

mine whether a particular dimer has an oxy- or a hydroxy-bridged structure.

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Infrared Intensities of the Molecular Nitrogen and Carbonyl Stretching Vibrations in Iridium(I) Complexes

Sir:

Since the discovery of the first transition metal-molecular nitrogen compound¹ there has been a considerable amount of discussion concerning the nature of the metal-nitrogen bond.²⁻⁵ In order to gain further insight into the nature of this bonding we have undertaken spectroscopic studies of comparable molecular nitrogen and carbonyl compounds.

We report here our initial investigation containing integrated infrared intensity data for the compounds $\text{Ir}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Cl}$ and $\text{Ir}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Cl}$.

Procedure.—Chlorocarbonylbis(triphenylphosphine)iridium(I) and chloronitrogenbis(triphenylphosphine)iridium(I) were obtained from Strem Chemicals Inc. as pure crystalline compounds. This was confirmed by C, H, and N analysis and by melting point data. Spectroscopic grade chloroform was used without further treatment. Samples were prepared by weighing out the solid material on a Cahn electrobalance to ± 0.01 mg. The solids were then added to volumetric flasks of appropriate size and the flasks were accurately filled with solvent. Linear Beer's law plots were observed. Spectra were obtained as soon as possible after complete dissolution of compounds, usually within 5–10 min. It was found that the nitrogen complex decomposed in solution under the conditions at which the spectra were observed to the extent of 18% during the course of a spectral measurement, whereas the carbonyl analog decomposed by only 5%. All intensity measurements reported are corrected for these effects.

Infrared spectral measurements were made on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. The spectral slit width of the instrument was 1.75 cm^{-1} . Recording was at a rate of approximately $10 \text{ cm}^{-1}/\text{min}$ on an expanded scale. Proper attention to double-beam bal-

ancing, zero transmission setting, etc., was emphasized. Sodium chloride cells (1 mm) calibrated by the interference fringe technique were employed in the measurements.

The areas under the bands were determined with a planimeter. In some cases, Simpson's rule was applied in determining the integrated absorbance which gave good agreement with values obtained by direct planimeter measurements. Intensities were determined at a number of concentrations and extrapolated

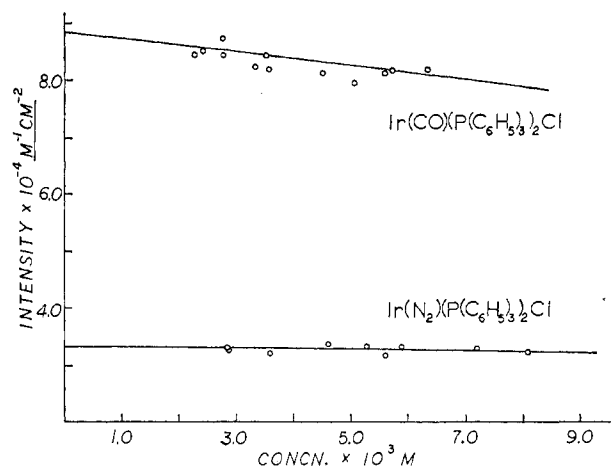


Figure 1.—Intensity vs. concentration for the N_2 and CO vibrational modes in the respective Ir(I) complexes.

to zero concentration (Figure 1). Data were analyzed by the linear least-squares method.

Results and Discussion.—On the basis of infrared frequency shifts (coordinated ligand vs. free ligand) it is evident that the infrared frequency properties of the N_2 and CO complexes are very similar when the groups are bound to identical iridium(I) species ($\Delta\nu_{\text{N}_2} = 221 \text{ cm}^{-1}$ and $\Delta\nu_{\text{CO}} = 178 \text{ cm}^{-1}$). Collman, *et al.*,³ have interpreted these shifts as meaning that N_2 is a better π^* acceptor than CO . This is unexpected since the $2p\pi^*$ orbitals of N_2 are at higher energy than those of CO . Also, in CO the π^* orbital is derived from about 68% carbon $2p$ orbital^{6,7} thereby resulting in better overlap with the metal's d orbitals than would the corresponding π^* orbitals on N_2 which employ equally populated $2p$ orbitals. Indeed, the difference in the metal-ligand bond is reflected in the thermal stabilities of the two complexes, the nitrogen complex being considerably more unstable.

Chatt and coworkers⁴ attributed this discrepancy between infrared results and stability mainly to nitrogen's poor σ -donor property as compared with CO , since these frequency shifts are a complex function of both the σ and π properties of the ligand. Purcell concluded, on the basis of overlap populations, the π^* orbitals on N_2 are more destabilizing to the $\text{N}\equiv\text{N}$ bond than those of CO are to the $\text{C}\equiv\text{O}$ bond.⁵ That is, in the instance of equal population of N_2 and CO π^* orbitals, the decrease in N_2 π overlap population will be greater than that of

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CO, thereby leading to a larger frequency shift in the nitrogen complex. Therefore, it is not necessary for the π^* -acceptor ability of N_2 to be greater than that of CO in order for a larger frequency shift to occur.

It is quite apparent from this discussion that frequency values alone cannot lead to meaningful conclusions as to the relative π^* -acceptor ability of the N_2 and CO groupings.

Integrated infrared intensity measurements of the CO stretching vibrations in transition metal-carbonyl and carbonyl-nitrosyl complexes have provided additional information on the electronic character of the bonded CO group.⁸⁻¹⁹ The intensities have been shown to be highly dependent on the π -electron density in the M-CO bond.^{14,17} In nitrosyl-carbonyl complexes the N-O stretching vibration has a higher intensity value than does the corresponding carbonyl vibration.¹⁹ This is the order expected from the greater π^* -acceptor ability of NO as compared to CO.

Due to the great similarity between the M-CO and M-NN bonds, we propose to assess the relative extent of π -electron delocalization on the basis of intensity measurements. These results are shown in Table I. It is easily seen that unlike the frequency measurements there are significant differences between

the integrated infrared intensities in comparable CO and N_2 compounds.

The dipole moment derivatives were calculated as previously described¹⁴ using the equation

$$I = G_{tt}\mu'_{ML}{}^2 \quad (1)$$

where I is the measured intensity $\times 10^{-4}$, G_{tt} equals the inverse mass of a CO or N_2 grouping, and μ'_{ML} is the respective change in group dipole moment with symmetry coordinates. The μ'_{MCO} compares closely with those found in molybdenum (9.00), cobalt (7.56), and iron (7.74) substituted carbonyl compounds.^{17,18} However, the μ'_{MNN} value is considerably smaller than any of these.²⁰ This may be taken as direct evidence that the acceptor ability of the N_2 π^* orbital is much less than that of CO.

Inasmuch as the CO molecule is a stronger base than N_2 , any increase in the base strength of N_2 when bound to a metal over that of CO would have to result from a greater π -acceptor ability of the N_2 molecule. Since we conclude that N_2 is a weaker π acceptor than CO, it necessarily follows that the N_2 σ -donor strength must also be considerably less than that of CO.

These results demonstrate the utility of integrated infrared intensity measurements in assessing π -electronic delocalization in transition metal-molecular nitrogen compounds. A limitation not encountered in frequency measurements is the availability of pure molecular nitrogen complexes, essential for accurate measurements. We are presently attempting to study other complexes of N_2 in order to extend this initial exploration.

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(20) We have considered here ν_{CO} and ν_{N_2} to be "pure" vibrations. Strictly speaking, this is not true; however, due to the large energy separation between these vibrations and other skeletal vibrations in the molecule, this is not at all a bad assumption. The far-infrared spectra in $CHCl_3$ solution observed between 600 and 250 cm^{-1} were found to be practically superimposable for the two compounds. Any coupling would be more pronounced in the CO complex since ν_{CO} is closer in energy to the other vibrations and would thereby be coupling more strongly. The net result would be a decrease in the CO intensity measured, leading to an even greater difference between μ_{MCO} and μ_{MNN} .

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TABLE I

FREQUENCIES, BAND HALF-WIDTHS, INTENSITIES, AND CALCULATED DIPOLE MOMENT DERIVATIVES FOR N_2 AND CO COMPLEXES OF Ir(I)

ν , cm^{-1}	2109 ± 1	1965 ± 1
$\Delta\nu_{1/2}$, cm^{-1}	24 ± 1	27 ± 1
I , $M^{-1} cm^{-2}$	$(3.29 \pm 0.06) \times 10^4$	$(8.82 \pm 0.12) \times 10^4$
μ'_{ML} ^b	4.80	7.78

^a Defined as $(2.303/cl) \int_{\text{band}} \log(I_0/I) d\nu$, where c equals the concentration in moles per liter and l equals the cell path length in centimeters. The errors listed are the standard deviations from least-squares analyses of the intensity vs. concentration plots. ^b The μ'_{ML} 's are effective group dipole moment derivatives which involve both MC or MN and CO or NN stretching motions.¹⁴ The units employed here are arbitrary; the intensities are expressed in units of $10^4 M^{-1} cm^{-2}$, and the G terms are based on atomic mass units.

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