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Correlation between the Stretching Frequency and the Absolute Infrared Intensity of the Dinitrogen Ligand in Isoelectronic Transition Metal Compounds

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Previously we have shown the usefulness of integrated infrared intensity measurements of the ν_{N_2} vibration in assessing π electronic delocalization in transition metal molecular nitrogen compounds.[1,2] An extension of these studies to include absolute infrared intensity measurements of the dinitrogen stretching vibration in $Re(Ph_2PCH_2CH_2PPh_2)_2(N_2)Cl$, $Re(Me_2PhP)_4(N_2)Cl$, and *trans*-$M(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$ (M = Mo and W) is reported here. These compounds are of particular interest since they contain some of the lowest N_2 stretching frequencies observed to date for transition metal–dinitrogen species. In fact, the N_2 moiety in $Re(Me_2PhP)_4(N_2)Cl$ has been found to interact with Lewis acids[3,4] (*e.g.*, $TiCl_3 \cdot 3THF$), presumably due to extensive delocalization of π-electronic charge from the transition metal to the dinitrogen ligand.

TABLE I

INFRARED FREQUENCIES, HALF-BANDWIDTHS, EXTINCTION COEFFICIENTS, INTENSITIES, AND GROUP DIPOLE MOMENT DERIVATIVES FOR THE ν_{N_2} VIBRATION IN Re(I), W(0), AND Mo(0) COMPLEXES

Compd	Vib, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	$10^{-2}\varepsilon$,[a] M^{-1} cm^{-1}	$10^{-4}A$,[b] M^{-1} cm^{-2}	μ'_{MN_2}[c]
$Re(Ph_2PCH_2CH_2PPh_2)_2(N_2)Cl$	1971.5 (A_1)	29.4	9.70	8.95 ± 0.11	7.92
$Re(Me_2PhP)_4(N_2)Cl$	1921.0 (A_1)	24.4	13.7	10.8 ± 0.12	8.71
$W(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$	1945.1 (A_{2u})	19.0	35.4	18.9 ± 0.22	8.14
	2007.9 (A_{1g})	(19.0)	(1.9)	(1.0 ± 0.10)[d]	
$Mo(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$	1973.5 (A_{2u})	19.7	34.0	19.4 ± 0.15	8.24
	2038.6 (A_{1g})	(19.2)	(4.2)	(2.3 ± 0.10)[d]	

[a] Obtained from the least-squares slope of absorbance *vs.* concentration plots. [b] Defined as $(2.303/cl) \int \log (I_0/I)\, d\nu$, 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. [c] These are calculated as described in ref 1 with an additional factor of 2 in the equation for the bis-dinitrogen complexes of molybdenum and tungsten, *i.e.*, $I = 2G_{tt}\mu'_{MN_2}{}^2$. [d] The intensity of the A_{1g} vibration (infrared forbidden) is presumably borrowed from the A_{2u} species mode. Including this intensity in the A_{2u} mode will not alter the correlation between ν_{N_2} and intensity significantly.

Experimental Section

$Re(Ph_2PCH_2CH_2PPh_2)_2(N_2)Cl$ and $Re(Me_2PhP)_4(N_2)Cl$ were synthesized and purified by the method of Chatt and co-workers.[5] *Anal.* Calcd for $Re(Ph_2PCH_2CH_2PPh_2)_2(N_2)Cl$: C, 59.7; H, 4.6; N, 2.7. Found: C, 59.85; H, 4.76; N, 2.81. Calcd for $Re(Me_2PhP)_4(N_2)Cl$: C, 48.0; H, 5.5; N, 3.5. Found: C, 48.20; H, 5.63; N, 3.86. The *trans*-$M(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$, where M = Mo and W, were generous gifts of Dr. R. L. Richards. These gave the following analyses. Calcd for $Mo(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$: C, 65.8; H, 5.09; N, 5.90. Found: C, 65.73; H, 5.17; N, 6.01. Calcd for $W(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$: C, 60.24; H, 4.66; N, 5.40. Found: C, 60.13; H, 4.72; N, 5.53.

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

Infrared spectra were measured on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. Spectra of the Re(I) complexes were determined in spectrograde chloroform; however, because of their reactivity with halogenated solvents, spectra of the W(0) and Mo(0) complexes were determined in spectrograde carbon disulfide.

Results and Discussion

The results of intensity studies on the Re(I), W(0), and Mo(0) complexes are given in Table I and the data are plotted in Figure 1. A linear relationship between ν_{N_2} or the force constant[6-8] and the absolute intensity (A) in these and isoelectronic Os(II) complexes has been established. The least-squares line for all the points thus far determined for the isoelectronic series of Os(II), Re(I), and W(0) compounds may be expressed as ν_{N_2} (cm^{-1}) = $2298.9 - 3.61 \times 10^{-3}A$, with a standard deviation (σ) of 8.9 cm^{-1}, or as k_{N_2} (mdyn/Å) = $21.29 - 5.66 \times 10^{-3}A$, with a σ value of 0.12 mdyn/Å.

The qualitative relationship between ν_{N_2} or k_{N_2} and the absolute intensity can be thought of in the same manner as that proposed for metal carbonyls with ν_{CO} less than 2143 cm^{-1}.[9] That is, the infrared intensity of the dinitrogen stretching vibration is largely determined by the extent of π-electronic charge transferred from the transition metal to the dinitrogen ligand during the N_2 stretching motion.

This is indeed substantiated by the significant effect of a change in nuclear charge of the central metal in a closely related isoelectronic series in which the intensity increases as the nuclear charge decreases.[10] The extent

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(6) The force constants were calculated assuming no interaction between the N_2 stretching mode and other deformations of the molecule. In the mono-dinitrogen complexes the force constant is therefore simply proportional to the square of the frequency, *i.e.*, $4\pi^2c^2\nu^2 = \mu_{N_2}k_{N_2}$, where μ_{N_2} is the reciprocal of the reduced mass of the N_2 group. However, for the bis-dinitrogen species an interaction constant (k_i) for the trans N_2 groups is necessary. This leads to the expressions[7] $\lambda_{A_{1g}} = 4\pi^2c^2\nu^2 = \mu_{N_2}(k_{N_2} + k_i)$ and $\lambda_{A_{2u}} = \mu_{N_2}(k_{N_2} - k_i)$. The k_i's are calculated to be 0.55 and 0.53 in the Mo and W derivatives, respectively. It follows that k_{N_2} in these cases is very dependent on the value of the interaction constant. Jones, *et al.*,[8] have shown that the interaction constants in metal carbonyls are extremely sensitive to the force field employed. Therefore, it is felt that the frequency correlation is probably more meaningful although the force constant correlation leads to the same conclusions.

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(10) The intensity of the W(0) complex is somewhat less than might be expected on the basis of this argument. However, in this complex the N_2 ligand is trans to a good π-acceptor ligand, N_2.

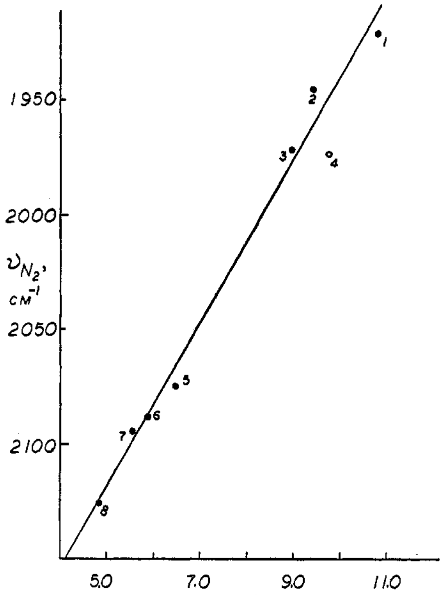

Figure 1.—Correlation of ν_{N_2} and absolute intensity (A). The numbers correspond to the following compounds: 1, $Re(N_2)Cl(Me_2PhP)_4$; 2, $W(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$; 3, $Re(N_2)Cl(Ph_2PCH_2CH_2PPh_2)_2$; 4, $Mo(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$; 5, $Os(N_2)Cl_2(Et_2PhP)_3$; 6, $Os(N_2)Cl_2(Me_2PhP)_3$; 7, $Os(N_2)Br_2(Me_2PhP)_3$; 8, $Os(N_2)Br_2(Me_2PhP)_2P(OMe)_2Ph$. Intensity data for the Os(II) complexes are found in ref 2.

of π bonding from the metal increases with a decrease in nuclear charge in an isoelectronic series. At the same time there is a concomitant decrease in the N_2 stretching frequency. The larger dipole moment derivatives in the Re(I) complexes as compared with those of the Os(II) complexes are in line with the greater stability of the Re(I) species. In addition, the large value for the intensity of the N_2 stretch in $Re(Me_2PhP)_4(N_2)Cl$ is in agreement with the reactivity of the terminal nitrogen of the N_2 ligand toward Lewis acids. Electron emission spectra from the nitrogen 1s orbitals of rhenium(I)–dinitrogen complexes also suggest that the N–N bond has considerable polarity with the terminal nitrogen having a small negative charge. It is also observed in these studies that as the N_2 stretching frequency increases, this polarity of the N–N bond decreases.[11]

It is noteworthy that the intercept ($A = 0$) in Figure 1 lies close to the Raman frequency of free dinitrogen (2330 cm^{-1}).

The above discussion implies that transition metal–molecular nitrogen complexes with large infrared intensity values for the dinitrogen stretching frequency are those most likely to interact with Lewis acids. This type of interaction is expected to be very important in the reduction of the dinitrogen ligand.[3] Indeed, this interaction has been shown to be essential in the reduction of the dinitrogen ligand in cobalt[12] and iron[13] complexes.

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Some Rhodium(III) and Iridium(III) Hydride Complexes Obtained by Protonation with Trifluoroacetic Acid

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Recently our work here has centered around the protonation of zerovalent platinum complexes and in this study we have obtained a hydride from the reaction of $Pt(PPh_3)_4$ with trifluoroacetic acid where the anion is a *dimer* of hydrogen-bonded trifluoroacetate groups.[1] In a related study we have found that the complexes $Pt(MeOPPh_2)_3$ and $Pt(BuOPPh_2)_4$ are also readily protonated by carboxylic acids but that the resulting hydride complexes are difficult to isolate in a pure state.[2] Because of phosphine exchange, several of these hydride complexes showed sharp lines in the ^1H nmr spectrum with no observable J_{P-H} coupling, and we were interested to see if this occurred with alkoxydiphenylphosphine hydride complexes of other transition metals. In this note we report our results on the protonation of the methoxydiphenylphosphinerhodium(I) complex.

Experimental Section

Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz., except for the fluorine analyses which were carried out by A. Bernhardt, Müllheim-Ruhr, Germany. Nuclear magnetic resonance spectra were obtained on a Varian T-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrometer as Nujol mulls. Far-infrared spectra were obtained on a Perkin-Elmer FIS spectrometer as vaseline mulls. Melting points were obtained on a Fischer-Johns apparatus and are uncorrected. Methoxydiphenylphosphine and *n*-butoxydiphenylphosphine were purchased from Arapahoe Chemicals Inc., and platinum metals as chloro salts, from Engelhard Industries Inc. Conductivity measurements were carried out as solutions in nitrobenzene using an Industrial Instruments Model RC 16B2 conductivity bridge. Chlorodicarbonylrhodium(I) dimer[3] and chlorobis(ethylene)rhodium(I) dimer[4] were prepared by previously published methods.

Dihydridocarbonyltris(triphenylphosphine)iridium(III) Hydrogen Bis(trifluoroacetate).—To a solution of hydridocarbonyltris(triphenylphosphine)iridium(I) in CH_2Cl_2 was added excess CF_3COOH. The yellow color of the solution discharged, and the addition of hexane or ether to the concentrated solution gave the *complex* as colorless crystals which were filtered, washed with hexane, and dried *in vacuo*, mp 145°. *Anal.* Calcd for $C_{59}H_{48}F_6IrO_5P_3$: C, 57.3; H, 3.92; F, 9.22; P, 7.52. Found: C, 57.5; H, 3.99; F, 9.26; P, 7.49. ν_{Ir-H} 2170, 2130 cm^{-1}; ν_{C-O} 2025 cm^{-1}; ν_{COO} 1780, 1740 cm^{-1}. The acid proton resonance in nmr is at τ −3.5.

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