The Chemistry of Heteroarylphosphorus Compounds. Part 15.[1] Phosphorus-31 Nuclear Magnetic Resonance Studies of the Donor Properties of Heteroarylphosphines towards Selenium and Platinum(II)

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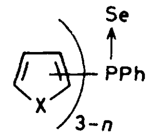
The donor properties of a series of heteroarylphosphines (bearing 2- and 3-furyl, 2- and 3-thienyl, and 1-methylpyrrol-2-yl groups directly bound to phosphorus) towards selenium and platinum(II) acceptors have been investigated by ^{31}P n.m.r. studies of the one-bond coupling constants $^1J(^{77}\mathrm{Se}-^{31}\mathrm{P})$ and $^1J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$. It is shown that the respective coupling constants increase as the heteroaryl groups become more electron withdrawing, indicating an increased *s* character for the phosphorus lone pair. The implications of this for the relative donor properties of the heteroarylphosphines and $\mathrm{PPh_3}$ are considered.

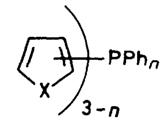
WE have been investigating the chemistry of organophosphorus compounds in which one or more heteroaromatic substituents are directly attached to phosphorus, in order to study the interactions between heteroaromatic systems and phosphorus in a wide variety of situations. In previous papers in this series we have reported on the effects of 2- and 3-furyl, 2- and 3-thienyl, 2-pyrrolyl, and 1-methylpyrrol-2-yl substituents on the rate and course of reactions involving nucleophilic attack at phosphorus in phosphonium salts [2-6] (and related phosphonium betaines [7,8]), phosphine oxides, phosphinate,[9] and phosphonate [10] esters and also on the rate of quaternization of phosphines.[11] We have found that for the above heteroaryl substituents there is considerable variation in electronic properties, depending on the nature of the heteroatom and its position with respect to phosphorus. In general, the 2-furyl and 2-thienyl groups behave as moderately strongly electron-withdrawing substituents, whereas the 2-pyrrolyl group is significantly less electron withdrawing. The following order of apparent electron-withdrawing power applies in many of the systems studied: 2-furyl > 2-thienyl > phenyl > 2-pyrrolyl (and 1-methylpyrrol-2-yl). The 3-furyl and 3-thienyl substituents appear to be much less electron withdrawing than the 2-isomers, presumably a reflection of the greater distance of the electronegative heteroatom from phosphorus.

However, a study of the donor properties of a series of (2-thienyl)phosphines towards nickel(II) and cobalt(II) ions surprisingly showed [12] that these phosphines appear to be better donors than triphenylphosphine, as indicated by band positions in the crystal-field spectra of pseudo-tetrahedral complexes of the type $[\mathrm{ML_2X_2}]$ (L = phosphine, X = halogen). As this result appeared to be in conflict with the general conclusions reached from the above studies, we were interested to make further investigations of the donor properties of heteroarylphosphines.

We have attempted to gain further insight into the effects of the heteroaryl substituents on the availability of the lone pair at phosphorus from a study of one-bond n.m.r. coupling constants between phosphorus and adjacent acceptor atoms. It is well known that coupling constants between directly bonded atoms arise predominantly from the Fermi-contact interaction between nuclear moments and electron spins in *s* orbitals,[13,14] and there have been a number of suggestions in the literature that there is a correlation between the magnitude of such coupling constants and the lengths of the bonds between adjacent atoms.[15-19] In this paper, we report studies of selenium–phosphorus coupling in a series of heteroarylphosphine selenides, (1), and platinum–phosphorus coupling in a series of platinum(II) complexes of the heteroarylphosphines (2).



(1) n = 0–2
X = O, S, or NMe



(2) n = 0–2
X = O or S

RESULTS AND DISCUSSION

Tertiary phosphines react readily with selenium in refluxing chloroform or toluene solution to form the corresponding phosphine selenide. There has been considerable recent interest in such compounds, particularly with regard to the nature of the phosphorus–selenium bond, and to studies of $^1J(^{77}\mathrm{Se}-^{31}\mathrm{P})$ coupling. The magnitude of $^1J(^{77}\mathrm{Se}-^{31}\mathrm{P})$ is very much dependent upon the nature of the organic groups bound to phosphorus, electron-withdrawing groups causing the coupling constant to increase whereas electron-donating and bulky groups cause it to decrease. It has been concluded that the phosphorus–selenium bond in phosphine selenides has little $\mathrm{P}_{3d\pi}$–$\mathrm{Se}_{4d\pi}$ character,[20,21] and the effects of substituents at phosphorus on the magnitude of the coupling constant have been discussed in terms of the degree of occupation by the lone pair of the phosphorus 3*s* orbital (although it should be remembered that the expression for the one-bond coupling constant contains a number of other terms which could also vary). Electron-withdrawing groups result in an increase in the *s* character of the lone pair, whereas electron-donating groups result in a decrease in *s* character,[22,23] these effects being commonly discussed in terms of Bent's rule.[24] The presence of bulky substituents at phosphorus likewise results in a decrease in the *s* character of the lone pair as a result of the widening of intervalence angles.[23]

The ^{31}P n.m.r. parameters for a range of heteroaryl and arylphosphine selenides are presented in Table 1.

TABLE 1

Phosphorus-31 n.m.r. data for heteroarylphosphine selenides [a]

Phosphine, $PR^1_2R^2$	$\delta(PR_3)$/ p.p.m.	$\delta(PR_3Se)$/ p.p.m.	$^1J(^{77}Se-^{31}P)$/ Hz
$R^1 = R^2 = Ph$	−4.7	35.9	732
$R^1 = Ph$, $R^2 =$ 2-thienyl	−19.3	20.6	743
$R^1 =$ 2-thienyl, $R^2 = Ph$	−33.6	9.3	752
$R^1 = R^2 =$ 2-thienyl	−45.8	−4.2	757
$R^1 = R^2 =$ 3-thienyl	−43.2	−1.4	740
$R^1 = Ph$, $R^2 =$ 2-furyl	−26.6	16.9	754
$R^1 =$ 2-furyl, $R^2 = Ph$	−50.8	−2.0	774
$R^1 = R^2 =$ 2-furyl	−76.4	−22.1	793
$R^1 = R^2 =$ 3-furyl	−81.9	−20.3	745
$R^1 = Ph$, $R^2 =$ 1-methylpyrrol-2-yl	−29.7	17.5	728
$R^1 = Ph$, $R^2 =$ *o*-tolyl	−13.0	32.6	730
$R^1 = R^2 =$ *m*-trifluoromethylphenyl	−4.3	35.5	766
$R^1 = R^2 =$ *p*-methoxyphenyl	−9.3	−39.7	708 [b]

[a] Recorded in dichloromethane. [b] Ref. 23.

It can be seen that progressive replacement of the phenyl groups in PPh_3 by 2-thienyl groups causes the selenium–phosphorus coupling constant to increase, indicating that the *s* character of the phosphorus lone-pair orbital is increasing, presumably a reflection of the electron-withdrawing nature of the 2-thienyl group. A similar, but more pronounced effect, is seen for the 2-furyl group, and it is of interest to compare the effects of these heteroaryl substituents with those of the *m*-trifluoromethylphenyl and *p*-methoxyphenyl groups as indicated by the magnitudes of $^1J(^{77}Se-^{31}P)$ in the related triarylphosphine selenides. The 2-furyl group appears to be appreciably more electron withdrawing than *m*-trifluoromethylphenyl. In contrast to the substituent effects of the 2-furyl and 2-thienyl groups, the 1-methylpyrrol-2-yl group appears to be slightly electron donating with respect to phenyl, although in this case there could also be a steric effect due to the *N*-methyl group, comparable to the *o*-tolyl group. As expected from earlier studies of phosphonium salt hydrolysis,[8] the 3-furyl and 3-thienyl groups are less electron withdrawing than the 2-isomers but nevertheless still more electron withdrawing than phenyl.

The larger coupling constants for the above 2- and 3-furyl and -thienyl phosphine selenides indicate that the phosphorus lone pair has greater *s* character compared with that in triphenylphosphine selenide, due to the greater electron-withdrawing nature of the heteroaryl substituents. In consequence, the bonds from phosphorus to selenium in these compounds would therefore be expected to be shorter than in PPh_3Se. We have shown recently [25] that the increase in selenium–phosphorus coupling constants in a series of dibenzophosphole selenides compared to those observed in a series of related acyclic phosphine selenides can be correlated with a corresponding increase in the selenium–phosphorus i.r. stretching frequency, presumably indicating that the bond is stronger in the phosphole selenides as a result of the increased *s* character of the phosphorus lone pair caused by the geometrical constraints imposed by the ring system on the intervalence angles at phosphorus. Unfortunately, a similar correlation of coupling constants with i.r. data for the phosphorus–selenium bond in the above heteroarylphosphine selenides was not possible, owing to the superimposition of ν(P–Se) and skeletal bands arising from the heterocyclic rings. However, there are a number of indications in the literature that an increase in the magnitude of single-bond coupling constants, *e.g.* between phosphorus and platinum in phosphine or phosphite complexes of platinum(II) halides (as a result of the increased electron-withdrawing nature of the phosphorus substituents), is paralleled by a shortening of the phosphorus–platinum bond, although it has also been pointed out that such a shortening may not necessarily lead to a strengthening of the bond.[15-19]

In addition to the above studies on the heteroarylphosphine selenides, we have also prepared a series of complexes of the above heteroarylphosphines with platinum(II) chloride, and the ^{31}P n.m.r. data for these complexes are presented in Table 2. As indicated from the magnitude of the coupling constants, all of the complexes have the *cis* square-planar structure. The changes in the coupling constants as phenyl groups are replaced by the 2-furyl or 2-thienyl groups are broadly similar to those reported above for the related heteroarylphosphine selenides, although ^1J(Pt–P) for the complex of 2-furyldiphenylphosphine is smaller than for that of PPh_3. In the case of platinum complexes derived from tris(3-furyl)- and tris(3-thienyl)-phosphine, the 3-heteroaryl substituents appear to be less electron withdrawing relative to phenyl compared to the situation in the corresponding phosphine selenides. Although the changes in coupling constant noted here are much smaller *

TABLE 2

Phosphorus-31 n.m.r. data for dichlorobis(heteroarylphosphine)platinum(II) complexes *

Phosphine $PR^1_2R^2$	$\delta(PR_3)$/ p.p.m.	$\delta(R_3P-Pt)$/ p.p.m.	$^1J(^{195}Pt-^{31}P)$/ Hz
$R^1 = R^2 = Ph$	−4.7	15.0	3 678
$R^1 = Ph$, $R^2 =$ 2-thienyl	−19.3	4.5	3 685
$R^1 =$ 2-thienyl, $R^2 = Ph$	−33.6	−7.0	3 699
$R^1 = R^2 =$ 2-thienyl	−45.8	−17.7	3 728
$R^1 = R^2 =$ 3-thienyl	−43.2	−18.6	3 662
$R^1 = Ph$, $R^2 =$ 2-furyl	−26.6	−1.5	3 665
$R^1 =$ 2-furyl, $R^2 = Ph$	−50.8	−18.3	3 698
$R^1 = R^2 =$ 2-furyl	−76.4	−36.3	3 716
$R^1 = R^2 =$ 3-furyl	−81.9	−42.1	3 649

* Recorded in dichloromethane.

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* Greater changes in ^1J(Pt–P) occur when phenyl is replaced by 2-furyl or 2-thienyl when attached to platinum rather than to phosphorus (C. Eaborn, K. J. Odell, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1978, 357). We thank a referee for pointing this out.

than those that are the subject of earlier correlations [15-19] between coupling constants and bond lengths in phosphine–platinum(II) halide complexes, it presumably follows that the above 2-heteroarylphosphine ligands form shorter bonds to platinum than does PPh_3 as a result of the electron-withdrawing nature of the heteroaryl substituents and the corresponding increase in the *s* character of the phosphorus lone pair. Consequently, it is now possible to rationalise our earlier observations [12] that phosphines bearing 2-thienyl substituents cause a greater perturbation of the metal-ion *d* orbitals in pseudo-tetrahedral complexes of nickel(II) than does PPh_3, and also that the metal–ligand bond in (2-thienyl)-phosphine–nickel(II) complexes appears (from a consideration of the Racah parameters) to have a greater degree of covalency than is the case for the triphenylphosphine complexes.

Finally, we would wish to draw attention to the effects of replacing the phenyl groups of PPh_3 by heteroaryl substituents on the phosphorus-31 chemical shift of the phosphines, the phosphorus becoming increasingly shielded (Table 1). The factors which affect ^{31}P chemical shifts of phosphines have been considered at length [26-29] and it has been concluded that the following are important: (*a*) the electronegativity of the groups attached to phosphorus, the more electron withdrawing the greater is the shielding; (*b*) the bond angles at phosphorus; and (*c*) the effects of π bonding between the substituent and phosphorus. Mann [29] has concluded that π bonding between phenyl rings and phosphorus is unlikely and that the ^{31}P chemical shifts of tertiary arylphosphines are dominated by bond-angle changes. In the above heteroarylphosphine series, the 2-furyl and 2-thienyl groups behave consistently as electron withdrawing relative to phenyl, and so the progressive increase in shielding at phosphorus on introduction of these groups could be accounted for in terms of group electronegativity effects. However, a comparison of the chemical shifts for the monoheteroaryldiphenylphosphines shows that the 1-methylpyrrol-2-yl group has a greater shielding effect than 2-furyl in spite of its much reduced electron-withdrawing character as indicated by reactivity studies and the above coupling-constant data. Similarly, it is seen that the 3-furyl and 3-thienyl groups have a greater shielding effect than the related 2-isomers, the phosphorus in tri(3-furyl)phosphine having a very high chemical shift for a tertiary arylphosphine. Furthermore, it would not seem to be possible to account for the above phosphorus chemical-shift data on the basis of bond-angle changes at phosphorus. Tolman [15] has pointed out that, in general, the phosphorus becomes increasingly deshielded as the cone angles (and hence the intervalence angles at phosphorus) increase. However, for *o*-tolylphosphines, this generalisation does not seem to apply, since the phosphorus of tri(*o*-tolyl)-phosphine ($\delta = -24.6$ p.p.m.) is shielded with respect to that in tri(*p*-tolyl)phosphine ($\delta = -2.5$ p.p.m.). In the above heteroarylphosphine series, it is unlikely that steric effects are of major significance, except perhaps in the case of the 1-methylpyrrol-2-yl group, which appears similar to the *o*-tolyl group. Nevertheless, a comparison of the chemical-shift data for (1-methylpyrrol-2-yl)diphenylphosphine and diphenyl(*o*-tolyl)-phosphine shows that the phosphorus of the former is shielded to a greater extent to that of the latter, and hence other factors would seem to be involved. In conclusion, it is therefore difficult to account for the heteroarylphosphine chemical-shift data in terms of the above factors.

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded on a JEOL PFT-100 Fourier-transform n.m.r. spectrometer at 40.48 MHz with proton-noise decoupling. Chemical shifts are reported on the δ scale with respect to external 85% H_3PO_4 and are accurate to ±0.1 p.p.m. Shifts to high field are negative in sign. Coupling constants are reported in Hz and are accurate to ±1.2 Hz.

Preparation of Phosphine Selenides.—The phosphine selenides were prepared by the reaction of the phosphine (10^{-3} mol) with selenium (0.3 g, excess) under reflux for 5 h in chloroform (2.5 cm^3). The excess of selenium was removed by filtration, and the filtrate evaporated to give the following compounds: *(2-furyl)diphenylphosphine selenide*, m.p. 128 °C (from EtOH) (Found: C, 57.8; H, 3.90. $C_{16}H_{13}OPSe$ requires C, 58.0; H, 3.95%); *di(2-furyl)phenylphosphine selenide*, m.p. 120 °C (from (EtOH) (Found: C, 51.95; H, 3.30. $C_{14}H_{11}O_2PSe$ requires C, 52.3; H, 3.45%); *phenyldi(2-thienyl)phosphine selenide*, m.p. 146 °C (from EtOH) (Found: C, 47.75; H, 3.25. $C_{14}H_{11}PS_2Se$ requires C, 47.6; H, 3.15%); *tri(3-furyl)phosphine selenide*, m.p. 107 °C (from EtOH) (Found: C, 46.4; H, 2.90. $C_{12}H_9O_3PSe$ requires C, 46.3; H, 2.90%); *(1-methylpyrrol-2-yl)-diphenylphosphine selenide*, m.p. 101 °C (from EtOH) (Found: C, 59.2; H, 4.60. $C_{17}H_{16}NPSe$ requires C, 59.3; H, 4.70%); *tris(3-trifluoromethylphenyl)phosphine selenide*, m.p. 105 °C (from hexane–EtOH, 4 : 1 v/v) (Found: C, 46.5; H, 2.15. $C_{21}H_{12}F_9PSe$ requires C, 46.25; H, 2.20%).

Also prepared by the above method were the following known compounds: triphenylphosphine selenide,[30] tri(2-furyl)phosphine selenide,[31] tri(2-thienyl)phosphine selenide,[32] tri(3-thienyl)phosphine selenide,[32] diphenyl(*o*-tolyl)-phosphine selenide,[33] and diphenyl(2-thienyl)phosphine selenide.[25]

Preparation of Platinum(II) *Chloride Complexes of Phosphines.*—To a hot solution of the phosphine (5×10^{-4} mol) in ethanol (2 cm^3) was added dropwise a cold solution of potassium tetrachloroplatinate(II) (2.5×10^{-4} mol) in water (0.5 cm^3). The resulting mixture was heated for 5 min and then allowed to cool, to give crystals of the following new complexes: *dichlorobis[tri(2-furyl)phosphine]platinum*(II), m.p. > 288 °C (decomp.) (Found: C, 39.4; H, 2.35. $C_{24}H_{18}Cl_2O_6P_2Pt$ requires C, 39.45; H, 2.45%); *dichlorobis[di(2-furyl)phenylphosphine]platinum*(II), m.p. >300 °C (decomp.) (Found: C, 45.1; H, 2.80. $C_{28}H_{22}Cl_2O_4P_2Pt$ requires C, 44.8; H, 2.95%); *dichlorobis[(2-furyl)diphenylphosphine]platinum*(II), m.p. > 294 °C (decomp.) (Found: C, 50.1; H, 3.25. $C_{32}H_{26}Cl_2O_2P_2Pt$ requires C, 49.85; H, 3.40%); *dichlorobis[tri(3-furyl)phosphine]platinum*(II), m.p. > 288 °C (decomp.) (Found: C, 39.8; H, 2.40. $C_{24}H_{18}Cl_2O_6P_2Pt$ requires C, 39.45; H, 2.45%); *dichlorobis[tri(2-thienyl)phosphine]platinum*(II), m.p. > 310 °C (decomp.)

(Found: C, 34.65; H, 2.25. $C_{24}H_{18}Cl_2P_2PtS_6$ requires C, 34.85; H, 2.20%); *dichlorobis*[*phenyldi*(2-*thienyl*)*phosphine*]*platinum*(II), m.p. > 310 °C (decomp.) (Found: C, 41.75; H, 2.95. $C_{28}H_{22}Cl_2P_2PtS_4$ requires C, 41.25; H, 2.70%); *dichlorobis*[*diphenyl*(2-*thienyl*)*phosphine*]*platinum*(II), m.p. > 310 °C (decomp.) (Found: C, 48.0; H, 3.30. $C_{32}H_{26}Cl_2P_2PtS_2$ requires C, 47.85; H, 3.25%); *dichlorobis*[*tri*(3-*thienyl*)*phosphine*]*platinum*(II), m.p. > 325 °C (decomp.) (Found: C, 35.25; H, 2.30. $C_{24}H_{18}Cl_2P_2PtS_6$ requires C, 34.85; H, 2.20%).

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REFERENCES

[1] Part 14, D. W. Allen and H. Ward, *Z. Naturforsch., Teil B.*, 1980, **35**, 754.

[2] D. W. Allen, *J. Chem. Soc. B*, 1970, 1490.

[3] D. W. Allen and B. G. Hutley, *J. Chem. Soc., Perkin Trans. 2*, 1972, 63.

[4] D. W. Allen and B. G. Hutley, *J. Chem. Soc., Perkin Trans. 2*, 1972, 67.

[5] D. W. Allen, I. Harness, B. G. Hutley, and I. W. Mowat, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1912.

[6] D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1690.

[7] D. W. Allen, B. G. Hutley, and T. C. Rich, *J. Chem. Soc., Perkin Trans. 2*, 1973, 820.

[8] D. W. Allen and B. G. Hutley, *J. Chem. Soc., Perkin Trans. 1*, 1978, 675.

[9] D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1705.

[10] D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 1977, 789.

[11] D. W. Allen, J. R. Charlton, and B. G. Hutley, *Phosphorus*, 1976, **6**, 191.

[12] D. W. Allen and D. F. Ashford, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1953.

[13] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[14] J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, 1969, **2**, 345.

[15] C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313 and refs. therein.

[16] G. A. Mather, A. Pidcock, and G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.*, 1973, 2095.

[17] P. B. Hitchcock, B. Jacobson, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2038; 2043.

[18] I. MacLeod, L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, and R. Walker, *J. Organomet. Chem.*, 1975, **97**, C7.

[19] A. N. Caldwell, L. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1977, 2265.

[20] W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1973, 2162.

[21] S. O. Grim and E. D. Walton, *Inorg. Chem.*, 1980, **19**, 1982.

[22] W. Stec, A. Okruszek, B. Uznański, and J. Michalski, *Phosphorus*, 1972, **2**, 97.

[23] R. P. Pinnell, C. A. Megerle, S. L. Manatt, and P. A. Kroon, *J. Am. Chem. Soc.*, 1973, **95**, 977.

[24] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

[25] D. W. Allen and B. F. Taylor, *J. Chem. Res.* (*S*), 1981, 220.

[26] J. H. Letcher and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 75, 169.

[27] G. Mavel, *Annu. Rev. NMR Spectrosc.*, 1973, **5B**, 1.

[28] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.

[29] B. E. Mann, *J. Chem. Soc., Perkin Trans. 2*, 1972, 30.

[30] A. Michaelis and H. Köhler, *Chem. Ber.*, 1876, **9**, 519, 1053.

[31] E. Niwa, H. Aoki, H. Tanaka, and K. Munakata, *Chem. Ber.*, 1966, **99**, 712.

[32] H. J. Jakobsen and J. A. Nielsen, *J. Mol. Spectrosc.*, 1970, **33**, 474.

[33] P. A. W. Dean and L. Polensek, *Can. J. Chem.*, 1980, **58**, 1627.