

ON THE σ AND π CHARGE TRANSFERS IN Ni(PF₃)₄ AND Ni(PCl₃)₄

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ABSTRACT

A comparative study of the Ni(PF₃)₄ and Ni(PCl₃)₄ complexes has been performed using the SCF-Multiple Scattering X α method. It is found that PCl₃ is a poorer π -acceptor and a somewhat better σ -donor than PF₃. The results are used to provide a quantitative test of the different models for the Ni-P bonding and its dependence on the electronegativity of the phosphorus substituents. The present work brings further support to the hyperconjugation model of the transition metal-P interaction and also is in agreement with the qualitative assumption that the π -acceptor ability parallels the electronegativity of the phosphorus substituents.

1. INTRODUCTION

A recent study of the electronic structure of the tetrakis-trifluorophosphine nickel Ni(PF₃)₄¹ has clearly indicated that the phosphorus 3p orbital is largely involved in the π -back-donation process with a comparatively small participation of the 3d orbital. The main role of the phosphorus 3d orbital is to hybridize with the 3p to give a pd hybrid orbital better suited for electron acceptance from the transition metal. In the present paper our main interest will be the analysis of the relation between the σ and π -bonding in transition metal complexes with substituted phosphines and the electronegativity of these substituents. It has been commonly assumed that the higher the electronegativity of the atoms or groups attached to the phosphorus atom the larger the metal-P π -bonding and the lower the σ -bonding². The increase in the π -bonding is easily related to the larger withdrawal of charge from the phosphorus atom a process which mainly empties the 3p valence shell. Since the π^* acceptor level on phosphorus is essentially of 3p character¹ we must expect an enhancement in its π -electron acceptor ability. A more positive phosphorus atom will in turn retain more strongly its lone pair and as a consequence it will be less available for σ -donation into the metal 3d and/or 4s, 4p shells. In this case, however, the relation with the electronegativity of the phosphorus substituents is not so simple as for the π -bonding and subtle electronic effects such as the interaction between lone and bond pairs in the ligand molecule can indeed alter the expected trends³. The metal \rightarrow P charge transfer through π -back-donation will also partially neutralize the inductive effect of the phosphorus substituents⁴ and the availability of the lone pair for σ -donation will not be reduced to the same extent as it would be in the absence of π -bonding.

As a consequence, σ and π charge shifts should be of about the same magnitude, their absolute value depending on the electronegativity of the atoms linked to the phosphorus. On the basis of this model it would be expected that σ and π charge transfers will both be larger for Ni(PF₃)₄ than for Ni(PCl₃)₄. More recently and based on CNDO calculations⁵ a completely opposite scheme has been proposed, i.e. σ and π bonding would both be less important in Ni(PF₃)₄ than in Ni(PCl₃)₄. It was claimed that a decrease in both σ and π charge transfers with the increase in the electronegativity of the phosphorus substituents could give a satisfactory interpretation of all the physico-chemical quantities in phosphorus complexes⁵. However, IR spectroscopic data clearly indicates that PF₃ is a better π -acceptor than PCl₃⁶. Moreover, experimental data seems also to support that the higher the electronegativity of the phosphorus substituents the smaller the σ charge transfer and the larger the π back-transfer⁶.

The hyperconjugation model of the metal-P π -bonding considers the interaction of the π, π^* pair belonging to the PX₃ (X = F, Cl, etc.) molecule with the metal 3d orbitals¹. The higher the electronegativity of the atoms attached to the phosphorus the lower the 3p character in π and the larger in π^* . For the X character the opposite trend is followed, i.e. larger in π and smaller in π^* . Since this model is primarily intended to give a description of the role of the P 3p orbital in the metal \rightarrow P π -back-donation, no considerations were made about the σ -bonding. In T_d symmetry σ and π levels can mix in t₂, however, they do not do so to any large extent except in the HOMO orbital. As it will be discussed in the next section it seems that the σ -donor properties are mainly depending on the electronic structure of the free ligand molecule rather than on the influence of charge shifts after coordination.

In the present paper we shall describe the results obtained from Multiple Scattering (MS)-X α ⁷ calculations for Ni(PF₃)₄ and Ni(PCl₃)₄. The computational details are the same as in reference 1. A regular T_d symmetry was assumed for both molecules and the PX₃ were kept fixed. For Ni(PF₃)₄ the Ni-P and P-F distances obtained from electron diffraction⁸ were used. For Ni(PCl₃)₄ we have assumed the same Ni-P distance as in Ni(PF₃)₄ and for the P-Cl distance the value corresponding to the free PCl₃ was used. Overlapping atomic spheres were defined following the same criteria as in reference 1. σ and π charge transfers were obtained from the calculated ground state wave function using the techniques previously described^{9,10}. It is found that our results support neither the Chatt⁴ nor the Savariault et al.⁵ schemes. Instead we find that the π -back-donation increases with the electronegativity of the phos-

phorus substituents and the σ -donation decreases. However, the increase in the π -back-donation seems to be larger than the decrease in the σ -bonding. For a given ligand, the extension of both the σ -donation and the π -back-donation are not equivalent, the former being systematically larger. A more detailed discussion will be given in the next section.

In the previous study of the electronic structure of $\text{Ni}(\text{PF}_3)_4$ we have been able to check the correctness of our calculated energy spectrum with the experimental photoelectron spectrum. Unfortunately similar experimental information is not available for $\text{Ni}(\text{PCl}_3)_4$. The MS model has already been applied to a number of transition metal complexes containing π -acceptor ligands and it was found to give results in qualitative and also quanti-

tative agreement with the experiments¹¹. We then can reasonably expect that the present MS calculation will adequately reproduce the main features and the correct trends in the electronic structure of both $\text{Ni}(\text{PF}_3)_4$ and $\text{Ni}(\text{PCl}_3)_4$.

2. THE σ AND π BONDING IN $\text{Ni}(\text{PF}_3)_4$ AND $\text{Ni}(\text{PCl}_3)_4$

The calculated orbital energies, charge densities, and orbital characters for the $\text{Ni}(\text{PF}_3)_4$ and $\text{Ni}(\text{PCl}_3)_4$ complexes are presented in Table I and II, respectively. Electron populations for the Ni 3d, 4s, and 4p valence shells are also given. The number of valence shells in both complexes are, of course, identical, however, some impor-

TABLE I

Orbital energies, Integrated charge density (in % of one electron charge) and orbital characters and electron populations for the Ni atom for $\text{Ni}(\text{PF}_3)_4$.

| ORBITAL | ORBITAL ENERGY (-Ry) | CHARGES IN MUFFIN-TIN SPHERES | | | ELECTRON POPULATION FOR THE Ni ATOM | | | ORBITAL CHARACTER |
|----------------------|----------------------|-------------------------------|-------|-------|-------------------------------------|------|------|---|
| | | Ni | P | F | 4s | 4p | 3d | |
| 9a ₁ | 1.408 | 1.44 | 37.34 | 60.35 | 0.05 | | | PF ₃ 6a ₁ |
| 10a ₁ | 1.062 | 4.62 | 16.68 | 59.11 | 0.18 | | | PF ₃ 7a ₁ |
| 11a ₁ | 0.774 | 19.97 | 27.78 | 37.36 | 0.82 | | | PF ₃ 8a ₁ , Ni 4s |
| 1a ₂ | 0.896 | 0.0 | 0.0 | 89.32 | | | | PF ₃ 1a ₂ |
| 4e | 1.202 | 0.15 | 22.19 | 74.20 | | | 0.00 | PF ₃ 4e |
| 5e | 0.980 | 0.01 | 4.51 | 82.65 | | | 0.00 | PF ₃ 5e |
| 6e | 0.933 | 0.38 | 2.23 | 85.39 | | | 0.01 | PF ₃ 6e |
| 7e | 0.555 | 88.09 | 2.55 | 2.18 | | | 3.68 | Ni 3d |
| 8e | 0.055 | 5.27 | 13.61 | 12.58 | | | 0.31 | PF ₃ 7e, Ni 3d |
| 4t ₁ | 1.203 | 0.02 | 21.32 | 72.59 | | | | PF ₃ 4e |
| 5t ₁ | 0.979 | 0.0 | 4.61 | 83.28 | | | | PF ₃ 5e |
| 6t ₁ | 0.927 | 0.02 | 2.03 | 86.87 | | | | PF ₃ 6e |
| 7t ₁ | 0.901 | 0.0 | 0.04 | 88.58 | | | | PF ₃ 1a ₂ |
| 11t ₂ | 1.365 | 0.81 | 36.19 | 62.68 | | 0.07 | 0.01 | PF ₃ 6a ₁ |
| 12t ₂ | 1.162 | 0.07 | 20.15 | 74.91 | | 0.01 | 0.04 | PF ₃ 4e |
| 13t ₂ | 1.011 | 2.16 | 12.94 | 70.94 | | 0.19 | 0.04 | PF ₃ 7a ₁ |
| 14t ₂ | 0.970 | 0.55 | 3.95 | 81.21 | | 0.00 | 0.02 | PF ₃ 5e |
| 15t ₂ | 0.936 | 0.16 | 1.75 | 84.22 | | 0.02 | 0.00 | PF ₃ 6e |
| 16t ₂ (a) | 0.740 | 35.11 | 32.09 | 24.35 | | 1.04 | 1.49 | PF ₃ 8a ₁ , Ni 3d, 4p |
| 17t ₂ | 0.481 | 57.09 | 13.39 | 7.23 | | 0.98 | 3.49 | Ni 3d, 4p, PF ₃ 8a ₁ , 7e |
| 18t ₂ | 0.106 | 9.83 | 22.29 | 8.32 | | 0.08 | 0.79 | PF ₃ 7e, Ni 3d |
| 19t ₂ | 0.015 | 2.68 | 22.64 | 17.85 | | 0.27 | 0.13 | PF ₃ 9a ₁ |

a) HOMO orbital.

TABLE 2

Orbital energies, Integrated Charge density (in % of one electron charge), orbital characters and electron populations for the Ni atom for Ni(PCl₃)₄.

| ORBITAL | ORBITAL ENERGY (-Ry) | CHARGES IN MUFFIN-TIN SPHERES | | | ELECTRON POPULATION FOR THE Ni ATOM | | | ORBITAL CHARACTER |
|---------------------------------|----------------------|-------------------------------|-------|-------|-------------------------------------|------|------|---|
| | | Ni | P | Cl | 4s | 4p | 3d | |
| 12a ₁ | 1.381 | 5.73 | 40.50 | 45.97 | 0.22 | | | PCl ₃ , 9a ₁ |
| 13a ₁ | 1.019 | 13.41 | 27.28 | 40.56 | 0.57 | | | PCl ₃ , 10a ₁ , Ni 4s |
| 14a ₁ | 0.814 | 9.26 | 10.10 | 67.14 | 0.41 | | | PCl ₃ , 11a ₁ , Ni 4s |
| 15a ₁ | 0.362 | 3.73 | 36.72 | 45.85 | | | | PCl ₃ , 12a ₁ |
| 2a ₂ | 0.759 | 0.0 | 0.0 | 90.45 | | | | PCl ₃ , 2a ₂ |
| 8e | 1.017 | 2.85 | 23.80 | 68.21 | | | 0.08 | PCl ₃ , 8e |
| 9e | 0.841 | 0.14 | 2.28 | 82.40 | | | 0.01 | PCl ₃ , 9e |
| 10e | 0.792 | 30.06 | 2.06 | 58.44 | | | 1.18 | PCl ₃ , 10e, Ni 3d |
| 11e | 0.759 | 57.54 | 0.53 | 35.12 | | | 2.34 | Ni 3d, PCl ₃ , 10e, 11e |
| 12e | 0.200 | 7.23 | 46.28 | 28.14 | | | 0.39 | PCl ₃ , 11e, Ni 3d |
| 9t ₁ | 0.999 | 0.06 | 24.09 | 74.52 | | | | PCl ₃ , 8e |
| 10t ₁ | 0.827 | 0.01 | 1.40 | 84.24 | | | | PCl ₃ , 9e |
| 11t ₁ | 0.788 | 0.0 | 0.70 | 87.65 | | | | PCl ₃ , 10e |
| 12t ₁ | 0.761 | 0.01 | 0.55 | 90.22 | | | | PCl ₃ , 2a ₂ |
| 18t ₂ | 1.331 | 4.23 | 44.24 | 46.57 | | 0.32 | 0.09 | PCl ₃ , 9a ₁ |
| 19t ₂ | 0.983 | 1.04 | 23.50 | 71.63 | | 0.07 | 0.04 | PCl ₃ , 8e |
| 20t ₂ | 0.949 | 29.78 | 28.33 | 32.23 | | 0.75 | 1.36 | PCl ₃ , 10a ₁ , Ni 3d |
| 21t ₂ | 0.868 | 3.87 | 1.42 | 76.83 | | 0.02 | 0.21 | PCl ₃ , 9e |
| 22t ₂ | 0.818 | 5.82 | 1.34 | 78.11 | | 0.0 | 0.34 | PCl ₃ , 10e |
| 23t ₂ | 0.784 | 14.41 | 1.80 | 74.02 | | 0.02 | 0.88 | PCl ₃ , 11a ₁ , Ni 3d |
| 24t ₂ ^(a) | 0.647 | 39.97 | 14.38 | 28.97 | | 1.17 | 2.40 | Ni 3d, 4p, PCl ₃ , 10a ₁ , 11a ₁ , 12e |
| 25t ₂ | 0.330 | 5.67 | 41.40 | 33.58 | | 1.09 | 0.07 | PCl ₃ , 12a ₁ , Ni 4p |
| 26t ₂ | 0.278 | 7.39 | 41.41 | 19.32 | | 0.0 | 0.61 | PCl ₃ , 11e, Ni 3d |

a) HOMO orbital.

tant differences in the ordering and composition of these levels are found. They are essentially due to the larger metal-ligand admixture in Ni(PCl₃)₄: the Ni 3d charge is distributed among the different orbitals belonging to e and t₂ symmetries instead of being concentrated in a few orbitals as in Ni(PF₃)₄. The distribution of the 4s charge among the a₁ orbitals is also different for both complexes. In the trifluoro-phosphine complex the highest a₁ orbital has almost all the 4s charge. In the trichlorophosphine complex the largest fraction of the 4s charge is found in the next-to-highest a₁ orbital and to a less extent in the highest orbital. The 3d and 4p components are also larger for the 20t₂ orbital which corresponds to the PCl₃ 10a₁, and considerably lower (particularly in the case of the 4p component) for the 23t₂ orbital, the PCl₃ 11a₁ level.

These differences between both complexes are easily understood by considering the electronic structure of the free ligand molecules. The PCl₃ valence levels are closer to the Ni valence levels than the PF₃ valence levels and this will facilitate the mixing between Ni and PCl₃ orbitals. On the other hand, the PF₃ 8a₁ level has a strong lone pair character which is almost completely absent from the remaining a₁ orbitals. It is also very high in energy compared with the other valence levels. In PCl₃ the lone pair character is distributed between both the 11a₁ and 10a₁ (highest and next-to-highest, respectively) levels and they also are very close in energy. It is interesting to note that if PF₃ is quite similar to CO as a ligand, PCl₃ can also be considered quite similar to N₂. The total amount of π-back-donated charge is almost the same for Ni(PCl₃)₄ and

Ni(N₂)₄ and most of the 4s and 4p charge is found to be in a MO corresponding to the next-to-highest PCl₃ σ₁ or N₂ σ orbital¹¹. However, this analogy must not be pushed further: the σ-bonding in the N₂ complex is weaker than in the CO while the opposite is true for the PCl₃ and PF₃ complexes.

The net charge in Ni valence shells and the total π-back-donated charge for both e and t₂ symmetries are shown in Table 3.

TABLE 3

Total electronic charge and π-back-donated charge for the Ni atom in Ni(PF₃)₄ and Ni(PCl₃)₄.

| | Ni(PF ₃) ₄ | Ni(PCl ₃) ₄ |
|-----------------------|-----------------------------------|------------------------------------|
| 3s | 1.99 | 1.99 |
| 3p | 5.98 | 5.93 |
| 3d | 8.38 | 8.91 |
| 4s | 1.05 | 1.20 |
| 4p | 2.31 | 2.35 |
| π-back-donated charge | | |
| e | 0.47 | 0.39 |
| t ₂ | 1.15 | 0.68 |
| total | 1.62 | 1.07 |

We have corrected the values obtained before for Ni(PF₃)₄¹ by taking account of the charge in the intersphere region. As was pointed out before¹ the virtual levels are extremely diffuse with a large fraction of their charge lying in the intersphere and outer regions. The values obtained for the π-back-donated charge are thus underestimated particularly for the e symmetry. The values obtained here seems to be more reasonable and the PF₃ results to be a slightly better π-acceptor than the CO itself. This fact is in agreement with the experimental data¹². It is interesting to note that the d-d splitting is larger in Ni(PCl₃)₄ than in Ni(PF₃)₄. This fact seems to be also consistent with the larger π-acceptor ability of PF₃ and agrees with experimental information available for various phosphorus ligands³.

In Ni(PCl₃)₄ as in Ni(PF₃)₄ the π-back-donated charge is going into a predominantly P 3p orbital with a minor 3d component. For the reasons indicated before it is very hard to estimate quantitatively the P 3p and 3d composition of this orbital. Inspection of the coefficients in the corresponding MS wave-function reveals that the 3p

to 3d ratio is larger for Ni(PCl₃)₄ than for Ni(PF₃)₄. Since the 3p component in the trifluorophosphine complex is expected to be larger than in the trichlorophosphine (see below) it is possible to conclude that the 3d component should also be larger for the former. The 3d component in the Ni(PCl₃)₄ LUMO orbital is then expected not to exceed 10% of its total atomic composition.

In Ni(PF₃)₄ the 4e, 4t₁ and 12t₂ MO's correspond to the PF₃ 4e π-orbital. These MO's have 22.19%, 21.30% and 20.15% of total 3p+3d character. In Ni(PCl₃)₄ the 8e, 9t₁ and 19t₂ MO's correspond to the PCl₃ 8e π-orbital and their total P character is 23.80%, 24.09% and 23.50%, respectively. Due to the diffuse nature of the unoccupied levels a similar comparison is not possible for MO's corresponding to the PF₃ and PCl₃ π*-orbitals, however, it is clear that in this case the total P character must be larger for the trifluorophosphine complex. These results give further support to the hyperconjugation model of the Ni-P π-bonding¹.

The σ-donation into the metal 4s and 4p shells is more important for Ni(PCl₃)₄ than for Ni(PF₃)₄. In a given complex the σ-bonding is considerably larger than the π-back-bonding. This is consistent with previous results for the Ni tetracarbonyl and tetradinitrogen complexes¹⁰. On the other hand, one can be surprised for the large values obtained in our calculations for both 4s and 4p occupancies. The net charge on the Ni atom is found to be very large and negative. However, this is not true: the calculated 4s and 4p charge is not really lying on the Ni atom but is largely delocalized on the ligand region (figure 7 in reference 10). More realistic 4s and 4p atomic occupancies can be calculated¹¹ and we still get a slightly negative charge on the transition metal atom. The π-back-donation is also probably overestimated in MS calculations mainly as a consequence of the use of a local exchange potential¹³. All this seems to indicate that the ligand to metal σ-donation is the most important contribution to the stability of the bond. Since the difference between σ and π charge transfers tends to be lower as the electronegativity of the phosphorus substituents increases, the net charge on the transition metal atom will be less negative in the same direction.

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