Aryl-bis(triorganylphosphine)nickel phenoxides

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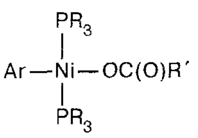
Compounds of general formula *trans*-$ArNi(PR_3)_2OAr'$ (R = Et, cyclohexyl; Ar = $2\text{-}MeC_6H_4$, $2\text{-}FC_6H_4$; Ar′ = $4\text{-}FC_6H_4$, $4\text{-}NO_2C_6H_4$) were synthesized by the reaction of Ar′OK with cationic nickel complexes generated by treatment of $ArNi(PR_3)_2Cl$ with $TlBF_4$. Syntheses of 4-fluorophenoxide complexes, $ArNi(PR_3)_2OC_6H_4F\text{-}4$, additionally give some quantities of *trans*-$[ArNi(PR_3)_2OC_6H_4F\text{-}4]\cdots[HOC_6H_4F\text{-}4]$ adducts. Exchange reactions $MeC_6H_4Ni(PEt_3)_2OC_6H_4F\text{-}4 + XC_6H_4OH \rightleftharpoons 2\text{-}MeC_6H_4Ni(PEt_3)_2OC_6H_4X + 4\text{-}FC_6H_4OH$ were studied in THF. The equilibrium is shifted to the right as the acidity of ArOH increases. A linear relationship between $\lg K_{eq}$ and pK_a of XC_6H_4OH in DMSO was found. A conclusion concerning the strong polarization of the Ni—O bond was made on the basis of an analysis of the chemical shifts of fluorine atoms in $2\text{-}MeC_6H_4Ni(PEt_3)_2OC_6H_4F\text{-}4$.

Key words: aryl-bis(triorganylphosphine)nickel phenoxides, hydrogen bond, substituted phenols, exchange reactions, ^1H NMR, ^{19}F NMR, ^{31}P NMR, bond polarity.

Previously we presented a series of works (see Refs. 1—3 and the references cited therein) reporting on the syntheses of σ-aryl-bis(triorganylphosphine)nickel carboxylates (**1**) and studies of their structures in solutions.



$$\mathrm{Ar{-}\overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{Ni}}{-}OC(O)R'}$$

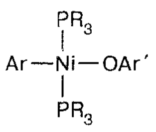
1

Ar = $2\text{-}FC_6H_4$, $2\text{-}MeC_6H_4$;
R = Et, Cy, Ph, $4\text{-}FC_6H_4$;
R′ = Ph, $4\text{-}FC_6H_4$, $4\text{-}MeC_6H_4$; $4\text{-}NO_2C_6H_4$, $4\text{-}Me_2NC_6H_4$, Me
Cy is cyclohexyl

Based on three independent approaches to the estimation of the polarity of the Ni—O bond in these compounds (determination of chemical shifts of the fluorine atom (CSF) for compounds **1**, R = $C_6H_4F\text{-}4$,[1] exchange equilibria,[2] and IR spectroscopy of hydrogen bonds[3]), we established that this bond is strongly polarized. It was also shown that the polarity of the Ni—O bond in compounds **1** increases in the following series of phosphines: $Cy_3P < (4\text{-}FC_6H_4)_3P < Et_3P < Ph_3P$, which does not coincide either with the order of increasing electron-donating ability of phosphines[4] or with the order of their increasing steric requirements.[5]

Results and Discussion

It was of interest to determine whether the previously revealed dependence of the Ni—O bond polarity on the nature of the phosphine is also valid in less sterically hindered organonickel derivatives containing the Ni—O bond. With this purpose, we synthesized σ-aryl-bis(triorganylphosphinenickel) phenoxides (**2a—g**) and studied them by NMR spectroscopy.



$$\mathrm{Ar{-}\overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{Ni}}{-}OAr'}$$

2

2	R	Ar	Ar′
a	Et	$2\text{-}MeC_6H_4$	$C_6H_4F\text{-}4$
b	Et	$2\text{-}MeC_6H_4$	$C_6H_4NO_2\text{-}4$
c	Et	$2\text{-}FC_6H_4$	$C_6H_4F\text{-}4$
d	Cy	$2\text{-}MeC_6H_4$	$C_6H_4F\text{-}4$
e	Cy	$2\text{-}FC_6H_4$	$C_6H_4F\text{-}4$
f	Ph	$2\text{-}MeC_6H_4$	$C_6H_4F\text{-}4$
g	Ph	$2\text{-}FC_6H_4$	$C_6H_4F\text{-}4$

It should be noted that compounds **2**, in which the organonickel moiety is bonded to the rigid phenoxide anion,[6] are convenient objects for determining quantitative relations of the effect of ligands on the rigidity of the above moiety by the exchange equilibrium method.

It follows from an analysis of literature data that of organonickel phenoxides, only σ-methyl compounds of nickel, $MeNi(L)_2OAr$ (L = PMe_3, Ar = Ph, $C_6H_4Me\text{-}4$,[7] and $C_6H_4Ph\text{-}4$ [8]), usually synthesized by protolysis of the corresponding Me_2NiL_2 compounds with phenol, have been reported. The compound with L = PEt_3 and Ar = Ph has not been isolated due to its instability in solutions.[8] The corresponding σ-aryl compounds of nickel are poorly studied, probably because of their even lower stability. There are only two examples of phenoxide σ-arylnickel complexes stabilized due to the presence of *ortho*-chlorine atoms, namely, σ-pentachlorophenylnickel pentachlorophenoxides, *trans*-

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$C_6Cl_5Ni(PEt_3)_2OC_6Cl_5$ and *cis*-$C_6Cl_5Ni(DPPE)OC_6Cl_5$. The former compound was obtained by treatment of $C_6Cl_5Ni(PEt_3)_2Cl$ with silver pentachlorophenoxide.[9] The latter compound was synthesized *via* an intermediate nickel complex formed by the reaction between $C_6Cl_5Ni(DPPE)Cl$ and silver perchlorate in acetone followed by treatment of the reaction mixture with potassium pentachlorophenoxide.[10]

In the present work we obtained compounds **2** by the previously developed procedure[1] for synthesizing compounds **1**. The procedure involved the reaction of the corresponding aryl-bis(triorganylphosphine)nickel with thallium fluoroborate in THF followed by treatment of the reaction mixture with KOAr′:

$$\mathrm{ArNi(PR_3)_2Cl} \xrightarrow{\text{1) TlBF}_4\text{; 2) KOAr}'} \mathbf{2}. \qquad (1)$$

It should be noted that replacement of Cl^- by ArO^- in this reaction occurs more readily than replacement of Cl^- by $ArC(O)O^-$ in a similar synthesis of compounds **1**. In the latter case, the reaction should be carried out in ethanol, since it does not proceed to the end in THF (^{31}P NMR data). It should also be pointed out that the direct reaction between aryl-bis(triethylphosphine)nickel chloride with potassium phenoxide does not afford the target compounds. In addition, according to ^{19}F NMR data, treatment of bis(*o*-tolyl)bis(triethylphosphine)nickel with 4-fluorophenol in organic solvents does not result in dearylation.

The hitherto unknown phenoxides **2a—e** are yellow crystalline compounds. They were characterized by elemental analyses (Table 1) as well as ^1H, ^{19}F, and ^{31}P NMR spectral data (Table 2). Phenoxide complexes **2** are less stable than the corresponding benzoate complexes **1**. Complexes **1** are rather stable in the solid state and are unstable only in solutions, whereas compounds **2** slowly decompose even in the solid form under argon, as evidenced by a change in their color from yellow to green. Compounds **2** are even less stable in solutions. The stability of compounds **2** depends on the nature of the phosphine in the same manner as in the case of compounds **1**: compounds stabilized by PEt_3 are the most stable, whereas those stabilized by Ph_3P are the least stable. It is impossible to isolate compound **2g** from the reaction mixture. The ^{19}F NMR spectrum of a solution of this compound in benzene does not contain signals of fluorine atoms in the region typical of compounds **2** ($Ar = 2\text{-}FC_6H_4$, $Ar' = 4\text{-}FC_6H_4$) containing other phosphine ligands ($\delta \sim -25$ and 21, respectively). Instead of the above signals, the ^{19}F NMR spectrum contains signals at δ 1.5 and 12.2, which probably correspond to 2,2′-difluorodiphenyl and 4-fluorophenol; this suggests that decomposition of **2g** occurs. Compound **2f** can be isolated from the reaction mixture. The ^{19}F NMR spectrum of its solution in benzene contains two signals of fluorine atoms at δ 13.1 and 22.1. The former signal corresponds to 4-fluorophenol, while the latter signal, with lower intensity, corresponds to the 4-fluorophenoxide ligand. The ^1H NMR spectrum of a solution of **2f** in C_6D_6 contains signals of protons in aromatic rings along with two signals in the region of *o*-methyl group protons at δ 3.30 and 2.98. We were unable to obtain a satisfactory elemental analysis for this compound.

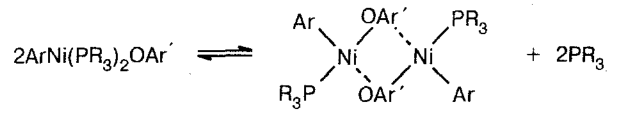
^{31}P NMR spectra. Bis(triethylphosphine) nickel complexes **2a—c** display ^{31}P singlet signals at δ 7, which indicates a *trans*-structure of these compounds. In addition to this signal, the 4-fluorophenoxide complex **2c** displays a weak (~10 %) signal around δ 50 corresponding to $POEt_3$. The ^{31}P NMR spectra of bis(tricyclohexylphosphine) complexes **2d** and **2e** contain the main signal of the coordinated PCy_3 ligand at δ 6—7 along with a signal at δ 10, which corresponds to uncoordinated PCy_3. The ratio of signal intensities from the coordinated and uncoordinated PCy_3 is 6 : 1 and 1.5 : 1 for compounds **2d** and **2e**, respectively. The ^{31}P NMR spectrum of compound **2d** also contains two weaker signals at δ 25.8 and 30.2, which is evidence of partial decomposition of this compound.

^1H NMR spectra. Complexes **2a—f** display characteristic multiplet signals of protons in aromatic as well as PEt_3 or PCy_3 ligands. In addition, the spectra of *o*-tolyl complexes **2a,b,d** contain a signal of protons in the *o*-tolyl group at δ ~ 3. The addition of 4-fluorophenol to a solution of compound **2a** in C_6D_6 results in an increase in intensity of the weak and poorly resolved multiplet with a center at δ 6.845 and in the appearance of a broadened signal of an OH-proton at δ 8.71. The spectrum of compound **2d** contains the main characteristic signals along with a significant number of foreign signals from decomposition products.

^{19}F NMR spectra. The spectra of 4-fluorophenoxide complexes **2a,c,e** contain the main fluorine signal around δ 20—22 as well as a less intense signal at δ ~ 13—14. Compound **2d** displays a signal at 21.79 as well as two signals at δ ~ 13. In addition, 2-fluorophenyl complexes **2c** and **2e** display a triplet signal of the 2-F atom [$^4J(^{19}F, ^{31}P) = 2.3$ Hz] in the region of δ −24 to −29. The addition of 1 equiv. 4-fluorophenol to a solution of compound **2a** in benzene results in an increase in the signal at δ 14.5 and its downfield shift (δ 12.8) towards the signal of 4-fluorophenol (δ 11), while the signal at δ 21.4 is also shifted 1 ppm downfield. It was shown for compound **2a** as an example that the ratio of the signals at δ 21 and 14 (9 : 1) depends on the purity of the starting KOC_6H_4F-4 used in the synthesis (see Experimental). The shape of the ^{19}F NMR spectra of compound **2a** does not depend significantly on its concentration in benzene and THF as well as on temperature down to −70 °C in THF and down to 90 °C in decalin. The ^{19}F NMR spectra of a **2a**—4-fluorophenol mixture (1 : 1) heated in decalin were also found to be independent of temperature.

When discussing the data obtained, it should first be noted that the elemental analyses of triethyl- and tricyclohexylphosphine complexes **2a**—**e** are in good agreement with theoretical considerations. On the other hand, the ^{19}F NMR spectra suggest that the solutions contain additional compounds containing the 4-FC_6H_4O group. In addition, the ^{31}P NMR spectra of 4-fluorophenoxide complexes containing the triethylphosphine (**2c**) and tricyclohexylphosphine (**2e**) ligands reveal the presence of some amounts of $POEt_3$ and PCy_3, respectively.

One could assume the following possible explanations for the presence of additional signals in NMR spectra. Partial dimerization with liberation of the free phosphine can occur in solutions of compounds **2c**,**e**:



PEt_3 is readily oxidated into $POEt_3$, whereas PCy_3 is very difficult to oxidate and is present in solution in the free state. For example, it is known that PCy_3, unlike $POEt_3$, is not oxidated in air.[11] It can be expected from general considerations that the nuclei of fluorine in μ^2-type bridge compounds should be deshielded in comparison with non-bridge compounds, and hence their signals can appear in the region of δ 13—14. When 4-fluorophenol is present, rapid exchange of the 4-fluorophenoxide moieties can occur between the free phenol and the dimer, which results in averaging of the chemical shift of fluorine (CSF). The possibility of formation of such dimers as a side product in the syntheses of methylnickel compounds, $MeNi(PMe_3)_2OR$ (R = Ph, 4-MeC_6H_4), has been noted in Ref. 7.

Table 1. Melting points and elemental analysis data for compounds **2**, **6**, and **7**

Compound	Molecular formula	Yield (%)	M.p./°C (dec.)	Found / Calculated (%) C	H	P
2a	$C_{25}H_{41}FNiOP_2$	62	70—73	60.56 60.39	8.48 8.31	11.98 12.46
2b	$C_{25}H_{41}NiNO_3P_2$	62	155—158	57.20 57.28	8.06 7.88	11.32 11.82
2c	$C_{24}H_{38}F_2NiOP_2$	54	87—90	58.12 57.51	7.65 7.64	12.27 12.36
2d	$C_{49}H_{77}FNiOP_2$	42	160—163	71.18 71.62	9.78 9.44	6.70 7.54
2e	$C_{48}H_{74}F_2NiOP_2$	76	163—166	69.76 69.82	9.00 9.03	7.30 7.50
6 · H_2O	$C_6H_6KFO_2$	~100		42.64 43.44	3.49 3.60	—
7 · H_2O	$C_6H_6KNO_3$	~100		36.80 36.91	3.06 3.09	—

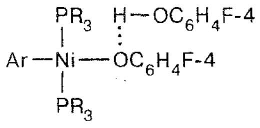
Table 2. ^{1}H, ^{31}P, and ^{19}F NMR spectral data for compounds **2**

Compound	δ^{1}H in C_6D_6	δ^{31}P (in C_6D_6)*	Chemical shift of F (in C_6D_6)*
2a	0.70—1.34 (m, Et, 30 H); 3.045 (s, Me, 3 H); 6.847 m, 7.459 (d, 2-MeC_6H_4, 4 H); 7.05 (m, 4-FC_6H_4, 4 H)	7.52(10) 51.58(1)	21.56(4) 14.45(1)
2b	0.74—0.95 (m, Et,30 H); 2.970 (s, Me,3 H); 6.84 m, 7.31 (m, 2-MeC_6H_4, $NO_2C_6H_4$, 6 H); 8.27 (d, $NO_2C_6H_4$, 2 H)	7.71	
2c	0.89—1.08 (m, Et, 30 H); 6.60—7.46 (m, 2-FC_6H_4, 4-FC_6H_4, 8 H)	7.58(9.5) 50.56(1)	20.04(3) 13.62(1) −24.07(3)
2d	0.86—2.28 (m, Cy, 66 H); 3.593 (s, Me, 3 H); 6.81—7.17 (m, 2-MeC_6H_4, 4-FC_6H_4)**	6.35(1.5) 10.6(1) 25.8(0.4) 30.2(0.2)	21.79 13.33 12.64
2e	0.91—2.24 (m, Cy, 66 H); 6.51—7.40 (m, 2-FC_6H_4, 4-FC_6H_4, 8 H)	7.51(6) 10.50(1)	21.18(4) 13.26(1) −29.79(4)
2f	2.88 (s, Me), 3.30 (s,Me)**		22.13(1) 13.14(4)

* The relative intensities of signals are given in parentheses.
** The ^{1}H NMR spectra contain many signals from decomposition products.

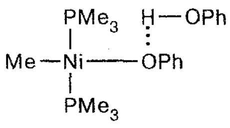
There are several objections to the above interpretation of the experimental data. First, there are no additional signals of protons in the 2-methyl group region or fluorine atom signals in the region of the 2-fluoromethyl group in the spectra of compounds **2a** and **2c**, respectively, while the ^{31}P NMR spectra do not contain additional signals of coordinated phosphine molecules. In principle, shielding of the corresponding indicator atoms in the monomer and dimer can be different.[7] Second, the number of $POEt_3$ molecules in compound **2c** (10 %) and that of PCy_3 molecules in **2e** (15 %) are less than one would expect based on the ^{19}F NMR spectra of compounds **2c** (25 %) and **2e** (20 %). It should, however, be taken into account that if the synthesis involves dimerization, the released PR_3 (or POR_3) molecules can be partially removed when the product is crystallized. However, the addition of 2 equiv. PEt_3 to a solution of **2c** in benzene does not cause considerable changes in the ^{19}F NMR spectrum, which is evidence against the existence of monomer—dimer equilibrium in solution.

It seems more reasonable to explain the results obtained by the assumption that solutions of compounds **2** contain some quantity of their complexes (**3**). Similar complexes of σ-methylnickel **4** were recently isolated and characterized by spectroscopic methods and X-ray diffraction analysis.[12]



$$\mathrm{Ar{-}Ni(PR_3)_2{-}OC_6H_4F\text{-}4\cdots H{-}OC_6H_4F\text{-}4}$$

3



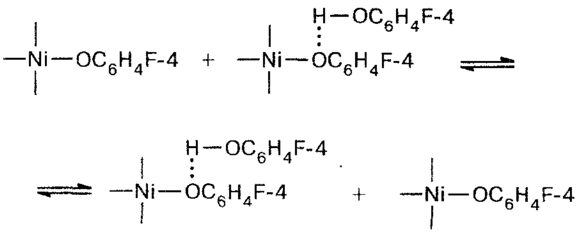
$$\mathrm{Me{-}Ni(PMe_3)_2{-}OPh\cdots H{-}OPh}$$

4

Unfortunately, compounds of σ-arylnickel **2** are quite unstable, and we were unable to obtain crystals of these compounds for performing an X-ray diffraction analysis. Despite our attempts, we failed to obtain analytically pure adduct **3a**. Treatment of **2a** with an equimolar amount of 4-fluorophenol in THF or performing reaction (1) in the presence of 4-fluorophenol afforded an oily product, which is a mixture of compound **3a** and $POEt_3\cdots HOC_6H_4F$ complex (**5**) in a 4 : 1 ratio, according to elemental analysis and ^{19}F and ^{31}P NMR spectral data. In addition, the IR spectrum of this product in decalin, along with two very broad bands with centers at 3350 and 3150 cm^{-1}, which refer to the OH group in the hydrogen-bonded complexes **3a** and **5**, also contains a band of free 4-fluorophenol at 3616 cm^{-1}.

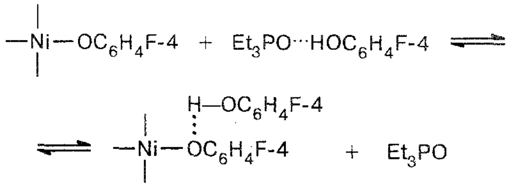
The currently available experimental data do not allow one to solve the problem of whether complexes **3** are formed in the course of the syntheses of compounds **2** or they result from the instability of these compounds and their partial decomposition in solution. The presence $POEt_3$ or PCy_3 in solutions can also suggest decomposition. Based on elemental analysis data, it is impossible to make unambiguous conclusions. For example, according to calculations, the content of C, H, and P in complex **3a** is 61.08, 7.55, and 10.18 % (60.39, 8.31 and 12.46 % for **2a**); hence, the existence of small amounts of **3a** should not considerably affect the results of analysis of **2a**. On the other hand, according to ^{19}F NMR data, the amount of complex **3a** in the solution of **2a** depends on the quality of the starting potassium 4-fluorophenoxide, which can suggest partial formation of **3a** during the synthesis of **2a**. The reason for this can be the presence of crystallization water in the starting $4\text{-}FC_6H_4OK$, which, in addition, is taken in some excess relative to the starting $ArNi(PR_3)_2Cl$ in reaction (1) (see Experimental).

The presence of single fluorine signals in the ^{19}F NMR spectra of **2a** or an authentic mixture of **2a** and 4-fluorophenol in the regions of 4-fluorophenol (~14 ppm) and 4-fluorophenoxide (~21 ppm) indicates that the exchange between **2a** and **3a**



$$\mathrm{{-}Ni{-}OC_6H_4F\text{-}4 + {-}Ni{-}OC_6H_4F\text{-}4\cdots H{-}OC_6H_4F\text{-}4 \rightleftharpoons {-}Ni{-}OC_6H_4F\text{-}4\cdots H{-}OC_6H_4F\text{-}4 + {-}Ni{-}OC_6H_4F\text{-}4}$$

or between **3a** and **5**



$$\mathrm{{-}Ni{-}OC_6H_4F\text{-}4 + Et_3PO\cdots HOC_6H_4F\text{-}4 \rightleftharpoons {-}Ni{-}OC_6H_4F\text{-}4\cdots H{-}OC_6H_4F\text{-}4 + Et_3PO}$$

by 4-fluorophenol occurs quickly in the NMR time scale at temperatures down to −90 °C.

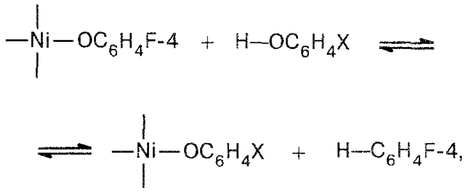
On the other hand, tautomeric exchange of 4-fluorophenoxide moieties in compound **3**

$$\mathrm{R{-}O(M)\cdots H{-}O{-}R \rightleftharpoons R{-}O{-}H\cdots O(M){-}R}$$

$(R = C_6H_4F\text{-}4;\ M = 2\text{-}MeC_6H_4Ni(PEt_3)_2)$

is slow in the NMR time scale down to −90 °C, which is proved by the absence of dynamics in the ^{19}F NMR spectra of **2a** or the mixture of **2a** with 4-fluorophenol. It is interesting to note that similar exchange with phenoxide ligands in methylnickel complexes [$R = Ph$, $M = MeNi(PMe_3)_2$] occurs by an intramolecular mechanism rather quickly in the ^{13}C NMR time scale even at room temperature.[12]

The intermolecular exchange with aroxyl groups between **3a** and substituted phenols in THF



$$\mathrm{{-}Ni{-}OC_6H_4F\text{-}4 + H{-}OC_6H_4X \rightleftharpoons {-}Ni{-}OC_6H_4X + H{-}C_6H_4F\text{-}4,} \quad (2)$$

$X = 4\text{-}Me, H, 4\text{-}Cl, 4\text{-}Br, 3\text{-}Cl, 4\text{-}NO_2,$

occur quickly: the equilibrium is established immediately after preparation of samples and recording the ^{19}F NMR spectra. The equilibrium constants are given in Table 3. An increase in phenol acidity results in a shift of equilibrium to the right, towards the formation of an organonickel derivative of a more acidic phenol. According to Ref. 2, the latter fact suggests the higher polarity of the Ni—O bond as compared with the H—O bond.

It was found that the logarithms of constants of equilibrium (2) in THF correlate well with polar constants of substituents and with pK_a of ArOH in DMSO (Table 3). The fact that the above correlations exist is indirect evidence of the existence of the following linear

Table 3. Equilibrium constants for the reaction
$\mathbf{2a} + XC_6H_4OH \rightleftharpoons 2\text{-}MeC_6H_4Ni(PEt_3)_2OC_6H_4X + 4\text{-}FC_6H_4OH$
(in THF)

X	σ(X)	σ°(X)	pK_a ArOH DMSO[13]	pK_a ArOH DMSO[14]	K_{eq}
4-NO_2	0.78	0.73	11.27	13.90	5.2
3-Cl	0.37	0.37	14.62	15.83	3.2
4-Br	0.23	0.26	15.24	16.81	1.5
4-Cl	0.23	0.27	15.32	16.74	2.0
H	0	0	16.47	18.03	0.44
4-Me	−0.17	−0.15	16.96	18.86	0.29

Parameters of the correlation equations

$\lg K_{eq} = (1.94\pm0.03)\,\sigma^{o} - (0.28\pm0.12)$; $r = 0.995$; $S = 0.06$.

$\lg K_{eq} = (1.81\pm0.05)\,\sigma - (0.24\pm0.15)$; $r = 0.989$; $S = 0.10$.

$\lg K_{eq} = (-0.28\pm0.01)\mathrm{p}K_a(\mathrm{ArOH}) + (4.5\pm1.8)$; $r = -0.958$; $S = 0.19$; (pK_a ArOH in DMSO, according to the data in Ref. 13).

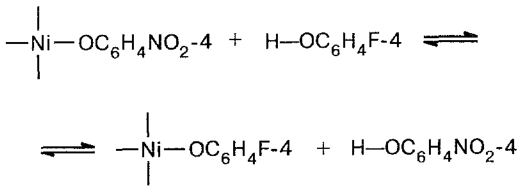
$\lg K_{eq} = (-0.368 \pm 0.003)\mathrm{p}K_a(\mathrm{ArOH}) + (6.4\pm1.8)$; $r = -0.988$; $S = 0.08$; (pK_a ArOH in DMSO, according to the data in Ref. 14).

relations between the dissociative ability of Ni—O and H—O bonds:

$$\lg K_D(\mathrm{Ni{-}O}) = A\cdot\lg K_D(\mathrm{H{-}O}) + B$$

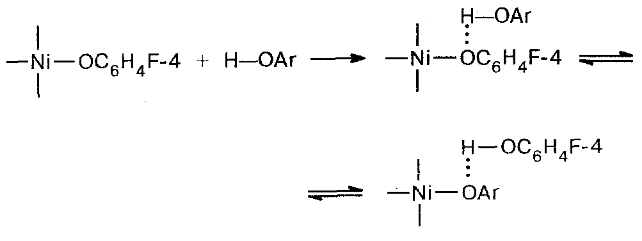
for substituted phenols and their organonickel derivatives.

It is interesting to note that exchange between the 4-nitrophenoxide complex **2b** and 4-fluorophenol



$$\overset{|}{\underset{|}{-\mathrm{Ni}}}-OC_6H_4NO_2\text{-}4 + H{-}OC_6H_4F\text{-}4 \rightleftharpoons \overset{|}{\underset{|}{-\mathrm{Ni}}}-OC_6H_4F\text{-}4 + H{-}OC_6H_4NO_2\text{-}4$$

does not occur under ordinary conditions, although the corresponding equilibrium Ar = 4-$NO_2C_6H_4$) is established quickly. The reason for the observed distinction is probably that the exchange is preceded by formation of a complex involving an H-bond, the exchange event occurring in this complex:



$$\overset{|}{\underset{|}{-\mathrm{Ni}}}-OC_6H_4F\text{-}4 + H{-}OAr \longrightarrow \overset{|}{\underset{|}{-\mathrm{Ni}}}-\overset{H-OAr}{\overset{\vdots}{O}}C_6H_4F\text{-}4 \rightleftharpoons \overset{|}{\underset{|}{-\mathrm{Ni}}}-\overset{H-OC_6H_4F\text{-}4}{\overset{\vdots}{O}}Ar$$

In the case of 4-nitrophenoxide derivative **2b**, the formation of a complex of this type can be hindered due to insufficient basicity of oxygen in this complex. According to the data in Ref. 12, $MePd(PMe_3)_2OC_6H_4CN\text{-}4$ does not form an adduct with 4-cyanophenol. However, the formation of $MePd(PMe_3)_2OAr\cdots HOAr$ was observed for those ArO^- which are more basic than $4\text{-}CNC_6H_4O^-$.

When analyzing the CSF values for compounds **2**, it is necessary to take into account the presence of adducts **3** in their solutions and a decrease in the electron-withdrawing effect of the Ni-containing moiety under the action of a hydrogen bond. This is suggested by a decrease in shielding of fluorine by 1 ppm upon addition of 4-fluorophenol to **2a** in 1 : 1 ratio, *i.e.*, in the case when the solution mostly contains adduct **3a**. The actual shielding of fluorine in **2a** should be 0.1 ppm higher than in the presence of 10 % **3a**, and the CSF for pure **2a** should be *ca.* δ 21.5. Assuming that the changes in CSF for compounds **2d** and **2f** due to formation of their adducts **3** with 4-fluorophenol are the same and do not depend on the nature of PR_3, one can expect that CSF for **2d** and **2f** should be *ca.* δ 22.0 and 23.0, respectively.

The following conclusions can be made based on the above values of CSF for $2\text{-}MeC_6H_4Ni(PR_3)_2OC_6H_4F\text{-}4$. First, the fluorine nuclei in these compounds are strongly shielded, and the CSF values approach δ 24.5, *i.e.*, the same value as we obtained for a solution of $4\text{-}FC_6H_4OK$ in DMSO, which probably has an ionic structure. It should be noted that this value is close to the CSF of $4\text{-}FC_6H_4ONa$, which is δ 25 as measured by Taft.[15] Taking into account that the CSF for the previously studied organometallic derivatives of 4-fluorophenol, $L_nMOC_6H_4F\text{-}4$, with other moieties L_nM containing heavy non-transition metals as central atoms do not exceed δ 17, and that for 4-fluorophenol is δ 11.7 in relatively inert benzene and δ 13.3 in solvating DMSO,[16] it can be considered that the Ni—O bonds in the nickel complexes of interest are considerably polarized and approach a purely ionic bond (Fig. 1).

Second, it follows from the CSF values that the electron-donating effect of the $MeC_6H_4Ni(PR_3)_2$ moiety increases in the following series of phosphines: $PEt_3 < PCy_3 < PPh_3$, which suggests that the polarity of the Ni—O bond increases in the same series of phosphines. The positions occupied by PCy_3 and PEt_3 in this series differ from that found previously for the effect of the nature of a tertiary phosphine for nickel 4-fluorobenzoate complexes.[1] Thus, the sequence observed for complexes **1** does not coincide either with the order of increasing electron-donating ability of phosphines, $PPh_3 < PPEt_3 < PCy_3$,[4] or with the order of increasing steric requirements: $PEt_3 \approx PPh_3 < PCy_3$.[5] Hence, the effect of phosphine nature on the polarity of the Ni—O bond for the spatially less hindered compounds **2** is also determined by the mutual action of the steric and polar effect of the substituent R.

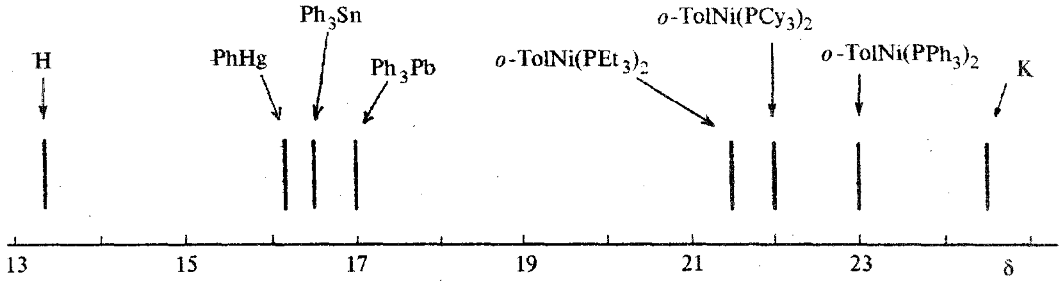


Fig. 1. Diagram of chemical shifts of fluorine (CSF) for compounds $4\text{-}FC_6H_4OQ$. (The CSF values are presented in ppm relative to PhF; the "+" sign corresponds to upfield shifts of a signal. The CSF for Q = H, HgPh, $SnPh_3$, $PbPh_3$, and K are measured in DMSO, those for Q = $2\text{-}MeC_6H_4Ni(PR_3)_2$ are measured in THF, while compounds **2** are unstable in DMSO.)

Experimental

^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY spectrometer with working frequencies of 200.13, 188.31, and 81.01 MHz, respectively. The chemical shifts of protons were measured for solutions in C_6D_6 relative to the background signal (δ 7.15) and were recalculated to the $SiMe_4$ scale. The CSF values were measured by the replacement method relative to a solution of fluorobenzene in benzene. Positive CSF values correspond to an increase in the shielding of fluorine atoms. The accuracy of CSF determination was no worse than ±0.05 ppm. The chemical shifts of ^{31}P nuclei were measured by the replacement method relative to 85 % H_3PO_4 with an accuracy no worse than ±0.01 ppm. Resonance conditions were stabilized using the signal from deuterium in D_2O placed between the walls of a 5 mm tube and a 4 mm insertion containing a solution of the sample (in the case of ^{19}F NMR spectra) or between the walls of a 10 mm tube and an 8 mm insertion containing a solution of the sample in benzene (in the case of ^{31}P NMR spectra).

Organonickel chlorides, $2\text{-}XC_6H_4Ni(PR_3)_2Cl$, were synthesized by the procedure in Ref. 1. Potassium phenoxides used in this study were obtained by the procedure in Ref. 17. According to elemental analysis data, the freshly prepared $4\text{-}FC_6H_4OK$ (**6**), which was used in the syntheses, is a monohydrate **6** · H_2O. The purity of **6** was monitored by ^{19}F NMR. The CSF for a solution of freshly prepared **6** is δ 22.1. The CSF for **6** measured after storage of a solid sample in an inert atmosphere changes by up to several ppm towards decreased shielding, *i.e.*, towards 4-fluorophenol (δ 14.1), which can be due to partial decomposition of **6** into free 4-fluorophenol and rapid exchange of hydrogen and potassium ions. When other than freshly prepared sample of **6** is used in the syntheses, the target compounds **2** contain a considerable amount of 4-fluorophenol. According to elemental analysis data, the $4\text{-}NO_2C_6H_4OK$ (7) used for synthesizing compound **2b** is also a hydrate, **7** · H_2O. On the other hand, compound **2b** obtained contains ~5 % 4-fluorophenol (^1H NMR data).

In this respect, it is interesting to note that an attempt to synthesize a cresolate complex $MeC_6H_4Ni(PEt_3)_2OC_6H_4Me\text{-}4$ (**8**) by reaction (1) from potassium 4-cresolate, which is also a monohydrate, gives only the **8**···$HOC_6H_4Me\text{-}4$ adduct (1 : 1) instead of compound **8** (^1H NMR data). Thus, an increase in ArOH acidity (change from $4\text{-}NO_2C_6H_4OH$ and $4\text{-}FC_6H_4OH$ to $4\text{-}MeC_6H_4OH$) results in an increase in the amount of the **2**···HOAr adduct formed.

All experiments concerning syntheses of organonickel compounds and preparation of solutions for spectroscopic measurements were carried out in an argon atmosphere. The solvents used were previously distilled in argon. The general procedure for synthesizing aryl-bis(triorganylphosphine)nickel phenoxides was as follows. THF (40 mL) was added to a mixture of $2\text{-}XC_6H_4Ni(PR_3)_2Cl$ (1 mmol) and $TlBF_4$ (1.2 mmol). The mixture was stirred for 3 h at -20 °C, then the precipitate of KBF_4 that formed was filtered off. The mother liquor was added to the corresponding potassium phenoxide (1.3 mmol). The mixture was stirred for 3 h at -20 °C, the precipitate of KBF_4 was filtered off, and the mother liquor was concentrated to dryness. The residue was twice crystallized, first from ether and then from pentane. It was found that keeping of a sample of **2a** *in vacuo* over wet alkali results in a decrease in 4-fluorophenol content from 20 to 10 %. In the attempts to obtain compounds **2** using equimolar amounts of ArOK, reaction (1) does not proceed to the end. The target product is formed as a mixture with the starting $ArNi(PR_3)_2Cl$ which is hard to remove by crystallization. In addition, some amount of $POEt_3$ is formed in the case of R = Et. For example, reaction (1) starting from the compound with Ar = $2\text{-}MeC_6H_4$, R = Et, and Ar′ = $4\text{-}FC_6H_4$ gives 50 % of compound **2a** and 33 % of adduct **5** (^{31}P NMR data). The mixture also contains 17 % of the starting $ArNi(PEt_3)_2Cl$.

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