

# Molecular Orbital Calculations on the Interaction of Ni and Cu Atoms with PN

H. Itoh \* and G. Ertl

Institut für Physikalische Chemie, Universität München

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Ab initio MO calculations for PN predict a pronounced electron transfer from the P to the N atom. Only very weak interactions result for M-PN ( $M = \text{Ni, Cu}$ ) configurations whereas bond formation is predicted if the N atom couples to the metal. The bond strength for Ni (10.5 kcal/mole) is about twice as large as for the Cu-NP complex (4.6 kcal/mole). Coupling occurs mainly with the  $7\sigma$ -level (HOMO) of the ligand whose energy is lowered below that of the  $2\pi$ -level.

## 1. Introduction

A large variety of thermally unstable complex compounds between transition metal atoms and diatomic ligands such as CO,  $\text{N}_2$  or  $\text{O}_2$  has become experimentally accessible by the matrix isolation technique [1]. An interesting candidate of this class is PN for which some evidence (based on IR studies) for complex formation with group Ib (Cu, Ag, Au) and VIII metals (Co, Ni, Pd) has been reported by Atkins and Timms [2]. By analogy with  $\text{N}_2$ -complexes [3] it is quite likely that the ligand is attached in "end-on" configuration, but so far it is unclear whether bond formation occurs through the P or the N atom (i. e. M-PN or M-NP). The aim of the present work is to give an answer to this question on the basis of theoretical calculations for M-L ( $M = \text{Ni, Cu}$ ) for both structures.

Possible analogies can be found in the literature by comparing results for  $\text{PH}_3$  and  $\text{NH}_3$ : An ab initio calculation for Li [4] showed that the bond strength is much larger with  $\text{NH}_3$  (0.63 eV at an equilibrium distance  $r_{\text{eq}} = 2.07 \text{ \AA}$ ) than with  $\text{PH}_3$  (0.02 eV at  $r_{\text{eq}} = 3.03 \text{ \AA}$ ). This result suggests that PN might be bonded through the N atom which will indeed be confirmed by the present work. The quoted data for Li- $\text{NH}_3$  are very similar to those obtained for Ni- $\text{NH}_3$  by the present authors [5] ( $E_b = 0.65 \text{ eV}$  at  $r_{\text{eq}} = 2.12 \text{ \AA}$ ) which provides some confidence in the applied method.

\* Present address: Laboratory of Catalysis, Institute of Physical and Chemical Research, Wako-Shi, 351, Japan.

Reprint requests to Prof. G. Ertl, Institut für Physikalische Chemie der Universität München, Sophienstraße 11, 8000 München 2.

## 2. Method and Model

The calculations were performed by the restricted Hartree-Fock (HF) theory. The Ne core of the P atom and the Ar cores of the Ni and Cu atoms were replaced by their effective potentials [6]. Single zeta basis sets for P and N were taken from Refs. [7] and [8], respectively.  $[2s1p2d]$  basis sets for the metal atoms (M) were used according to Wachters and Hay [9, 10]. The 4s and 3d functions were composed of 4 and 6 primitives, respectively. Contraction coefficients were determined by HF calculations for the metal atoms with  $3d^n - 14s^1$  electron configurations. The basis sets for the N and metal atoms were the same as those used in previous work [5].

Two linear configurations, M-PN and M-NP, were considered, as already mentioned. The P-N distance was held fixed at the experimental value of the free molecule (1.491 Å) [11], whereas the M-L distance was optimized to within  $\pm 0.01 \text{ \AA}$ . In addition, some preliminary results for Ni- $\text{PH}_3$  will be presented in order to obtain some further insight into the difference of the binding properties between N and P.

## 3. Results and Discussion

Table 1 compares the calculated orbital energies for free PN with its experimentally obtained negative ionisation potentials [12]. Because of the use of Koopmans' theorem (i. e. neglect of relaxation energies) the theoretical values are too low, but show the correct ordering. It should be noted in this context that calculations using double zeta or better basis sets [13] yield the reverse ordering of the

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a) Orbital energies (theory) and negative ionization potentials (experiment [12]) in [eV]:

Level	Theory	Exp.
7σ	− 12.74	− 11.88
2π	− 12.90	− 12.30
6σ	− 18.29	− 15.74
5σ	− 32.00	

b) Electron populations:

P	N
4.532	7.468

Table 1. Data for free PN.

a) Equilibrium distances and bond energies

	Ni-NP	Cu-NP
$r_{eq}$ [Å]	2.13	2.42
$E_b$ [eV]	0.46	0.20

b) Orbital energies [eV]

Level	Ni-NP	Cu-NP
7σ	− 14.64	− 14.21
2π	− 14.40	− 13.90
6σ	− 19.98	− 19.33
5σ	− 33.23	− 32.90

c) Electron populations

	Free PN	Ni-NP	Cu-NP
P	4.532	4.388	4.431
N	7.468	7.473	7.466
M	—	10.140	11.103

Table 3. Calculated results for M-NP.

two highest orbitals, quite similar as in the case of  $N_2$  [14]. This fact is considered as justification for the use of single zeta basis sets.

The electron population analysis shows a pronounced electron transfer ( $0.47 e_0$ ) from P to N from which a rather large dipole moment for the PN molecule is predicted.

Theoretical results for the configurations M-PN and M-NP are listed in Tables 2 and 3, respectively. It is quite evident that coupling of the metal atom to the (positively charged) P atom would yield an almost negligible bond strength. The equilibrium distance would be quite large, and there is almost no influence on the orbital energies and electron populations of the ligand.

By contrast, fairly pronounced interactions result for the structure M-NP, as can be seen from

a) Equilibrium distances and bond energies

	Ni-PN	Cu-PN
$r_{eq}$ [Å]	4.08	4.28
$E_b$ [eV]	0.02	0.01

b) Orbital energies [eV]

Level	Ni-PN	Cu-PN
7σ	− 12.75	− 12.73
2π	− 12.89	− 12.88
6σ	− 18.29	− 18.27
5σ	− 31.99	− 31.98

c) Electron populations

	Ni-PN	Cu-PN
N	7.464	7.466
P	4.541	4.537
M	9.995	10.997

Table 2. Calculated results for M-PN.

Table 3. The bond energy for Ni-NP (10.5 kcal/mole) is about twice as large as for Cu-NP (4.6 kcal/mole) which suggests that stable compounds of this type could be formed at low enough temperatures. Accordingly the Ni-NP distance (2.13 Å) is shorter than that for Cu-NP (2.42 Å). Of course no experimental data for bond lengths in NP-complexes are available. But there exist some data for M-NP<sub>x</sub> compounds in which the M-N distance ranges between 2.0 and 2.4 Å [15–18], which compare qualitatively with the present calculated values. The differences between Ni and Cu are consistent with the electronic properties of these atoms [19]: If the Ni 3d<sup>9</sup>4s<sup>1</sup> and Cu 3d<sup>10</sup>4s<sup>1</sup> configurations are compared it turns out that the 4s<sup>1</sup> orbital energies (− 6.42 and − 6.47 eV respectively) as well as orbital extensions are quite similar, whereas the Ni-3d orbital energy (− 12.44 eV) is about 0.9 eV higher than that for Cu (− 13.35 eV). In addition the 3d-states in Cu are completely occupied. It is therefore concluded that about equal contributions to the coordination bond arise from the 4s-orbitals of Ni and Cu, whereas the Cu 3d-levels exhibit only very small additional contributions in contrast to Ni. These results are quite similar to those obtained by analogous calculations for NH<sub>3</sub> and H<sub>2</sub>O ligands [4]. Also the experimental adsorption energies for PF<sub>3</sub> or CO are about twice as large on Ni than on Cu surfaces [20].

The bond formation involves mainly the HOMO 7σ-level of the ligand which as a consequence is

energetically stabilized and "pulled down" below the  $2\pi$  level as can be seen from Table 3. This level shift arises mainly from interaction with the metal  $4s$ -orbital and is quite analogous to the findings for CO,  $\text{PF}_3$  and  $\text{NH}_3$  ligands [5, 21, 22]. The electron population analysis suggests a slight electron transfer from PN to the metal atom whereby the P atom becomes even more positive, which is again similar to the conclusions reached for  $\text{N-NH}_3$  and  $\text{M-OH}_2$  complexes [4, 5].

The conclusion whereafter a metal atom interacts stronger with N than with P can be generalized if also  $\text{NH}_3$  and  $\text{PH}_3$  are compared: Corresponding results for Li [4] had already been mentioned in

the introduction. Preliminary calculations for  $\text{Ni-PH}_3$  yielded a very small binding energy of 0.02 eV at a bond length of 3.96 Å which has to be compared with the data (0.65 eV and 2.12 Å, respectively) for  $\text{Ni-NH}_3$  [5].

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