On the Bonding and the Photoelectron Spectra of $Ni(PF_3)_4$ and $Pt(PF_3)_4$

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Summary The bonding in the complexes $Ni(PF_3)_4$ and $Pt(PF_3)_4$ is discussed with the aid of their photoelectron spectra, reported here.

THE bonding in transition-metal complexes of phosphine and substituted phosphines is generally described in terms of the σ-donor and π-acceptor properties of the ligands. A study of the simple co-ordination compound PF_3O has shown that a quantitative understanding of the bonding may be obtained from the photoelectron spectrum coupled with the results of *ab initio* SCF–MO calculations.[1] Although such calculations on the complexes $Ni(PF_3)_4$ and $Pt(PF_3)_4$ are not possible at present, we here report the photoelectron spectra of these molecules and present an interpretation of the results following that of PF_3O. A gas-phase electron diffraction study of the structure of the ligand in these molecules suggests that differences in their mode of bonding exist.[2]

The photoelectron spectra of these two complexes and that of the free ligand are shown in the Figure. The vertical ionization potentials measured are $Ni(PF_3)_4$: 9·69, 10·74, 13·17, 14·65, 15·97, 17·48, and 19·42 ev; $Pt(PF_3)_4$: 9·83, 12·45, 14·54, 15·87, 17·53, 19·40 ev. Vertical I.P. for PF_3 have already been reported;[1] the spectrum shows considerable fine structure when examined at higher resolution. Data for the nickel complex substantially agree with those obtained by other workers.[3] The first two I.P. in the complexes correspond to ionization from the orbitals, mainly of metal *d*-character, of t_2 and *e* symmetry (in T_d). The remaining I.P. have counterparts in the free ligand, that at 13·2 ev in the nickel and at 14·5 ev in the platinum complex corresponds to ionization from orbitals chiefly

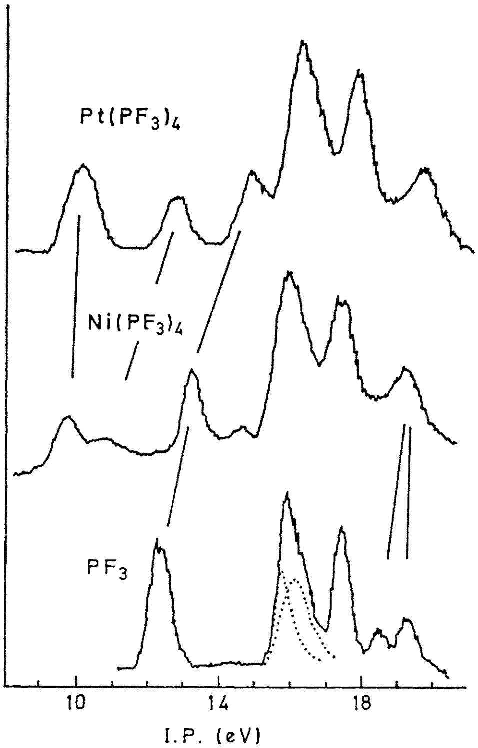

FIGURE. *Photoelectron spectra of* PF_3 *and its* Ni *and* Pt *complexes. The dotted lines in the* PF_3 *spectrum show the components of the second band.*

localized on the phosphorus atoms (lone pair) and may be compared with the value of 12·3 ev in the free ligand. The final three I.P. at 15·97, 17·48, and 19·42 ev in $Ni(PF_3)_4$ and 15·87, 17·53, and 19·4 ev in $Pt(PF_3)_4$ are due to ionization from molecular orbitals mainly derived from fluorine $2p$-atomic orbitals. These values may be compared with the corresponding values of 16·3, 17·5, 18·6, and 19·4 ev in PF_3. The assignment of the very weak band at 14·65 ev in $Ni(PF_3)_4$ is tentative but it probably originates from the four totally non-bonding a_2 orbitals of $PF_3(C_{3v})$ at 15·8 ev in the free ligand which yield a t_1 and a_2 orbital in T_d, the latter remaining totally non-bonding. In the platinum complex it may be obscured by the strong band at 14·54 ev.

The change in the energy of the phosphorus lone-pair orbital is brought about by delocalization over the transition metal and is a measure of the σ-donation from the lone pair. The lowering of the orbital energy is substantially greater in the platinum than in the nickel complex indicating a greater degree of σ-donation in the former. This is in accord with the increased t_2–e splitting in the platinum complex, for the t_2 metal orbital has a σ-antibonding component involving the phosphorus lone pair orbitals, which will be greater the larger the σ-donation. On complex formation the change in energy of the non-bonding fluorine orbitals is due mainly to the change in potential experienced by the non-bonding electrons and therefore reflects the net result of σ- and π-bonding. The data show very little difference between the I.P. of these non-bonding electrons in the two complexes and in the free ligand, in contrast to the results for PF_3O where a shift of *ca.* 1 ev is observed. Thus, in each complex, σ-donation (from the lone pair) is compensated by π-back-bonding to produce little net charge migration; however, the extent of delocalization by both mechanisms appears to be greater in the platinum than in the nickel complex.

The change in geometry of the PF_3 ligand on co-ordination may be correlated with the degree of σ-donation from the lone-pair orbitals. *Ab initio* calculations of PF_3[1] show that although this orbital is strongly localized on the phosphorus atom there is a significant anti-bonding component involving the phosphorus $3s$ and fluorine $2p$ orbitals. Thus, σ-donation will tend to shorten the P–F bond lengths which are found to decrease from 1·569 Å in PF_3 to 1·561 Å in $Ni(PF_3)_4$ and to 1·546 Å in $Pt(PF_3)_4$. This suggests that there is substantially more σ-donation in $Pt(PF_3)_4$ than in $Ni(PF_3)_4$, a conclusion which we also reach from the photoelectron spectra.

(*Received, August 5th*, 1970; *Com.* 1295.)

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[1] P. J. Bassett, D. R. Lloyd, I. H. Hillier, and V. R. Saunders, *Chem. Phys. Letters*, in the press.

[2] J. C. Marriott, J. A. Salthouse, M. J. Ware, and J. M. Freeman, *Chem. Comm.*, 1970, 595.

[3] A. F. Orchard, personal communication.