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

IV. Electronic Structure and Magneto-Optical Behaviour of Some $Ni(PX_3)_4$ (X = F, OCH_3, Cl, CH_3, H): A Critical Analysis of Chatt and Wilkinson's Scheme for the Electronic Content of Metal-Ligand Bonds

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The electronic structure and the conformational analysis of some $Ni(PX_3)_4$ (X = F, OCH_3, Cl, CH_3, H) complexes are investigated within the framework of the previously described extended CNDO/2 method in order to interpret their magneto-optical behaviour and to propose a suitable scheme for the electronic content of a metal-ligand ($\sigma + \pi$) dative bond. Chatt and Wilkinson's pattern, used up to now, is criticized and a new scheme is proposed which - taking accurately the role of electronegativity into account and abiding by Pauling's principle of electroneutrality - fits well the sets of available physico-chemical data and allows us to understand why *ab initio* bonds overlap populations as well as IR force constants are low for any metal-ligand ($\sigma + \pi$) dative bond.

Key words: Nickel complexes - Chatt and Wilkinson's scheme

1. Introduction

Although the general pattern (Fig. 1) proposed in 1950 by Chatt and Wilkinson [1] in order to describe the electronic content of a metal-ligand dative bond is nowadays widely admitted, many controversies were developed through the literature about the relative magnitude of σ and π components. In the sixties, for example, Cotton [2] on the one hand, Bigorgne and Angelici [3] on the other hand, both starting from the *same* infrared data, concluded in opposite ways, the former being in favour of a constant σ part and a varying π part into a given chemical series, the latter claiming the very reverse.

Actually, most of the physico-chemists trust - on the basis of an intuitive approach - in an intermediate scheme in which the contrary σ and π charge transfers would respect Pauling's electroneutrality principle. But it must be emphasized that the scarce *quantitative* results, provided by *ab initio* calculations dealing with some standard transition metal complexes ($Ni(CO)_4$ [4, 5], $Cr(CO)_6$ [5], $[Ni(CN)_4]^{2-}$ [4]), do not fit really well the intuitive idea the chemist has obtained on the basis of Chatt and Wilkinson's model.

$$\mathrm{M} \underset{\sigma}{\overset{\pi}{\rightleftarrows}} \mathrm{D}$$

Fig. 1.

Moreover, magneto-optical studies of many $Ni(PXYZ)_4$ complexes in the transparent region [6] have induced us to conclude - without any calculation, simply considering electronegativity, steric hindrance and so on - that the magnetic rotation, ρ(Ni-P), of the nickel-phosphorus bond in such a series was all the more large as its multiplicity was lower. This result is surprisingly opposite to the well-known concept which says that the higher the multiplicity of a covalent bond the larger its magnetic rotation [7]. From this point of view, a choice had to be made between the interpretation based on the magneto-optical behaviour of the (Ni-P) bond and the interpretation based on the charge distribution resulting from the Cotton and Wilkinson scheme.

The previously proposed extended CNDO/2 method [8, 9] [1] was used to solve this problem (theoretical and experimental) and to approach the *variations* of the Ni-P electronic content into a suitable set of $Ni(PXYZ)_4$ complexes.

In order to save hours of computing time and to simplify the conformational analysis of such systems which must be preformed - when necessary - prior to any calculation of electronic structure [10], our work was limited to five symmetrical $Ni(PX_3)_4$ compounds covering the whole field of X electronegativities (X = F, OCH_3, Cl, CH_3, H).

Among the five complexes studied, $Ni[P(OMe)_3]_4$ is the only one needing a preliminary conformational analysis which has to be developed.

2. Theoretical Conformational Analysis of $P(OMe)_3$ and $Ni[P(OMe)_3]_4$

Using Naumov's geometrical set provided by electron diffraction for $P(OMe)_3$ [11], we have performed, as usual [12], a theoretical conformational analysis of this molecule; the total energy was computed as a function of rotations around the three (P-O) bonds. In such conditions, the preferred conformation (Fig. 2) is the one of C_3 symmetry which had been proposed by Naumov [11].

The theoretical conformational analysis showed that four such entities may be grafted on a Ni(0) atom without any conformational modifications, each phosphite group being staggered with respect to the three (Ni-P) bonds other than the one which links this group to the Ni atom.

In spite of the steric hindrance effects, the interlocking posibility of the $P(OMe)_3$ ligands permits the existence of the stable complex $Ni[P(OMe)_3]_4$. However, it may be noted that with the even bulkier $P(NMe_2)_3$ group this interlocking of ligands is excluded and the corresponding $Ni[P(NMe_2)_3]_4$ complex does not exist [13].

3. Electronic Structure of $Ni(PX_3)_4$ (X = F, OCH_3, Cl, CH_3, H)

The geometry in the gas phase of $Ni(PF_3)_4$ has been determined by Marriott [14] and Almenningen [15] using electron diffraction,[2] whereas the geometries of the other terms of the series are still unknown.

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[1] Calculations were performed using the IBM 370/168 computer of the CNRS (Orsay, France) and the original program written for this purpose in collaboration with Cassoux, Pelissier and Serafini.

[2] The extended CNDO/2 procedure was recently applied [16] to the calculation of barriers to internal rotation of the PF_3 groups in $Ni(PF_3)_4$ and an explanation was given to the inconsistency which seems to exist between these two works about the "free rotation or not" of PF_3.

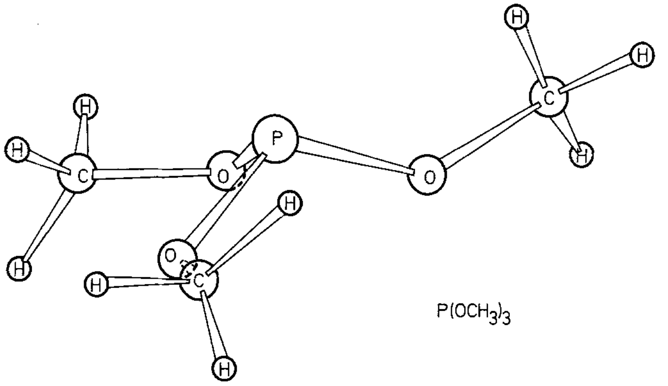

Fig. 2.

Then, we used again [16] a Gordon and Pople-like standard geometrical model, i.e. the four ligands were assumed to keep the bond lengths and angles they have in other isologous complexes ([PF_3 as in $Ni(PF_3)_4$ [14, 15], $P(OMe)_3$ as in $Ni[P(OCH_3)_3]_2\{[(CF_3)_2C_2]_3\}$ [17], PCl_3 as in $OPCl_3$ [18], $P(CH_3)_3$ as in $NiBr_2[P(CH_3)_3]_3$ [19], and PH_3 as in $Cr(CO)_2(PH_3)_4$ [20]]). The (Ni-P) bond length was kept constant and equal to 2.19 Å.[3] Such a process will undoubtedly reduce the variations of all the electronic quantities through the series, which we will keep in mind when discussing our results.

Under such conditions, orbital populations and Ni-P Wiberg indices [23][4] are gathered in Table 1.

As for atomic charges, it may just be mentioned that if Q_{Ni} is *positive* (lack of electrons due to a π release towards the phosphorus atoms which is larger than the σ withdrawing from P to Ni) in $Ni(PF_3)_4$, as in metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ [8, 9] and related $Fe(PF_3)_5$ and $Cr(PF_3)_6$ [16] compounds, it becomes *negative* (−0.22 in $Ni[P(OMe)_3]_4$, −0.04 in $Ni(PCl_3)_4$, −0.13 in $Ni(PMe_3)_4$, −0.09 in $Ni(PH_3)_4$) in the other complexes.

Getting back to Table 1, we may divide its analysis in two parts:

1. First of all, we observe that inside the $Ni(PF_3)_4$, $Ni[P(OMe)_3]_4$, $Ni(PCl_3)_4$ series - for which magneto-optical data are available - the $3d$(Ni) population decreases, the $3d$(P) population increases and the W^{π}_{NiP} increases too when going from the most electronegative ligand (PF_3) to the least (PCl_3). In other words, *the higher the electronegativity of atoms or groups linked to phosphorus, the higher the π order of the* (Ni-P) *bond.* This result is the very reverse of the one which had been predicted on the basis of Chatt and Wilkinson's pattern. The establishment of this fundamental feature allows us to cancel the hypothesis of the so-called anomaly we thought to reveal about the magneto-optical behaviour of (Ni-P) bonds (the magnetic rotation recovering under such conditions its increasing character with π bond order). We must also emphasize that it has been demonstrated that careless use of electronegativity in such cases may lead to dramatic errors when predicting the magnitude of the π back-bonding.

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[4] These calculations being performed with a z axis located on one of the (Ni-P) bonds, we were able to share the total W_{NiP} Wiberg index in its σ and π components, despite the fact that, strictly speaking, the notation σ and π is valid only for linear and planar molecules [22].

[3] This value differs slightly from the ≃ 2.10 Å one which characterizes the (Ni-P) bond in $Ni(PF_3)_4$ [14, 15], but we thought that it would be more realistic to use an *average* value (from the (Ni-P) bond lengths available for some other nickel-phosphorus complexes [21]) to describe a *mean* situation with respect to the electronegativity of ligands on phosphorus.

Table 1.

Atom	Orbital	$Ni(PF_3)_4$	$Ni[P(OMe)_3]_4$	$Ni(PCl_3)_4$	$Ni(PMe_3)_4$	$Ni(PH_3)_4$
Ni	$4s$	0.78	0.77	0.76	0.75	0.76
	$4p$	0.38	0.77	0.72	0.77	0.70
	$3d \begin{cases} t_2 \end{cases}$	5.18	5.15	5.12	5.11	5.11
	e	3.52	3.52	3.44	3.50	3.52
P	$3s$	1.51	1.50	1.46	1.43	1.42
	$3p$	1.58	1.82	2.13	2.52	2.84
	$3d$	1.39	1.42	1.44	1.13	0.66
	Wiberg Indices					
	W_{NiP}	0.86	0.85	0.84	0.84	0.95
	W_{NiP}^{σ}	0.44	0.42	0.40	0.37	0.45
	W_{NiP}^{π}	0.42	0.43	0.44	0.47	0.50

2. Looking now at the right-hand side of Table 1 (area in which very few experimental data are available) we observe that if W_{NiP}^{π} continues increasing consistently with the left-hand side of the table, a break in the $3d$(Ni) and $3d$(P) population variation is made conspicuous. The analysis becomes ambiguous but we may connect such breaks with the ones which are experimentally observed for ^{31}P NMR of $Ni(PMe_3)_4$ [24] and $Ni(PMeCl_2)_4$ [6] and for the Faraday effect of $Ni(PMeCl_2)_4$ [6] when the corresponding representative points are plotted on the monotonous variation curves which exist [6, 25] between $\Delta P = \delta^{31}P\,(Ni(PX_3)_4) - \delta^{31}P\,(PX_3)$ or $\rho(Ni\,.\,P)$ and the electronegativity x_X of ligands grafted on phosphorus.

Thus, the preceding discussion gives rise to an intricate question. Are our calculations a support or not to Chatt and Wilkinson's model?

We have mentioned in previous papers [8, 9, 16] that a metal-carbon or a metal-phosphorus bond is characterized by a surprisingly low (i.e. less than unity) Wiberg index. The same situation is observed here. Such low values are consistent both with the very small (M-C) bond overlap populations obtained by *ab initio* calculations in $Ni(CO)_4$ (0.116) and $Cr(CO)_6$ (0.244) [5] and with the extremely low IR force constants of the metal-carbon and metal-phosphorus bonds [26].

Moreover, as the total charge transfers upon coordination of ligands on the metal are in any case very small, Pauling's electroneutrality principle is fairly well respected in transition metal complexes.

We thus propose the following quite new scheme to describe the electronic content of a metal-ligand dative bond:

a) let us consider the free ligand X_3P when approaching the metal. The larger the electronegativity of X, the stronger the lone pair of phosphorus will be retained on this atom and the smaller the σ charge transfer from P to M;
b) in agreement with Pauling's electroneutrality principle, the smaller this σ charge transfer, i.e. the larger the electronegativity of X, the smaller the back π charge transfer from M to P.

In other words, the new scheme we propose may be applied as follows (Fig. 3): The σ and π charge transfers will both be less important in $Ni(PF_3)_4$ than in $Ni(PCl_3)_4$. This conclusion - in opposition to the one based on Chatt and Wilkinson' pattern - allows a satis-

$$\mathrm{Ni(PF_3)_4} \qquad \mathrm{Ni} \xrightarrow{\pi} \quad \xleftarrow[\sigma]{} \mathrm{P}$$

$$TC_\sigma + TC_\pi \simeq 0$$

$$\mathrm{Ni(PCl_3)_4} \qquad \mathrm{Ni} \xrightarrow{\pi} \quad \xleftarrow[\sigma]{} \mathrm{P}$$

$$TC_\sigma + TC_\pi \simeq 0$$

Fig. 3.

factory interpretation of the evolution of all the physico-chemical quantities (NMR, Faraday effect, IR spectroscopy. . .).

Moreover, such a scheme helps us to understand why the bond overlap populations provided by *ab initio* calculations (or the Wiberg indices in an extended CNDO/2 method) and, consequently, the corresponding IR force constants are so small.

Thus, it seems quite obvious that the extended CNDO/2 calculations of the electronic structure of $Ni(PX_3)_4$ complexes we have performed emphasized the dangers which arise when predicting empirically the electronic content (and mainly the magnitude of the π component) of a $(\sigma + \pi)$ metal-ligand dative bond.

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