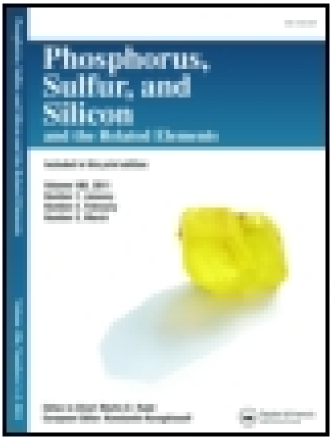

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PERI-INTERACTIONS IN NAPHTHALENES, 2^1. SUBSTITUENT EFFECTS IN (8-DIMETHYLAMINO-NAPHTH-1-YL)- AND [2-(DIMETHYLAMINO-METHYL)PHENYL]-PHOSPHINES ON THE ^{31}P-NMR SIGNAL POSITIONS

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Contrary to claims in the literature, the ^{31}P NMR signal positions of ortho-dimethylaminomethyl-substituted triarylphosphines do not provide evidence for hypercoordination at phosphorus; the observed highfield shifts relative to triphenylphosphine are rather due to the *ortho-effect*. In (8-dimethylamino-naphth-1-yl)phosphines, the signal positions similar to that of triphenylphosphine are the result of the highfield *ortho-effect* and a lowfield peri-substituent effect of about the same magnitude whose nature remains to be explored.

Keywords: Hypercoordination of phosphorus; ^{31}P NMR signal positions; ortho effect; naphthalene geometry

INTRODUCTION

In tetraarylphosphonium cations, the positively charged phosphorus is sufficiently electrophilic as to react with very strong nucleophiles, *e. g.* with aryl lithium compounds to give pentaarylphosphoranes with trigonal bipyramidal (*TBP*) geometry.[2] Not surprisingly, in these pentaorgano phosphoranes, the electrophilicity of the phosphorus is greatly reduced so that hexacoordination of phosphorus, *i.e.* octahedral geometry, is achieved only under particularly favourable conditions. These include the use of the

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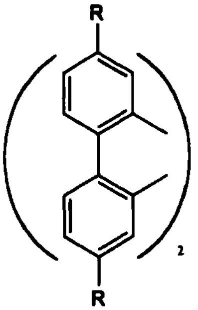
* Corresponding Author.

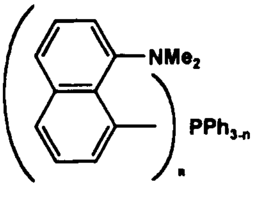
bis(2,2′-biphenylylen)phosphonium cation (**1a**) (and ring-substituted derivatives thereof, **1b**) and of a bidentate bis(organo lithium) reagent, *viz.* a very strong nucleophile for both hypercoordination steps. The reaction products were hexaorgano phosphates whose negatively charged phosphorus atom was devoid of electrophilic properties even towards very strong nucleophiles. In spite of the considerable sterical hindrance, naphth-1-yl lithium and even 8-substituted derivatives thereof reacted smoothly with **1a,b**, though only in a 1:1 ratio to give the respective phosphorane.[3] Among the peri-substituents investigated was the dimethylamino group, hence a substituent which *is* a nucleophile albeit a rather poor one compared with organo lithium compounds. In an 8-dimethylamino-naphth-1-yl ("*DAN*") phosphorus compound of "ideal" geometry, the lengths of a N-$C_{arom.}$ bond (ca. 140 pm[4]) and a P-$C_{arom.}$ bond (182.8 pm in Ph_3P[5]) and the parameters of the "perfect" naphthalene skeleton (planar, bond length C(1,8)-C(9) 142.5 pm,[6] all angles 120°) would place the nitrogen and the phosphorus atoms at a distance of 250 pm,[7] 36% longer than the sum of the covalent radii (N: 74, P: 110 pm[8]), hence at a distance where there would be no significant bond energy (compare the potential energy curve of the H-H bond in the H_2 molecule[9]). Because of the rigidity of the naphthalene skeleton, approximation of the N and P atoms to normal N-P bond length (*i.e.* to increased bond energy) would necessitate a considerable deformation of the "natural" bond angles of the C_{10} unit. A gain of energy by bond formation upon approximation would thus be counterbalanced by the energy required for this distortion. In the DAN-phosphoranes, both reasons should be detrimental for the formation of a dative N→P bond,[10] *i.e.* no hexacoordination would be anticipated,[11] and in fact, from the ^{31}P NMR signal positions, Hellwinkel et al.[3] concluded that there was none. This was later corroborated by Day and Holmes[12] who determined the P-N distance d = 281.0 pm, 12% *longer* than the "ideal" peri-distance and hence evidence for steric repulsion[7] rather than for incipient bond formation.[13] Day and Holmes aptly concluded that, "*while this [P-N distance] is shorter than the van der Waals sum of 3.4 Å, it is not indicative of a bonding interaction of any appreciable magnitude*".[14]

Though still hampered by the poor donor strength of the substituent and of the rigidity of the C_{10} unit, DAN-phosphonium cations should be better candidates for an intramolecular dative N→P bond. However, the results of our method of counterion induced shifts (*CIS*[15]) as well as the ^{31}P NMR signal position typical for phosphonium salts[16] unambiguously showed



1

1	R
a	H
b	Me



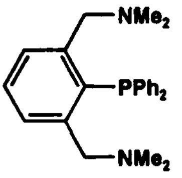
2

2, 6-29	n
a	1
b	2
c	3

that (in solution) even pentacoordination did not occur. Because of the higher electron density and the unshared electron pair at P, this would be expected to hold true even more for the corresponding phosphine,[17] **2a**, and we felt that this was indeed indicated by its ^{31}P NMR signal position (**2a**: δ –0.12 ppm) similar to that of triphenylphosphine (δ –5.6 ppm).[16] Though without adequate discussion of the earlier work, the debate was re-opened by the claim of Corriu, Chuit, Reyé et al. that in **2a**, one dative N→P bond is formed[18,19] and that in bis(DAN)(phenyl)phosphine (**2b**)[19,20] and in tris(DAN)phosphine (**2c**)[19,21] the additional nitrogen atom(s) form(s) (a) further N→P bond(s), so that the phosphorus atom becomes *pseudo-penta-*[18,19], *pseudo-hexa-*[19,20] and *pseudo-hepta-coordinate*[19,21] *with the same ease* (*pseudo* designating the electron pair as a *pseudo-substituent*). Following a pandemic (though untenable) view that any interatomic distance shorter than the sum of the respective van der Waals radii (Σr_{vdW}) is evidence of some sort of (covalent, i. e. anisotropic) bonding, the authors based their conclusions solely on the fact that the N-P distances, between 271 and 285 pm as revealed by x-ray structure determination, and thus in the same range as in Hellwinkel's phosphorane,[12] are considerably shorter than Σr_{vdW} of N and P. However, as in related DAN-silanes,[1] the geometry of the C_{10} unit forces *any* peri-substituents into sub-van der Waals distances so that from the very fact no such conclusions can be drawn. Obviously, other criteria are needed to decide whether Day's and Holmes'[12] or Corriu's[18–21] interpretation of the peri-N-P distances is correct. ^{31}P NMR is a promising property but requires a much more sophisticated treatment than hitherto applied.

RESULTS AND DISCUSSION

Tetracoordinate, positively charged phosphorus, as in tetraorgano phosphonium cations and O- and S-deprotonated hydroxy- and mercapto-triorgano phosphonium cations (*"phosphine oxides"*, *"phosphine sulfides"*[22]), usually absorbs at ca. δ +25 ppm,[23] "pseudo-tetracoordinate" phosphorus, *i. e.* P in phosphines, at distinctly higher field (*e. g.* Ph_3P at ca. δ –6 ppm[24]), the electronic influence of meta- and para-substituents being small (*vide infra*). Pentaorgano phosphoranes exhibit their ^{31}P NMR signal at much higher field (*e. g.* Ph_5P at –88.7 ppm[25]). The δ range for *pseudo*pentacoordinate P species, R_4P^-, is not known, since so far no such compounds have unambiguously been shown to exist (Hellwinkel's bis(2,2′-biphenylylene)(hydrido)phosphorane[26] is the conjugate acid of a pertinent species; a modest ability of proton/deuterium exchange testifies some acidity which, however, is apparently very weak, and as a consequence, no ^{31}P NMR spectrum of the conjugate base has been obtained). Hexaorgano phosphorus compounds absorb at even higher field,[3] again no data being available for *pseudo*hexacoordinate phosphorus. The various ranges are reasonably well separated so that usually safe decisions can be made. Whether *weak dative bonds* of variable length, *i. e.* a bond-forming continuum between, *e. g.*, (pseudo-) tetracoordinate and (pseudo-) pentacoordinate phosphorus structures, are a sound concept and, if so, whether the strengths of such bonds are manifested by a continuum of ^{31}P NMR highfield shifts, are presently unanswered questions.



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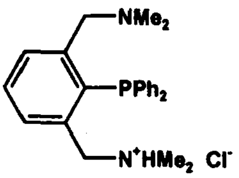

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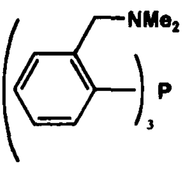


5

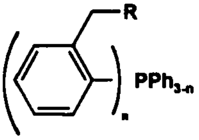
Corriu et al. reported that, when in one of the phenyl rings of Ph_3P, dimethylaminomethyl (*DAM*) groups were introduced into the two ortho positions (*cf.* **3**), the ^{31}P NMR signal was shifted to higher field by 11 ppm.[27] Upon protonation of one of the nitrogen atoms (*cf.* **4**), the ^{31}P NMR signal experienced an additional highfield shift of $\Delta\delta = -4.3$ ppm.

When a $Me_2N\text{-}CH_2$- group was introduced into *one* ortho-position of *each* phenyl group of Ph_3P (*cf.* **5**), a highfield shift of 28 ppm was observed.[21] In all cases, the highfield shift was interpreted as due to "*a weak N→P interaction*", *N→P* being the symbol of a *dative bond* from N to P, consistently being used in many papers of the authors, in several cases in conjunction with the term *dative bond.*[28] Independent support for this *N→P interaction* was believed to be provided by the x-ray structure of **5** with a mean N-P distance of 302.7 pm, only 7% less than Σr_{vdW},[29] but exceeding Σr_{cov}(N, P) by 65%. In the DAN-phosphines **2a-c**, the N-P distances fall short of Σr_{vdW} by 16, 14 and 13%, in average double as much as in **5**, according to Corriu et al. indicative of stronger N→P interaction, and yet, ^{31}P NMR absorbance is consistently at *lower* field than in Ph_3P ($\Delta\delta = 5.03$[30]; 8.92; 10.32 ppm, respectively), in the case of the tris(DAN)-phosphine **2c** (allegedly with pseudo-heptacoordinate phosphorus[19,21]) by about the same amount as the *high*field shift in **3**. The contradictory conclusion, then, is that a weak N→P interaction does provoke the anticipated highfield shift, while a stronger interaction does not, but causes the opposite effect. The discrepancy prompted us to conduct a systematic study.

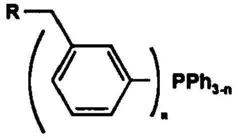
The case of (2-dimethylaminomethyl-phenyl)phosphines

The concept of a N→P dative interaction implies that the electron pair at the nitrogen atom is an essential feature; in fact, it has been adduced as an argument for such interaction that the lone pair points in direction of the P (or Si in corresponding silanes) atom.[31] For a countercheck, we therefore omitted the NMe_2 group, replacing it by H as well as by CH_3. In order to be on safe ground, we investigated the complete set of phosphines **6** and **7**, and in order to account for the (presumably small) electronic effects of alkyl groups, included their meta- and para-isomers **8–11**. For the sake of consistency, all data are given in $\Delta\delta$, referring to the value $\delta(Ph_3P)$ used in the respective set of data, our own value being $\delta(Ph_3P)$ −4.49 ppm, in good agreement with the value $\delta(Ph_3P)$ −4.84 ppm reported by Yamashoji et al.[32]

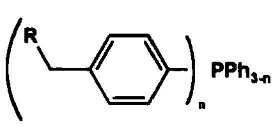
meta- and para-Alkyl groups have a negligible influence upon δ (see Table I: **8-11**). Though always smaller than 1 ppm per alkyl group, the signal displacements are almost strictly additive within each series of compounds **8–11**, the effects of meta-ethyl groups slightly exceeding those of



	R
6	H
7	Me
21	OMe



	R
8	H
9	Me



	R
10	H
11	Me

meta-methyl groups (*cf.* **9** with **8**). Though the Hammett σ constants of meta- and para-alkyl groups are both negative (and insignificantly different for methyl and ethyl),[33] meta-alkyl groups consistently cause a minute downfield shift and para-alkyl groups a very small highfield shift. As a consequence, no Hammett correlation $\delta = a \cdot \Sigma\sigma + b$ (a and b constants) can be set up. Being, therefore, neither clear-cut sterical nor electronic, the nature of the effect of meta-, para-alkyl upon δ remains unexplained, but the effect of ortho-alkyl groups is greater by one to two powers of 10 so that in the further discussion, the role of meta/ para-alkyl substituents can be neglected.

Again with remarkably strict additivity, *ortho*-alkyl groups cause a highfield shift of about 8–10 ppm per alkyl group, ethyl groups being more efficient than methyl groups by about 20%. This is in accord with the "*ortho-effect*" which since its discovery by Grim and Yankowsky[34] has been found to be a general phenomenon.[35] **5** ($\Delta\delta = -28$ ppm) exhibits a highfield shift between those of the corresponding methyl compound **6c** ($\Delta\delta = -24.36$ ppm) and the ethyl compound **7c** ($\Delta\delta = -29.18$ ppm), closer to the latter which certainly is the closer analogue. The proper reference compounds for **3**, **4** would be (2,6-diethyl- and (2,6-dimethyl-phenyl)di(phenyl)phosphine (**12a**, **13a**) which were not at hand. Instead, we chose (mesityl)di(phenyl)phosphine (**14a**) and accounted for the additional para-methyl group by referring not to $\delta(Ph_3P)$, but to δ(**10a**). *Two* ortho-methyl groups in *one* phenyl group of Ph_3P, then, cause a highfield shift of $\Delta\delta = -11.9$ ppm, virtually identical with (formally 8% greater than) the highfield shift in **3**. Literature data of the xylyl phosphines **13a,c** and the mesityl phosphines **14a-c**[35b] gave very similar results (*cf.* Table I). The highfield shift exerted by two ortho,ortho′-methyl groups,

$\Delta\delta$(**13a**/Ph_3P) = −16.8 ppm, slightly exceeds the combined effects of one ortho-Me_2N-CH_2- and one ortho-Me_2HN^+-CH_2-substituent ($\Delta\delta$(**4**/Ph_3P) = −15.3 ppm) (*cf.* Table I).

TABLE I ^{31}P NMR Signal positions of substituted triphenylphosphines

Phosphine	$\Delta\delta$ *[ppm]*[a]	$\Delta\Delta\delta$ *[ppm]*[a]		*mean* $\Delta\Delta\delta$ *[ppm]*[a,b]	
Ph_3P	0.00				
3	−11[c,27]	**3**/Ph_3P	−11	**3**	−11
4	−15.3[c,27]	**4**/Ph_3P	−15.3	**4**	−15.3
5	−28[21]	(**5**/Ph_3P):3	−9.3	**5**	−9.3
6a[d,43]	−8.00	**6a**/Ph_3P	−8.00		
6b[43]	−15.91	**6b**/**6a**	−7.91	**6**	−8.12
6c[44]	−24.36	**6c**/**6b**	−8.45		
7a[45]	−9.90	**7a**/Ph_3P	−9.90		
7b[45]	−19.36	**7b**/**7a**	−9.46	**7**	−9.73
7c[45]	−29.18	**7c**/**7b**	−9.82		
8a[46,47]	+0.04	**8a**/Ph_3P	+0.04		
8b[47,48]	+0.11	**8b**/**8a**	+0.07	**8**	+0.06
8c[47,49]	+0.18	**8c**/**8b**	+0.07		
9a[45]	+0.22	**9a**/Ph_3P	+0.22		
9b[45]	+0.41	**9b**/**9a**	+0.19	**9**	+0.22
9c[45]	+0.65	**9c**/**9b**	+0.24		
10a[46]	−0.92	**10a**/Ph_3P	−0.92		
10b[50]	−1.70	**10b**/**10a**	−0.78	**10**	−0.84
10c[49]	−2.52	**10c**/**10b**	−0.82		
11c[45]	−2.48	(**11c**/Ph_3P):3	−0.83	**11**	−0.83
13a	−16.8[c,e,35b]	**13a**/Ph_3P	−16.8		
13c	−30.8[c,e,35b]	(**13c**/Ph_3P):3	−10.3	**13**	−10.3
14a	−12.8[c,e,35b]	**14a**/**10a**	−11.9		
14b	−18.6[c,e,35b]	(**14b**/**10b**):2	−8.5	**14**	−10.2
14c	−32.7[c,e,35b]	(**14c**/**10c**):3	−10.1		
15a[51]	−11.06	**15a**/Ph_3P	−11.06		
15b[51]	−20.86	**15b**/**15a**	−9.80	**15**	−9.90
15c[51]	−29.71	**15c**/**15b**	−8.85		
16a[51]	−5.74	**16a**/Ph_3P	−5.74		

Phosphine	*Δδ [ppm]*[a]	*ΔΔδ [ppm]*[a]		*mean ΔΔδ [ppm]*[a,b]	
16b[51]	−10.20	**16b/16a**	−4.46	**16**	−5.10
17a[51]	+0.12	**17a**/Ph_3P	+0.12		
17b[51]	+0.26	**17b/17a**	+0.14	**17**	+0.13[f]
18a[51]	+0.38	**18a**/Ph_3P	+0.38		
18b[51]	+0.81	**18b/18a**	+0.43	**18**	+0.40[f]
19a[51]	−0.30	**19a**/Ph_3P	−0.30	**19**	−0.30[f]
20a[51]	−0.53	**20a**/Ph_3P	−0.53		
20b[51]	−1.11	**20b/20a**	−0.58	**20**	−0.57[f]
20c[51]	−1.73	**20c/20b**	−0.61[g]		
21a[52]	−10.41	**21a**/Ph_3P	−10.41		
21b[53]	−20.62	**21b/21a**	−10.21	**21**	−10.31
22a[54,55]	−13.44	**22a**/Ph_3P	−13.44	**22**	−13.44
23a[55]	−22.65[c]	**23a/22a**	−9.21		
iso-24a[h,56]	+0.33				
25a[57]	−1.07	**25a**/Ph_3P	−1.07		
25c[57]	−3.21	(**25c/25a**):2	−1.07	**25**	−1.07
26a[57,58]	−1.12	**26a**/Ph_3P	−1.12	**26**	−1.12
27c	−61.54[c,32]	(**27c**/Ph_3P):3	−20.51		
28c[59]	−2.14	(**28c**/Ph_3P):3	−0.71	**28**	−0.71

a. Δδ = δ of the respective phosphine − δ(Ph_3P); own measurements except for **3**, **4**, **5**, **13a,c**, **14a-c**, **27c**; positive = downfield from δ(Ph_3P), negative = highfield from δ(Ph_3P). To obtain δ, add −4.49 (−5.6 to Δδ(**3**, **4**, **5**)).

b. *i. e.* mean ^{31}P NMR signal displacement per substituent, in **3**, **4**, **13c**, **14** per one ortho, ortho′- disubstituted aryl group.

c. ortho, ortho′-Disubstitution.

d. References added to compound numbers refer to the method of synthesis.

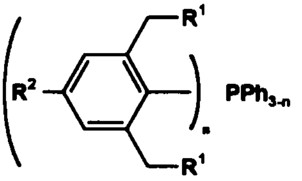
e. Since Culcasi et al.[35b] gave no δ(Ph_3P) value, only an external reference is possible. The figures in Table I are based on our value δ(Ph_3P) −4.49. Comparison, wherever possible, of Culcasi's and our own data suggests that, indeed, δ(Ph_3P) −4.49 is a more appropriate reference than the frequently used literature value δ(Ph_3P) −5.6. The use of the latter value changes the figures slightly, but does not affect the argument.

f. Mean (absolute) signal displacement per substituent of all meta-, para-series **17–20**: 0.39 ppm.

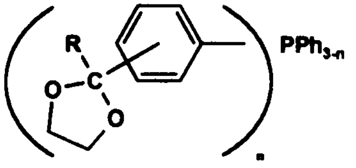
g. Apparent discrepancy due to round-off.

h. meta-Isomer of **24a**.

To assess the possible influence of electronegative substituents on the *ortho-effect*, we turned to triarylphosphines in which one or two hydrogen atoms of a methyl group or of the CH_2 group of an ethyl group have been replaced by oxygen. Since the σ-donicity of ether-type oxygen is very low, the possibility of a dative interaction $O\rightarrow P$ need not seriously be considered.[36] Again, we included the meta- and para-isomers in order to get an insight into possible electronic effects (see Table I, **15–21**). As meta-, para-substituents at the benzene rings, these substituents would be expected to have a negligible π-electronic effect, since the (small) electron-donating power of alkyl groups should be more or less cancelled (possibly overcompensated) by the -I effect of the oxygen atom(s) (*cf.* the σ_{para} constants of $ClCH_2$-, +0.184, and of NC-CH_2-, +0.007[33]). In fact, both in the meta- and in the para-series (**17, 18** and **19, 20**, respectively), the dioxolanyl phosphines closely resemble their alkyl analogues **8–11**, all signal displacements being of negligible magnitude with respect to the *ortho-effect.* Within each series, the additivity is, again, excellent (*cf.* Table I, $\Delta\Delta\delta$).



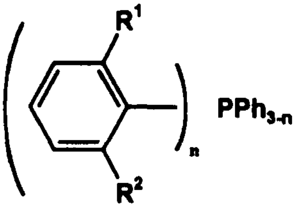
	R¹	R²
12	Me	H
13	H	H
14	H	Me



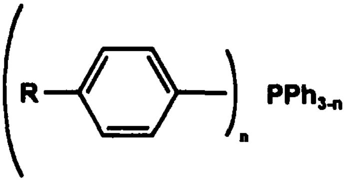
	position of substituent	R
15	2	H
16	2	Me
17	3	H
18	3	Me
19	4	H
20	4	Me

In the two ortho-dioxolanyl series, the mean substituent effect exceeds the mean (absolute) signal displacement per substituent in the meta-, para-series by a factor of 25 (**15**) and 13 (**16**). In detail, the effects differ from those in the alkyl series: The α-substituted ethyl substituents (in **16**) cause *smaller* highfield shifts than the O_2-substituted methyl groups (in **15**), and in both series, the effect decreases with increasing n. However, no such trend is exhibited by the MeO-CH_2- compounds **21**. The mean highfield signal displacement per substituent is in the same range as in the alkyl series (**6**: −8.12; **7**: −9.73; **15**: −9.90; **16**: −5.10; **21**: −10.31 ppm). The effect per group of MeO-CH_2- (in **21**) is 10% *greater* than that of

Me_2N-CH_2- (in **5**), a fact which certainly cannot be reconciled with the difference of σ-donicity of amine nitrogen and ether oxygen.



	R¹	R²
22	F	H
23	F	F
27	OMe	OMe



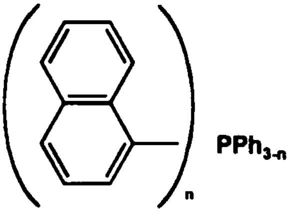
	R
24	F
25	Cl
26	Br
28	Ph

In the bis-ortho-substituted compounds **3**, **4**, protonation of one amino group resulted in a slight highfield shift ($\Delta\Delta\delta = -4.3$ ppm). Within the reasoning of Corriu et. al., the effect cannot be attributed to a change from pseudo-hexacoordination in **3** to pseudo-pentacoordination in **4**. On the other hand, it does not provide evidence for hypercoordination in either species, since δ is still within the range of the *ortho-effect. E. g.*, one ortho-fluorine causes a highfield shift of −13.44 ppm (**22a**/Ph_3P), 2,6-difluoro substitution one of −22.65 ppm (**23a**/Ph_3P), well above the substituent effect in **4** (−15.3 ppm, **4**/Ph_3P). The effect cannot be due to a π-electronic effect of F, because 1) $\sigma_{p\text{-}F} = +0.062^{33} \approx 0$, and 2) the effect of *para*-halogen is negligible: $\Delta\delta = -1.07$ (**25a**/Ph_3P), −1.12 ppm (**26a**/Ph_3P). (The fluorine compound **24a** was not at hand; its meta-isomer had $\Delta\delta = +0.33$ ppm.) In view of the poor σ-donicity of C-bound fluorine[37] and the large P-F distance (301 pm according to a model calculation with P-C(1) = 182.8 pm and C(1)-C(2) = 140.2 pm as in triphenylphosphine,[5] C-F = 133 pm as in fluoroaromatics[38] and 120° angles throughout, slightly shorter than $\Sigma r_{vdW} = 320$ pm[29] as a geometric necessity,[39] but 65% longer than $\Sigma r_{cov} = 182$ pm[8] and hence out of reach for any significant bonding interaction), it cannot be due to dative F→P interaction either, so that **22a**, **23a** can safely be taken as normal examples for the *ortho-effect*. Other examples with 2,6-substituents of very low σ-donicity and similar distances from P are known, *e. g.* **27c**, $\Delta\delta = -61.54$ ppm (**27c**/Ph_3P),[40] *i. e.* $\Delta\Delta\delta = -20.5$ ppm per 2,6-disubstituted phenyl ring.

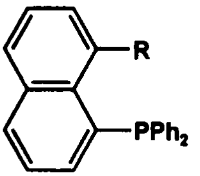
After all, the Me_2N-CH_2- substituent shows *no* peculiarities which might be indicative of any N→P interaction.

The case of (8-dimethylamino-naphth-1-yl)phosphines

On the other hand, our data permit to regard (naphth-1-yl)-phosphines as 2,3-di(carbon)substituted phenyl-phosphines. Comparison of **11c** ($\Delta\delta = -2.48$ ppm) with its phenyl analogue **28c** ($\Delta\delta = -2.14$ ppm) indicates that an *aromatic* carbon atom instead of Et in a non-ortho-position has a negligible influence; meta-alkyl groups have a particularly small effect (Table I: **8, 9**). Introduction of a 3-Me group into each phenyl ring of **6c** ($\Delta\delta = -24.36$ ppm) has, indeed, virtually no effect ($\Delta\delta$ ($[2,3\text{-}Me_2C_6H_3]_3P/Ph_3P$) = ca. −22.9 ppm[41]). For the (naphth-1-yl)-phosphines **29a-c**, then, $\Delta\delta$ (**29**/Ph_3P) values of ca. −8 to −10 (n = 1), −16 to −20 (n = 2) and −24 to −30 ppm (n = 3) would be predicted. Indeed, we found $\Delta\delta = -8.88$ ppm for **29a**; the data of Budzelaar et al.[35c] for Ph_3P and **29c** provide $\Delta\delta = -27.7$ ppm for **29c** or −9.23 ppm as mean value for the replacement of one phenyl by one naphth-1-yl group. (2-Fluoro-naphth-1-yl)di(phenyl)phosphine would be expected to have $\Delta\delta$ between the values of **13a** (estimated as −11.9 ppm from **14a/10a**, *vide supra*) and **23a** (found −22.65 ppm) and has in fact −20.38 ppm.



29



30-34

	R
30	F
31	Br
32	I
33	PPh_2
34	$P^+MePh_2\ I^-$

Upon peri-substitution, very surprisingly, the *ortho-effect* exerted by benzoanellation (*e. g.* **29a**/Ph_3P) is retained in only two of the investigated cases (**32, 33**), slightly reduced in **34**, moderately so in **31**, but cancelled or even slightly overcompensated by peri-F (**30**) and peri-NMe_2 (**2a-c**). The case of **30** is particularly noteworthy in view of the enhanced *ortho-effect* exerted by fluorine in **22a, 23a**. We therefore conclude that both the "high-field shifts" exhibited by **3, 4, 5**[18,20,21] as well as the absence of such an effect in **2a**[16] are artefacts created by the choice of an unsuitable reference, *viz*. triphenylphosphine (rather than **12a, 13a** for **3, 4; 6c, 7c** for **5**, and **29a** for **2a**). The ^{31}P NMR signal positions of the DAN-phosphines are the result of the counteraction of the *ortho-effect* causing a highfield shift, and of a peri-lowfield effect of about equal strength whose nature presently remains obscure. It must be pointed out that Hellwinkel's phosphoranes do not show this effect: A peri-NMe_2 group has no influence at all, whereas 8-F, 8-Cl, 8-Br, 8-CH_3 and 8-OMe cause an almost constant downfield shift of ca. 6 ppm.[3] In the phosphines, the downfield effect of NMe_2 is obviously incompatible with Corriu's reasoning in favour of dative N→P interaction.

TABLE II ^{31}P NMR signal positions of (naphth-1-yl)phosphines

Phosphine	*peri-substituent*	*Δδ(No./Ph_3P) [ppm]*[a]	*ΔΔδ(No./**29a**[b]) [ppm]*[a]
29a[a,60]	H	−8.88	0.00
29c	H	−27.7[a,35c]	−18.8
			(-9.4 per 1 $C_{10}H_7$ group)
iso-30[c]	H (2-F)	−20.38	−11.50
30	F	+5.10	+13.98
31	Br	−1.32	+7.56
32	I	−8.03	+0.85
33[61]	PPh_2	−9.68	−0.80
34[61]	$P^+MePh_2I^-$	−7.63	+1.25
2a[16]	NMe_2	+5.03	+13.91[d]
2b[20,62]	NMe_2	+8.92	+27.21[e]
			(+13.60 per 1 NMe_2 group[d])
2c[21,62]	NMe_2	+10.32	+38.02[f]
			(+12.67 per 1 NMe_2 group[d])

a. *Cf.* notes[a,c] in Table I.

b. Reference **29a** in the mono(subst. naphth-1-yl) series and for **29c** only.

c. 2-Isomer of **30**.

d. **2a-c**: Mean downfield shift per 1 $N(CH_3)_2$ group: $\Delta\Delta\delta = 13.39$ ppm. Whether the formal decrease of ΔΔδ with increasing number of $N(CH_3)_2$ groups is significant, is doubtful; if so, it might point to an influence of steric crowding around P.

e. Reference: **29b**; $\Delta\delta = -18.29$ as interpolated between Δδ(**29a**) = −8.88 and Δδ(**29c**) = −27.7 ppm.

f. Reference: **29c**.

CONCLUSION

^{31}P NMR, after all, does not support the claim of N→P interaction in both the DAN and the (DAM-phenyl) phosphines. Since the N-P distances do not provide pertinent evidence either,[42] we conclude that there is none.

EXPERIMENTAL

^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer at 81.015 MHz (ext. ref. 85% H_3PO_4) on solutions of ca. 0.25 mol phosphine / *l* $CDCl_3$. Most spectra were obtained within 72 days; the reproducibility was repeatedly checked by measurements on new solutions of selected compounds. *E. g.*, after 397 days, the nominally recorded difference for Ph_3P was < 0.8 Hz (< 0.01 ppm). ^{19}F NMR spectra were recorded on the same instrument at 188 MHz (ext. ref. CCl_3F). – Most phosphines were available in our compound collection. For hydrogen/lithium or halogen/lithium exchange, a commercial solution of n-butyl lithium (1.6 molar) in petrol ether was used. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

(2,6-Difluorophenyl)di(phenyl)phosphine (23a)[55]

2.41 g (21.1 mmol) 1,3-difluorobenzene were lithiated by lithium-diisopropylamide prepared *in situ* from 2.70 ml (20.6 mmol) diisopropylamine dissolved in 10 ml dry diethyl ether and 12.8 ml (20.5 mmol) n-butyl lithium.[63] To this solution, 3.70 ml (20.6 mmol) (chloro)di(phenyl)phosphine were slowly added at –80°C. After conventional workup, a brown oil was obtained which crystallized. Recrystallisation from ethanol yielded 3.93 g (64%) colourless crystals, m.p. 81–82°C. NMR: ^{19}F ($CDCl_3$): δ –98.22, d, $^{3}J(F,P) = 42$ Hz; ^{31}P: δ –27.14, t, $^{3}J(F,P) = 42$ Hz. MS (EI): $^{m}/_{z}$[%] 298, 144 [100, 10]. $C_{18}H_{13}F_2P$ (298.3): P calc. 10.38, found 10.2. For further characterization, (2,6-difluorophenyl)(methyl)di(phenyl)phosphonium tetraphenylborate was prepared from a diethyl ether solution of **23a** and methyl iodide, precipitation of the tetraphenylborate from an aqueous solution of **23a**-methiodide upon addition of aqueous sodium tetraphenylborate and recrystallization from acetone/ethanol (2:3); m.p. 180–182°C.

NMR (CD_2Cl_2): ^1H: P^+-CH_3 δ +2.11, dt, 3H, $^2J(H,P) = 13.5$ Hz, $^5J(H,F) = 2.3$ Hz; ^{19}F: δ −95.54; ^{31}P: δ +15.66. $C_{43}H_{36}BF_2P$ (632.5): P calc. 4.90, found 4.80.

(8-Fluoro-naphth-1-yl)di(phenyl)phosphine (30)[55]

(8-Fluoro-naphth-1-yl) lithium was prepared by addition of 13.0 ml (20.8 mmol) n-butyl lithium to a solution of 4.16 g (18.5 mmol) 1-bromo-8-fluoronaphthalene (obtained by thermal decomposition of (8-bromonaphthalene)diazonium tetrafluoroborate[64]) in 20 ml tetrahydrofuran within 30 min at −60°C (maximum). To this was added a solution of 3.50 ml (18.9 mmol) (chloro)di(phenyl)phosphine in 10 ml tetrahydrofuran within 30 min. Conventional workup and two recrystallizations from benzene/ethanol (1:1) yielded colourless crystals; yield 4.47 g (73%); m.p. 162–163°C. NMR: ^{19}F: δ −104.19, d, $^4J(F,P) = 194$ Hz; ^{31}P: δ +0.61, d, $^4J(F,P) = 194$ Hz.[65] MS (CI): $^m/_z = 330$ (100%). $C_{22}H_{16}FP$ (330.3): P calc. 9.38, found 9.22.

(2-Fluoro-naphth-1-yl)di(phenyl)phosphine (iso-30)[55]

Was prepared from 1-bromo-2-fluoro-naphthalene[66], as described for **30b**; yield 76%, m.p. 136–138°C. NMR: ^{19}F: δ −93.05, d, $^3J(F,P) = 4.8$ Hz; ^{31}P: δ −24.87, d, $^3J(F,P) = 4.8$ Hz; MS (EI): $^m/_z = 329$ (100%), (CI): $^m/_z = 331$ (100%). $C_{22}H_{16}FP$ (330.3): P calc. 9.38, found 9.26.

(8-Bromo-naphth-1-yl)di(phenyl)phosphine (31)[67] and (8-iodo-naphth-1-yl)di(phenylphosphine (32)[67,68]

Were prepared in the same way by mono-lithiation of 1-bromo-8-iodo-naphthalene[69] and 1,8-diiodo-naphthalene,[70] respectively, with the stoichiometric amount of n-butyl lithium and subsequent reaction with (chloro)di(phenyl)phosphine. In order to preclude quaternization of **31** with n-C_4H_9I formed by the halogen/metal exchange, an equimolar amount of (n-C_4H_9)$_3$P was added before the addition of $ClP(C_6H_5)_2$. Because of the reduced reactivity of **32** due to increased sterical hindrance, this precaution was considered unnecessary in this case. – **31**: Yield 77%; m.p. 128–131°C. NMR: ^{31}P: δ −5.81. $C_{22}H_{16}BrP$ (391.2):

Br calc. 20.42, found 20.8; P calc. 7.92, found 7.88. **32**: Yield 33%; yellow crystals, m.p. 137–138°C; NMR: ^{31}P: δ −12.52. $C_{22}H_{16}IP$ (438.2): I calc. 28.96, found 28.5; P calc. 7.07, found 6.95. – Evidently, some dilithiation occurred:[71]After conventional workup, the crude materials of **31, 32** contained some **29a**, whose formation can be ascribed to protonation of 8-Li-$C_{10}H_6$-(1)-P$(C_6H_5)_2$ by water during workup. After recrystallization from ethanol, **29a**-free samples of **31, 32** were obtained, but in the reaction of crude **31** with sulfur, the sterically less hindered **29a** reacted preferentially so that mixtures of phosphine sulfides were obtained which, according to the elemental analyses, consisted of ca. 75–80% **31**-sulfide and ca. 25–20% **29a**-sulfide. In one run of **32** (formal yield 79%), after the reaction with sulfur and recrystallization from methanol, a phosphine sulfide was obtained whose elemental analyses corresponded to the emprirical formula $C_{22.9}H_{16.9}I_{0.0}P_{1.0}S_{1.0}$.

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41. Culcasi et al.[35b]: δ –28.5. Since no δ value for Ph_3P was given, we refer to the frequently used literature value of –5.6 ppm.[24] With our value for Ph_3P, $\Delta\delta = -24.0$ ppm is obtained.
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