

## COMPOUNDS $R^1R^2EMMe_3$ (E = P, As; M = Si, Sn) – CONVENIENT AND VERSATILE REAGENTS FOR THE SYNTHESSES OF TERTIARY (FLUOROARYL)PHOSPHANES AND -ARSANES

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*Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organofluorine chemistry.*

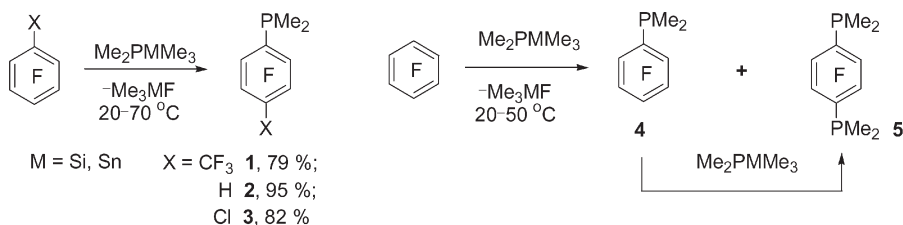
Synthetic and mechanistic aspects of nucleophilic replacement of fluorine in fluorobenzenes, fluoropyridines and fluoroquinolines by phosphanyl and arsanyl groups via their reactions with  $R^1R^2EMMe_3$  (E = P, As; M = Si, Sn;  $R^1, R^2 = Me, i\text{-Pr}, t\text{-Bu}, Ph$ , etc.) reagents are considered.

**Keywords:** Arsanes; Phosphanes; Phosphines; Polyfluoroarenes; Fluorinated ligands; Fluoropyridines; Rhodium complexes.

Tertiary (fluoroaryl)phosphanes<sup>1</sup> and -arsanes<sup>2</sup> are of interest as ligands in catalytically active transition metal complexes and as starting materials for the preparation of phosphanyl- and arsanyl-substituted derivatives of fluorinated heterocycles, such as dibenzodioxin, phenoxathiin, phenoxazine, with a probably higher biological activity than that of the unsubstituted analogues<sup>3,4</sup>. The preparation of arylphosphanes and -arsanes using aryl halides as precursors is one of the commonly used methods which can be realized using various synthetic routes<sup>1,3</sup>. A particularly convenient procedure is the nucleophilic reaction of the chosen aryl halide with an alkali metal salt  $MER_2$  (E = P, As), generated from the corresponding secondary derivative  $HER_2$  with phenyllithium<sup>5</sup>, potassium *tert*-butoxide<sup>6</sup> or KOH<sup>7</sup>. The nucleophiles  $MPPh_2$  may also be prepared via cleavage of triphenylphosphane with lithium, sodium or potassium<sup>8</sup>. This method, however, shows some experimental difficulties due to the high basicity of the metal

salts  $\text{MER}_2$ . To overcome this problem, trimethylsilyl and -stannyl reagents  $\text{R}^1\text{R}^2\text{EMMe}_3$  ( $\text{E} = \text{P}, \text{As}$ ;  $\text{M} = \text{Si}, \text{Sn}$ ) were proposed.

$\text{Me}_3\text{SiPMe}_2$  reacts with polyfluorobenzene derivatives  $\text{C}_6\text{F}_5\text{X}$  ( $\text{X} = \text{F}, \text{CF}_3, \text{Cl}, \text{H}$ ) at an appreciable rate already at room temperature, without solvent or in benzene, to give the corresponding para substituted derivatives **1–3** almost quantitatively; the isolated yields are between 79–95% (Scheme 1)<sup>9</sup>. In the case of  $\text{C}_6\text{F}_5\text{Cl}$  the ortho and meta substituted derivatives  $\text{Me}_2\text{PC}_6\text{F}_4\text{Cl}$  are also formed in yields up to 11 and 3%, respectively. In the case of hexafluorobenzene, not only (dimethylphosphanyl)pentafluorobenzene (**4**) is formed, but also the product of its further conversion, 1,4-bis(dimethylphosphanyl)-2,3,5,6-tetrafluorobenzene (**5**). The degree of disubstitution can be reduced by increasing the initial molar ratio  $\text{C}_6\text{F}_6:\text{Me}_3\text{SiPMe}_2$ ; thus, with a tenfold amount of  $\text{C}_6\text{F}_6$ , the yields of **4** and **5** are 65 and 15%, respectively, at room temperature after 125 h. On the contrary, at the molar ratio 1:2 of  $\text{C}_6\text{F}_6$  and  $\text{Me}_3\text{SiPMe}_2$ , **5** was obtained as the main product.



SCHEME 1

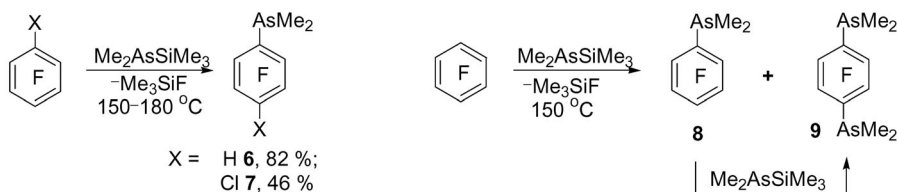
$\text{Me}_3\text{SnPMe}_2$  also reacts with polyfluoroarenes to yield basically the same substitution products as demonstrated for  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{F}_5\text{H}$ ,  $\text{C}_6\text{F}_5\text{Cl}$  (ref.<sup>9</sup>). The reactivity of the tin compound is approximately twice as high as that of the silicon analogue.

Kinetic investigations of the reactions of polyfluorobenzene derivatives with  $\text{Me}_3\text{SiPMe}_2$  (Scheme 1) showed that the reaction rates are somewhat higher in the absence of benzene as solvent. Raising the temperature to 50–70 °C results in a considerable increase in the rate with a temperature coefficient of ca. 2.4, but without any change in the composition of the product mixture. The second-order rate constants  $k(\text{X}) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$  obtained for the reactions in benzene at 20 °C and without solvent at 17–20 °C are, respectively,  $k(\text{Cl}) = 4.8 \pm 1.0$  and  $6.3 \pm 1.3$ ;  $k(\text{PMe}_2) = 4.7 \pm 1.0$  and  $3.1 \pm 0.7$ ;  $k(\text{H}) = 2.2 \pm 0.4$  and  $1.1 \pm 0.2$ ;  $k(\text{F}) = 1.1 \pm 0.2$  and  $0.6 \pm 0.1$ . Thus, the influence of the substituent X on the reaction rate follows the sequence  $k(\text{Cl}) > k(\text{PMe}_2) > k(\text{H}) > k(\text{F})$ . The reactivity is considerably enhanced with

increasing electron-withdrawing character of the substituent X in the substrates  $C_6F_5X$  when passing from X = H, Cl, F,  $PMe_2$  to X =  $CF_3$ , and even more so for pentafluoropyridine. Depending on the number of fluorine atoms, the reactivity of fluorobenzenes follows the order: pentafluorobenzene > hexafluorobenzene  $\gg$  tri-, difluorobenzenes > fluorobenzene (see below). All these features correspond, in principle, to those observed for the reactions of polyfluoroarenes with O-, S-, and N-centred nucleophiles, conventionally rationalized in terms of the  $SNAr$  mechanism<sup>10</sup>. However, a concerted one-step ANDN mechanism<sup>11</sup> cannot be excluded.

*Ab initio* calculations were performed for the model gas-phase reactions of 4-fluoropyridine with  $PH_3$  or  $H_3SiPH_2$  (ref.<sup>9</sup>). In both cases extremely high activation energies ( $>50$  kcal mol<sup>-1</sup>) were predicted. In contrast, the calculation for the reaction of the same substrate with the  $H_2P^-$  anion in benzene gave a considerably lower activation energy of 8.5 kcal mol<sup>-1</sup>. These data led to the conclusion that the active reagent in the case of nucleophile  $Me_2PSiMe_3$  could be the  $Me_2P^-$  anion formed via cleavage of  $Me_2PSiMe_3$  by fluoride anion. The possibility of an ionic mechanism with dimethylphosphanide as nucleophile and fluoride anion as catalyst was tested by reactions of  $C_6F_5Cl$  with  $LiPMe_2$  or  $Me_3SiPMe_2$  in the presence of a fluoride anion source ( $CsF$ ,  $Et_4NF$ )<sup>12</sup>. It turned out that the first reaction resulted mainly in chlorine replacement to give **4** and **5** (Scheme 1) along with phosphane **3** and its isomers. In the reaction with  $Me_3SiPMe_2$  no appreciable difference in the product ratios was found from those observed without the additives. Thus, participation of the  $Me_2P^-$  anion as active reagent in the reactions of  $Ar_FX$  with  $Me_2PSiMe_3$  can be excluded. Obviously,  $Me_2PSiMe_3$  participates in the reactions with polyfluoroarenes without dissociation. However, both  $SNAr$  and ANDN mechanisms proposed may occur in condensed phase.

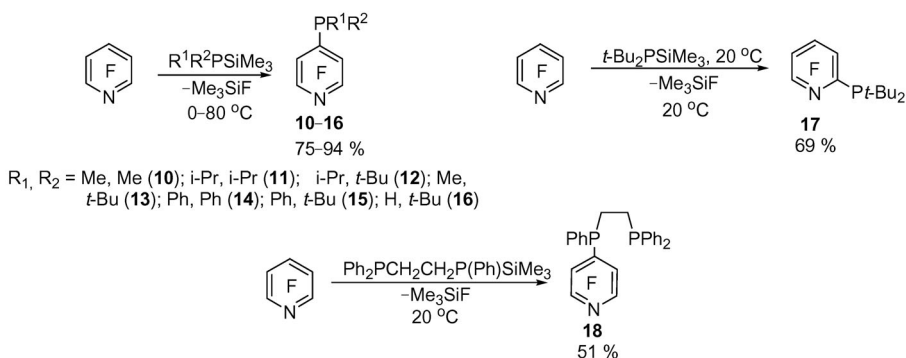
$Me_3SiAsMe_2$  was also successfully applied in the substitution of fluorine in polyfluorobenzenes by  $Me_2As$  groups according to Scheme 2<sup>13</sup>.



SCHEME 2

Pentafluorobenzene reacts with the silylarsane at 150–180 °C via replacement of F-3 to form regioselectively the dimethylarsanyl derivative **6** isolated in 82% yield. In the case of C<sub>6</sub>F<sub>5</sub>Cl, a mixture of product **7** (90%) of fluorine substitution in the position para to the chlorine atom and of its ortho and meta isomers (10%) was obtained in a total yield of 83% after heating at 150 °C. The para isomer was isolated from the mixture by crystallization in 46% yield. In the reaction of hexafluorobenzene, monosubstituted product **8** and para disubstituted compound **9** were formed and isolated in 48 and 43% yields, respectively. This result corresponds to that found for the analogous reaction of C<sub>6</sub>F<sub>6</sub> with Me<sub>3</sub>SiPMe<sub>2</sub> (Scheme 1). Therefore, the ratio **8/9** could be changed by varying the ratio Me<sub>3</sub>SiAsMe<sub>2</sub>/C<sub>6</sub>F<sub>6</sub>.

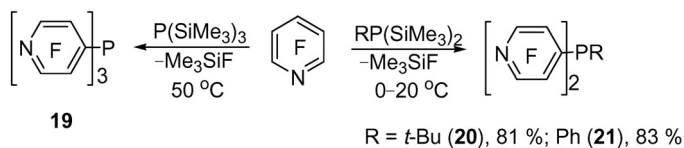
Dimethyl(trimethylsilyl)phosphane<sup>9</sup> and its analogues R<sup>1</sup>R<sup>2</sup>PSiMe<sub>3</sub> (R<sup>1</sup>, R<sup>2</sup> = Me, *i*-Pr, *t*-Bu, Ph, H)<sup>14</sup> react easily with pentafluoropyridine at 0–80 °C to give the corresponding compounds **10–16**, the products of F-4 replacement, isolated in 75–94% yields (Scheme 3). The reactivity of these nucleophiles was found to depend on the R<sup>1</sup>/R<sup>2</sup> combination and follows the order Ph, Ph; *t*-Bu, Ph; *t*-Bu, H < Me, *i*-Pr; Me, *t*-Bu < Me, Me. The reagent *t*-Bu<sub>2</sub>PSiMe<sub>3</sub> containing two bulky *tert*-butyl groups reacts at 20 °C to yield the 2-substituted instead of the 4-substituted tetrafluoropyridine.



SCHEME 3

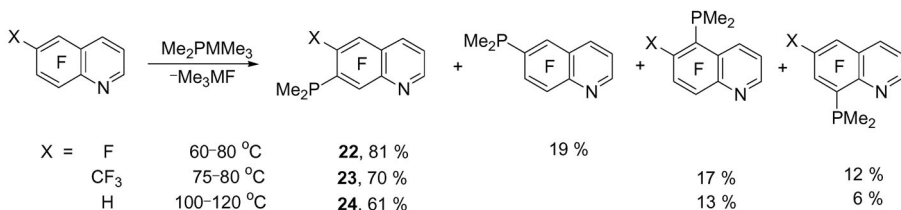
Recently, tetrafluoropyridyl-substituted diphosphane **18** was prepared by reaction of Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPhSiMe<sub>3</sub> with pentafluoropyridine<sup>15</sup>.

The application of tris- and bis(trimethylsilyl)phosphane in similar reactions with pentafluoropyridine enabled the preparation of the corresponding tris- and bis(tetrafluoropyridin-4-yl)phosphanes **19–21** (Scheme 4)<sup>14</sup>.



SCHEME 4

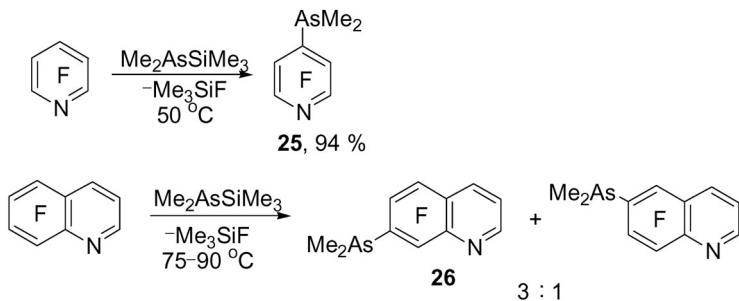
5,6,7,8-Tetrafluoroquinoline and its 6-substituted derivatives react with  $\text{Me}_3\text{SiPMe}_2$  at higher temperatures than polyfluorobenzene derivatives  $\text{C}_6\text{F}_5\text{X}$ , producing mainly compounds **22–24** with fluorine substituted in position 7 (Scheme 5)<sup>16</sup>.



SCHEME 5

The observed regioselectivity was explained in terms of the  $\text{S}_{\text{N}}\text{Ar}$  mechanism by a concerted influence of the heteroatom N and the collective effect of the fluorine substituents on the stabilization of the “ $\sigma$ -complex type” transition states.

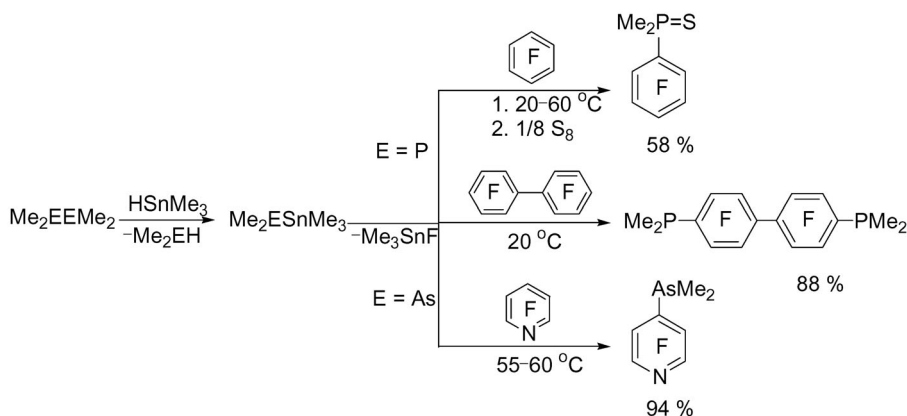
Homologous  $\text{Me}_2\text{AsSiMe}_3$  was also successfully used for the substitution of fluorine in pentafluoropyridine with a  $\text{Me}_2\text{As}$  group; this reaction gave 4-(dimethylarsanyl)tetrafluoropyridine (**25**) at 50 °C within 1 h in 94% yield (Scheme 6)<sup>13</sup>.



SCHEME 6

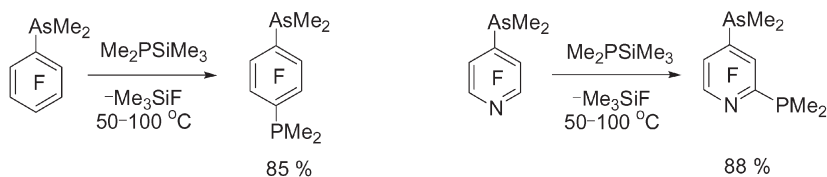
5,6,7,8-Tetrafluoroquinoline reacts at 75–90 °C, affording a mixture of **26** (31% yield) and its 6-substituted isomer<sup>16</sup>. Both results, as expected, are similar to those found for the corresponding reactions of pentafluoropyridine and 5,6,7,8-tetrafluoroquinoline with  $\text{Me}_2\text{PSiMe}_3$  (Scheme 5). On the whole, the reactions of polyfluoroarenes with  $\text{Me}_2\text{AsSiMe}_3$  exhibit the same regioselectivity, but are significantly slower than those with  $\text{Me}_2\text{PSiMe}_3$  and  $\text{Me}_2\text{PSnMe}_3$ .

Since the trimethyltin reagents  $\text{Me}_2\text{ESnMe}_3$  ( $\text{E} = \text{P}, \text{As}$ ) can easily be generated by cleavage of diphosphane  $\text{P}_2\text{Me}_4$  or diarsane  $\text{As}_2\text{Me}_4$  with trimethyltin hydride  $\text{Me}_3\text{SnH}$  at room temperature, a very convenient one-pot preparation of  $\text{Me}_2\text{E}$ -substituted polyfluoroarenes ( $\text{E} = \text{P}, \text{As}$ ) has been developed<sup>9,13</sup> (Scheme 7).



SCHEME 7

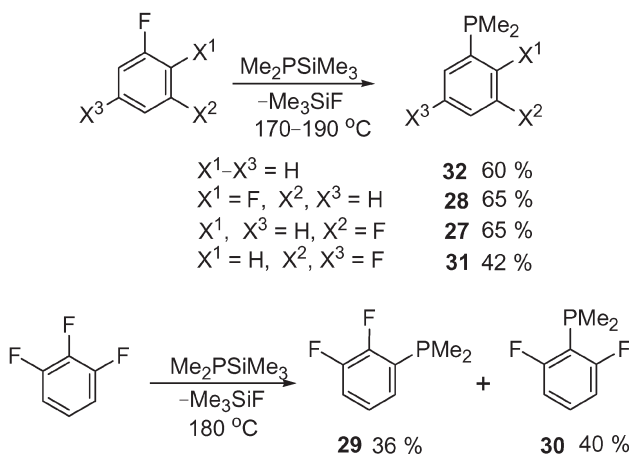
The most convenient route to heterodisubstituted derivatives, bearing simultaneously  $\text{Me}_2\text{As}$  and  $\text{Me}_2\text{P}$  groups, was realized in two steps. In the first step the monosubstituted  $\text{Me}_2\text{As}$  derivative is produced, followed in the second step by the reaction of isolated (dimethylarsanyl)polyfluoroarene with the more nucleophilic  $\text{Me}_3\text{SiPMe}_2$  (Scheme 8)<sup>13</sup>.



SCHEME 8

Attempts to prepare heterodisubstituted derivatives by reacting  $\text{Me}_2\text{P}$ -substituted products of the first reaction step, such as 4-( $\text{Me}_2\text{P}$ ) $\text{C}_5\text{F}_4\text{N}$ , 4-( $\text{Me}_2\text{PS}$ ) $\text{C}_5\text{F}_4\text{N}$  or 1-( $\text{Me}_2\text{PS}$ )-4- $\text{HC}_6\text{F}_4$ , with  $\text{Me}_3\text{SiAsMe}_2$  failed.

Reactions of relatively weak electrophiles mono-, di- or trifluorobenzene with  $\text{Me}_2\text{PSiMe}_3$  require temperatures between 170 and 190 °C. They were carried out in sealed ampoules either in benzene solution or without solvent. Thus, the monosubstituted products **27–31**<sup>17</sup> and **32**<sup>9</sup> were prepared in yields (for **27**, **28** and **31**) ranging between 42–65% (Scheme 9).

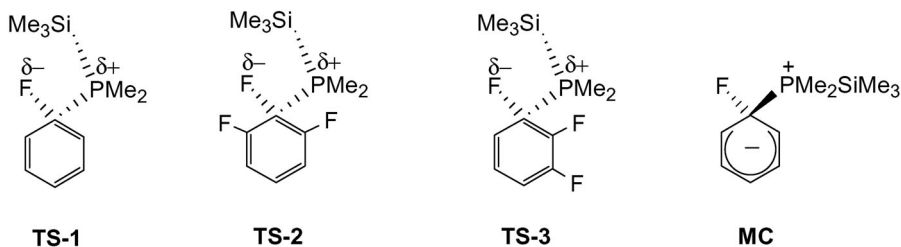


SCHEME 9

With the purpose of elucidating the mechanism of these transformations, competitive reactions of 1,2- vs 1,3-difluorobenzene and 1,2,3- vs 1,3,5-trifluorobenzene with reagents  $\text{Me}_2\text{PM}$  ( $\text{M} = \text{SiMe}_3, \text{SnMe}_3$  or  $\text{Li}$ ) were investigated. The correlation of the partial rate factors found ( $f_{o-F} > f_{m-F}$ ) is opposite to that observed for the reactions of these substrates with  $\text{MeONa}$  in  $\text{DMSO}/\text{CH}_3\text{OH}$ , which are believed to proceed via the  $\text{S}_{\text{N}}\text{Ar}$  mechanism<sup>18</sup>. The quantum-chemically calculated energy profiles of the gas-phase reactions of  $\text{C}_6\text{H}_5\text{F}$  or 1,2,3- $\text{F}_3\text{C}_6\text{H}_3$  with  $\text{Me}_2\text{PSiMe}_3$  suggest in both cases the one-step synchronous ANDN mechanism of aromatic nucleophilic substitution with the single transition states **TS-1**, **TS-2** or **TS-3**, shown below.

The principal reason for the observed reaction, i.e. to avoid the  $\text{S}_{\text{N}}\text{Ar}$  mechanism, is the disfavored Meisenheimer complex (**MC**) in gas phase due to the separation of opposite charges. The concerted ANDN mechanism should diminish the degree of such charge partition in comparison with

the S<sub>N</sub>Ar mechanism. One may believe, therefore, that in the TSs of the ANDN mechanism, due to the lack of structure units for effective resonance stabilization of the anionic ring system, a negative charge is built up mainly on an outcoming fluoride anion, being stabilized by the proximity of the positively charged E-atom. Thus, it cannot be excluded that, as an additional reason, the energy of the forming C–P bond does not contribute enough to compensate the energy expenses of transforming a benzene system into an anionic cyclohexadienyl one.

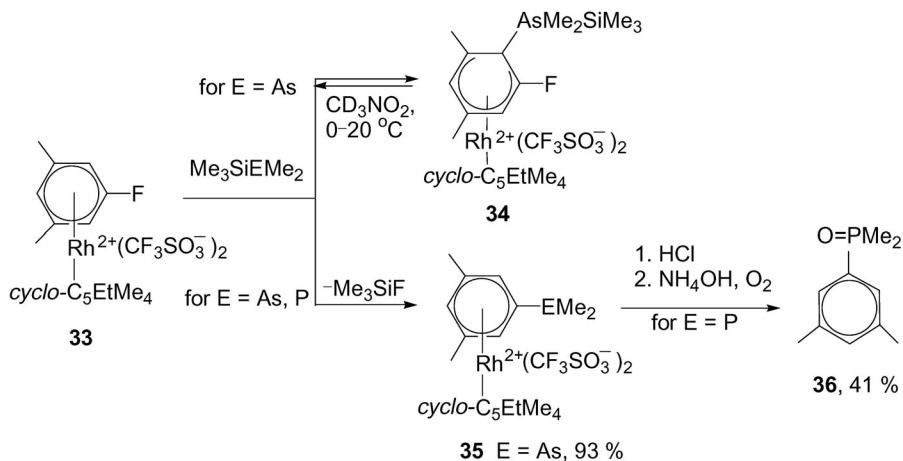


As the reactions were carried out in essentially nonpolar media, the calculations performed for the gas phase seem to be quite adequate to the experimental conditions. So, the ANDN mechanism is fairly consistent with the experimentally observed and calculated substrate and positional selectivities. Both reactivity patterns also correspond qualitatively to the calculated correlations of the reaction exothermicities. The key structure features of the TSs responsible for this kinetics/thermodynamics parallelism are believed to be as follows: First, the ring can obviously maintain a considerable degree of benzenoid resonance instead of changing to a cyclohexadienyl anion-like structure, while both entering and leaving groups, due to their out-of-plane deviation, lose efficient resonance interaction with the ring  $\pi$ -system. Second, the ortho position of two fluorine atoms on a benzene ring is destabilizing compared to the meta location (*o*-difluorobenzene is higher in energy by 3.5–3.6 kcal mol<sup>-1</sup> relative to its meta isomer<sup>19</sup>). Obviously, the fluorine out-of-plane deviation in the TSs relieves this tension and acts in favor of the nucleophilic attack at the neighboring CF unit. Third, because of a benzenoid-like ring moiety in the TS, the *o*-fluorine does not exert considerable  $p,\pi$ -repulsion, but its  $-I$  effect facilitates the nucleophilic attack more than that of the *m*-F, obviously by strengthening the forming carbon–nucleophile bond. Therefore, 1,2-difluorobenzene and 1,2,3-trifluorobenzene are more reactive in the aggregate than 1,3-difluorobenzene and 1,3,5-trifluorobenzene, respectively. For the regioselectivity of 1,2,3-trifluorobenzene, it can be significant that



the ring in **TS-2** is *m*-difluorobenzene-like and thus being more favorable than the *o*-difluorobenzene-like ring in **TS-3**. All these features are in favor of the observed reaction products and in accordance with the kinetics/thermodynamics parallelism.

Fluorine substitution in monofluoroarenes by  $\text{Me}_2\text{E}$  groups by the reaction with  $\text{Me}_2\text{ESiMe}_3$  ( $\text{E} = \text{As}, \text{P}$ ) has also been accomplished, using the activating effect of arene  $\pi$ -coordination to an electron-withdrawing metallocomplex fragment according to Scheme 10<sup>20</sup>.



SCHEME 10

In the reaction with the arsane, complex **33** was completely transformed within 5 min to an equimolar mixture of product **34**, formed by nucleophilic addition to an unsubstituted position of the arene ligand, and **35**, the product of fluorine substitution. The former species obviously arises from a kinetically preferred reversible reaction and is completely transformed within 20 min into **35** obtained in 93% yield. In the reaction of **33** with  $\text{Me}_2\text{PSiMe}_3$ , the fluorine atom was also rapidly replaced by the  $\text{Me}_2\text{P}$  group, giving rise, however, to a complex product mixture from which (3,5-dimethylphenyl)dimethylphosphane oxide (**36**) could be isolated in 41% yield.

The activating effect of arene  $\pi$ -coordination to the doubly charged fragment  $\text{Rh}(\eta^5\text{-C}_5\text{EtMe}_4)^{2+}$  for nucleophilic attack is comparable with the influence of three nitro groups in ortho and para positions to the C-Hal unit in a noncoordinated haloarene<sup>21</sup>. So, complex **33** is the most active substrate hitherto applied in reactions with  $\text{Me}_2\text{ESiMe}_3$  ( $\text{E} = \text{P}, \text{As}$ ). The initial formation of complex **34**, which can be considered as a metallocomplex

analogue of the classical Meisenheimer intermediate, allows to suggest the S<sub>N</sub>Ar mechanism for the observed replacement of fluorine in **33** (Scheme 10).

The results presented here clearly demonstrate the ability of the Me<sub>2</sub>ESiMe<sub>3</sub> (E = As, P) reagents to introduce the Me<sub>2</sub>E group into arene transition metal complexes by nucleophilic substitution of halogen atoms in arene ligands. The Me<sub>2</sub>E groups thus introduced can serve as additional coordination centers and allow to modify and tune catalytic and other useful properties of the synthesized complexes.

The observed characteristic features of the phosphane and arsane reagents Me<sub>2</sub>EMMe<sub>3</sub> (E = P, As; M = Si, Sn), which distinguish them from the related nucleophiles Me<sub>2</sub>EH and Me<sub>2</sub>E<sup>-</sup>, are caused by their relatively weak nucleophilic activity in combination with their high selectivity and make them convenient and versatile synthons for a variety of syntheses.

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