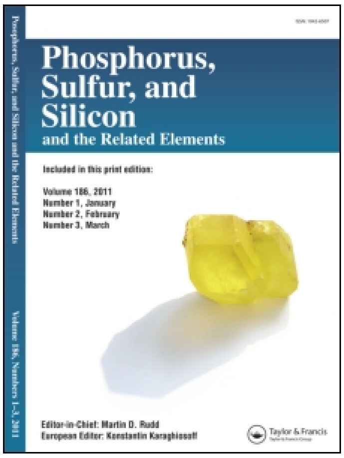

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ON THE PHOSPHORUS-31 CHEMICAL SHIFTS OF SUBSTITUTED TRIARYLPHOSPHINES

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The ^{31}P chemical shifts of eleven $(4\text{-}ZC_6H_4)_3P$ compounds show a slight correlation with the Hammet σ_{para} constant of Z. The unusually large upfield chemical shifts of $(2\text{-}ZC_6H_4)_3P$ compounds are attributed to an extreme "gamma" effect caused by the restricted conformations due to the steric influence of the ortho substituents. Chemical shifts are given for about thirty triarylphosphines, and group contributions to phosphine chemical shifts are listed for twenty-one aryl groups.

INTRODUCTION

Some years ago we had prepared a number of substituted aryl tertiary phosphines[1] for studies of phosphine coordination compounds.[2] Although many of these tertiary phosphines have been reported by us[1] and others [3-11] and in various physical studies,[1b,2,12-16] a considerable number of these compounds and their physical properties have not yet been published. These substituted aryl tertiary phosphines and their phosphorus-31 chemical shifts are reported here.

RESULTS AND DISCUSSION

Thirty substituted aryl tertiary phosphines prepared in this study are listed in Table I along with melting points, methods of preparation, yields, and phosphorus-31 chemical shifts. Included are eleven tris(4-substituted aryl) phosphines, six tris(3-substituted aryl) phosphines, three tris(2-substituted aryl) phosphines and ten mixed arylphosphines.

The chemical shifts of phosphorus have been the subject of numerous theoretical[17,18] and empirical[19-22] treatments and have been shown to depend on bond angles about phosphorus, other steric effects, electronegativity of groups bonded to phosphorus, molecular orbital occupancy and excitation energies. Application of quantum mechanical theory to the prediction and explanation of phosphorus chemical shifts requires numerous assumptions and often empirical correlations are more useful, if not more satisfying. Some observations from the list of chemical shifts of the substituted arylphosphines follow. First, the group additivity concept[23] applies. For example, the series $(2\text{-}CH_3C_6H_4)_3P$, $(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$, and $(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$ has chemical shifts of −30.0, −21.4, and −13.4 ppm, respectively. The *o*-tolyl group thus has a group contribution of −10.0 ppm. Other group contributions are listed in Table II. The consistent application of the additivity concept for all these compounds would predict a chemical shift of about −21 ppm for $(2\text{-}ClC_6H_4)_3P$ in sequence with the observed chemical shifts of −15.8 and −10.9 ppm, respectively for $(2\text{-}ClC_6H_4)_2(C_6H_5)P$ and $(2\text{-}ClC_6H_4)(C_6H_5)_2P$. The synthesis of $(2\text{-}ClC_6H_4)_3P$ was unsuccessful in our laboratory and was prepared only in low yield earlier.[7b] For these reasons we feel that the reported chemical shift of −9.2 ppm[8b] for $(2\text{-}ClC_6H_4)_3P$ is probably in error.

Secondly, the phosphines with ortho substituents have unusually large upfield chemical shifts[1c] compared to triphenylphosphine and meta and para-substituted arylphosphines. We believe this is an illustration of an extreme "gamma" effect. The gamma effect, an upfield contribution to the chemical shift caused by a substituent in the position gamma to the nucleus in question, was first recognized in ^{13}C chemical shifts[24] and also has been noticed in ^{31}P chemical shifts.[19] The steric cause of the gamma effect for ^{31}P shifts has been espoused by L. D. Quin.[22] In tertiary alkylphosphines, where the gamma substituent is free to rotate toward (above the lone pair of electrons or tucked under the phosphorus pyramid) or away from the phosphorus atom, the gamma contribution to the ^{31}P chemical shift is only a few ppm (*ca.* 3 ppm). However, in $(2\text{-}CH_3C_6H_4)_3P$ the

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TABLE I

^{31}P Chemical shifts and melting points for some substituted aryl tertiary phosphines

Tertiary phosphine	mp (°C)	Prep. method[a]	Yield (%)	δ p(ppm)[b]
$(4\text{-}CH_3C_6H_4)_3P$	146 (146)[c]	B	71	−8.0
$[4\text{-}(CH_3)_2CHC_6H_4]_3P$	144–146	A	19	−7.8
$[4\text{-}(CH_3)_3CC_6H_4]_3P$	236–239	A	59	−9.1
$(4\text{-}CF_3C_6H_4)_3P$[d]	68–70 (71–73)[e]	A	14	−6.0
$(4\text{-}CH_3OC_6H_4)_3P$	130 (131)[c]	A	41	−10.2 (−9.8)[f]
$(4\text{-}CH_3SC_6H_4)_3P$[g]	–	–	–	−8.3
$[4\text{-}(CH_3)_2NC_6H_4]_3P$	271–275 (278–282)[h]	B	43	−11.5
$[4\text{-}(CH_3)_3SiC_6H_4]_3P$	187–189 (95–96)[i]	A	89	−5.8
$(4\text{-}FC_6H_4)_3P$	77–79 (77–80)[k]	A	76	−9.0 (−8.8)[j] (−9.4)[f] (−10.0)[l]
$(4\text{-}ClC_6H_4)_3P$	102 (103)[n]	A	75	−8.5 (−9.2)[m] (−9.6)[l]
$(4\text{-}BrC_6H_4)_3P$[g]	118–119	A	–	−8.2
$(3\text{-}CH_3C_6H_4)_3P$	99–100 (100)[n]	B	69	−5.3
$(3\text{-}CF_3C_6H_4)_3P$[d]	bp 130–132/0.2 mm	A	low	−5.0
$(3\text{-}CH_3OC_6H_4)_3P$	114–115 (115)[n]	A	51	−2.1
$[3\text{-}(CH_3)_3SiC_6H_4]_3P$	oil	A	39	−5.6
$(3\text{-}ClC_6H_4)_3P$	64–66 (67)[n]	A	17	−4.4 (−5.6)[l]
$(3\text{-}FC_6H_4)_3P$	(62)[c]	A	low	−6.5 (−6.5)[j] (−5.6)[l]
$(2\text{-}CH_3C_6H_4)_3P$	123–125 (125)[n]	B	64	−30.0 (−30.2)[p]
$(2\text{-}CF_3C_6H_4)_3P$	164–165	C	21	−18.5
$(2\text{-}CH_3OC_6H_4)_3P$	202–203 (204)[c]	A	23	−38.5
$(2\text{-}ClC_6H_4)_3P$	(185)[n]	–	–	(−9.2)[m,q]
$(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$	77–79	B	43	−21.4
$(2\text{-}CF_3C_6H_4)_2(C_6H_5)P$[d]	126–127	C	53	−14.5
$(2\text{-}CH_3OC_6H_4)_2(C_6H_5)P$	148–150 (164–165)[u]	A	27	−27.2
$(2\text{-}ClC_6H_4)_2(C_6H_5)P$	137–138 (133–134)[r]	A	33	−15.8
$(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$	66–67 (67–68)[s]	B	58	−13.4
$(2\text{-}CF_3C_6H_4)(C_6H_5)_2P$	86–87	C	45	−12.0
$(2\text{-}CH_3OC_6H_4)(C_6H_5)_2P$	119–120 (122.5–123.5)[u]	A	55	−16.3 (−13.5)[u]
$(2\text{-}ClC_6H_4)(C_6H_5)_2P$	107–108 (107–108)[t]	A	49	−10.9
$(4\text{-}CH_3C_6H_4)(2\text{-}CH_3C_6H_4)_2P$	73–75	B	52	−22.1
$(4\text{-}CH_3C_6H_4)_2(4\text{-}ClC_6H_4)P$	115–117 (115)[c]	A	72	−8.2

[a] See experimental section.
[b] Negative chemical shifts in CH_2Cl_2 solution are upfield from 85% H_3PO_4. See also Ref. 30.
[c] Ref. 8a.
[d] Ref. 1b.
[e] Ref. 10a.
[f] W. McFarlane, *Org. Mag. Resonance* **1**, 3 (1969).
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[p] C. A. Tolman, *J. Am. Chem. Soc.* **92**, 2956 (1970).
[q] Probably in error, see text.
[r] Ref. 7c.
[s] Ref. 6a.
[t] F. A. Hart, *J. Chem. Soc.* 3224 (1960).
[u] Ref. 11.

TABLE II
Phosphorus chemical shift group contributions[a] for aryl groups in tertiary phosphines

Group	Group contribution	Group	Group contribution
4-$(CH_3)_3SiC_6H_4$	−1.9	3-$CH_3OC_6H_4$	−0.7
4-$CF_3C_6H_4$	−2.0	3-ClC_6H_4	−1.5
4-$(CH_3)_2CHC_6H_4$	−2.6	3-$CF_3C_6H_4$	−1.7
4-$CH_3C_6H_4$	−2.7	3-$CH_3C_6H_4$	−1.8
4-BrC_6H_4	−2.7	3-$(CH_3)_3SiC_6H_4$	−1.9
4-ClC_6H_4	−2.8	3-FC_6H_4	−2.2
4-$CH_3SC_6H_4$	−2.8	2-$CF_3C_6H_4$	−6.2
4-FC_6H_4	−3.0	2-ClC_6H_4	−6.9
4-$(CH_3)_3CC_6H_4$	−3.0	2-$CH_3C_6H_4$	−10.0
4-$CH_3OC_6H_4$	−3.4	2-$CH_3OC_6H_4$	−12.8
4-$(CH_3)_2NC_6H_4$	−3.8		

[a] See Ref. 19.

methyl group is cis to phosphorus on the benzene ring with the rings arranged such that the methyls are conformationally favored to be above the pyramid of the phosphorus and the C_1-C_4 axes of the phenyl groups.[13] The crystal structure[14] of $(2\text{-}CH_3C_6H_4)_3P$ has confirmed this earlier prediction. Thus, the proximity of the gamma group to the lone pair of phosphorus probably causes this enhanced gamma effect. Further evidence for this proposal is that the unusually large gamma effect in the tris-(2-substituted)-arylphosphines is lost when the lone pair of phosphorus is quaternized.[25] The chemical shifts of the resulting phosphonium salts are not vastly different from the respective meta and para-substituted analogues.[25-26]

Third, there appears to be some correlation of the chemical shifts of $(4\text{-}ZC_6H_4)_3P$ with the Hammet σ_{para} parameter[27] of Z (Figure 1). Previously, in the case of $(4\text{-}ZC_6H_4)PH_2$ no correlation was observed,[28] but the larger number and variety of compounds in this study permits such a correlation. The $(4\text{-}Me_3SiC_6H_4)_3P$ falls substantially off the curve, indicating that the phosphorus is less shielded than anticipated from the σ-parameter. This is not an unusual circumstance for the *p*-trimethylsilyl group, which enhances the acid strength of phenol and decreases the base strength of aniline,[29] indicating an electron withdrawing property. The correlation coefficient is only 0.69 for all the para-substituted compounds, but increases to 0.84 when $(4\text{-}Me_3SiC_6H_4)_3P$ is excluded. Admittedly, this is still not a good correlation, however it is clear that the compounds with para electron withdrawing groups have less shielded phosphorus atoms than those with electron releasing groups. The trend is not very clear in the meta-substituted compounds where the electronegative OCH_3 and Cl groups cause the expected lower shielding of phosphorus (−2.1 and −4.4 ppm, respectively)[30] but $(3\text{-}FC_6H_4)_3P$ has unexpectedly higher shielding at phosphorus (−6.5 ppm).

Finally, we found the melting point of $(4\text{-}Me_3SiC_6H_4)_3P$ to be 187–189° whereas the reported[31] melting point is 95–96°. This discrepancy is unexplained. Our compound has good microanalyses, the expected ^{31}P chemical shift, the expected proton nmr spectrum [Ph, multiplet, 7.2 ppm; Me_3Si, sharp singlet, 0.26 ppm; intensity ratio, 12:27.7 (theoretical 12:27)], and is oxidized with aqueous H_2O_2 to give the oxide with $\nu_{P=O}$ at 1188 cm^{-1} (absent in the phosphine) and a ^{31}P shift of +30.0 ppm. The similar $[4\text{-}(CH_3)_3CC_6H_4]_3P(O)$ has a ^{31}P chemical

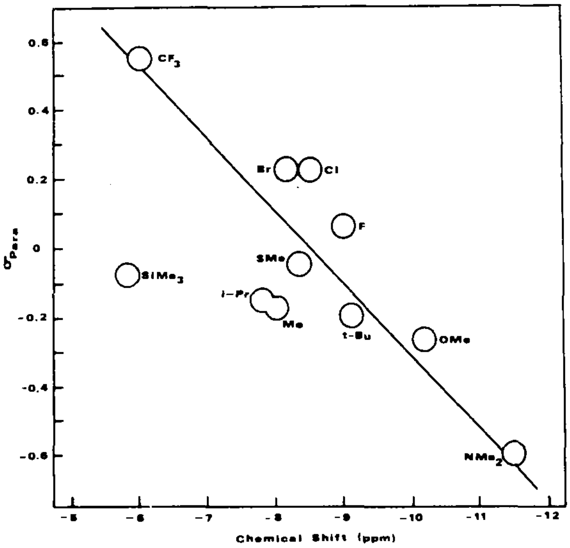

FIGURE 1 Hammett σ constants *vs.* ^{31}P chemical shift for para-substituted triarylphosphines.

shift of +31.4 ppm.[2,26] The melting point of 187-189° might at first seem unusually high for a triarylphosphine but the somewhat similar $[4\text{-}(CH_3)_2CHC_6H_4]_3P$ and $[4\text{-}(CH_3)_3CC_6H_4]_3P$ have melting points of 144-146° and 236-239°, respectively, which makes the melting point of the trimethylsilyl compound seem quite reasonable.

EXPERIMENTAL

Phosphorus-31 nmr spectra of CH_2Cl_2 solutions were measured in 13 stationary tubes with a 3 mm reference tube of 85% H_3PO_4 fixed concentrically in the larger tube. A Varian DP60 spectrometer at 24.3 MHz was employed with calibration accomplished by the side band technique. The chemical shifts are accurate to ±0.3 ppm and are positive when downfield from H_3PO_4.[30]

Proton magnetic resonance spectra were obtained on a Varian A-60A or a Perkin-Elmer R-20A spectrometer with TMS as the internal standard.

The tertiary phosphines were prepared under N_2 from the appropriate phosphorus chloride and Grignard or organolithium reagents. In Table I, Method A refers to the Grignard method; Method B to an organolithium reagent formed from the aryl halide and lithium wire; and Method C from the aryllithium reagent formed from the exchange reaction between *n*-BuLi and the aryl halide.

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