decomp). Calcd for $Os(N_2)Cl_2(P(CH_3)_2C_6H_5)_3$: C, 41.0; H, 4.70; N, 4.00. Found: C, 40.89; H, 5.00; N, 4.30 (mp 148–150° decomp). These compounds had physical and spectral properties identical with those of samples supplied by Professor Basolo.

$Os(N_2)Br_2(P(CH_3)_2C_6H_5)_3$ and $Os(N_2)Br_2(P(CH_3)_2C_6H_5)_2P(OCH_3)_2C_6H_5$ were also generously donated by Professor Basolo. These compounds gave the following elemental analyses. *Anal.* Calcd for $Os(N_2)Br_2(P(CH_3)_2C_6H_5)_3$: C, 36.4; H, 4.2; N, 3.50. Found: C, 36.44; H, 4.50; N, 3.82. Calcd for $Os(N_2)Br_2(P(CH_3)_2C_6H_5)_2P(OCH_3)_2C_6H_5$: C, 35.0; H, 4.03; N, 3.40. Found: C, 35.25; H, 4.05; N, 3.70.

$Os(CO)Cl_2(P(C_2H_5)_2C_6H_5)_3$ (isomers I and II) were prepared in a manner similar to the preparation of the $P(CH_3)_2C_6H_5$ analog described by Basolo.[6] A 1.3-g sample of $OsCl_3(P(C_2H_5)_2C_6H_5)_3$ in 30 ml of tetrahydrofuran was added to a zinc amalgam (0.19 g of zinc, 20 mesh, and 5.0 ml of mercury) with stirring under nitrogen. Carbon monoxide was slowly bubbled through the solution for approximately 45 min during which time the solution turned from dark red to yellow. The yellow solution was filtered and THF was removed at room temperature under vacuum. The product was then divided into two portions. The first portion was recrystallized from a THF–methanol mixture to yield a yellow solid. This product turned yellow-white at 179° but remained solid and then melted at 226.5–228°. This is isomer I.

The second portion was heated at 150–165° for 30 min under a nitrogen atmosphere. This material was cooled to room temperature and recrystallized from THF–methanol to yield a white powder, mp 234–235°. This is isomer II. *Anal.* Calcd for $Os(CO)Cl_2(P(C_2H_5)_2C_6H_5)_3$: C, 47.2; H, 5.76. Found: C, 46.8; H, 5.53.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Infrared Spectra.—Infrared spectra in the N_2 and CO stretching region were measured on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer in Spectrograde chloroform. Samples were prepared by weighing out the solid material on a Cahn Electrobalance to ±0.01 mg. Linear Beer's law plots were observed in all cases (Figure 1). No decomposition of samples in solution over a prolonged period in the infrared cell was noted. The spectrophotometer was calibrated in the region above 2000 cm^{-1} against the spectrum of carbon monoxide and below 2000 cm^{-1} against the spectrum of water vapor. The spectral slit width of the instrument was set at 1.5 cm^{-1}. Recordings were made on an expanded abscissa scale (5.0 cm^{-1}/cm) and areas under bands were determined with a planimeter. One-millimeter sodium chloride cells calibrated by the interference fringes method were employed in the measurements. Far-infrared spectra were measured in 1-mm CsI cells in Spectrograde chloroform or carbon disulfide. Intensities were determined at a number of concentrations and extrapolated to zero concentration (Figure 2). All data were analyzed by the linear least-squares method.

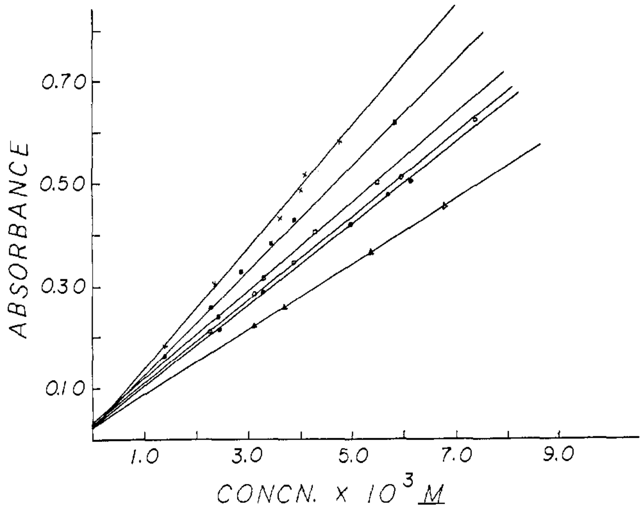

Figure 1.—Beer's law plots for $Os(N_2)X_2(PR_2C_6H_5)$ complexes in chloroform solution in a 1.0-mm cell: ×, $Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$ (I); ■, $Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$ (II); □, $Os(N_2)Cl_2[P(C_2H_5)_2C_6H_5]_3$; ○, $Os(N_2)Cl_2[P(CH_3)_2C_6H_5]_3$; ●, $Os(N_2)Br_2[P(CH_3)_2C_6H_5]_3$; △, $Os(N_2)Br_2[P(CH_3)_2C_6H_5]_2[P(OCH_3)_2C_6H_5]$.

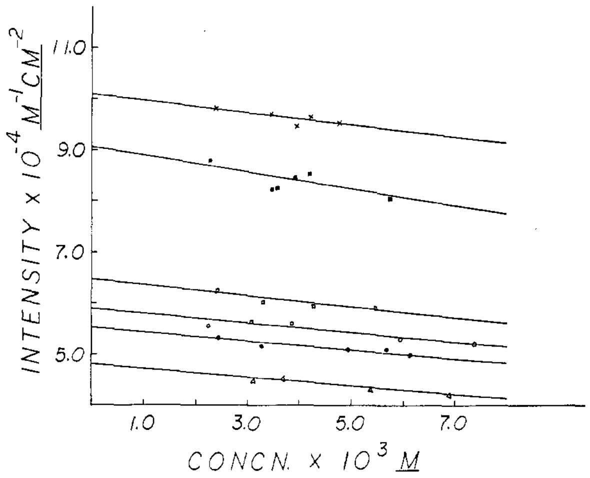

Figure 2.—Intensity *vs.* concentration for the N_2 and CO vibrational modes in Os(II) complexes. Labels are the same as in Figure 1.

Calculations.—Machine calculations were performed on a CDC 6400 at the State University of New York at Buffalo Computing Center. Infrared band shape analyses were carried out using a program based on the work of R. N. Jones and J. Pitha of the Division of Pure Chemistry, National Research Council of Canada, and modified for use on the CDC system in our laboratory.[15,16] The program fits a Cauchy–Gauss product or sum function to an infrared absorption band envelope and will handle up to 20 bands simultaneously.

Results and Discussion

The stereochemistries of both the $Os(N_2)X_2[PR_2C_6H_5]_3$ and $Os(CO)X_2[PR_2C_6H_5]_3$ complexes, where R is methyl, were determined using proton nmr by Maples, Basolo, and Pearson.[6] The stereochemistries of cases where R is ethyl were assumed to be similar,

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[14] J. Chatt, G. L. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc. A*, 2636 (1968).

[15] R. N. Jones and J. Pitha, Bulletin No. 12, National Research Council of Canada, 1968, and references contained within.

[16] The details of these calculations are available from the author upon request.

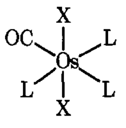
TABLE I

INFRARED FREQUENCIES, BAND HALF-WIDTHS, EXTINCTION COEFFICIENTS, AND INTENSITIES FOR THE νN_2 AND νCO VIBRATIONS IN Os(II) COMPLEXES

Compound	Vibration, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	$10^{-2}\bar{\epsilon}$,[a] M^{-1} cm^{-1}	$10^{-4}I$,[b] M^{-1} cm^{-2}
$Os(N_2)Cl_2[P(C_2H_5)_2C_6H_5]_3$	2074.8	26.1	8.30	6.46 ± 0.07
$Os(N_2)Cl_2[P(CH_3)_2C_6H_5]_3$	2088.3	25.2	7.81	5.88 ± 0.09
$Os(N_2)Br_2[P(CH_3)_2C_6H_5]_3$	2094.6	23.9	7.66	5.54 ± 0.09
$Os(N_2)Br_2[P(CH_3)_2C_6H_5]_2$-$[P(OCH_3)_2C_6H_5]$	2125.9	26.9	6.11	4.81 ± 0.05
$Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$[c]	1946.0, 1932.0	30.3	11.29	10.08 ± 0.09
	(1946.6, 1932.0)	(16.9, 17.5)		
$Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$[d]	1924.0, 1916.0	25.3		
	(1924.5, 1911.7)	(18.1, 17.5)	9.91	9.05 ± 0.18

[a] Obtained from the least-squares slope of absorbance *vs.* concentration plots. [b] Defined as $(2.303/Cl)\int_{\text{band}} \log (I_0/I)\, d\nu$, where C is the concentration in moles per liter and l is the cell path length in cm. The errors listed are the standard deviations from least-squares analyses of the intensity *vs.* concentration plots. [c] This is isomer I; parameters in parentheses were computed as in ref 15. [d] This is isomer II.

since an analysis of their complex nmr patterns was not attempted. The dinitrogen complexes were shown to exist as isomer II, whereas, in contrast, the carbonyl analogs were found to exist as both isomers I and II. In these cases, isomer II is the thermodynamically more stable isomer.



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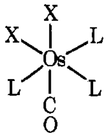

II

The infrared spectra in the CO stretching vibration region of isomers I and II of $Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$ in chloroform solution show rather broad, unresolved peaks under high-resolution conditions (Figure 3).

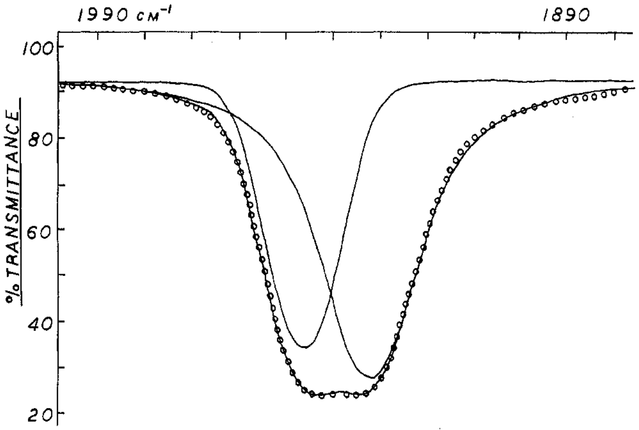

Figure 3.—Observed and calculated band shapes for the CO vibrations in $Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$ (I) in chloroform solution: O, observed; —, calculated.

This asymmetry indicates that two or more bands may be contributing to these peaks. It may arise from the existence of more than one conformer of each isomer in solution as a result of the bulky asymmetric diethylphenylphosphine ligands. It was possible satisfactorily to fit the observed infrared spectra of both isomers with two symmetric band envelopes. These band fits were obtained using Cauchy–Gauss product and sum functions as described previously.[15] In contrast, the N_2 stretching vibrations of isomer II complexes in chloroform solution were observed as single, symmetrical bands.

The N_2 and CO stretching frequencies, band parameters, and integrated intensities are found in Table I.

The group dipole moment derivatives were calculated as previously described using the equation

$$I = G_{tt}\left(\frac{\partial \mu_{ML}}{\partial S}\right)^2 = G_{tt}\mu'_{ML}{}^2$$

where I is the measured intensity × 10^{-4}, G_{tt} equals the inverse mass of an N_2 or CO grouping (0.14278 and 0.14585, respectively), and μ'_{ML} is the respective change in group dipole moment with symmetry coordinates. Tabulated values of μ'_{OsNN} and μ'_{OsCO} are listed in Table II.

TABLE II

GROUP DIPOLE MOMENT DERIVATIVES FOR THE N_2 AND CO STRETCHING VIBRATIONS IN OSMIUM(II) COMPLEXES[a]

Compound	μ'_{OsN_2}	μ'_{OsCO}
$Os(N_2)Cl_2[P(C_2H_5)_2C_6H_5]_3$	6.73	. . .
$Os(N_2)Cl_2[P(CH_3)_2C_6H_5]_3$	6.42	. . .
$Os(N_2)Br_2[P(CH_3)_2C_6H_5]_3$	6.23	. . .
$Os(N_2)Br_2[P(CH_3)_2C_6H_5]_2$-$[P(OCH_3)_2C_6H_5]$	5.80	. . .
$Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$[b]	. . .	8.32
$Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$[c]	. . .	7.88

[a] Dipole moment derivative values are accurate to ±0.1 unit. The units employed here are arbitrary. [b] Isomer I. [c] Isomer II.

As is shown in Tables I and II the integrated intensities or group dipole moment derivatives for the carbonyl compounds were found to be considerably larger in magnitude than the comparable values for the dinitrogen compounds. During the N_2 or CO stretching motions there is a significant transfer of π-electronic charge from the osmium–nitrogen or osmium–carbon linkage to N≡N or C≡O and a concomitant change in the dipole moment for the Os—N_2 or Os—CO linkages. This π-electronic charge transfer, which is responsible for a major part of the OsNN or OsCO group dipole moment change with N_2 or CO stretching motions, occurs between d_π orbitals centered on the metal and π^* orbitals on N_2 or CO. Therefore the moment vector is from the metal atom to the center of charge of the π^* orbitals on N_2 or CO. In the case of the Os—NN grouping the charge center is the center of the N≡N bond whereas in Os—CO the charge center lies closer to the carbon atom than to the oxygen atom. Hence, in the case of equal π-electronic charge transfer from the metal to either N_2 or CO, the moment created would be expected to be greater in the case of OsN_2 since the metal–nitrogen and metal–carbon as well as the NN and CO bond distances are quite similar.[17] It therefore follows that since the μ'_{OsCO}'s are considerably larger than the corresponding values for $\mu'_{\mathrm{OsN_2}}$, the acceptor ability of the N_2 π^* orbital is much less than that of the CO π^* orbital.[18] This necessitates concluding that N_2 is also a poorer σ-donating ligand than CO in these osmium complexes. The free CO molecule is a stronger Lewis base than the free N_2 molecule; *e.g.*, CO readily forms a complex with BH_3 while N_2 does not. Any increase in the base strength of the bound N_2 over that of a similarly bound CO group would therefore have to result from the synergistic relationship between σ and π effects. However, this effect will be more important for carbon monoxide than for dinitrogen since CO is concluded to be the better π acceptor.

The $\mu'_{\mathrm{OsN_2}}$'s are observed to decrease for the halide complexes as the nature of the attached cis phosphine ligands changes in the order $P(C_2H_5)_2C_6H_5 > P(CH_3)_2C_6H_5 > P(OCH_3)_2C_6H_5$. There is a less dramatic decrease in $\mu'_{\mathrm{OsN_2}}$ as the trans chloride ligand is replaced by bromide. A similar trend was observed for ν_{N_2} values in $Os(N_2)X_2(PR_2C_6H_5)_3$[13] and $Ir(N_2)X(PR_3)_2$[3] complexes as the phosphine ligands were varied. Since the dipole moment gradients are primarily a function of the π-electronic charge in the metal–nitrogen bond, these results would indicate that the extent of metal–nitrogen π bonding is also decreasing in the same order. It is interesting to note in this connection that if a plot of the intensities *vs.* ν_{N_2} is extrapolated to zero intensity, this occurs in the approximate vicinity of 2330 cm^{-1}, the vibrational frequency of the free N_2 molecule. These results are consistent with the decreasing σ-donor and increasing π-acceptor properties of the phosphine ligands in the order $P(C_2H_5)_2C_6H_5 > P(CH_3)_2C_6H_5 > P(OCH_3)_2C_6H_5$.[19]

The fact that the phosphine ligands are acting as π acceptors in these complexes is adequately demonstrated in the difference in μ'_{OsCO} values for the two isomers of $Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$. There is a sizable increase (6%) in the dipole moment derivative of isomer I over isomer II despite the apparent decrease in π-electronic charge in the OsC bond as indicated by an increase in ν_{CO}. This is consistent with a vibronic transfer of π-electronic charge from the trans phosphine group in isomer I through the metal to the CO group during the CO vibration. Similar vibronic contributions to the group dipole moment derivative were observed in substituted molybdenum carbonyls containing phosphine ligands trans to carbonyl groups.[10]

In an attempt to study further the osmium–nitrogen and osmium–carbon bonds, the far-infrared spectra in solution were observed. The far-infrared spectra are complicated by the fact that bands due to the phosphine ligands obscure much of the region between 600 and 300 cm^{-1} where bands of interest are expected to occur. These spectra were recorded in chloroform or carbon disulfide solution in order to obtain maximum resolution (Figure 4). Frequency data and relative intensities are presented in Table III.

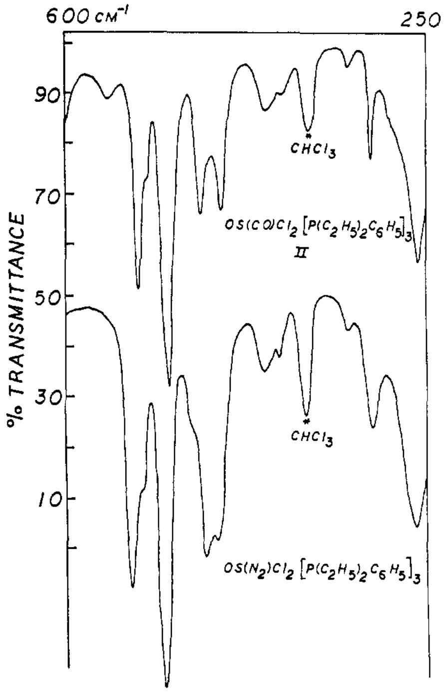

Figure 4.—Far-infrared spectra of $Os(CO)Cl_2[P(C_2H_5)_2C_6H_5]_3$ (II) and $Os(N_2)Cl_2[P(C_2H_5)_2C_6H_5]_3$ in chloroform solution.

TABLE III

FAR-INFRARED SPECTRA (600–250 CM^{-1}) OF N_2 AND CO COMPLEXES OF OSMIUM(II)

Compound	ν_{OsCl}, cm^{-1}	Other bands,[a] cm^{-1}
$P(C_2H_5)_2C_6H_5$	. . .	517.4 w, 495.0 s, 484.0 vs, 433.8 m, 402.5 w, 362.5 w
$Os(N_2)Cl_2(P(C_2H_5)_2C_6H_5)_3$	300.5 m, 253.0 s	*534.4* s, 523.6 sh, m, 498.8 vs, *475.0* sh, w, *461.2* s, 449.5 s, 403.9 w, 389.5 w
$Os(CO)Cl_2(P(C_2H_5)_2C_6H_5)_3$ (I)	298.5 s, 278.2 w	*593.7* s, *580.0* m, 529.4 w, 509.4 s, 497.5 vs, *466.5* s, 445.0 s, 399.0 w, 386.2 w, *362.5* w
$Os(CO)Cl_2(P(C_2H_5)_2C_6H_5)_3$ (II)	303.0 w, 256.0 s	*557.9* w, *527*.4 s, 521.8 sh, w, 499.0 vs, *469*.8 m, 447.7 m, 405.0 w, 392.0 w

[a] Italic bands are attributed to vibrations in the complexes other than those of the phosphine ligands.

By a comparison of the bands and their relative intensities in the phosphine ligand $P(C_2H_5)_2C_6H_5$ free and bound in the complexes it appears to be possible to separate bands which are assignable to the $\delta(Os–N_2)$ or $\delta(Os–CO)$ and osmium–nitrogen, –carbon, or –phosphorus stretching frequencies. Since the $\delta(Os–CO)$ vibrations generally occur at higher frequency than the $\nu(Os–C)$ vibrations,[20,21] the high-frequency absorptions are assigned to $\delta(Os–N_2)$ or $\delta(Os–CO)$ deformation vibrations. In $Os(NH_3)_5N_2^{2+}$ species a band at approximately 540 cm^{-1} has been assigned to the Os–N_2

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[17] B. R. Davis, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 1240 (1969).

[18] It should again be pointed out[9] that we have considered ν_{CO} and ν_{N_2} to be "pure" vibrations. Strictly speaking, this is not true; however, since the far-infrared spectra are shown to be quite similar in the two types of compounds, we expect the degree of mixing of vibrations to be similar in the two cases. Any coupling would be expected to be more pronounced in the CO complex since ν_{CO} is closer in energy to the other skeletal vibrations in the molecule and would thereby be coupled more strongly. The net result would be an underestimate of the dipole moment derivative for the CO molecule. Hopefully, using simpler complexes, we may be able to determine the error involved in this assumption.

[19] This is the same trend observed for the variations in rates and activation parameters for N_2 dissociation in $Os(N_2)X_2(PR_2C_6H_5)_3$ complexes. At the same time the OsCO group was observed to be substitution inert.[6]

[20] D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1967.

[21] C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **7**, 2365 (1968).

stretching vibration.[22] However the possibility of this being the bending vibration δ(Os–NN) is not excluded. The low-frequency absorptions may be assignable to either the ν(Os–N), ν(Os–C), or ν(Os–P) stretching vibrations, all of which should occur in the region between 500 and 300 cm^{-1}. Therefore, it is rather difficult to gain useful information from a study of the far-infrared spectra of these type complexes. A similar conclusion was reached by Chatt and coworkers[13] for the Nujol mull spectra of several dinitrogen–osmium complexes observed in the far-infrared region.

Conclusions

Data from infrared intensity measurements, as contrast with relative infrared frequency shifts of ν_{N_2} and ν_{CO} in metal dinitrogen and analogous metal carbonyl complexes, correlate exceeding well with other observations, such as Mössbauer studies, stability and reactivity studies, and molecular orbital calculations. All of these studies indicate the metal–N_2 bond to be less stable than the metal–CO bond in analogous complexes. However, the decrease in ν_{N_2} or μ'_{OsN_2} in a series of dinitrogen complexes can be attributed to differences in the stabilities of the Os–N_2 bonds.

Acknowledgments.—The author is most grateful to Professor Fred Basolo for making his article available prior to publication and for the gift of several dinitrogen complexes. He also thanks the Petroleum Research Fund administered by the American Chemical Society for Grant 1705-G3 which supported this research.

(22) A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

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The Ion Dihydridobis(ethylenediamine)osmium(IV)

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Reduction by zinc amalgam of an acidic solution containing $[OsO_2(en)_2]Cl_2$ leads to the formation in high yield of a salt having the composition $[OsH_2(en)_2]ZnCl_4$. Investigation of solutions by nmr shows two hydride hydrogens to be present for each osmium, and the structure of the part of the nmr spectrum attributable to the methylene protons of the coordinated amines suggests that the hydrides occupy cis positions. The hydrides are readily exchangeable for deuterium in an acidic solution in D_2O. In strongly basic solution, there is a shift in the nmr absorption but no change in the number of hydridic protons. The most likely explanation of the shift is that coordinated NH_2 is partly converted to NH^- by strong base. Three equivalents of iodine is consumed per mole of $OsH_2(en)_2^{2+}$ producing Os in the oxidation state 3+. The hydride does not produce Os(II) from Os(III) when mixed with it in equivalent amount.

Introduction

The reduction of $Os(NH_3)_6^{3+}$ to the dipositive state is known to be difficult.[2] The production of Os(II) in an environment of saturated ligands was of particular interest to us in our studies of the chemistry of N_2 as a ligand. Relying on experience with Ru,[3] which showed that the aquo ion is more easily reduced than the ammine, we turned to the reduction of the ion $OsO_2(en)_2^{2+}$ which is expected to form $Os(OH_2)_2(en)_2^{2+}$ when it is reduced to the 2+ state. Reduction of $OsO_2(en)_2^{2+}$ does take place, but instead of Os(II) being formed, the new species $OsH_2(en)_2^{2+}$ was encountered, where the protons shown are to be regarded as hydridic. Though in terms of its general composition the new ion is bracketed by $RhH_2(en)_2^{+}$ [4] on the one hand (metal in lower oxidation state) and ReH_7^{2-} and TeH_9^{2-} [5] on the other (metal in higher oxidation state and hydrogen: metal ratio higher), metal hydrides having only saturated amine ligands are rare enough to justify the description of the preparation and properties of this new ion being offered in this paper. In particular, it should be noted that all osmium hydrides thus far reported[6a] contain some unsaturated ligands.[6b]

Experimental Section

Only preparations of solid compounds will be dealt with in this section. The methods used for characterization of the ion were standard ones, and do not require discussion apart from that which is appropriate to the presentation of results in the next section.

$[OsO_2(en)_2]Cl_2$.—This compound has not heretofore been described. It was obtained by analogy with Gibbs' synthesis of $[OsO_2(NH_3)_4]Cl_2$.[7] In a typical preparation, a solution of 2.07 g of $K_2[OsO_2(OH)_4]$ dissolved in the minimum amount of water was added dropwise to a minimum volume aqueous solution containing 4 g of en·2HCl. The sparingly soluble product precipitated during this process. After filtration, a first crop (1.97 g) of crude $[OsO_2(en)_2]Cl_2$ was obtained, which was a dull yellow-orange product. By addition of sodium salts of Br^-, I^-, ClO_4^-, or tosylate, the osmyl salts of those anions were easily prepared from solutions of the chloride salt. *Anal.* Calcd for $[OsO_2(en)_2]Cl_2$: N, 13.61; H, 3.87; Cl, 17.2. Found: N, 13.4; H, 3.90; Cl, 17.3. Calcd for $[OsO_2(en)_2](ClO_4)_2$: C, 8.88; N, 10.4; H, 2.98; Cl, 13.1. Found: C, 8.76; N, 10.5; H, 2.82; Cl, 12.9. Potassium osmate, $K_2[OsO_2(OH)_4]$, was prepared by

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(1) National Academy of Sciences Overseas Research Fellow, University of São Paulo, Sao Paulo, Brazil, 1970–1972.

(2) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, p 88.

(3) (a) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); (b) R. E. Mercer and R. E. Buckley, *ibid.*, **4**, 1093 (1965).

(4) J. A. Osborne, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 3168 (1964); R. D. Gillard and G. Wilkinson, *ibid.*, 3594 (1963).

(5) A. P. Ginsberg and C. R. Sprinkle, *Inorg. Chem.*, **8**, 2212 (1969); A. P. Ginsberg, *ibid.*, **3**, 567 (1964).

(6) (a) See, for example, J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 6017 (1963); L. Vaska, *Inorg. Nucl. Chem. Lett.*, **1**, 89 (1965); W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, Chapter 3. (b) Phosphines are included among unsaturated ligands because they have the capacity to function as π acids, but we take no position on the question of the extent to which they function in this role in the combinations under consideration.

(7) L. Gibbs, *Amer. J. Chem.*, **3**, 233 (1881); L. Wintrebert, *Ann. Chim. Phys.*, **28**, 15 (1903).