

An Extension of the CNDO/2 Formalism for the Study of Transition Metal Complexes

III. $\text{Cr}(\text{PF}_3)_6$ and $\text{Fe}(\text{PF}_3)_5$

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A previously described extended CNDO/2 method is used for investigating the energy level distribution and electronic structure of trifluorophosphine metal complexes: $\text{Cr}(\text{PF}_3)_6$, $\text{Fe}(\text{PF}_3)_5$, $\text{Ni}(\text{PF}_3)_4$. The results are compared with the few experimental data which are known for these complexes. The metal-phosphorus bonds show large $\sigma(\text{P} \rightarrow \text{M})$ and $\pi(\text{M} \rightarrow \text{P})$ charge transfers but small *total* charge transfers ($\text{M} \rightarrow \text{P}$) which induce on the metal in any case a small *positive* charge.

Such ($\sigma + \pi$) coordination bonds seem to be generally characterized by small bond overlap populations (or small Wiberg indices).

Key words: Transition metal - $\text{Cr}(\text{PF}_3)_6$ - $\text{Fe}(\text{PF}_3)_5$ - Extended CNDO/2

1. Introduction

An extended CNDO/2 method was previously proposed for investigating the electronic structure of some transition metal complexes in the ground state: $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{PF}_3)_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ [1, 2]. The values of the β parameters and α exponents for the $4s$, $4p$ and $3d$ orbitals were fitted to the results of *ab initio* calculations of the energy level distributions and electronic structures which were available for three of these complexes [3-5]. Moreover a good agreement between experimental data (as provided by photoelectron spectroscopy, IR spectroscopy, thermodynamics, etc. . .) and the corresponding calculated quantities have been observed.

The purpose of this work is to test the validity of our method with its original parametrization for the study of the trifluorophosphine metal complexes $\text{Cr}(\text{PF}_3)_6$, $\text{Fe}(\text{PF}_3)_5$ - for which no *ab initio* calculations suitable for use as standards have been made - in order to interpret the physical and chemical behaviour of these molecules.

2. Molecular Geometry and Conformational Analysis

The metal-phosphorus bond lengths in $\text{Cr}(\text{PF}_3)_6$ and $\text{Fe}(\text{PF}_3)_5$ being unknown, the following distances were assumed: $d(\text{Cr}-\text{P}) = 2.35 \text{ \AA}$ and $d(\text{Fe}-\text{P}) = 2.23 \text{ \AA}$, based on the values

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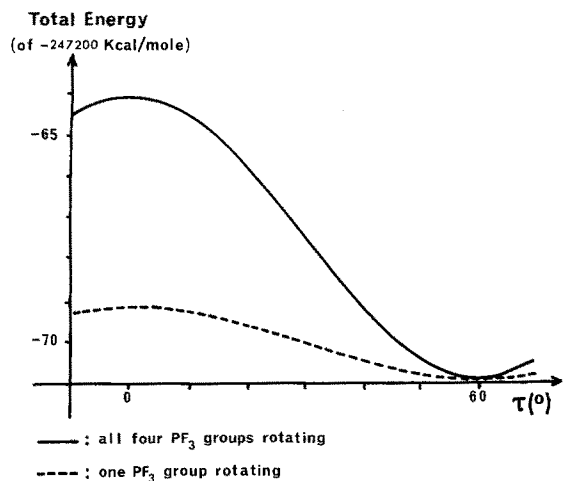


Fig. 1

observed for these bond lengths in similar complexes [6]. The P-F bond length, $d(\text{P-F}) = 1.561 \text{ \AA}$, and $\angle \text{FPF} = 98.4^\circ$ angle as measured in $\text{Ni}(\text{PF}_3)_4$ [7, 8] were kept constant and used for the chromium and iron complexes. This assumption is supported by the minor changes observed in the photoelectron spectra of these three complexes for the bonds relative to the PF_3 groups [9, 10]. The geometrical parameters for free PF_3 were taken as $d(\text{P-F}) = 1.569 \text{ \AA}$, $\angle \text{FPF} = 97.5^\circ$ [11].

In $\text{Ni}(\text{PF}_3)_4$, Almenningen fitted the experimental electron diffraction data by assuming that the PF_3 groups were freely rotating [7], while Marriott found a preferred conformation with a torsional angle $\tau = 40^\circ$ [8] ($\tau = 0^\circ$ when the P-F bonds of one PF_3 group are in an eclipsed conformation with respect to the Ni-P bonds linking nickel to the three other PF_3 groups). Using $d(\text{Ni-P}) = 2.099 \text{ \AA}$ [7], our calculations lead to a minimum of the total energy for $\tau = 60^\circ$ (Fig. 1). The electronic structure of this staggered conformation has been partly published [2]. We may however stress that the difference of energy between these eclipsed and staggered forms is 6.8 kcal/mole, that is four times the 1.7 kcal/mole value, calculated when only one PF_3 group is rotated. This shows that there is no interaction between the rotations of the different PF_3 groups. The rather low value for such a rotational barrier indicates that the PF_3 groups in $\text{Ni}(\text{PF}_3)_4$ are practically freely rotating. Moreover, a statistical analysis of the number of PF_3 groups characterized by a torsional angle τ as a function of the energy of the corresponding conformation, leads to a "most probable" model in which $\tau = 40^\circ$. As electron diffraction is known to determine only average interatomic distances, the last model is then in very good agreement with the "conformation" proposed by Marriott but it is not surprising that Almenningen had found that the PF_3 groups were freely rotating.

As for $\text{Fe}(\text{PF}_3)_5$, our calculations indicate that the equatorial PF_3 groups are freely rotating (rotational barrier ≈ 0.3 kcal/mole) while the axial PF_3 groups are staggered with respect to the equatorial Fe-P bonds ($\tau = 60^\circ$), the eclipsed/staggered gap of energy being equal to 8 kcal/mole. It may be noted that only one ^{31}P NMR signal is observed for this compound but the experiment was carried out at room temperature and no VT process had been performed [12].

For $\text{Cr}(\text{PF}_3)_6$, all the PF_3 groups were found to be in free rotation (rotational barrier ≈ 0.3 kcal/mole).

Table 1. Molecular orbital energies and experimental ionization potentials (eV)

| Cr(PF ₃) ₆ | | Fe(PF ₃) ₅ | | Ni(PF ₃) ₄ | | PF ₃ | |
|--|----------------------|---|----------------------|-----------------------------------|---------------------|--|---------------------|
| Orbital Energy | Experimental IP [10] | ^a Orbital Energy | Experimental IP [10] | ^a Orbital Energy | Experimental IP [9] | Orbital Energy | Experimental IP [9] |
| {14.81 14.91} (<i>t_{2g}</i>) | 9.0 | -14.40 (<i>e'</i>) | 8.9 | -14.33 (<i>t₂</i>) | 9.6 | | |
| {16.81 16.82} (<i>e_g</i>) | | -15.87 (<i>e''</i>) -16.08 (<i>a₁'</i>) | 10.2 | -17.10 (<i>e</i>) | 10.6 | | |
| {17.08 17.10} (<i>t_{1u}</i>) | 12.7 | -16.96 (<i>a₂'</i>) -18.98 (<i>e'</i>) | 13.0 | -19.06 (<i>t₂</i>) | 13.1 | -15.72 (<i>a₁</i>) | 12.3 |
| 18 { -21.33 -21.99 } | 15.8 | 9 { -21.20 -21.98 } | 15.9 | 5 { -21.16 -21.87 } | 15.8 | -19.52 (<i>a₂</i>) | 15.9 |
| 13 { -23.14 -24.10 } | 17.4 | 7 { -23.14 -23.92 } | 17.4 | 4 { -22.95 -23.62 } | 17.4 | -19.87 (<i>e</i>) -21.58 (<i>e</i>) | 17.4 18.5 |
| 17 { -24.47 -25.60 } | 19.5 | 9 { -24.33 -25.60 } | 19.3 | 4 { -24.73 -25.03 } | 19.3 | -23.10 (<i>a₁</i>) | 19.3 |
| 6 { -26.14 -26.52 } | | 4 { -26.00 -26.54 } | | 2 { -25.71 -26.22 } | | -23.16 (<i>e</i>) | |
| -37.74 (<i>a_{1g}</i>) | | -38.94 (<i>a₁'</i>) | | -39.04 (<i>a₁</i>) | | -24.58 (<i>a₁</i>) | |
| 14 { -47.02 -48.40 } | | 7 { -47.07 -47.82 } | | 3 { -46.96 -47.14 } | | -45.29 (<i>e</i>) | |

^a Number of levels grouped in each "band".

3. Results

3.1. Energy Level Distribution

In Table 1, the energies and symmetries of the occupied molecular orbitals (MOs) of the three studied complexes are shown together with the experimental adiabatic ionization potentials.

The highest filled orbitals, t_{2g} and e_g in $\text{Cr}(\text{PF}_3)_6$, e' , e'' and a'_1 in $\text{Fe}(\text{PF}_3)_5$, t_2 and e in $\text{Ni}(\text{PF}_3)_4$, have a predominant "metal $3d$ " character, as they had in the corresponding metal carbonyls $\text{M}(\text{CO})_n$ [2]. These orbitals mainly correspond to metal-phosphorus π back donation.

The other valence MOs are largely composed of ligand atomic orbitals. The levels of O_h and D_{3h} symmetry in $\text{Cr}(\text{PF}_3)_6$ and $\text{Fe}(\text{PF}_3)_5$ seem to be split: this is due to the linking of PF_3 groups of C_{3v} symmetry to the CrP_6 and FeP_5 skeletons. This splitting does not occur in $\text{Ni}(\text{PF}_3)_4$, where the C_{3v} symmetry of PF_3 does not destroy the T_d symmetry of the NiP_4 skeleton and would not occur in $\text{Cr}(\text{PF}_3)_6$ and $\text{Fe}(\text{PF}_3)_5$ if we had been able to introduce the free rotation of PF_3 groups in our calculations.

The orbitals t_{1u} in $\text{Cr}(\text{PF}_3)_6$, a''_2 and e' in $\text{Fe}(\text{PF}_3)_5$ and t_2 in $\text{Ni}(\text{PF}_3)_4$ are mainly composed of phosphorus s and p AOs and correspond to the ($\text{P} \rightarrow \text{M}$) σ dative bonds.

The lowest levels are mainly composed of fluorine AOs. A typical arrangement, which we call "band structure", is observed. In each band several of these levels of very close energies are grouped. The mean energy of such bands does not change with the nature of the metal. This is in agreement with the photoelectron spectra in which it was observed [9, 10] that the IPs assigned to the MOs built on the fluorine AOs are nearly constant upon coordination of PF_3 to the various metals. Therefore, according to the interpretation of Green *et al.* [9], our calculations confirm that the electronic content of PF_3 remains essentially unchanged upon coordination.

As shown in Table 1, the agreement between the calculated energies of the HOMO and the first IP as measured by photoelectron spectroscopy is not very good. It is well known that Koopmans' theorem is not generally valid for transition metal complexes, owing to orbital relaxation effects which are particularly important for the metal $3d$ AOs [3, 13]. Hillier corrects these effects in the case of $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$ by scaling the experimental IPs by a 0.92 empirical factor [4]. These orbital relaxation effects even seem to increase with the number of AOs [13] (in the case of $\text{M}(\text{PF}_3)_n$, the correction factor would be about 0.6).

3.2. Orbital Populations and Charge Transfers

In Table 2, the orbital populations and atomic charges of the studied complexes and free PF_3 are given. In Table 3, the corresponding charge transfers, observed *upon coordination*, are gathered.

In the three complexes, the metal atom has a formal *positive* charge which results from a small net electron migration from the metal to the phosphorus atoms when complexation occurs. This indicates that the ($\text{M} \rightarrow \text{P}$) π charge transfer has to be larger than the ($\text{P} \rightarrow \text{M}$) σ one. These charge transfers are both decreasing in the $\text{Fe} > \text{Cr} > \text{Ni}$ series, Fe being a better π donor and a better σ acceptor towards PF_3 than Cr and Ni. The same order in π

Table 2. Orbital populations and atomic charges

| Atom | Orbital | PF ₃ | Cr(PF ₃) ₆ | Fe(PF ₃) ₅ | | Ni(PF ₃) ₄ | | |
|---------------|---------|-----------------|-----------------------------------|-----------------------------------|-------------------------|-----------------------------------|-----------------------|------|
| M | 4s | | 0.68 | | 0.73 | | 0.77 | |
| | 4p | | 0.25 | | 0.31 | | 0.37 | |
| | 3d | | <i>t</i> _{2g} | 3.99 | <i>a</i> ' ₁ | 0.34 | <i>t</i> ₂ | 5.13 |
| | | | <i>e</i> _g | 0.69 | <i>e</i> ' | 1.39 | <i>e</i> | 3.50 |
| P | 3s | 1.76 | 1.46 | ax. | 1.44 | eq. | 1.50 | |
| | 3p | 1.45 | 1.66 | | 1.67 | | 1.60 | |
| | 3d | 1.13 | 1.43 | | 1.45 | | 1.41 | |
| F | 2s | 1.84 | 1.83 | | 1.82 | | 1.83 | |
| | 2p | 5.38 | 5.34 | | 5.34 | | 5.35 | |
| Atomic charge | | | | | | | | |
| M | | | +0.40 | | +0.36 | | +0.23 | |
| P | | +0.66 | +0.44 | +0.43 | +0.45 | | +0.49 | |
| F | | -0.22 | -0.17 | -0.17 | -0.18 | | -0.18 | |

donor and σ acceptor characters had been previously observed in the Fe(CO)₅, Cr(CO)₆, Ni(CO)₄ series [2].

In the PF₃ charge distribution, the (P → M) σ transfer corresponds to a decrease in the phosphorus 3s and the (M → P) π transfer to an increase in the phosphorus 3d orbital populations. If we compare the values of these σ and π charge transfers in M(PF₃)_n with those we have previously obtained, using the same method, for M(CO)_n [2], it appears that PF₃ is a better σ donor and a better π acceptor towards chromium, iron and nickel than CO.

In spite of the very high electronegativity of the fluorine atom, there is a small charge transfer upon coordination along the P-F bonds from fluorine to phosphorus. This is in agreement with the deshielding of the fluorine atom observed in ¹⁹F NMR when going from free to complexed PF₃: -34.6 ppm in Fe(PF₃)₅ and ~ -15 ppm in Ni(PF₃)₄ [14]. Moreover, the calculated (F → P) charge transfer and experimental deshielding are both larger in Cr(PF₃)₆ than in Ni(PF₃)₄.

3.3. Wiberg Indices

The nature of the bonding may also be inferred from the Wiberg indices of the bonds [15] which are given in Table 4, together with their IR force constants.

Table 3. Charge transfers upon coordination

| Charge Transfer | Cr(PF ₃) ₆ | Fe(PF ₃) ₅ | | Ni(PF ₃) ₄ |
|---|-----------------------------------|-----------------------------------|------|-----------------------------------|
| | | ax. | eq. | |
| CT _{σ} (P → M) | 0.45 | 0.49 | 0.44 | 0.32 |
| CT _{π} (M → P) | 0.52 | 0.55 | 0.51 | 0.38 |
| CT(M → P) total | 0.06 | 0.06 | 0.07 | 0.06 |
| CT(F → P) total | 0.05 | 0.06 | 0.04 | 0.04 |

Table 4. Wiberg indices and force constants

| Molecule | W_{MP} | k_{MP} (mdynes/Å) | W_{PF} | k_{PF} (mdynes/Å) |
|-----------------------------------|----------|------------------------|----------|--------------------------|
| PF ₃ | — | — | 1.26 | { 5.17 [16] 6.14 [17] |
| Cr(PF ₃) ₆ | 0.77 | 2.9 [18] | 1.27 | 7.80 [18] |
| Fe(PF ₃) ₅ | ax. 0.84 | — | 1.27 | — |
| | eq. 0.85 | — | 1.26 | — |
| Ni(PF ₃) ₄ | 0.88 [2] | { 2.20 [19] | 1.25 | { 6.15 [19] |
| | | { 2.71 [16] | | { 7.73 [16] |

The W_{MP} Wiberg indices of the (M-P) bonds are smaller than unity. These low values may be surprising for such multiple bonds but compare well with the also very low values of the corresponding force constants. In the $M(CO)_n$ complexes, W_{MC} was even smaller than W_{MP} and k_{MC} was smaller than k_{MP} [2]. This result confirms our earlier conclusion that the strength of the metal-phosphorus bond is larger than the strength of the corresponding metal-carbon bond. It is interesting to note that *ab initio* calculations also yield very low values for the bond overlap population of such metal-carbon coordination bonds: 0.116 in Ni(CO)₄ and 0.244 in Cr(CO)₆ [4]; 0.284 in Ni(CN)₄²⁻ [5].

As expected on the basis of the relative magnitude of the charge transfers, W_{FeP} is larger than W_{CrP} , but W_{NiP} is even larger and we have no explanation for this last result.

W_{PF} remains unchanged upon coordination of PF₃ to the various metals and this is in agreement with the negligible changes in the geometrical structure and photoelectron spectra and is also in agreement with the values of k_{PF} which are reasonably close, considering that they were determined by different authors.

4. Concluding Remarks

A satisfactory general agreement is observed between the energy level distributions and electronic structures of Cr(PF₃)₆, Fe(PF₃)₅ and Ni(PF₃)₄, as calculated by our extended CNDO/2 method, and the corresponding few experimental data which are known for these molecules. It therefore seems interesting to make use of this simple and inexpensive method for a series of such large molecules (135 AOs in Cr(PF₃)₆) for which *ab initio* calculations are not yet available and would anyhow be very expensive. However, *ab initio* calculations of *some* reference molecules still seem to be essential for testing the validity of the parametrization of a semi-empirical method like the one we use.

The very low charge transfers observed along the metal-phosphorus bonds - as well as along the metal-carbon bonds in the metal carbonyls [2] - lead to another conclusion of this work: the classical description [20] of the coordination bond as a *covalent bond characterized by a large charge transfer* seems to be valid only for pure σ bonds (as for example in H₃N · BH₃ [21]), and not for ($\sigma + \pi$) coordination bonds. A ($\sigma + \pi$) coordination bond finally seems to be better characterized by very small bond overlap populations (or by small Wiberg indices in CNDO/2) and very small force constants.

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