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## Force Constants of Coordinated CO and $\beta$ -amino Substituted Isocyanides Using Infrared Spectroscopy

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### Abstract

Metal carbonyls and isocyanides have characteristic peaks in infrared spectra. While the energies are useful in a qualitative determination of relative bond strengths, a more quantitative approach is needed to cross-compare similar complexes. Using a harmonic oscillator approximation, it is possible to determine the effective force constants of carbon-oxygen and carbon-nitrogen bonds. This allowed me to show that negatively charged bis(diphenylphosphinomethyl)diphenylborate used in our laboratory is a better donor than its neutral analogue 1,2-bis(diphenylphosphino)ethane.

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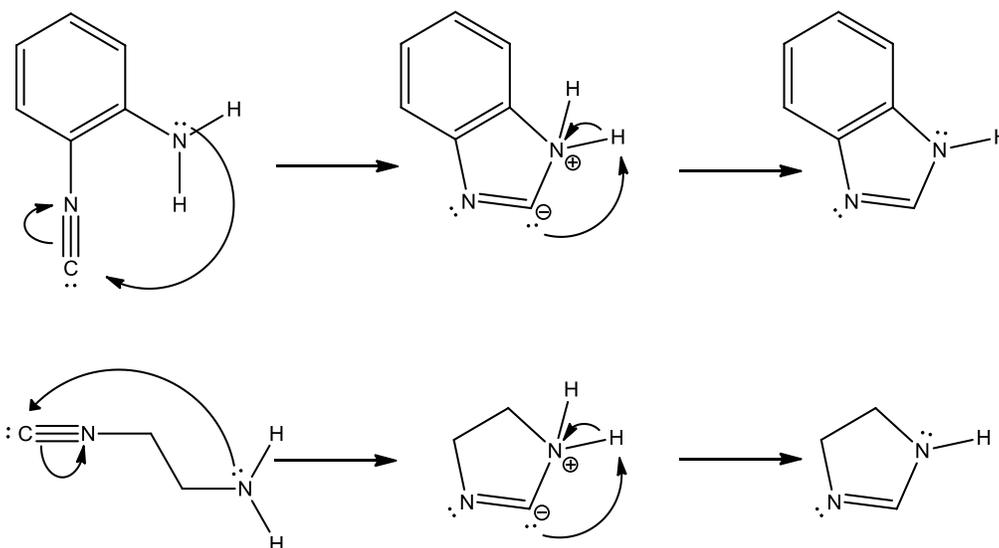
# Force Constants of Coordinated CO and $\beta$ -amino Substituted Isocyanides Using Infrared Spectroscopy

## Cover Page Footnote

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## Introduction

2-amino functionalized isocyanides are neither thermodynamically nor kinetically stable. A heterocyclic product is formed instead via 1,2 - nucleophilic addition of the amino group to the electrophilic isocyanide carbon. For example, 2-aminophenyl isocyanide is not known as free species. It immediately cyclizes to yield benzimidazole similarly as 2-aminoethyl isocyanide that yields 4,5-dihydroimidazole (Scheme 1).



**Scheme 1. Intramolecular cyclization of 2- aminophenyl isocyanide and 2-aminoethyl isocyanide to yield benzimidazole and 4,5 – dihydroimidazole**

However, if  $\beta$ -amino functionalized isocyanides are coordinated onto a sufficiently electron rich metal center, the nucleophilic attack of the amino nitrogen can be prevented because the carbon cannot accommodate the electrons from amino group anymore. Hahn and coworkers showed that zerovalent Mo and

W complexes of neutral 1,2-bis(diphenylphosphino)ethane (dppe) can stabilize  $\beta$ -amino functionalized isocyanides<sup>1</sup>. We became interested in whether additional stability of these complexes could be achieved if an anionic (negatively charged) ligand was coordinated onto the metal, making the metal center more electron rich and enhancing the backbonding effect. The anionic bis(diphenylphosphinomethyl)diphenylborate<sup>2</sup>  $[Ph_2B(CH_2PPh_2)_2]^-$  ligand was chosen. The 5-azonia-spiro[4.4]nonane (ASN) salt of this ligand was reported by J. Peters' group in 2003. Complexes of  $[Ph_2B(CH_2PPh_2)_2]^-$  were shown to have a more electron rich metal center relative to those with neutral bidentate (meaning binds through 2 atoms of the same molecule) phosphine ligands.

Metal carbonyls and isocyanides have characteristic peaks in infrared spectra. This allows chemists to effectively monitor the reaction progress and get important information about structure of the studied molecule. Frequencies in infrared spectra are related to energy that is required to stretch or compress the bonds. This allows for comparison of relative bond strength, however, a more quantitative method is needed to effectively compare different bonds. In 1962 Cotton and Kraihanzel showed that it is possible to determine the stiffness

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<sup>1</sup> Dumke C. A, Pape T., Kösters J., Feldmann K., Schulte to Brinke K., F. Hahn E., *Organometallics*, **2013**, 32 (1), 289-299

<sup>2</sup>Thomas J. C, Peters J. C., *J. Am. Chem. Soc.*, **2003**, 125 (29), 8870-8888

constant in metal carbonyls using the harmonic oscillator approximation<sup>3</sup>. This method has since been used to determine the force constant of other IR active bonds by adjusting the reduced mass<sup>1</sup>.

## Results and Discussion

Molybdenum complexes of bis(diphenylphosphinomethyl)diphenylborate with 2-aminoethyl isocyanide was prepared in our laboratory using similar strategies to Hahn's<sup>4</sup>. Solution infrared spectra were acquired on a Nicolet iS10 spectrometer with samples sealed in 0.1 mm gastight NaCl cells.

Force constants of isocyanides were first found since there is only one C≡N triple bond per each molecule and thus the vibrational mode is simple. It was assumed that interactions of CN stretching with other deformations in the molecule can be neglected. Also no anharmonicity corrections were made. The force constant is related to the vibrational frequency by equation:

$$\omega^2 = \frac{k}{\mu} = \nu^2 \cdot 5.8890 \cdot 10^{-5}$$

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<sup>3</sup> Cotton F. A., Kraihanzel C. S. *J. Am. Chem. Soc.*, **1962**, 84, 4432-4438

<sup>4</sup> Fischer P. J.; Avena L.; Bohrmann T. D.; Neary M. C.; Putka G. K.; Sullivan K. P. *Organometallics*, **2014**, 33, 1300-1309

Where  $k$  is the force constant (N/m),  $\mu$  is the reduced mass (amu) and  $\nu$  is the frequency read from the IR spectra in wavenumbers. The correction constant is needed to take care of unit differences.

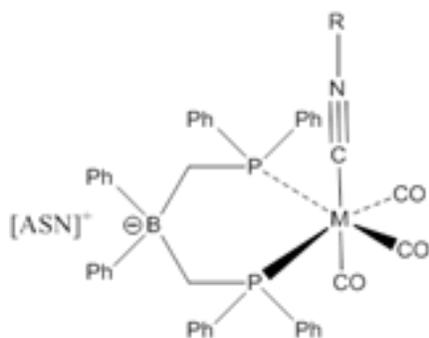
Calculations of force constants for coordinated carbon monoxide ( $\text{C}\equiv\text{O}$ ) ligands are more complicated since there are three such ligands per molecule and thus the stretching modes are more complicated. Additionally, a positive correction factor  $k_c$  has to be introduced due to the stretch-stretch interactions. The reason for this is that as a CO bond is stretched, the  $\pi$  bonding within it is weakened (there are 2  $\pi$  bonds and 1  $\sigma$  bond in every triple bond) and the  $\pi$  antibonding orbital drops in energy so that it more nearly matches the energy of the metal  $d\pi$  orbitals. This causes increased metal-CO  $\pi$  interaction resulting in a drift of  $d\pi$  electrons to this MCO grouping and decreasing the availability of these electrons for M-C  $\pi$  bonding in the other MCO groups of the molecule. This in turn permits the carbon  $p\pi$  orbitals in these other CO groups to participate more fully in CO  $\pi$  bonding which strengthens the other CO bonds and increases their resistance to stretching.

Methods of group theory have to be implemented to determine the number and symmetry of IR active stretching modes<sup>5</sup>. For analysis of the symmetry of metal carbonyls it is often beneficial to focus on the metal-carbonyl part only. The molecules of interest in this project all have slightly distorted octahedral geometry

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<sup>5</sup> For details on application of group theory in inorganic chemistry see Miessler, Gary L., Paul J. Fischer, and Donald A. Tarr. *Inorganic Chemistry*. N.p.: Prentice Hall, 2013. Print

with all three CO's on the face of octahedron based on single crystal X-ray analysis. This corresponds to  $C_{3v}$  symmetry group that has two IR active modes –  $A_1$  and  $E^{3,5}$ .



**Figure 1. Schematic drawing of the octahedral molecules prepared and studied in this project. Three CO ligands are on the face of the octahedron thus corresponding to  $C_{3v}$  symmetry group.**

Symmetries of the vibrational modes can also be found using group theory<sup>5</sup>. The vibrational mode that corresponds to  $A_1$  symmetry in these molecules is just a simple symmetric stretching of all three CO bonds. The mode that corresponds to E symmetry is a little more complicated – one of the bonds is stretching twice as much as the other two are compressing. With the knowledge of the symmetries of the stretching modes one can easily write the equations that describe the vibrational frequency:

$$A_1 : \omega^2 = \frac{k+2k_c}{\mu}$$

$$E: \omega^2 = \frac{k-k_c}{\mu}$$

With this information we have all the tools needed to solve for the force constants of CN and CO bonds in complexes prepared in our research laboratory and by Hahn. Table 1 summarizes the results.

$\nu$ (CN), $\text{cm}^{-1}$	2026 (w)	2097 (m)	2093 (m)
$k$ (CN), N/m	1629	1675	1668
$\nu$ (CO), $\text{cm}^{-1}$	1918 (s) 1829 (s)	1927 (s) 1831 (s)	1926 (s) 1838 (s)
$k$ (CO), N/m	1396	1403	1409
$k_c$ , N/m	45	49	45

**Table 1. Summary of frequencies and force constants of CO and CN bonds.**

## Conclusions

The metal framework with anionic bis(diphenylphosphinomethyl)diphenylborate has enough electron density on the metal center to stabilize  $\beta$ -amino substituted isocyanides, however, IR data alone are not conclusive enough to prove that the CO and CN bonds were noticeably weaker. To get a more quantitative insight force constants of the bonds were calculated using harmonic oscillator approximation. The calculations clearly show

that the force constants of our molecules are smaller than the ones prepared by Hahn. This means that the metal center in complexes of the anionic bis(diphenylphosphinomethyl)diphenylborate has a higher electron density than the ones of 1,2-bis(diphenylphosphino)ethane and thus are able to donate more into the  $\pi$ -antibonding system of carbonyls and isocyanides. More work could be done in future to find out the limits of the force constant needed prevent the intramolecular cyclization of  $\beta$ -amino substituted isocyanides.