The Structure of Tetrakis(trifluorophosphine)nickel and Tetrakis(trifluorophosphine)platinum Determined by Gas-phase Electron Diffraction

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Summary The principal structural parameters of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ have been determined by gas-phase electron diffraction, assuming a molecular point group T; the geometry of the PF_3 ligands in the nickel compound differs very little from that of the free molecule.

DESPITE the large number of transition-metal complexes of trifluorophosphine now known,[1] there appear to be no published molecular structure determinations of such molecules by X-ray or electron diffraction. A theoretical study[2] of the bonding in trifluorophosphine makes it desirable to compare the geometry of this molecule in the free and co-ordinated states, particularly in view of the recent accurate redetermination[3] of the structure of trifluorophosphine itself.

Tetrakis(trifluorophosphine)nickel was prepared as described by Nixon[4] and purified by standard vacuum techniques. The platinum analogue was kindly donated by Dr. H. G. M. Edwards.[5] Electron-diffraction data were recorded photographically using the Balzers apparatus[6] at the University of Manchester Institute of Science and Technology. Camera distances of 100, 50, and 25 cm were employed and the data were processed and reduced at Cambridge, using the methods of Rankin, Robiette, Sheldrick, and their co-workers.[7]

The experimental radial distribution curves $P(r)/r$ [the Figure depicts that of $Ni(PF_3)_4$, which is typical] show the expected peaks for P–F, F · · · F, M–P, and M · · · F scattering, but no sharp non-bonded P · · · P peak can be discerned, although this should be clearly apparent at about 3·4Å if the MP_4 skeleton is regular tetrahedral. However, the i.r. and Raman spectra[5,8] of these molecules are fully consistent with a T_d molecular skeleton; moreover they show that the deformational modes δ(PNiP) of symmetry species e and t_2 lie at very low frequency, *ca.* 54 cm^{-1}. An approximate calculation for the e mode, assuming a Simple Valence Force Field and point masses, indicates a skeletal bending force constant (f_δ/r^2) of about 0·04 m dyn Å^{-1} and a corresponding mean amplitude for P · · · P motion in the order of 0·2 Å which would result in a greatly broadened P · · · P peak in the radial distribution curve. The long non-bonded distances, P · · · F and F · · · F, will also be influenced in this way and by hindered rotation of the PF_3 groups. We find that the radial distribution curve for r greater than 3·4 Å can satisfactorily be represented by a single molecular conformation of point group T, in which each PF_3 group is twisted by about 40° from the position where it eclipses the NiP_4 skeleton, and the mean amplitudes of vibration for the P · · · P, the long P · · · F, and F · · · F distances are rather large (0·2—0·3 Å). With this model assumed, the well-defined distances, P–F (1·561 Å), Ni–P (2·116 Å), Ni · · · F (3·177 Å), and short F . . . F (2·372 Å), could be satisfactorily refined. The mean square amplitudes associated with these four peaks are of the expected magnitude. The bond lengths and ∠FPF angle calculated from the four refined distances are summarised in the Table, and there compared with those of free PF_3,[3] and of PF_3BH_3.[9] The results for the nickel compound agree well with the values obtained[10] by Norwegian workers. Our estimated standard deviations (given in parentheses) are three times the values obtained in the least-squares refinements.

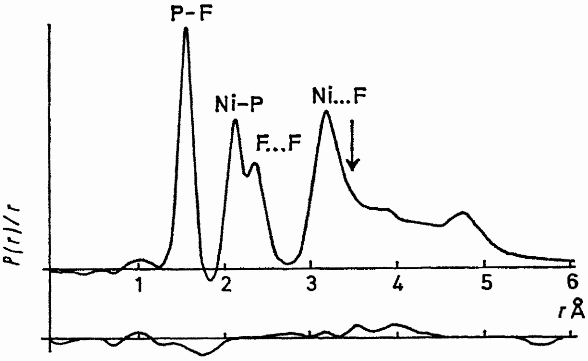

FIGURE. *Experimental and difference radial distribution curves for* $Ni(PF_3)_4$. *The arrow marks the expected position of the* P · · · P *peak for a regular tetrahedral* NiP_4 *skeleton.*

It is noteworthy that the geometry of the PF_3 group is little changed in going from the free molecule to the co-ordinated molecule in $Ni(PF_3)_4$, whereas there is a marked contraction of r(P–F) in PF_3BH_3, and a lesser but probably significant contraction in $Pt(PF_3)_4$.

A comparison of the structural parameters of trifluorophosphine and its derivatives

Molecule	r(P–F) Å	<(FPF)°	r(M–P) Å
PF_3[a]	1·569(1)	97·7(2)	—
$Ni(PF_3)_4$[b]	1·561(5)	98·4(8)	2·116(10)
$Pt(PF_3)_4$[b]	1·546(6)	98·9(7)	2·230(10)
PF_3BH_3[c]	1·538(8)	99·8(1·0)	1·836(12)

[a] Electron diffraction data from ref. 3, r_a values.
[b] This work, r_a values.
[c] Mixed r_s/r_0 structure from microwave data, ref. 9.

σ-Donation from the highest filled orbital of PF_3 (the "lone-pair" of a_1 symmetry which is antibonding with respect to the fluorine atoms[2]) might be expected to shorten r(P–F), and π-acceptance into the first virtual orbital of PF_3 (symmetry e, which is largely localised on the phosphorus atom) may tend to lengthen r(P–F). In PF_3BH_3

it appears that σ-donation is the dominant factor; in $Ni(PF_3)_4$ the negligible change in r(P–F) may be attributed to a synergic effect. The latter observation is in harmony with the data from photoelectron spectroscopy,[11] in which the relevant molecular ionization energies of $Ni(PF_3)_4$ are but little displaced from those of PF_3 itself. The results for the platinum compound hold interesting implications which are being investigated.

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