Helium-I Photoelectron Spectra of Tetrakis(trifluorophosphine)-nickel(0), -palladium(0), and -platinum(0)

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He(I) Photoelectron (p.e.) spectra of the title compounds are reported and discussed. Discrepancies between earlier reports are analysed. The spectra are related to ionisation potential data for the free atoms, free PF_3, and other compounds, and evidence is put forward which suggests that the bonding is strongest for the Pt compound, and that charge shifts from σ- and π-bonding cancel each other in these molecules.

COMPARISON of valence-region photoelectron (p.e.) spectra of sets of related molecules within a group of the Periodic Table has given much useful information, but the majority of such studies has been concerned with main-group compounds.[1-4] Comparison of vertical triads within the transition series should also be interesting, but often the differences in chemistry between the three series make it difficult to assemble complete sets of compounds of small molecules. The only triad whose spectra have been reported so far is the set of Group 6A hexacarbonyls.[5]

Tetrakis compounds of PF_3 with the Ni group are another possible set to investigate. These compounds have the formal electron configuration d^{10}, in a tetrahedral environment, and the closely related nickel tetracarbonyl has been shown to have the p.e. spectrum expected from elementary ligand-field considerations.[6] A preliminary report on the spectra of $[Ni(PF_3)_4]$ and $[Pt(PF_3)_4]$ has appeared,[7] but this disagrees in some important detail with another study.[8] We give more details of our earlier work here and also report the spectrum of the thermally unstable $[Pd(PF_3)_4]$.

EXPERIMENTAL

The nickel and platinum compounds were provided by Dr. M. J. Ware, and their spectra were obtained on a Perkin-Elmer PS15 spectrometer. The direct-inlet system described earlier was used;[9] this ensures that the residence time of the molecules in the inlet is as short as possible. No problems were encountered with the nickel compound, but since the band at 14·7 eV has no equivalent in the spectrum of $[Pt(PF_3)_4]$, it was investigated carefully.† The sample was held at various temperatures between +25 and −45 °C, but no variation in the intensity of this band relative to the others was observed. The sample was prepared from bis(η-cyclopentadienyl)nickel, and no impurities were detected in the mass spectrum, so it is probable that the weak band is a genuine feature of the spectrum. The $[Pt(PF_3)_4]$ was held at room temperature, and the first spectrum obtained from the sample was identical with that of PF_3. This was slowly replaced by the spectrum shown in Figure 1(*a*), which was then invariant over several days. At an intermediate stage the spectrum was identical with that reported for $[Pt(PF_3)_4]$.[7] Calibration methods have been described.[9]

The complex $[Pd(PF_3)_4]$, which decomposes above −20 °C, was supplied by Dr P. L. Timms. Attempts to obtain the spectrum with a PS16 spectrometer were largely unsuccessful. The sample was held at *ca.* −30 °C and was shielded from light. The inlet valve was fully open, minimising the time that the molecules encountered surfaces at room temperature. However, the spectrum

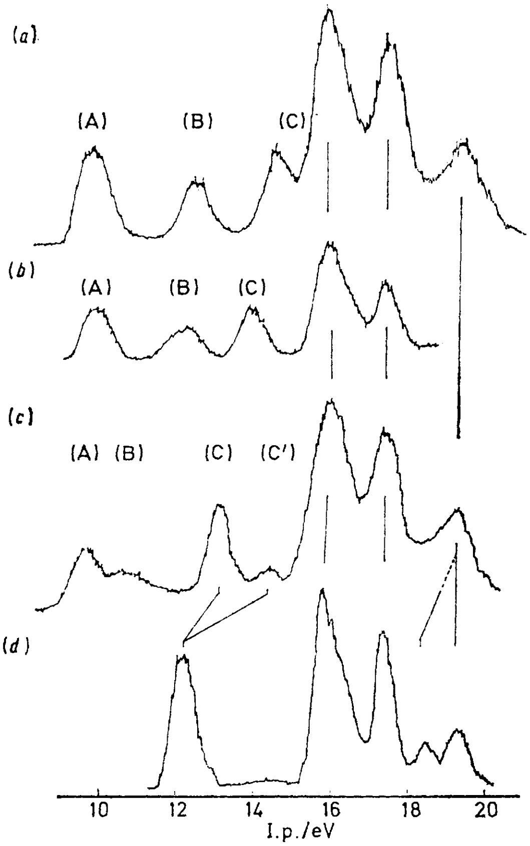

FIGURE 1 He(I) Photoelectron spectra of (*a*) $[Pt(PF_3)_4]$, (*b*) $[Pd(PF_3)_4]$, (*c*) $[Ni(PF_3)_4]$, and (*d*) PF_3

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† 1 eV ≈ 1·60 × 10^{-19} J.

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[3] A. W. Potts and W. C. Price, *Proc. Roy. Soc.*, 1972, **A326**, 165, 181.

[4] P. J. Bassett and D. R. Lloyd, *J.C.S. Dalton*, 1972, 248.

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[6] I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1974, **27**, 215.

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[8] I. H. Hillier, V. R. Saunders, M. J. Ware, P. J. Bassett, D. R. Lloyd, and N. Lynaugh, *Chem. Comm.*, 1970, 1316.

[9] D. R. Lloyd, *J. Phys.*, 1970, **E3**, 629.

was essentially that of PF_3, except that a weak band at 9·9 eV was also present, with less than 5% of the intensity of the 12·3 eV band of PF_3. The spectrum of $[Pd(PF_3)_4]$ was finally obtained on an instrument in which the entire inlet system can be cooled.[10] The electron analyser on this instrument is a hemispherical electrostatic deflector subtending 157·5° with principal orbit radius 20·3 cm. The ionisation chamber is pumped by a liquid-nitrogen trap with an estimated pumping speed of *ca.* 150 l s^{-1} for condensables. The inlet system is a heavy copper bar drilled axially which terminates in a slot 0·1 cm × 1·5 cm. The slot is aligned with the photon beam and the analyser entrance slit. The system thus approximates to a molecular-beam system, and the majority of the molecules ionised are at the temperature of the bar. The bar was held at −40 °C by external cooling and the sample was held at −45 °C. A small section of glass tubing immediately before the bar could not be cooled below 5 °C. Initially the spectrum of PF_3 was obtained, which gradually changed to that in Figure 1. The slight asymmetry on the leading edge of band (B) is probably due to traces of PF_3. The pseudo-beam operation consumes large amounts of compound, and to conserve as much as possible the pumping speed of the cold trap was reduced to *ca.* 10 l s^{-1} with a plug in the connecting line for measurements of the ionisation potential (i.p.). No deterioration of the spectrum was observed under these conditions, but deposition of Pd on the spectrometer surfaces gave substantial zero shifts in the spectra and reduced the spectrometer sensitivity to zero for electrons of kinetic energy less than 2 eV. Thus the apparent absence in Figure 1(*b*) of a band corresponding to the 19·3 eV bands of the Ni and Pt compounds is not significant. Calibration was carried out using N_2 and Xe ionisation, but, because of the rapid consumption of the compound and the calibration shifts, it was not possible to obtain data as precisely as for the other compounds.

RESULTS AND DISCUSSION

The spectra are shown in Figure 1, together with that of PF_3, and the measured i.p.s are reported in Table 1.

TABLE 1

Ionisation potentials (eV) for $[Ni(PF_3)_4]$, $[Pd(PF_3)_4]$, and $[Pt(PF_3)_4]$

Band	Assignment		$[Ni(PF_3)_4]$	$[Pd(PF_3)_4]$	$[Pt(PF_3)_4]$
(A)	t_2(M)	a	8·82 (6)		8·89 (3)
		v	9·69 (4)	9·9 (1)	9·83 (2)
(B)	e	a			11·53 (1)
		v	10·74 (4)	12·2 (1)	12·45 (1)
(C)	t_2(P)	a	12·56 (2)		13·59 (2)
		v	13·17 (4)	13·7 (1)	14·54 (2)
(C′)	a_1	v	14·65 (2)		
	F lone pair	v	15·97 (1)	15·84 (5)	15·87 (1)
		v	17·48 (2)	17·4	17·53 (1)
	P–F bond	v	19·42 (1)		19·40 (2)

a = Adiabatic i.p., v = vertical i.p. Quantities in parentheses are standard deviations, calculated from at least five independent measurements.

The $[Ni(PF_3)_4]$ spectrum is identical with that in ref. 7 except for the presence of an additional weak band at 14·7 eV. It is unlikely that the band in our spectrum is due to impurities for the reasons outlined above, and also because the samples used in both investigations [7,8] came from the same preparation,[11] so we believe that the band is genuine. The spectrum of a completely independent sample has also been reported,[12] and though there is no comment on this band in the report it can be seen in the spectrum illustrated. The spectrum of $[Pt(PF_3)_4]$ reported in ref. 7 appears to contain bands due to appreciable amounts of PF_3, perhaps from thermal decomposition on the walls of the inlet system, but the first i.p., which is not perturbed by PF_3 ionisations, is in good agreement with our value.

It can be seen in Figure 1 that, except for the first two bands (A) and (B), there is a general resemblance of all the spectra to that of free PF_3, and the bands (C), *etc.*, are assumed to arise from ionisation of orbitals localised mainly on the ligands. In the spectrum of $[Ni(PF_3)_4]$, bands (A) and (B) are almost identical in form, and very similar in i.p. to the first two bands in the $[Ni(CO)_4]$ spectrum which have been assigned to ionisation of mainly metal-localised t_2 and e orbitals.[6] Since the local symmetry around the metal atom is tetrahedral in the PF_3 complexes, at least for those of Ni and Pt,[13] we assign bands (A) and (B) to the metal t_2 and e orbitals. Occupation of these orbitals gives the formal d^{10} configuration of the metal atom in oxidation state 0. A substantial increase in intensity of bands (A) and (B) with respect to the rest of the spectrum was observed on changing from Ni to Pt. Such a 'heavy-atom effect' was also observed in metal carbonyl p.e. spectra.[5]

The metal–ligand bonding is expected to arise mainly from interaction of symmetry-adapted combinations, $a_1 + t_2$, of the highest-lying 'lone-pair' orbitals of the PF_3 ligands with the metal valence orbitals. In tetrahedral compounds of main-group elements p.e. spectra show pairs of bands with a *ca.* 3 : 1 intensity ratio which are assigned to the corresponding $t_2 + a_1$ molecular orbitals (m.o.s); the a_1 orbital always has the higher i.p.[1,3,14] The reasons for the orbital sequence $t_2 > a_1$ in main-group compounds certainly include the fact that the a_1 orbital has central-atom ns character, whereas t_2 has np character (and possibly nd character), but there is also a ligand–ligand interaction which stabilises a_1 and destabilises t_2.[15] In a transition-metal compound the main metal contribution to t_2 will come from the $(n-1)d$ orbitals which lie below the ns orbitals. Thus it is not immediately evident that the $t_2 > a_1$ sequence will still be found in the metal compounds. However, though the corresponding bands in the spectrum of $[Ni(CO)_4]$ cannot be identified with certainty, from comparison with *ab initio* m.o. calculations [6] it seems probable that the a_1 orbital lies *ca.* 1 eV below the t_2 orbitals. Also, in the spectra of $TiCl_4$

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[11] M. J. Ware, personal communication.

[12] J. Müller, K. Fenderl, and B. Mertschenk, *Chem. Ber.*, 1971, **104**, 700.

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

[14] M. B. Hall, M. F. Guest, I. H. Hillier, D. R. Lloyd, A. F. Orchard, and A. W. Potts, *J. Electron Spectroscopy*, 1972—1973, **1**, 497.

[15] C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' Benjamin, New York, 1965, pp. 109, 118.

and VCl_4 it seems likely that the a_1 orbital has the lowest energy.[1,16]

Returning to Figure 1, it is reasonable to correlate the bands beyond 15 eV with those of PF_3 as shown on grounds of intensity and i.p. The two remaining bands (C) and (C′) in $[Ni(PF_3)_4]$ are therefore assigned to ionisation from the Ni–P bonding t_2 and a_1 orbitals. This differs from the earlier assignment of (C′) as due to a combination of F lone pairs.[8] However, if (C′) were due to this then the F–F repulsions would be expected to produce more perturbations of the rest of the spectrum. Band (C′) was not observed in the spectra of the Pt or Pd analogues, but in these (C) is at higher i.p., and if there is a similar shift of (C′) it will be hidden under the remainder of the spectrum. Alternatively if (C′) maintains a constant i.p. it will be overlapped by (C). Thus (C) is assigned to ionisation from the t_2 M–P bonding orbitals in all three compounds, but the i.p. of the a_1 orbital is unknown for the Pd and Pt compounds. In the subsequent discussion the orbitals giving rise to band (C) will be referred to as the t_2 (P) set, and those giving rise to band (A) as the t_2 (M) set. If it is assumed that (—i.p.) sequences are the same as those of orbital energies, as required by Koopmans' approximation, then this discussion of the spectrum of $[Ni(PF_3)_4]$ may be summarised in the qualitative m.o. diagram shown in Figure 2, in which the separation of e and t_2 (M) orbitals arises from the antibonding interaction of the PF_3 lone pairs with the d orbitals.* Koopmans' approximation has been shown to provide a qualitatively accurate description of the p.e. spectrum of $[Ni(CO)_4]$.[6] For completeness, interactions of the $4p$ orbitals are included in Figure 2, but there is no experimental evidence for this. According to the calculations,[6] in $[Ni(CO)_4]$ the t_2 (M) orbital set have 9% $4p$ contribution.

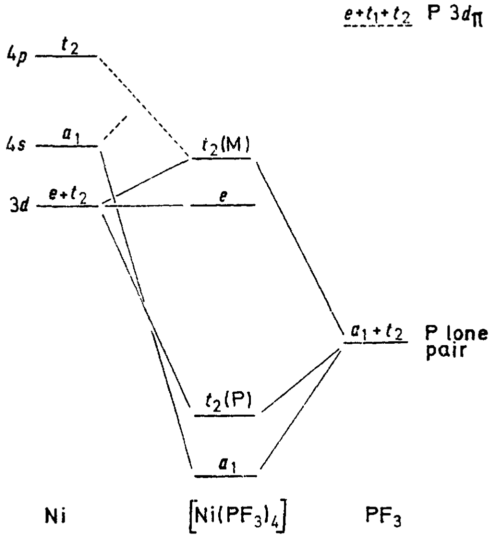

FIGURE 2 The σ-bonding scheme for $[Ni(PF_3)_4]$. The effects of interaction with the P $3d_\pi$ orbitals are discussed in the text

The increase in separation of the e and t_2 (M) i.p. on descending the Group is interesting. Increases in d-orbital splitting on descending a Group are frequently observed in the optical spectra of transition-metal compounds, though these usually involve metal atoms in positive oxidation states.[18] However, in the optical spectra the changes between first- and second-row elements are comparable with those between the second and third rows, but in the PF_3 compounds the e—t_2 (M) separations for Pt and Pd are similar and substantially greater than that for Ni. As the e—t_2 (M) separation increases so does the i.p. of the t_2 (P) orbitals, but in this case the greatest change occurs between the Pd and Pt compounds. These variations may be partially related to the orbital i.p. for the free atoms.

Although atomic-spectral data are sparse for heavier transition elements,[19] there are only a small number of terms involved in the calculation of average i.p. for the filled or nearly filled shell configurations involved here, and for d ionisation from $(n-1)d^{10}$ or s ionisation from $(n-1)d^9ns$ all the terms were observed. For p ionisation from $(n-1)d^9np$, all the terms were observed for Ni and Pd, but *ca.* ¼ of the $5d^96p$ terms were missing for Pt. The available terms [19] were averaged, weighting according to degeneracy in the usual manner,[20] and are set out in Table 2. Although the atomic ground configurations are different for all three atoms, there is a definite pattern in the average of configuration i.p., with the d-orbital i.p. being very similar for Pd and Pt, *ca.* 2·7 eV greater than for Ni. Variations in s- and p-orbital i.p. are smaller, but here the main difference is between Pd and Pt.

TABLE 2

Average of configuration ionisation energies (eV) for free atoms

Ionisation	Ni	Pd	Pt
$(n-1)d^{10} \rightarrow (n-1)d^9$	5·88	8·51	8·62
$(n-1)d^9ns \rightarrow (n-1)d^9$	7·54	7·44	8·75
$(n-1)d^9np \rightarrow (n-1)d^9$	3·98	3·71	4·6

Term energies were taken from Moore,[19] and were averaged according to degeneracy. The relative energies of ns and np orbitals may be inferred from these data, but not the relative energies of $(n-1)d$ and ns orbitals.

Similar variations were observed also in the i.p. of the e orbitals in the PF_3 compounds, which increased by 1·5 eV from Ni to Pd but only by 0·3 eV from Pd to Pt. Since the e orbitals cannot take part in σ-bonding to the ligands, this parallelism is expected. In terms of the σ-bonding scheme of Figure 2, a more stable d-orbital set should give a greater stabilisation of the t_2 (P) levels, and this was observed in the behaviour

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* A similar diagram [17] has some inaccuracies in the correlation lines.

[16] P. Cox, S. Evans, A. Hamnett, and A. F. Orchard, *Chem. Phys. Letters*, 1970, **7**, 414.

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[19] C. E. Moore, 'Atomic Energy Levels,' N.B.S. Circular 467, U.S. Government Printing Office, Washington D.C., 1958.

[20] Ref. 15, p. 120.

of band (C). A small stabilisation of the M–P bonding orbital of lowest i.p. was observed[21] through the sequence [Cr(PF_3)$_6$], [Fe(PF_3)$_5$], and [Ni(PF_3)$_4$], which also follows the sequence of *d*-orbital energy. The very substantial increase in the t_2 (P) i.p. from Ni to Pt indicates a stronger σ-bond,[8] and this is probably partly as a result of the more stable *d* orbital in Pt. However, the same shift in *d*-orbital i.p. from Ni to Pd produces very little change (0·5 eV) in the i.p. of t_2 (P). A reasonable but not rigorous deduction would be that σ-bonding in the Pd compound is weaker than in the Ni compound; it is certainly weaker than in the Pt compound. Discussion of the t_2 (M) i.p. is deferred until the high-i.p. portions of the spectra have been examined.

The substantial variations of the *e* and t_2 (P) i.p. are in marked contrast to the invariance of the i.p. beyond 15 eV. So far we have only discussed σ-bonding, but it is widely accepted that the stability of PF_3 compounds of transition metals is connected with an ability of this ligand to accept charge from the metal atom.[22,23] In amine–borane or –BF_3 compounds, where there is no obvious mechanism for such back donation of charge, p.e. spectra show a general increase in *all* ligand i.p.s by *ca.* 1 eV on formation of the complex.[24,25] Similar stabilisations of the F lone-pair and P–F bonding orbitals of PF_3 were observed[24] on forming the compounds PF_3,BH_3 and PF_3O, the stabilisation being slightly greater for the latter. In contrast, the corresponding region in the metal compounds is very similar to that of free PF_3, and this constancy of i.p. is most easily interpreted as the result of back donation. Since σ-bonding seems to be strongest for Pt, the π-back donation must also be greatest for this atom.[8] The back donation may also be expected to stabilise both the t_2 (M) and *e* orbitals, and the i.p.s of these orbitals are substantially greater than the *d*-orbital i.p. in Table 2 in all cases, but the stabilisation is smallest for Pd.

The only noticeable difference between the spectra of PF_3 and of the compounds beyond 15 eV is the disappearance of the 18·5 eV band of PF_3 in the compounds. The orbital assigned to this ionisation of free PF_3 is of a_1 symmetry[4] and has appreciable P character. In PF_3,BH_3 this orbital is destabilised by interaction with the lower-lying B 2*s* orbital;[24] correspondingly in the metal compounds at least the t_2 combinations of this orbital may be expected to be stabilised by interaction with the higher-lying t_2 (M) and t_2 (P) sets. A small stabilisation of this type will account for collapse of the last two bands of PF_3 in to one in the metal compounds.

The t_2 (M) orbitals have an almost constant i.p. in the set of three compounds. The constancy between Ni and Pt can readily be explained on the basis of Figure 2 as a cancellation between the greater initial *d*-orbital stability in Pt and the greater antibonding interaction with PF_3. However, on grounds of σ-interaction alone, this would lead to a significantly greater i.p. for t_2 (Pd) since σ-bonding appears to be weaker here and the corresponding antibonding destabilisation will be smaller than for Pt. This may be explained if π-back donation is also smaller for Pd.

In summary, the changes in *e*-orbital i.p. reflect mainly the changes in atomic *d*-orbital i.p., while the t_2 (P) i.p. changes include contributions from this and from differing σ-bonding effects. The constancy of the ligand i.p. suggests that back donation approximately cancels the charge donation in the σ-bonding, and interpretation of the constancy of the t_2 (M) i.p. needs to invoke cancellations in all three effects. Both σ- and π-bonding is strongest for Pt and is probably weakest for Pd. The accuracy of this picture of the bonding depends to some extent on the accuracy of Koopmans' theorem, but such inaccuracies as have been reported are mainly different relaxation energies for orbitals of very different localisation properties.[6,26,27] By comparing similar orbital i.p.s in different compounds such effects are reduced.

It is evident from the spectra reported here and elsewhere[20] that the i.p.s of the P–M bonding orbitals are very sensitive to the nature of the metal atom in these compounds. It would be interesting to have comparable data for C–M bonding orbitals in metal carbonyls, but interpretation of the carbonyl spectra is confused by overlapping of the ionisations of the CO π-orbitals. However, attempts have been made on the basis of comparison with calculations and of intensity changes to assign the M–C bonding-orbital i.p. in the hexacarbonyls of Cr, Mo, and W.[5] If these tentative assignments are accepted, then the i.p. of the corresponding t_{1u}, e_g, and a_{1g} orbitals are almost invariant to the metal: the values for t_{1u} are Cr 13·38, Mo 13·32, and W 13·27 eV. The reasons for this marked difference in behaviour of the CO and PF_3 lone pairs are not clear, but it is possible that this may be related to the greater stability of [Pt(PF_3)$_4$] compared to [Pt(CO)$_4$].

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