Synthesis and Reactivity of Nickel an Palladium Fluoride Complexes with PCP Pincer Ligands. A NMR-Based Assessment of Electron-Donating Properties of Fluoride and Other Monoanionic Ligands.

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Abstract: A series of complexes of the type [(^{iPr}PCP)M-L] (^{I}M = Ni, Pd), containing the 2,6-bis(diisopropylphosphiomethyl)phenyl (^{Pr}PCP) pincer ligand and simple monoanionic ligands L (F, Cl, Br, H, Me, Ph, NO_3 and OTf) have been synthesized and characterized. The fluoride derivatives [(^{iPr}PCP)M-F] were prepared from the halides [(^{iPr}PCP)M-X] (M = Ni, X = Br; M= Pd, X = Cl) by exchange reactions with AgF or, alternatively, by protonolysis of the methyl complexes [(^{iPr}PCP)M-Me] with $Et_3N{\cdot}3HF$ (TREAT-HF). A survey of the ^{13}C NMR data for the new complexes and previously reported ones with L = OH, OMe and NH_2 revealed significant trends that can be directly related to the electronic properties of the anionic ligands L coordinated to Ni(II) and Pd(II) centers. The chemical shift of the ^{13}C resonance of the metal-bound (ipso) is very sensitive to the σ-donating capacity of L, which increases in the order L = OTf > NO_3 > F > OAc > OMe > Cl > OH ≈ Br > I > NH_2 > Ph > Me > H. In addition, the reactivity of [(^{iPr}PCP)M-F] complexes was investigated. These readily undergo fluoride exchange with LiOMe, affording the corresponding methoxides [(^{iPr}PCP)M-OMe] and LiF. They also react with n-$C_{12}H_{13}$I to cleanly yield [(^{iPr}PCP)M-I] and n-$C_{12}H_{13}$F. Comparison of the rates of the latter reactions and analogous ones involving bromide or chloride complexes showed that the fluorides are significantly more nucleophilic, particularly the palladium derivative. This property was applied in a palladium-catalyzed reaction for the synthesis of alkyl fluorides using AgF as the fluoride source.

Introduction

In the last two decades, late transition metal complexes containing covalently bound hard monoanionic ligands, L, such as amides, alkoxides or fluorides have been subject of sustained interest.[1,2] This class of compounds is involved in many catalytic reactions, such as hydrogen transfer hydrogenations, aerobic oxidations or carbon-heteroatom couplings.[3] The ability to catalyze these processes is connected to the unique reactivity of the M-L linkage, which combines high nucleophilicity and basicity and the ability to undergo many typical organometallic reactions, e. g. insertion reactions, β-hydrogen elimination or C-heteroatom reductive couplings.[4]

Although the chemistry of late transition metal complexes containing terminal (non-bridging) M-N, M-O or M-F bonds has lately experienced a considerable development, their synthesis is still challenging. This is due to a number of reasons, such as the tendency of terminal ligands to bridge other metal centers, thermal instability or hydrolytic sensitivity. A useful strategy for minimizing such problems is using rigid PCP *pincer* chelates to stabilize the metal-containing moiety. We have previously prepared and studied several monomeric hydroxo, alkoxo or

amido complexes of Ni and Pd containing the strongly donor and relatively bulky 2,6-bis(iisopropylphosphino-methyl)phenyl ligand (^{iPr}PCP) which imparts a balance between stability and reactivity to such complexes.[5]

Late transition metal fluoride complexes have been recently the object of much attention, particularly in the context of C-F bond activation[6] and formation,[1b,7] as well as in relation with their use as sources of the hypernucleophilic (and elusive) "naked fluoride" anion.[8] In addition, fluoride complexes can be valuable starting materials in organometallic synthesis. For example, we have showed before that the fluoride ligand is cleanly displaced from the precursor complex [(dippe)Ni(Me)(F)] by lithium alkoxides and amides, providing a versatile route to monomeric methyl-alkoxo and methyl-amides that would have been difficult to prepare by a different method.[9] Although number of monomeric nickel and palladium fluorides stabilized by monodentate or bidentate ligands have been reported in the literature, but only a couple of examples contain *pincer*-type ligands.[10] These would be interesting candidates to participate in the generation of new C-F bonds, since many *pincer* complexes have found interesting applications as catalysts for coupling reactions.[11] Herein we report the synthesis of new Ni(II) and Pd(II) fluoride complexes, the pincer derivatives [(^{iPr}PCP)Ni-F] and [(^{iPr}PCP)Pd-F]. We also investigate the use of Ni and Pd pincer as starting materials for the synthesis of organometallic alkoxides and their ability to catalyze fluoride exchange between AgF and alkyl halides.

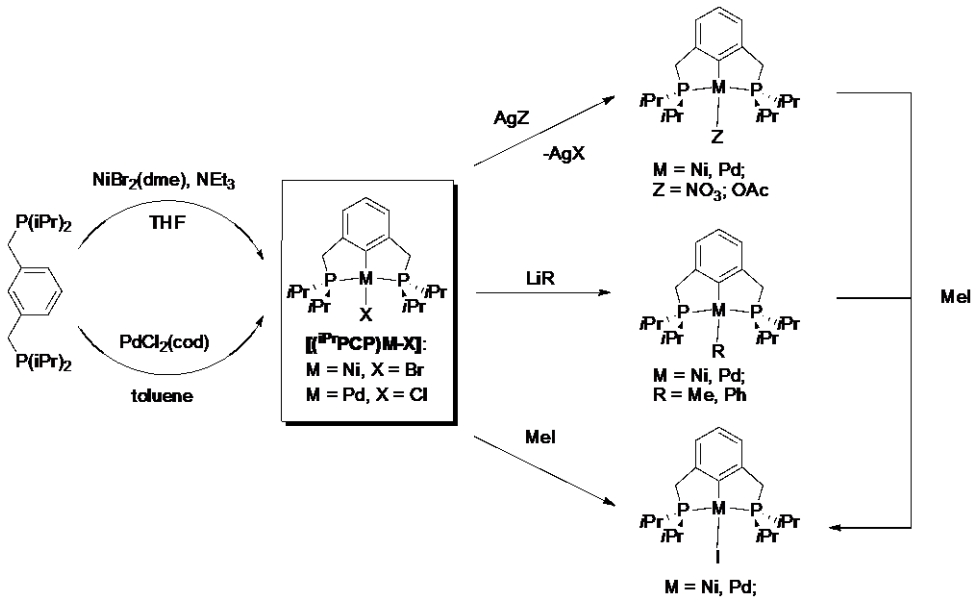
One of the most striking questions regarding the bonding and reactivity of late transition metal complexes with strongly π-electron donor ligands such as OR, NR_2 or F is to which extent these metal-ligand linkages are destabilized by non-bonding $d\pi$-$p\pi$ interactions between the filled *d* orbitals in the metal and the lone electron pairs in the heteroatom.[12] Answering this question would improve the understanding of the reactivity of compounds containing strong π-donor ligands such as fluoride. Spectroscopic data have been of critical importance to support the concept of repulsive $d\pi$-$p\pi$ interactions.[13,14] The availability of spectroscopic data for many pincer complexes of the type [(^{iPr}PCP)M-L] containing widely different anionic ligands L provides an unique opportunity for investigating their correlation to their σ/π donor capacity of L. With the aim of extending this comparison, we have prepared some new derivatives with L = triflate, nitrate, acetate, methyl, phenyl and hydride.

Results and Discussion.

Synthesis of new pincer derivatives of Ni and Pd. We have described previously the hydroxo, alkoxo and amido derivatives of Ni and Pd stabilized by the ^{iPr}PCP pincer ligand.[5] In this section we detail the synthesis of new complexes [(^{iPr}PCP)M-L] containing anionic ligands L with widely different electron-donor strengths, including different halides, triflates, nitrates, alkyls and hydrides.

We originally synthesized the nickel precursor [(^{iPr}PCP)Ni-Br] by oxidative addition of 1-bromo-2,6-bis(diisopropylphosphino)methylbenzene (^{iPr}PCBrP) to $Ni(cod)_2$. A similar reaction was used to prepare the Pd analogue [(^{iPr}(PCP)Pd-Br], using [Pd(η^5-Cp)(η^3-C_3H_5)], generated *in situ* from [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ and NaCp, as the Pd(0) source (see Experimental part). For the synthesis of [(^{iPr}PCP)Pd-Cl], we relied on literature procedures for involving direct palladation of the diphosphine 2,6-bis(diisopropylphosphino)methylbenzene (^{iPr}PCHP) by Pd(II) sources.[15] Several pincer derivatives of nickel have also been prepared by direct metallation,[16] including the chloro derivative [(^{iPr}PCP)Ni-Cl].[17] This method can be regarded more practical than those based on oxidative addition methods because it does not require the previous synthesis of organometallic precursors. Hence, we developed a new synthesis of [(^{iPr}(PCP)Ni-Br] involving direct reaction of (^{iPr}PCP)H and $NiBr_2$(dme), using triethylamine to

neutralize the resulting HBr. This method leads to the desired nickel complex in nearly the same yield as achieved by oxidative addition (ca. 80 %).



Scheme 1

As shown in Scheme 1, complexes [(^{iPr}(PCP)Ni-Br] and [(^{iPr}PCP)Pd-Cl] are starting materials for the synthesis of other compounds. We previously reported that the palladium nitrate complex is readily obtained by reacting the corresponding chloro precursor with silver nitrate.[5a] Similarly, the nickel analogue is also prepared from the corresponding bromide precursor and $AgNO_3$, but in this case special care should be taken to adjust 1:1 Ni/Ag stoichiometry. This is because an excess of the silver reagent causes the oxidation of the product to an stable Ni(III) complex, [(^{iPr}PCP)Ni(NO_3)$_2$], which will be described elsewhere.[18] The acetate complexes [(^{iPr}PCP)M-OAc] are obtained in analogous fashion from the halide precursors and an stoichiometric amount of silver acetate.

Transmetallation reactions of halide precursors with methyl or phenyllithium also proceed easily, affording the corresponding derivatives [(^{iPr}PCP)M-R] (R = Me or Ph) in good yields. The Pd phenyl derivative was mentioned in the literature before.[15a] We characterized the nickel methyl and phenyl complexes by X-ray diffraction. Figures 1 and 2 represent one of the two crystallographically independent molecules found in the unit cells of these complexes. The methyl complex has a typical square-planar configuration without remarkable features. Figure 2 shows that the rings of the phenyl and the pincer ligands are approximately perpendicular. Although electron π-backdonation from the Ni center to each of the aromatic systems is expected to be different due to their different orientations with regard to the metal coordination plane, the Ni-C bond distances are very similar (Ni1-C1: 1.940(2); Ni1-C21, 1.925(2) Å).

The methyl and phenyl complexes are thermally stable and they resist exposure to air for some time in the solid state. However, during one of the attempts to crystallize the nickel methyl complex we isolated colorless crystals which we subsequently identified as the diphosphine oxide 1-Me-2,6-($iPr_2P(O)CH_2$)$_2C_6H_3$·H_2O (Figure 3). Interestingly, a methyl group saturates the *ipso* position originally bound to nickel, suggesting that the reaction with oxygen induces the reductive coupling of the methyl and the pincer ligand. Although the molecule has no crystallographically imposed symmetry, it adopts a symmetric arrangement with both phosphine oxide

functionalities associated to a single water molecule through strong hydrogen bridges (oxygen-oxygen distances = 2.766(2) and 2.841(2) Å).

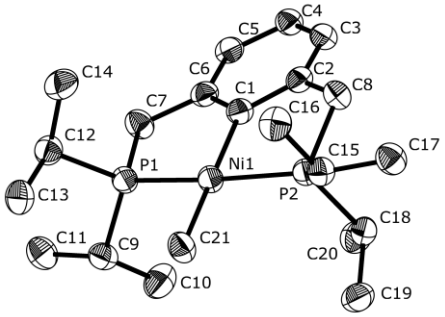


Figure 1. Crystal structure of [(^{iPr}PCP)NiMe] (one of two independent molecules). Selected bond distances (Å) : Ni1-C1, 1.954(2); Ni1-C21, 1.991(2); Ni1-P1, 2.1418(15); Ni1-P2, 2.1445(15). Angle between mean planes: ring C1-C6 NiP_2C_2, 9.1º.

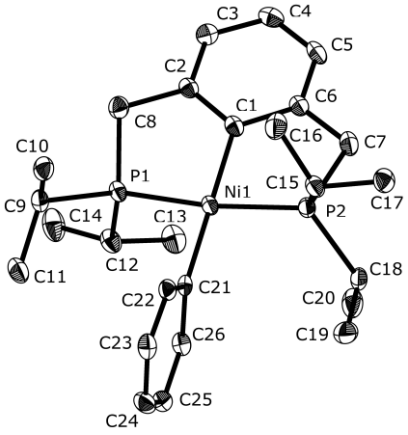


Figure 2. Crystal structure of [(^{iPr}PCP)NiPh] (one of two independent molecules) Selected bond distances (Å): Ni1-C1, 1.940(2); Ni1-C21, 1.925(2); Ni1-P1,2.1470(6); N11-P2, 2.1484(6). Angles between mean planes (deg): Ph NiP_2C_2, 79.3; Ring C1-C6 NiP_2C_2, 11.1; Ph ; Ring C1-C6, 88.1.

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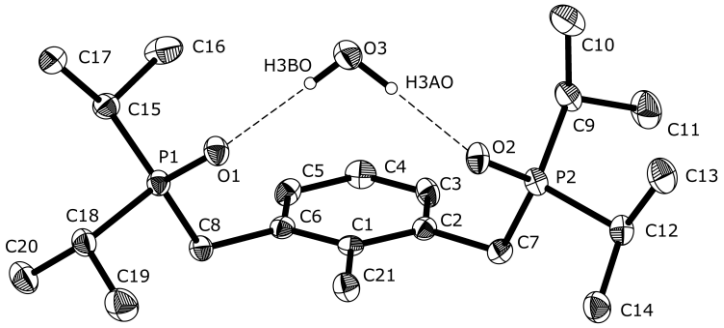
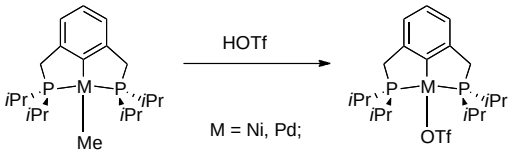


Figure 3. Crystal structure of 1-Me-2,6-($iPr_2P(O)CH_2)_2C_6H_3 \cdot H_2O$. Selected distances (Å) and angles (deg) : C1-C21, 1.509(3); P1-O1, 1.4978(14); P2-O2, 1.4867(13); O1-H3BO, 1.884(17); O3-H3BO, 0.881(15); O1-O3, 2.763(3); O2-H3AO, 1.93(2); O3-H3AO, 0.921(15); O2-O3, 2.842(3); O1-H3BO-O3, 175(2); O2-H3AO-O3, 174(2); H3BO-O3-H3AO, 104(2).

Both the nickel bromide and the palladium chloride react smoothly with MeI at 60 ºC affording the iodides [iPr(PCP)M-I] [15a,16d] in high yield. This appears to be a very general reaction for pincer complexes,[19] and other ^{iPr}PCP derivatives of Ni or Pd we tried react in a similar fashion with MeI. This reaction provides a simple method for recycling mixtures of these compounds, since the iodide complexes can easily be recovered by column chromatography on silica.

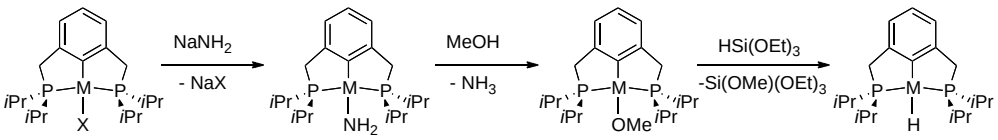
The synthesis of the palladium triflate [(^{iPr}PCP)PdOTf] from the chloride complex and silver triflate has been described previously in the literature.[15b] We found that the readily available Ni and Pd methyl derivatives react with triflic acid affording the corresponding triflates in good yields (Eq 1). This is a versatile route to complexes containing weakly coordinating anions that avoids the use of expensive and potentially reactive silver salts.



(1)

Nickel hydride complexes containing ^{R}PCP ligands (R = *i*Pr, *t*Bu, cyclohexyl) have been synthesized by the reaction of the corresponding halide precursors and different hydride sources.[17] In our hands, the reaction of [(^{iPr}PCP)Ni-Br] with $LiBHEt_3$ (*superhydride*) was clean and essentially complete, but the purification of the hydride from the boron byproducts was problematic, leading to erratic isolated yields. Alternatively, this compound can be prepared reacting [(^{iPr}PCP)Ni-OMe] with triethoxysilane. As shown in Scheme 2, the Ni methoxide is prepared by the previously reported method,[5b] from the amide [(^{iPr}PCP)Ni-NH_2] and methanol. It is not necessary to isolate the amido and methoxide intermediates because all three steps of this synthesis can be performed in sequential manner. Since most reagents and byproducts (methanol, $HSi(OEt)_3$, ammonia and $Si(OMe)(OEt)_3$) are volatile, this method minimizes side reactions and simplifies product isolation. The palladium hydride [(^{iPr}PCP)Pd-H] has also been prepared in the same way, in spite of the thermal instability of the corresponding amido complex [(^{iPr}PCP)Pd-NH_2].[5c] The identity of the latter intermediate has been confirmed spectroscopically and full NMR data (^{1}H, ^{13}C and ^{31}P) are supplied in the Experimental Section.

The crystal structure of the nickel hydride is shown in Figure 4. The crystals of this compound contain three crystallographically independent molecules and are isomorphous with those of the nickel fluoride derivative. Both complexes share an unusual crystal packing model, which is described in detail below for the fluoride complex. Although the quality of the X-ray data is not excellent, the hydride ligand was located at ca. 1.60 Å of the Ni center. The lengths of the N-C bonds in the three independent molecules are slightly different (1.943, 1.911 and 1.893 Å). The average length of the Ni-C bond found in the unit cell is 1.916 Å, somewhat shorter than in the methyl and phenyl complexes (1.94 – 1.95 Å) and very similar in the hydroxo and amido derivatives (1.917 and 1.929 Å), in spite of the widely different strengths of the *trans* influence of such ligands. This suggests that these M-C bonds can be significantly biased by the rigidity of the pincer scaffold and are not good indicators of the *trans* influence exerted by the anionic ligand.



Scheme 2.

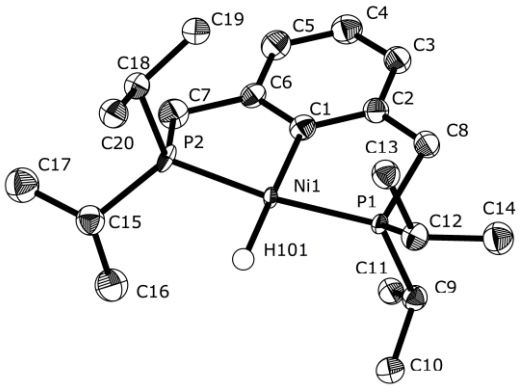


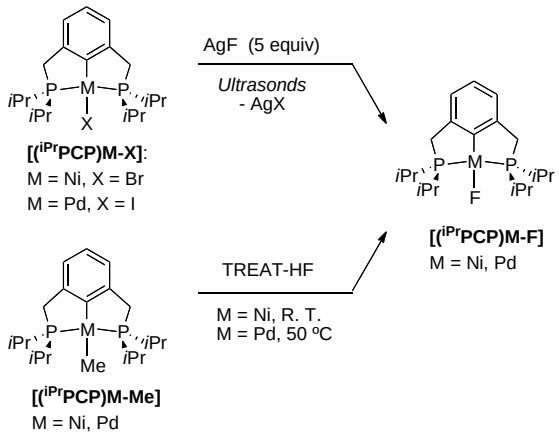
Figure 4. ORTEP view of [(^{iPr}PCP)Ni-H] (one of three independent molecules in the crystal). Selected bond distances (Å): Ni-H, 1.597(15); Ni1-C1, 1.946(13); Ni1-P1, 2.112(3); Ni1-P2, 2.121(3). Angle between mean planes ring C1-C6 and NiP_2C_2, 14.1º.

Synthesis of Ni and Pd fluoride complexes. In order to synthesize these compounds, we explored two general methods commonly used for the preparation of organometallic transition metal fluoride complexes: halide exchange with AgF and protonation of suitable precursors with $Et_3N{\cdot}3HF$ (TREAT-HF) (Scheme 3).[1a] We investigated the reaction of the halide precursors [(^{iPr}PCP)Ni-Br] and [(^{iPr}PCP)Pd-Cl] with an excess of AgF in toluene, assisted with ultrasounds. Under these conditions, the Ni precursor is transformed into the corresponding fluoride complex [(^{iPr}PCP)Ni-F] in good yield, but the Pd chloro complex only reacts very sluggishly. Grushin observed that palladium iodide complexes are better precursors for this purpose, probably because such exchange reactions are driven by the insolubility of AgI.[20] Hence, [(^{iPr}PCP)Pd-F] complex was satisfactorily obtained from the corresponding palladium iodide [(^{iPr}PCP)Pd-I] and AgF. We found that an excess of ≥ 2equiv of AgI was necessary to complete the formation of the nickel and palladium fluorides (Scheme 3). Although this could be attributed to the transformation of AgF into a less reactive mixed halide compound, analysis of the salt residue by powder X ray diffraction gave no indication of inorganic phases different from AgF and AgBr or AgI. Monitoring the halide exchange reactions by $^{31}P\{^1H\}$ NMR shows that after 12h of sonication, the initial resonances of the nickel bromide or palladium iodide precursors fully disappear and are replaced by broader signals of the products. Analytically pure samples of the yellow (M = Ni) or colorless (M = Pd) fluoride complexes [(^{iPr}PCP)M-F] were obtained after recrystallization from hexane. The $^{31}P\{^1H\}$ signals of the pure materials appear splitted in doublets by coupling with ^{19}F. These are significantly narrower and appear a few ppm below those observed for the crude reaction mixtures. The differences of line shape and chemical shifts of the ^{31}P spectra of the reaction mixtures could be due to the presence of small amounts of water, which is known to promote rapid intermolecular fluoride exchange.[21] However, since efforts were made to maintain rigorously anhydrous conditions, it can not be ruled out that the presence of small amounts of AgF could induce similar effects to those of water in the NMR spectra of the crude solutions.

The reaction of hydroxo complexes with TREAT-HF has proven to be an useful and versatile route for the synthesis of fluoride derivatives.[20] In addition, we showed that the methylnickel complex [$NiMe_2$(dippe)] also reacts readily with TREAT-HF, affording the methyl-fluoride complex [NiMeF(dippe)].[9] Since methyl derivatives [(^{iPr}PCP)M-Me] are robust and readily available, we decided to investigate their reaction with TREAT-HF. This reaction proceeds rapidly for M = Ni, affording [(^{iPr}PCP)Ni-F] in high yield. As with the AgF method, the $^{31}P\{^1H\}$ spectrum of the crude product is somewhat broad, but in this case the line broadening persists after recrystallization. This suggests the presence of small amounts of HF, probably retained in the form of fluxional bifluoride species that cannot be easily removed by recrystallization.[21] However, we found that THF solutions of the

crude material are effectively cleaned by stirring with CaH_2 for 24 h, affording [^{iPr}(PCP)Ni-F] with well resolved spectra. Presumably, CaH_2 reacts with the HF but not with the nickel fluoride complex, forming highly insoluble CaF_2.

At room temperature, the reaction of [(^{iPr}PCP)Pd-Me] with an equivalent amount of TREAT-HF is slow and incomplete. However, using an excess of the acidic reagent to force the reaction leads to ill-defined products that could not be purified by recrystallization. Treating this mixture with CaH_2 was unsuccessful because it leads to the formation of [(^{iPr}PCP)Pd-H], identified by its characteristic low-field ^{31}P signal at 71.7 ppm. Monitoring the reaction of TREAT-HF with [(^{iPr}PCP)Pd-Me] by $^{31}P\{^1H\}$ shows that full neutralization requires gentle warming at 50 ºC for 1 – 2 h. Clean samples of [(^{iPr}PCP)Pd-F] are obtained when a somewhat less than the stoichiometric amount of TREAT-HF is reacted with [(^{iPr}PCP)Pd-Me] at 50 ºC, since all the HF contained in the acidic reagent is consumed under these conditions. Therefore, careful adjustment of the TREAT-HF and the reaction temperature is essential for the successful preparation of [(^{iPr}PCP)Pd-F]. This can be routinely done by a two-stage addition method, as described in the Experimental Section.



Scheme 3

The room temperature $^{31}P\{^1H\}$ spectra of pure fluoride complexes [(^{iPr}PCP)M-F] in C_6D_6 show signals at 54.3 ppm (M = Ni) or 57.5 ppm (M = Pd), splitted in doublets by coupling to ^{19}F. The coupling constant $^2J_{PF}$ is larger for M = Ni (36.7 Hz) than for M = Pd (5.9 Hz). The *trans* ^{19}F – ^{13}C coupling is transmitted more efficiently in the case of the palladium complex, which gives a broad doublet at 155.2 ppm in its $^{13}C\{^1H\}$ spectrum for C *ipso* with $^2J_{CF}$ = 48.8 Hz, while the analogous signal of the Ni complex appears unresolved at 152.1 ppm. This signal splits in a doublet of triplets with $^2J_{CF}$ = 27.3 Hz and $^2J_{CP}$ = 16.0 Hz when the carbon spectrum is recorded at -75 ºC. The ^{19}F signals, which appear at -295.0 and -245.3 ppm for the Ni and the Pd complexes respectively, are too broad to allow resolving the ^{19}F-^{31}P splitting.

The nickel fluoride complex has been characterized by X-ray diffraction. The unit cell of the crystal contains three crystallographically independent molecules. These show no significant differences in their general configuration or intramolecular bond distances or angles. One of them is shown in Figure 5. The Ni center is found in a square-planar coordination environment, with nearly zero tetrahedral distortion. Intramolecular bond distances and angles are unexceptional. The Ni-F bond lengths are 1.844(2), 1.861(2) and 1.846(2) Å (1.850(2) Å in average), which are comparable to other monomeric nickel fluoride complexes. As mentioned previously, the nickel fluoride and hydride complexes form isomorphous crystals characterized by very similar cell parameters. The

crystal packing of these compounds is worth some comment. This is shown in Figure 6 for [(^{iPr}PCP)Ni-F]. The molecules pile themselves, forming columnar structures separated by narrow channels of about 1.6 Å wide. Each C1-Ni-L vector (L = H or F) is twisted ca. 120º with respect to the next one, in such a way that the columns resemble screw threads making one turn for each set of three molecules. The Ni-L bonds are oriented pointing outwards from the columns. This arrangement allows short inter-columnar contacts involving the fluoride or hydride and the C-H bonds of neighboring molecules. Although in the case of the fluoride complex it would be tempting to attribute these contacts to non-classical hydrogen bridges, this appears less likely for the hydride since the Ni-H bond is much less polar than the Ni-F. No signs of other intermolecular interactions, e. g., π-stacking, seem to stabilize the columnar arrangement. Thus, it seems likely that the peculiar crystal packing of these compounds stems from the shape of their molecules, rather than from the existence of strong intermolecular forces.

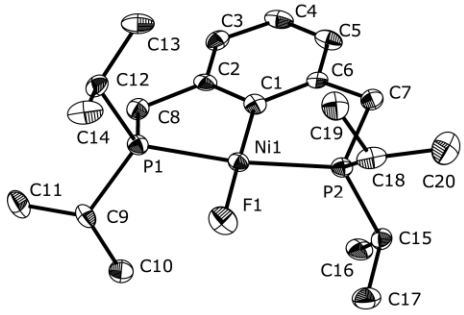


Figure 5. Crystal structure of [(^{iPr}PCP)Ni-F] (one of three independent molecules). Selected bond distances (Å): Ni1-F1, 1.844(2) ;Ni1-C1, 1.901(4); Ni1-P1; 2.1606(13); Ni1-P2, 2.1608(12).

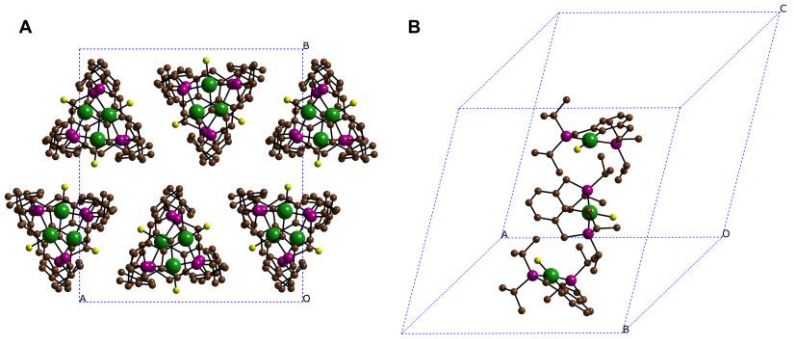


Figure 6. Crystal packing of [(^{iPr}PCP)Ni-F]. **A**) view along axis C, showing the columnar motif from the top . **B**) Detail of one of the columns formed by three crystallographically independent molecules.

Assessment of the σ and π bonding strength of anionic ligands L⁻ on the basis of the ^{13}C NMR spectra of [(^{iPr}PCP)M-L] complexes. The special reactivity of late transition metal complexes containing strongly π-basic ligands such as fluoride, alkoxo or amido complexes has been explained in the light of different theories.[1,22] One of the most appealing ideas is the existence of nonbonding *dπ-pπ* interactions between the filled *d* orbitals in the metal and the ligand lone pairs.[12] These would destabilize the metal-ligand bond, increasing the reactivity of the complexes. Unfortunately, quantification of such effects has proven to be a difficult task. Precise measurements of the relative metal-alkoxide and metal-amido bond strengths in Ni(II) , Pt(II) and Ru(II) complexes have been interpreted in terms of electrostatic and covalent contributions to essentially σ bonds, leading to the conclusion that *dπ-pπ* interactions are weak or non-existent.[23] However, analysis of spectroscopic data for late transition metal

complexes containing π-donor ligands has led to different conclusions. A study by Caulton and Eisenstein on Ru(II) carbonyl complexes [RuHL(CO)(PR_3)$_2$] showed that the frequency of the ν(CO) band depends on the relative π-donor strength of the anionic ligands L^- present in the molecule, decreasing in the order I < Br < Cl < F < OEt.[14] Since the metal *d* orbitals of π symmetry are all occupied, the observed decrease ν(CO) was assumed to be induced by a *push-pull* effect: the metal *d* orbitals become destabilized by the nonbonding M-L $p\pi - d\pi$ interactions, which exalt the π-backbonding capacity of the Ru(II) center to the carbonyl. Theoretical calculations supported this interpretation and reproduced the experimental trend of the ν(CO) frequency. This suggested that ν(CO) provides an indication of the intensity of the filled-filled π interactions. Accordingly, fluoride and alkoxide are among the stronger π donor ligands towards the Ru center. Grushin has applied similar ideas to the analysis of the bonding in a series of palladium complexes of the type *trans*-Pd(Ar)(X)(PPh_3)$_2$ (Ar = Ph, 4-$C_6H_4NO_2$; X = F, Cl, Br, I). [24] In these compounds, the ^{13}C signal of the metal-bound carbon atom (C *ipso*) experiences a significant shift of ca. 10 ppm, growing increasingly shielded on going from iodide to fluoride. The trend is counterintuitive, because the *trans influence*[25] of the halide ligands, and therefore their electron-donor capacity, increases in the opposite order (as confirmed by the structural data gathered for this particular set of complexes). As a rationale, it was proposed that a π *push-pull* effect analogous to that suggested by Caulton and Eisenstein actually increases the electron density at the *ipso* carbon as the halogen varies from I to F, shifting ^{13}C resonance to lower frequency. This is schematically shown in Figure 7, A.

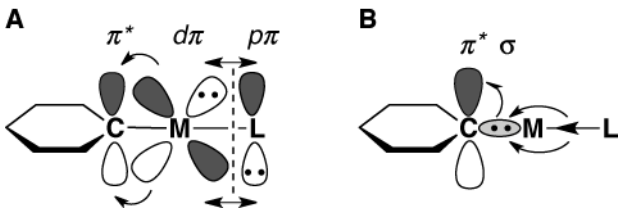


Figure 7. Mechanisms explaining the influence of the metal fragment on ^{13}C NMR shifts of the aryl ring. **A**) ligand promoted π-electron backdonation (*push-pull* effect). **B**) paramagnetic contribution to the chemical shift, due the to the mixing of the ground and excited states.

The availability of a series of ^{iPr}PCP pincer complexes of Ni and Pd provides an opportunity to extend the comparison to various monoanionic ligands besides halides. X-ray structural data are of little use for this purpose, because the influence of the anionic ligands on the rigid *pincer* fragment is small. However, the structural invariance of the [(^{iPr}PCP)M] moiety is a positive factor for analyzing spectroscopic properties, since any variations can be directly attributed to electronic effects. Table 1 collects selected ^{13}C NMR data for [(^{iPr}PCP)M-L] derivatives, analogous to the signals considered by Grushin in the analysis of arylpalladium complexes. Most of the ^{13}C data come from spectra recorded in C_6D_6, but in some cases the spectra were recorded in CD_2Cl_2 for solubility reasons. Although solvent effects on chemical shifts are fairly small, these have been minimized with the use of *coordination shifts,* $\Delta\delta$ ^{13}C, i.e. the differences between the chemical shifts of each signal in the complex and those in the free ligand (in the same solvent).

Table 1. Coordination shifts ($\Delta\delta$) for selected ^{13}C signals of [(^{iPr}PCP)M-L] complexes relative to free ^{Pr}PCHP ligand.[a]

	Δδ ^{13}C M = Ni					Δδ ^{13}C M = Pd				
L	***i*-C**	***o*-C**	***m*-C**	***p*-C**	**Ref.**	***i*-C**	***o*-C**	***m*-C**	***p*-C**	**Ref.**
OTf	16.1	12.5	-4.1	-4.5	*b, This work*	20.9	10.8	-3.5	-4.9	*b, This work*
ONO_2	21.8	12.1	-4.3	-5.0	*c, This work*	21.8	10.8	-3.3	-4.8	*c, This work*
F	23.5	13	-4.8	-6.1	*b, This work*	26.6	10.9	-4.2	-6.1	*b, This work*
OAc	26.1	12.6	-4.5	-5.5	*c, This work*	27.9	10.9	-4.0	-4.8	*c, This work*
OMe	29.1	11.7	-5.3	-6.7	*b, ref 5b*	30.6	10.6	-4.5	-6.3	*b, ref 5c*
Cl	29.6	12.5	-4.6	-5.5	*b, ref 17*	31.8	10.5	-3.8	-5.4	*c, This work*
Br	31.8	11.5	-5.3	-7.0	*c, This work*	31.7	10.0	-4.9	-6.8	*c, This work*
OH	32	12.3	-4.3	-5.1	*b, ref 5a*	34.0	10.5	-3.8	-5.3	*b, ref 5a*
I	36.3	12	-4.3	-5.0	*c, This work*	37.7	10.3	-4.0	-5.2	*c, This work*
NH_2	39.3	10.9	-5.2	-6.9	*b, ref 5b*	39.2	9.4	-5.0	-6.8	*b, This work*
Ph	46.8	11.6	-5.6	-5.8	*c, This work*	47.6	10.3	-5.4	-6.0	*c, This work*
Me	49.1	9.3	-5.7	-6.2	*c, This work*	50.7	10.7	-5.6	-6.2	*c, This work*
H	49.5	8.2	-6.0	-6.1	*c, This work*	51.1	10.0	-5.6	-5.8	*c, ref 5c*

a) NMR signals for the free ligand (C_6D_6, CD_2Cl_2): *i*- C, 128.5, *128.4*; *o*-C, 140.4, *140.5*; *m*-C, 127.0, *126.7*; *p*-C: 130.8, *130.6* ppm. b) Spectrum recorded in C_6D_6. c) Recorded in CD_2Cl_2.

Table 1 shows that changes in the coordination shifts are more pronounced for the *ipso* carbon than for the rest of ^{13}C resonances. Just as observed for the *trans*-[Pd(X)(Ar)(PPh_3)$_2$] complexes, this signal becomes increasingly deshielded on descending along the halide series, from F to I. The magnitude of the variation is also very similar in the two systems (10 – 13 ppm from F to I). The influence of the anionic ligand follows the same trend along the full series of nickel and palladium pincer complexes. This is confirmed by a plot of $\Delta\delta$ $^{13}C_{ipso}$ of nickel complexes *versus* the same parameter in their palladium analogues (Figure 8, A), which shows a good linear correlation (R = 0.993) with a slope close to 1. The points in the plot, each one corresponding to a single ligand, spread regularly along the straight line with $\Delta\delta$ $^{13}C_{ipso}$ increasing in the order OTf < NO_3 < F < OAc < OMe < Cl < OH ≈ Br < I < NH_2 < Ph < Me < H. This sequence matches the qualitative σ-donor strengths of the ligands, and suggests that $\Delta\delta$ $^{13}C_{ipso}$ bears little relation with the π-donor capacities of the anionic ligands. For example, extreme values of $\Delta\delta$ $^{13}C_{ipso}$ are observed for L = OTf and H, respectively the weakest and strongest σ-donor ligands, but both of them with little or no π-donor capacity. Good π-donors, such as F, NH_2, OH or OMe are not grouped together, but scattered along the series, and the effect of Ph, which has some π acceptor character, is comparable to that of Me. Furthermore, $\Delta\delta$ $^{13}C_{ipso}$ correlates with the electronegativity of atomic ligands, i.e., halides *and* hydride (Figure 8, plot B). This would not be expected if the π-donor capacity of these ligands were playing a substantial role, but is reasonable if $\Delta\delta$ $^{13}C_{ipso}$ is controlled by the σ-donor capacity of the *trans* ligand. The effect of anionic ligands on $\Delta\delta$ $^{13}C_{ipso}$ can be related to the familiar concept of *trans influence* since this is also linked to σ-donor capacity. The relationship between the electronegativity of ligands and their *trans influence* has been noted before.[25a]

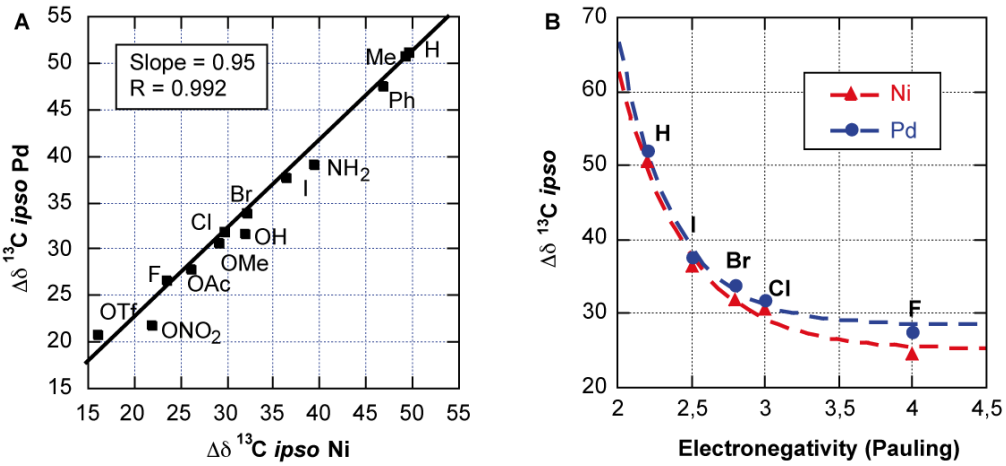


Figure 8. Plots of **A**) coordination shifts of the [(^{iPr}PCP)M-L] complexes *ipso*-C signal for M = Pd *vs* M = Ni; and **B**) coordination shifts for *ipso*-C of hydride and halide nickel and palladium complexes *vs* electronegativity of the anionic ligand.

Apparently, the progressive deshielding of the ^{13}C resonance of the *ipso* carbon as the ligand L becomes a stronger σ-donor contradicts basic ideas on the origin of the NMR chemical shift. However, it must be recalled that for nuclei heavier than H, chemical shifts are not only determined by the diamagnetic screening exerted by the surrounding electron density, but also by a paramagnetic contribution arising from the mixing of the molecule ground and excited states containing unpaired electrons. The intensity of this paramagnetic contribution depends inversely on the energy required to promote the electrons from the ground to the excited states. In part, the typical deshielding of the signals originated by aromatic systems (relative to saturated organic fragments) is due to the low energy of the empty aromatic π* orbitals. When an electron is promoted into them, orbital symmetry dictates that the effect of the paramagnetic contribution will oppose to that of the diamagnetic screening, shifting the NMR signals towards higher frequencies. The smaller the energy gap between occupied and empty orbitals, the larger the chemical shifts of the aromatic nuclei. This explains, for example, the very high frequency of the *ipso* ^{13}C carbon resonance in strongly polar aryllithium derivatives (ca. 200 ppm).[26] The polarized C–Li bond can be assimilated to a high-energy electron pair sitting on a carbon sp^2 hybrid orbital, therefore promotion of these electrons is relatively easy. Pregosin used the same argument to explain the unusually high frequency of the ^{13}C resonances of aromatic carbon atoms attached to Pd(II) centers.[27] As shown schematically in Figure 7 B, when the ligand placed in *trans* to the carbon atom is a strong σ-donor (e. g., H or Me) it raises the electron density at the σ Pd-C bond, shifting the ^{13}C towards higher frequency. On the contrary, electronegative ligands remove electron density from the *trans* position, stabilizing the bonding pair. In the limit for very electronegative ligands, the M-L bond is essentially ionic and $\Delta\delta\ ^{13}C_{ipso}$ is not influenced by the nature of L^-. This is in good agreement with the exponential form of the correlation between the $\Delta\delta\ ^{13}C_{ipso}$ and ligand electronegativity (Fig. 8 B).

Since the behavior of the ^{13}C resonance of the *ipso* carbon is controlled by the σ-donor capacity of the anionic ligands, it offers no indication of π effects such as $p\pi–d\pi$ repulsions. However, other spectroscopic parameters could provide some indications regarding such effect. Classic NMR studies on arylpalladium and arylplatinum complexes have shown that chemical shifts of the nuclei at the *para* positions of the aryl group (either of ^{13}C for ring carbon atoms or ^{19}F for attached fluorine substituents) can be interpreted in terms of inductive (σ) and resonance (π) effects caused by the metal fragment.[13] Since chemical shifts at the *meta* position are determined essentially by inductive effects, these are expected to cancel out in the differences δ_{para}-δ_{meta}, which were then used to gauge the

π interaction of the metal fragment with the aromatic ring. These differences show that Pt(II) or Pd(II) centers act as π-donors towards the aryl ligand, although this interaction is rather weak compared to organic groups with strong π-electron donor properties such as NR_2 or OR. The ^{13}C chemical shifts of the *meta* and *para* in the [(^{iPr}PCP)M-L] system are not very different to those of the free ligand, hence the corresponding coordination shifts $\Delta\delta\ ^{13}C$ are small. In spite of this, the differences $\Delta\delta\ ^{13}C_{para}$ - $\Delta\delta\ ^{13}C_{meta}$ show some interesting trends (Table 2). Noteworthy, the stronger π-donor ligands, F, NH_2, OH and OMe, are characterized by negative and relatively large values of this parameter, while this is almost zero for H or Me, suggesting that π effects are small for the latter (note that for the free ligand $\Delta\delta\ ^{13}C_{para}$ - $\Delta\delta\ ^{13}C_{meta}$ is zero by definition). Although these figures have to be taken with due caution, the trend is not likely to be entirely fortuitous and supports the ability of strongly π-donor ligands such as fluoride to destabilize the filled metal *d* orbitals increasing π-backdonation to the aromatic ring, as previously proposed by other authors. The NMR data suggests that π-donor strength of fluoride is comparable in magnitude with those of the OH and NH_2 groups, and at the same time it behaves as a weak σ-donor. As previously suggested in the literature,[1b,7a] the combination of these two factors tends to destabilize the metal-ligand bond rendering the fluoride complexes of Ni and Pd specially reactive in comparison with other halide complexes.

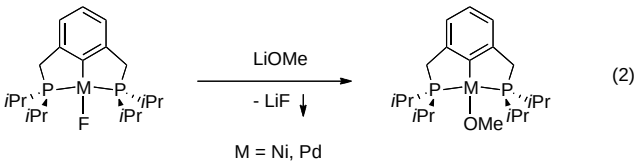
Table 2. Difference between coordination shifts of the *meta* and *ipso* carbons ($\Delta\delta\ ^{13}C$ *para* - $\Delta\delta\ ^{13}C$ *meta)* for different complexes.

Ligand	Ni	Pd
OH	-1,7	-1,9
NH_2	-1,7	-1,8
OMe	-1,4	-1,8
F	-1,3	-1,9
Cl	-0,9	-1,6
Br	-0,8	-1,5
ONO_2	-0,7	-1,5
I	-0,7	-1,2
OTf	-0,4	-1,4
Oac	-1	-0,8
Me	-0,5	-0,6
Ph	-0,2	-0,6
H	-0,1	-0,2

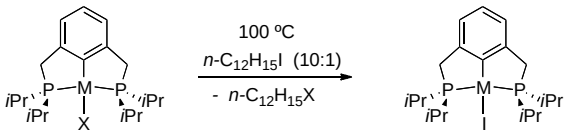
Reactivity of Ni and Pd pincer fluoride complexes. Due to the high reactivity associated to the M-F bond in late transition metal complexes, nickel and palladium pincer fluorocomplexes can be considered either as sources of the cationic [(^{iPr}PCP)M]$^+$ fragment or the anionic fluoride anion. As such, they may find useful applications in synthesis, both of new pincer organometallic complexes and of organic fluorides. We selected two simple reactions of the [(^{iPr}PCP)M-F] complexes for illustrating both aspects of their reactivity: displacement of fluoride by alkoxide at the metal center, and the reaction with an alkyl iodide leading to halide exchange at the carbon center (Eq 2 and Scheme 4).

The reaction of [(^{iPr}PCP)M-F] (M = Ni, Pd) with lithium methoxide in THF (Eq 2) is straightforward. The $^{31}P\{^1H\}$ spectra of the reaction mixtures indicate that these reactions are clean and quantitative. The resulting light precipitate of LiF is readily removed by centrifugation, leaving the corresponding methoxides [(^{iPr}PCP)M-OMe] as

the only products in solution, from where these products can be isolated in good yield. This reaction can be useful for *in situ* generation of reactive alkoxides that may be difficult to isolate otherwise.



As previously mentioned, methyl iodide reacts with [(^{iPr}PCP)M-L] complexes (M = Ni, Pd), cleanly affording the corresponding iodide complexes. In order to facilitate the identification of the organic products, we investigated the reactions of the fluoride complexes with dodecyl iodide at 100 ºC in C_6D_6. For comparison, the reactions of dodecyl iodide with nickel bromide and palladium chloride complexes were studied as well (Scheme 4). NMR, GC and GC-MS analyses of the reaction mixtures showed that the exchange reactions proceed cleanly in all cases, affording equimolar amounts of the corresponding iodide complexes and alkyl halides (fluoride, chloride, or bromide). The course of the reactions was monitored by $^{31}P\{^1H\}$. In the presence of a 10:1 excess of dodecyl iodide, these exhibit pseudo-first order kinetics. The apparent rate constants, expressed as half-lives, are shown in Scheme 4. Fluoride complexes are significantly more reactive than the bromide or chloride derivatives. The difference is particularly striking in the case of palladium: whilst 50 % conversion of the chloro derivative takes nearly one day, the fluoride is fully transformed within 40 min. The nickel fluoride complex is less reactive than its palladium analogue, but reacts significantly faster than the corresponding bromide. Noteworthy, the reaction rate of the nickel fluoride with dodecyl iodide increases significantly when carried out in THF instead of C_6D_6.



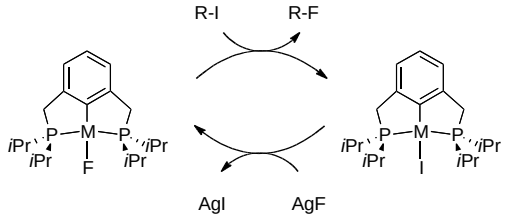
M	X	solvent	$t_{1/2}$ (h)
Ni	Br	C_6D_6	14.0(6)
Ni	F	C_6D_6	6.5(1)
Ni	F	THF	1.9(3)
Pd	Cl	C_6D_6	23.5(4)
Pd	F	C_6D_6	< 0.3

Scheme 4

From a mechanistic point of view, these halide exchange reactions are probably more intricate than their apparent simplicity may suggest. In the case of palladium complexes, the mechanism could involve unstable Pd(IV) intermediates formed by oxidative addition of the alkyl iodide, which would undergo reductive elimination to afford the Pd(II) iodide complex and alkyl fluoride. The recently observed decomposition of Palladium(IV) fluoride complexes by C-F reductive coupling adds support to this proposal.[4a,d] Although such mechanism is less likely in the case of the nickel complexes, an oxidative process involving paramagnetic Ni(III) intermediates cannot be ruled out in principle.[28,29] According to either of these mechanisms, the reactivity of complexes [(^{iPr}PCP)M-L] would be higher when L is a strong σ-donor, because this facilitates the oxidation of the metal center. This conclusion is not supported by the high reactivity of fluoride complexes, since fluoride is a very weak σ-donor ligand. The experimental trend of reactivity would be better understood if the mechanism is assumed to be ligand- rather than

metal-centered. In this view, the highly polarized $M^{\delta+}$-$F^{\delta-}$ retains part of the strong nucleophilicity of the naked fluoride anion. However, this does not explain why the palladium fluoride is much more reactive than its nickel analogue, since the polarity of the M-F bonds probably are not very different. The *d*π-*p*π repulsions theory could be useful here, because these interactions are probably more intense for Pd, due to the larger radial extension of the metal *d* orbitals in second-row transition elements.[30]

Independently of what might be the chemical behavior of the [(^{iPr}PCP)M-F] complexes, their high reactivity could be exploited in catalytic reactions. Thus, we decided to investigate if these compounds could catalyze fluoride exchange between alkyl halides and AgF, as shown in Scheme 5. Although AgF does react directly with alkyl iodides, the synthetic interest of this reaction is limited because it is not selective and alkyl fluorides are formed together with a number of byproducts.[31,32] Notwithstanding, the reaction has found some application in the synthesis of alkyl fluorides.[33] Very recently, Doyle *et al.* reported a Pd-catalyzed method for the stereoselective fluorination of allyl chlorides, involving an outer sphere fluoride from AgF to a π-allylpalladium intermediate.[34]



Scheme 5

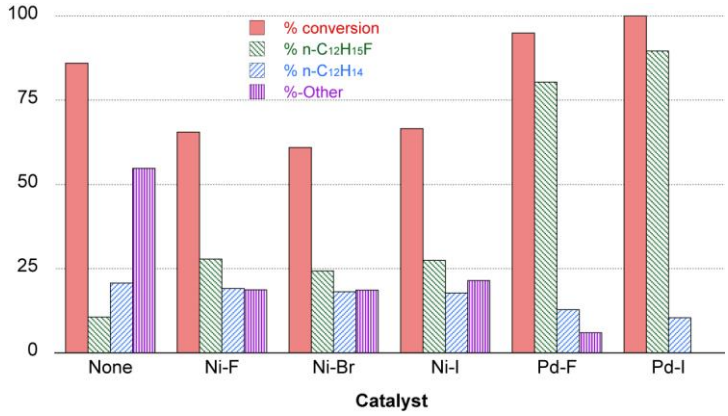


Figure 9. Conversion and selectivity of the reaction of dodecyl iodide with AgF in the presence of 10 mol% of [(^{iPr}PCP)M-X] (X = F, Br, I). Experimental conditions: Toluene, 100 ºC, 200 min, except for Pd-F (135 min).

The most important byproducts of the reactions of AgF with alkyl iodides are alcohols, but significant amounts of olefins and isomerization products are formed as well. Hence, a mechanism involving a carbocationic intermediate has been suggested for these reactions.[32] In agreement with this, the reaction of AgF with dodecyl iodide in toluene at 100 ºC yields a complex mixture containing roughly similar amounts of 1-dodecanol, 1-dodecene, and 1-fluorododecane and minor amounts of isomers of these substances, which were identified by GC-MS. The conversion reaches 75 % in 3.3 h. Figure 9 compares the effect of catalytic amounts of nickel and palladium halocomplexes [(^{iPr}PCP)M-L] (L = F, Br, I) on the latter reaction. The catalyst dose was adjusted to 10 mol% (with regard to R-I) to match the conditions used in stoichiometric halogen exchange experiments. Since the nickel and palladium fluoride, bromide or chloride complexes are converted by dodecyl iodide into the corresponding iodides, the choice of the catalyst precursor has only a minor influence on the catalytic process.

The halide complexes [(^{iPr}PCP)M-X] do influence the rate of the reaction of AgF with dodecyl iodide, but whilst this is appreciably accelerated by the palladium complexes, the overall rate of consumption of dodecyl iodide *decreases* in the presence of the nickel derivatives. The selectivity of the reaction improves significantly in either case: formation of byproducts is inhibited, and the yield of dodecyl fluoride increases. Actually, the net rate of production of alkyl fluoride is higher in the presence of both nickel and palladium complexes, although the acceleration is much more pronounced with the latter. This difference is not unexpected, since [(^{iPr}PCP)Pd-F] is much more reactive towards dodecyl iodide than its nickel analogue. When the palladium fluoride complex is used as catalyst, formation of dodecanol and other minor byproducts is almost suppressed and the only significant byproduct is 1-dodecene. Best results are obtained with [(^{iPr}PCP)Pd-I]: dodecyl iodide is fully converted within 2.3 h, producing dodecyl fluoride and a small amount of 1-dodecene (10 %) as the only detected byproduct. Although there is no obvious reason for the better performance of the iodide compared to the fluoride, this could be due to the fact that [(^{iPr}PCP)Pd-F] easily captures traces of water or other proton-donor impurities that may have some effect in the reaction.

GC monitoring of the catalyzed reactions confirmed that nickel complexes slightly accelerate the rate of formation of dodecyl fluoride and inhibit the formation of *n*-dodecanol. In contrast, palladium complexes not only improve the selectivity of the reaction but also catalyze actively the formation of dodecyl fluoride. This suggests that the effect of the pincer complexes on the course of the halide exchange reaction is two-fold: First, they inhibit the formation of products arising by a carbocationic pathway, probably because they are much better halide donors towards Ag^+ than dodecyl iodide. Second, they catalyze C-F bond formation *via* reaction of the fluoride complex with the alkyl halide. The fact that the rate of dodecyl fluoride formation increases only slightly in the presence of Ni complexes suggests that in this case most of this product is still formed by direct reaction with AgF. This is in line with the slow reaction rate of the reaction of [(^{iPr}PCP)Ni-F] with dodecyl iodide, which requires 6.5 h to produce 0.5 equivalents of the alkyl fluoride. The metal-catalyzed fluoride transfer reaction is significantly accelerated only in the case of the palladium complexes, due to the higher reactivity of [(^{iPr}PCP)Pd-F].

The $^{31}P\{^{1}H\}$ spectra of the reaction mixtures of catalysis experiments with Ni or Pd complexes are usually simple displaying one or two signals in the 54 – 60 ppm region. These signals show evident line broadening and are reminiscent of those of impure samples of the fluoride complexes. They probably correspond to rapidly exchanging mixtures of fluoride containing species, such as bifluorides. This observation indicates that the fluoride framework [(^{iPr}PCP)M] survives the catalytic process, which may allow catalyst recycling or achieving higher turnover numbers if the experimental conditions are optimized.

Conclusions

A series of nickel and palladium complexes containing the ^{iPr}PCP *pincer* ligand and different anions, including triflate, nitrate, alkyl, phenyl, hydride and halide were prepared and characterized. Together with the previously reported hydroxo, methoxo and amido derivatives, the new complexes constitute one of the widest known series of isostructural complexes with simple monoanionic anions. This facilitated the comparison of the electronic properties of fluoride with those of many other anionic ligands. Significant trends were observed in the ^{13}C NMR data corresponding to the aromatic ring of the pincer ligand. The position of the metal-bound carbon signal (C *ipso*) is very sensitive to the nature of the anionic ligand in the complex, shifting over a spectral interval of

ca. 35 ppm. The magnitude of the coordination shift is nearly identical for the nickel and palladium complexes, and is related to the qualitative σ-donor capacity of the anionic ligands. This is supported by a good correlation between the coordination shifts of C *ipso* and the electronegativity of the monoatomic ligands (hydride and halides). This relationship can be used to gauge the σ-donor capacity of the anionic ligands towards the Ni and Pd centers, which increases in the order OTf < NO_3 < F < OAc < OMe < Cl < OH ≈ Br < I < NH_2 < Ph < Me < H. Analysis of the chemical shifts of the *para* and *meta* resonances revealed a completely different pattern that could be related to the π-donor capacity of the ligands. The differences between the chemical shifts of the *para* and *meta* carbons are more negative in complexes containing strong π–donor ligands (OH, F, NH_2 or OMe) than those without this capacity (H, Me). This is consistent with an enhancement of π-backdonation from the metal to the aryl ring caused by nonbonding *p*π-*d*π interactions. These results are largely in agreement with long-standing ideas on the electronic properties of simple anionic ligands (e. g., fluoride is a weak σ-donor ligand, but a stronger π donor than the rest of the halides), but the new data offer the opportunity to directly compare very different ligands that are seldom found within the same system.

Two methods have been applied for the synthesis of the fluoride derivatives [(^{iPr}PCP)M-F]: halide exchange with AgF and protonation of the methyl derivatives [(^{iPr}PCP)M-Me] with TREAT-HF. Fluoride complexes [(^{iPr}PCP)M-F] exhibit an interesting reactivity pattern. The fluoride ligand is readily displaced from nickel or palladium by lithium alkoxides, cleanly leading to the corresponding pincer alkoxo derivatives. The fluoride complexes also react with dodecyl iodide affording iodide complexes and alkyl fluoride. Although analogous halide exchange reactions also take place between dodecyl iodide and chloride or bromide pincer complexes, these react much more slowly than the fluorides, indicating that the latter are more nucleophilic. Furthermore, the reaction of the fluorides with dodecyl iodide is at least 20 times faster for the palladium than for the nickel derivative. It is difficult to justify this difference on the basis of the degree of polarization of the M-F bonds since this is probably similar in the Ni and Pd complexes. However, the higher nucleophilicity of the palladium fluoride can be qualitatively explained by the larger degree of destabilization of the fluoride lone pairs by the filled metal *d* orbitals, which are more spatially extended in second than in first row transition elements.

The nucleophilic reactivity of the fluoride pincer complexes was exploited in a catalytic halide exchange reaction between AgF and RI to afford alkyl fluorides. Both nickel and palladium catalysts improve the selectivity of the reaction of AgF with dodecyl iodide, probably by avoiding the formation of reactive carbocationic intermediates. However, only the palladium complexes lead to a significant acceleration of the reaction, presumably due to the much higher nucleophilic reactivity of the fluoride complex.

Experimental Section.

All procedures and chemical manipulations were carried out under Ar or N_2 using Schlenk or glove box techniques. Solvents were rigorously dried and degassed before use. Commercially available reagents were used as received. The pincer ligand precursor, 2,6-bis(diisopropylphosphino)benzene[35] (^{iPr}PCHP) and the complex [(^{iPr}PCP)Pd-Cl][15b] were prepared according to literature methods. The brominated precursor 1-bromo-2,6-bis(diisopropylphosphino)benzene[36] (^{iPr}PCBrP) was prepared analogously to ^{iPr}PCHP from 1-bromo-α,α'-dibromoxylene. NMR spectra were recorded on Bruker DRX 300, 400 and 500 MHz spectrometers. Assignment of signals was assisted by combined monodimiensional (gated ^{13}C) and bidimensional techniques (HSQC). Chemical

shifts (δ) are in ppm. Solvent ^{1}H and $^{13}C\{^{1}H\}$ resonances were used as the internal standard but the chemical shifts are reported with respect to TMS, and ^{31}P spectra are referenced to external PPh_3 in C_6D_6 (δ −6.0 ppm). Multiplicity abbreviation is reported as: br, broad; s, singlet, d, doublet; t, triplet; m, mutiplet; v, virtual; dvt, doublet of virtual triplets. IR spectra were recorded in nujol mull on Bruker Vector 22 or Tensor 27 spectrophotometers. GC and GC-MS analyses were carried out in Agilent 6890 and Thermoquest Trace GC chromatographs equipped with a FID detector and an AutomassMulti mass spectrometer, respectively, using capillary polymethylsiloxane columns. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas.

Synthesis of complexes.

[(^{iPr}PCP)Ni-Br]: A solution of ^{Pr}PCHP in THF (0.5 M, 10 mL, 5 mmol) was added to a suspension of $NiBr_2$(dme) (dme= dimethoxyethane) (1.54 g, 5 mmol) in THF (60 mL) at −78 ºC , the resulting mixture was stirred and allowed to reach room temperature. Et_3N (5.5 mL, 50 mmol) was added and the reaction mixture heated at 125 ºC for 3 h. The solvent was evaporated under reduced pressure and the residue extracted with Et_2O (3 × 40 mL). The combined extracts were concentrated and cooled to -20 ºC, affording the [(^{iPr}PCP)Ni-Br] as a yellow solid in 90% yield. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz) δ 1.17 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 6.9 Hz, CH_3), 1.44 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.7 Hz, CH_3), 2.36 (m, 4H, CH), 3.09 (vt, 4H, J^{*}_{HP} = 4.0 Hz, CH_2), 6.90 (m, 3H, 2×$C_{ar}H_m$, $C_{ar}H_p$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 18.3 (s, CH_3), 19.0 (s, CH_3), 24.2 (vt, J^{*}_{CP} = 11.2 Hz *C*H), 33.0 (vt, J^{*}_{CP} = 12.9 Hz, *C*H_2), 122.4 (vt, J^{*}_{CP} = 8.9 Hz, $C_{ar}H_m$), 125.5 (s, $C_{ar}H_p$), 152.8 (vt, J^{*}_{CP} = 13.2 Hz, $C_{ar\text{-}o}$), 159.5 (t, $^{2}J_{CP}$ = 15.9 Hz, $C_{ar\text{-}i}$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 60.5. Anal. Calcd. for $C_{22}H_{35}BrNiP_2$: C, 50.46; H, 7.41; found: C, 50.35; H, 7.32.

[(^{iPr}PCP)Pd-Br]: 12 mL of a 0.085 M solution of NaCp in THF (1.02 mmol) were added to a solution of the palladium chloro(allyl) dimer [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.183 g, 0.5 mmol) in 40 ml of THF stirred at -80 ºC. The resulting red mixture was stirred for 1 h at room temperature and then cooled again to -80 ºC. A solution of ^{Pr}PCBrP (0.5 M in THF, 2 mL, 1mmol) was added. The mixture was allowed to warm at room temperature and stirred for 12 h. The solvent was evaporated under vacuum, and the resulting solid extracted with diethyl ether (3 x 20 mL). The solution was taken to dryness again and the residue purified by chromatography on a silica gel column, using diethyl ether/hexane 5:1 as eluent. The product was isolated as a pale yellow solid in 40 % yield. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz) δ 1.14 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.0 Hz, CH_3), 1.37 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.0 Hz, CH_3), 2.34 (m, 4H, CH), 3.19 (vt, 4H, J^{*}_{HP} = 4.0 Hz, CH_2), 6.91 (t, 1H, $^{3}J_{HH}$ = 7.4 Hz, $C_{ar}H_p$), 7.01 (d, 2H, $^{3}J_{HH}$ = 7.6 Hz, 2×$C_{ar}H_m$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 18.1 (s, CH_3), 18.9 (s, CH_3), 24.4 (vt, J^{*}_{CP} = 11.2 Hz *C*H), 33.4 (vt, J^{*}_{CP} = 11.5 Hz, *C*H_2), 122.9 (vt, J^{*}_{CP} = 10.8 Hz, $C_{ar}H_m$), 125.2 (s, $C_{ar}H_p$), 151.0 (vt, J^{*}_{CP} = 10.7 Hz, $C_{ar\text{-}o}$), 159.3 (s, $C_{ar\text{-}i}$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 61.4. Anal. Calcd. for $C_{22}H_{35}BrNiP_2$: C, 50.12; H, 7.36; found: C, 50.42; H, 7.43.

[(^{iPr}PCP)Ni-I]: To a solution of (^{iPr}PCP)Ni-Br (0.095 g, 0.2 mmol) in THF (5 mL), MeI (0.152 mL, 1 mmol) was added and the resulting mixture was heated at 60 ºC for 72 h. The solvent was removed under reduce pressure, and the residue extracted with hexane. The product was obtained as a yellow solid after evaporating the solvent under reduced pressure. Yield 70%**.** ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 1.15 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 6.9 Hz, 12H,

C*H*$_3$), 1.43 (dvt, $^3J_{HH} \approx J^*_{HP} \approx 7.7$ Hz, 12H, C*H*$_3$), 2.48 (m, 4H, C*H*), 3.14 (vt, $J^*_{HP} = 4.1$ Hz, 4H, C*H*$_2$), 6.95 (m, 3H, 2×C$_{ar}$H$_m$, C$_{ar}$H$_p$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 18.4 (s, *C*H$_3$), 19.3 (s, *C*H$_3$), 25.2 (vt, $J^*_{CP} = 11.8$ Hz, *C*H), 34.1 (vt, $J^*_{CP} = 13.0$ Hz, *C*H$_2$), 122.4 (vt, $J^*_{CP} = 8.9$ Hz, C$_{ar}$H$_m$), 125.6 (s, C$_{ar}$H$_p$), 152.5 (vt, $J^*_{CP} = 12.9$ Hz, C$_{ar-o}$), 163.8 (t, $^2J_{CP} = 15.9$ Hz, C$_{ar-i}$). ^{31}P{1H} NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 63.1. Anal calcd for $C_{20}H_{35}INiP_2$: C, 45.93; H, 6.74; found C, 45.59, H, 5.81.

[(*i*^{Pr}PCP)Pd-I]: MeI (0.152 mL, 1 mmol) was added to a solution of [(*i*^{Pr}PCP)Pd-Cl] (0.095 g, 0.2 mmol) in THF (5 mL), and the resulting mixture was heated at 60 ºC for 24 h. The solvent was removed under reduced pressure, the residue extracted with hexane, and the solution was taken to dryness affording [(*i*^{Pr}PCP)Pd-I] as a colourless solid. Yield 80%**.** ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 1.10 (dvt, $^3J_{HH} \approx J^*_{HP} \approx 7.2$ Hz, 12H, C*H*$_3$), 1.37 (dvt, $^3J_{HH} \approx J^*_{HP} \approx$ 8.0 Hz, 12H, C*H*$_3$), 2.44 (m, 4H, C*H*), 3.26 (vt, $J^*_{HP} = 4.3$ Hz, 4H, C*H*$_2$), 6.97 (t, $^3J_{HH} = 7.4$ Hz, 1H, C$_{ar}$H$_p$), 7.07 (d, $^3J_{HH} = 7.6$ Hz, 2H, C$_{ar}$H$_m$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 ºC, 75 MHz): δ 18.1 (s, *C*H$_3$), 19.3 (s, *C*H$_3$), 25.3 (vt, $J^*_{CP} =$ 11.9 Hz, *C*H), 34.9 (vt, $J^*_{CP} = 11.6$ Hz, *C*H$_2$), 122.7 (vt, $J^*_{CP} = 10.7$ Hz, C$_{ar}$H$_m$), 125.4 (s, C$_{ar}$H$_p$), 150.8 (vt, $J^*_{CP} =$ 10.6 Hz, C$_{ar-o}$), 165.2 (s, C$_{ar-i}$). ^{31}P{1H} NMR (CD_2Cl_2, 25 ºC, 121 MHz): δ 62.4. Anal calcd for $C_{20}H_{35}IP_2Pd$: C, 42.09; H, 6.18; found C, 42.27, H, 5.81.

[(iPrPCP)Ni-ONO$_2$]: A solution of [(iPrPCP)Ni-Br] (2.05 g, 4.3 mmol) in THF (50 mL) was added to a flask charged with $AgNO_3$ (0.750 g, 4.4 mmol). The reaction mixture was stirred at room temperature for 36 h. The solvent was evaporated under vacuumand the residue extracted with Et_2O (3×50 mL). The complex [(iPrPCP)Ni-ONO$_2$] was obtained as a yellow crystals after evaporating the solvent under reduced pressure and crystallizing from hexane to −30 ºC. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 0.91 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx 7.0$ Hz, C*H*$_3$), 1.25 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx$ 7.7 Hz, C*H*$_3$), 1.79 (m, 4H, C*H*), 2.58 (vt, 4H, $J^*_{HP} = 4.1$ Hz, C*H*$_2$), 6.73 (d, 2H, $^3J_{HH}$ =7.4 Hz, C$_{ar}$*H*$_m$), 6.95 (t, 1H, $^3J_{HH}$ = 7.4 Hz, C$_{ar}$*H*$_p$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 17.6 (s, *C*H$_3$), 18.2 (s, *C*H$_3$), 23.5 (vt, $J^*_{CP} = 10.1$ Hz *C*H), 30.4 (vt, $J^*_{CP} = 13.6$ Hz, *C*H$_2$), 122.4 (vt, $J^*_{CP} = 8.6$ Hz, C$_{ar}$H$_m$), 125.6 (s, C$_{ar}$H$_p$), 149.3 (t, $^2J_{CP} = 16.6$ Hz, C$_{ar-i}$), 152.6 (vt, $J^*_{CP} = 12.5$ Hz, C$_{ar-o}$) .^{31}P{^{1}H} NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 58.6 ppm. Anal. Calcd. for $C_{20}H_{35}NO_3P_2Ni$: C, 52.43; H, 7.70. N, 3.06; found: C, 52.51; H, 7.89. N, 2.97. IR (Nujol mull) ν(NO_2) 1456 cm^{-1}, ν(NO_2) 1282 cm^{-1}, ν(NO) 1026 cm^{-1}.

[(*i*^{Pr}PCP)Ni-OAc] and [(*i*^{Pr}PCP)Pd-OAc]: A solution of [(*i*^{Pr}PCP)Ni-Br] (0.238 g, 0.5 mmol) or [(*i*^{Pr}PCP)Pd-Cl] (0.240 g, 0.5 mmol) in THF (25 mL) was transferred to a flask charged with AgOAc (0.083 g, 0.5 mmol) and the resulting mixture was stirred at room temperature for 12 h. The solvent was evaporated under reduce pressure and the residue extracted with Et_2O (3 × 25 mL). The complex [(*i*^{Pr}PCP)Ni-OAc] was obtained as a yellow crystalline solid after addition of some hexane and cooling to −30 ºC. Yield 75%. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz) δ 1.24 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx 6.9$ Hz, C*H*$_3$), 1.36 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx 8.6$ Hz, C*H*$_3$), 1.73 (s, 3H, OCOC*H*$_3$), 2.18 (m, 4H, C*H*), 3.02 (vt, 4H, $J^*_{HP} = 4.1$ Hz, C*H*$_2$), 6.79 (m, 3H, 2×C$_{ar}$H$_m$, C$_{ar}$H$_p$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 ºC, 75 MHz) δ 18.1 (s, CH$_3$), 18.7 (s, CH$_3$), 24.1 (vt, $J^*_{CP} = 10.0$Hz, *C*H), 24.3 (s, COO*C*H$_3$), 31.4 (vt, $J^*_{CP} = 13.4$ Hz, *C*H$_2$), 122.2 (vt, $J^*_{CP} = 8.6$ Hz, C$_{ar}$H$_m$), 125.1 (s, C$_{ar}$H$_p$), 153.1 (vt, $J^*_{CP} = 13.1$ Hz, C$_{ar-o}$), 153.6 (t, $^2J_{CP} = 17.3$ Hz, C$_{ar-i}$), 175.9 (s, O*C*OCH$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 ºC, 121 MHz) δ 56.6 ppm. . Anal. Calcd. for $C_{22}H_{38}NiO_2P_2$: C, 58.05; H, 8.41;found: C, 58.09; H, 8.37. The complex [(*i*^{Pr}PCP)Pd-OAc] was obtained as a colourless microcrystalline solid after evaporating the solvent under reduce pressure. Yield 75%.^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 1.19 (dvt,

$^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.3 Hz, 12H, C*H*$_3$), 1.28 (dvt, $^{3}J_{HH} \approx$ 7.9 $J^{*}_{HP} \approx$ 7.9 Hz, 12H, C*H*$_3$), 1.85 (s, 3H, OCOC*H*$_3$) 2.29 (m, 4H, C*H*), 3.15 (vt, J^{*}_{HP} = 4.3 Hz, 4H, C*H*$_2$), 6.88 (t, $^{3}J_{HH}$ = 8.6 Hz, 1H, $C_{ar}H_p$), 6.96 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, $C_{ar}H_m$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 75 MHz): δ 18.0 (s, *C*H$_3$), 18.8 (s, *C*H$_3$), 24.2 (br s, OCO*C*H$_3$), 24.7 (vt, J^{*}_{CP} = 10.9 Hz, *C*H), 32.4 (vt, J^{*}_{CP} = 11.7 Hz, *C*H$_2$), 122.7 (vt, J^{*}_{CP} = 10.6 Hz, $C_{ar}H_m$), 125.8 (s, $C_{ar}H_p$), 151.4 (vt, J^{*}_{CP} = 10.6 Hz, C_{ar-o}), 155.4 (s, C_{ar-i}), 175.7 (s, O*C*OCH$_3$). $^{31}P\{1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 59.5. IR (Nujol mull) ν(C=O) 1580 cm^{-1}. Anal calcd for $C_{22}H_{38}O_2P_2Pd$: C, 52.54; H, 7.62; found C, 52.50, H, 7.48.

[(*i*^{Pr}PCP)Ni-Me] and [(*i*^{Pr}PCP)Pd-Me]: A solution of MeLi in Et_2O (1.6 M, 0.29 mL, 0.47 mmol) was added to a solution of [(*i*^{Pr}PCP)Ni-Br] (0.148 g, 0.31 mmol) in Et_2O (25 mL) or [(*i*^{Pr}PCP)Pd-Cl] (0.149 g, 0.31 mmol) at –50 ºC. The resulting mixture allowed to stir for 2 h at room temperature. Methanol (0.29 mL) was added and the reaction mixture stirred for 15 additional min. The mixture was evaporated under reduced pressure and the residue extracted with Et_2O (3×15 mL). The complex [(*i*^{Pr}PCP)Ni-Me] was obtained as an orange solid after evaporating the solvent under reduced pressure, and was recrystallized from hexane. Yield: 73%. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ −0.77 (t, $^{3}J_{HP}$ = 8.0 Hz, 3H, NiC*H*$_3$), 1.11 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 6.6 Hz, 12H, C*H*$_3$), 1.25 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.5 Hz, 12H, C*H*$_3$), 2.24 (m, 4H, C*H*), 3.20 (vt, J^{*}_{HP} = 4.0 Hz, 4H, C*H*$_2$), 6.82 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, $C_{ar}H_p$), 6.95 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, $C_{ar}H_m$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 75 MHz): δ −17.8 (t, $^{2}J_{CP}$ = 21.7 Hz, Ni*C*H$_3$), 18.4 (s, *C*H$_3$), 19.0 (vt, J^{*}_{CP} = 2.3 Hz, *C*H$_3$), 23.8 (vt, J^{*}_{CP} = 10.3 Hz, *C*H), 37.0 (vt, J^{*}_{CP} = 13.1 Hz, *C*H$_2$), 121.0 (vt, J^{*}_{CP} = 8.5 Hz, $C_{ar}H_m$), 124.4 (s, $C_{ar}H_p$), 151.2 (vt, J^{*}_{CP} = 13.8 Hz, C_{ar-o}) 176.6 (t, $^{2}J_{CP}$ = 13.5 Hz, C_{ar-i}). $^{31}P\{1H\}$ NMR (CD_2Cl_2, 25 ºC, 121 MHz): δ 62.4. Anal calcd for $C_{21}H_{38}P_2Ni$: C, 61.34; H, 9.32; found C, 31.34, H, 9.32.The complex [(*i*^{Pr}PCP)Pd-Me] was obtained as a white solid after evaporating the solvent under reduce pressure. Yield: 62%. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ −0.34 (t, $^{3}J_{HP}$ = 5.2 Hz, PdC*H*$_3$), 1.09 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 6.9 Hz, 12H, C*H*$_3$), 1.23 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.8 Hz, 12H, C*H*$_3$), 2.25 (m, 4H, C*H*), 3.35 (vt, J^{*}_{HP} = 4.1 Hz, 4H, C*H*$_2$), 6.86 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, $C_{ar}H_p$), 7.05 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, $C_{ar}H_m$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 75 MHz): δ −18.6 (t, $^{2}J_{CP}$ = 10.1 Hz, Pd*C*H$_3$), 18.2 (s, *C*H$_3$), 19.1 (vt, J^{*}_{CP} = 2.8 Hz, *C*H$_3$), 24.5 (vt, J^{*}_{CP} = 10.8 Hz, *C*H), 38.7 (vt, J^{*}_{CP} = 11.9 Hz, *C*H$_2$), 121.1 (vt, J^{*}_{CP} = 9.6 Hz, $C_{ar}H_m$), 124.1 (s, $C_{ar}H_p$), 149.8 (vt, J^{*}_{CP} = 10.8 Hz, C_{ar-o}) 178.2 (t, $^{2}J_{CP}$ = 4.1 Hz, C_{ar-i}). $^{31}P\{1H\}$ NMR (CD_2Cl_2, 25 ºC, 121 MHz) : δ 59.2. Anal calcd for $C_{21}H_{38}P_2Pd$: C, 54.96; H, 8.35; found C, 54.90, H, 8.30.

[(*i*^{Pr}PCP)Ni-Ph and [(*i*^{Pr}PCP)Pd-Ph]: A solution of PhLi in hexane (2.0 M, 0.15 mL, 0.3 mmol) was added to a solution of [(*i*^{Pr}PCP)Pd-Cl] (0.149 g, 0.31 mmol) or [(*i*^{Pr}PCP)Ni-Br] (0.148 g, 0.31 mmol) in Et_2O (25 mL) at –80 ºC. The cooling bath was removed and the mixture was allowed to stir until it warmed to the room temperature. The solvent was evaporated under reduced pressure and the remaining residue was extracted with Et_2O (3 × 10 mL). The extract evaporated under vacuum and the residue was taken up in hexane (20 mL). The products crystallized when the hexane solutions were concentrated to 1 or 2 mL and cooled to −30 ºC. [(*i*^{Pr}PCP)Ni-Ph]: yellow solid. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 0.86 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.4 Hz, 12H, C*H*$_3$), 1.09 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 6.9 Hz, 12H, C*H*$_3$), 2.04 (m, 4H, C*H*), 3.18 (vt, J^{*}_{HP} = 4.0 Hz, 4H, C*H*$_2$), 6.61 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, $C_{Ph}H_p$), 6.80 (m, 3H, $C_{ar}H_p$, and 2×$C_{Ph}H_m$), 6.91 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, $C_{ar}H_m$), 7.42 (dd, 2H, $^{3}J_{HH}$ = 7.8 Hz, $^{1}J_{HH}$ = 1.3 Hz, $C_{Ph}H_o$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 ºC, 75 MHz): δ 17.7 (s, *C*H$_3$), 18.5 (s, *C*H$_3$), 23.6 (vt, J^{*}_{CP} = 11.0 Hz, *C*H), 36.9 (vt, J^{*}_{CP} = 13.0 Hz, *C*H$_2$), 120.5 (s, $C_{Ph}H_p$), 121.1 (vt, J^{*}_{CP} = 8.7 Hz, $C_{ar}H_m$), 124.8 (s, $C_{ar}H_p$), 125.5 (s, $C_{Ph}H_m$), 140.1 (vt, J^{*}_{CP} = 2.5 Hz, $C_{ph}H_o$), 152.1 (vt, J^{*}_{CP} = 10.8 Hz, C_{ar-o}), 164.2 (t, $^{2}J_{CP}$ = 26.1 Hz, C_{ar-i}), 174.3 (t, $^{2}J_{CP}$ = 13.2 Hz, C_{ar-i}). $^{31}P\{1H\}$ NMR (CD_2Cl_2, 25 ºC, 121 MHz) : δ 56.3. Anal calcd for $C_{26}H_{40}P_2Ni$: C, 65.99; H, 8.52; found C, 65.95, H, 8.63.

[($^{i\text{Pr}}$PCP)Pd-Ph]: white solid, 62% yield. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300 MHz): δ 1.02 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.7 Hz, 12H, C*H*$_3$), 1.13 (dvt, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.2 Hz, 12H, C*H*$_3$), 2.13 (m, 4H, C*H*), 3.41 (vt, J^{*}_{HP} = 4.2 Hz, 4H, C*H*$_2$), 6.77 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, $C_{Ph}H_p$), 6.94 (m, 1H, $C_{ar}H_p$) 6.93 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, $C_{Ph}H_m$), 7.08 (dd, 2H, $^{3}J_{HH}$ = 7.4 Hz, $C_{ar}H_m$), 7.51 (dd, 2H, $^{3}J_{HH}$ = 7.6 Hz, $^{1}J_{HH}$ = 1.3 Hz, $C_{Ph}H_o$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 ºC, 75 MHz): δ 17.9 (s, *C*H$_3$), 18.6 (s, *C*H$_3$), 24.4 (vt, J^{*}_{CP} = 11.3 Hz, *C*H), 38.2 (vt, J^{*}_{CP} = 12.1 Hz, *C*H$_2$), 121.0 (s, $C_{Ph}H_p$), 121.3 (vt, J^{*}_{CP} = 9.3 Hz, $C_{ar}H_m$), 124.6 (s, $C_{ar}H_p$), 126.1 (s, $C_{Ph}H_m$), 140.6 (vt, J^{*}_{CP} = 2.5 Hz, $C_{ph}H_o$), 150.8 (vt, J^{*}_{CP} = 10.8 Hz, C_{ar-o}), 164.4 (t, $^{2}J_{CP}$ = 12.1 Hz, C_{Ph-i}), 175.1 (t, $^{2}J_{CP}$ = 4.1 Hz, C_{ar-i}). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 ºC, 121 MHz) : δ 55.1. Anal calcd for $C_{26}H_{40}P_2Pd$: C, 59.94; H, 7.74; found C, 59.99, H, 7.77.

[($^{i\text{Pr}}$PCP)Ni-OTf]: A solution of trifluoromethanesulfonic (triflic) acid (0.7M, 0.3 mL, 0.21 mmol) was added to a solution of [($^{i\text{Pr}}$PCP)Ni-Me] (0.082 g, 0.2 mmol) in Et_2O (15 mL) at −78 ºC. The product precipitated as a red solid when the mixture was allowed to warm to room temperature. The solution was filtered off, and the solid was washed with Et_2O (10 mL), dried under vacuum and recrystallized from dichloromethane-toluene. Yield 50%. ^{1}H NMR (C_6D_6, 25 ºC, 300MHz) δ 0.81 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 6.9 Hz, C*H*$_3$), 1.45 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.9 Hz, C*H*$_3$), 2.16 (m, 4H, C*H*), 2.52 (vt, 4H, J^{*}_{HP} = 3.7 Hz, C*H*$_2$), 6.66 (d, 2H, $^{3}J_{HH}$ =7.4 Hz, $C_{ar}H_m$), 6.91 (t, 1H, $^{3}J_{HH}$ = 7.4 Hz, $C_{ar}H_p$). ^{13}C{^{1}H} NMR (C_6D_6, 25 ºC, 75 MHz) δ 18.2 (s, *C*H$_3$), 19.2 (s, *C*H$_3$), 23.8 (vt, J^{*}_{CP} = 10.4 Hz *C*H), 29.5 (vt, J^{*}_{CP} = 13.9 Hz, *C*H$_2$), 120.2 (q, J^{*}_{CF} = 318.4 Hz, *C*F$_3$), 122.9 (vt, J^{*}_{CP} = 8.5 Hz, $C_{ar}H_m$), 126.3 (s, $C_{ar}H_p$), 144.7 (t, $^{2}J_{CP}$ = 16.2 Hz, C_{ar-i}) and 152.8 (vt, J^{*}_{CP} = 12.5 Hz, C_{ar-o}) .^{31}P{^{1}H} NMR (C_6D_6, 25 ºC, 121 MHz) δ 60.1 ppm. IR (Nujol mull) ν(SO) 1320, 1203, 1167 cm^{-1}. Anal. Calcd. for $C_{21}H_{35}F_3NiOP_2S$: C, 46.21; H, 6.45; S, 5.88 ; found: C, 46.21; H, 6.47; S, 5.98.

[($^{i\text{Pr}}$PCP)Pd-OTf]: A solution of trifluoromethanesulfonic (triflic) acid (0.7M, 0.3 mL, 0.21 mmol) was added to a solution of [($^{i\text{Pr}}$PCP)Pd-Me] (0.092 g, 0.2 mmol) in Et_2O (15 mL) at −78 ºC and the reaction mixture was allowed to warm to room temperature. The solvent was evaporated under reduced pressure and the residue extracted with CH_2Cl_2, the solution filtered and taken to dryness. The white residue was recrystallized from Et_2O at −30ºC to afford the product as colorless crystals. Yield 40%. ^{1}H NMR (C_6D_6, 25 ºC, 400MHz) δ 0.76 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.2 Hz, C*H*$_3$), 1.33 (dvt, 12H, $^{3}J_{HH} \approx J^{*}_{HP} \approx$ 7.7 Hz, C*H*$_3$), 2.15 (m, 4H, C*H*), 2.58 (vt, 4H, J^{*}_{HP} = 4.7 Hz, C*H*$_2$), 6.79 (d, 2H, $^{3}J_{HH}$ =7.5 Hz, $C_{ar}H_m$), 6.94 (t, 1H, $^{3}J_{HH}$ = 7.5 Hz, $C_{ar}H_p$). ^{13}C{^{1}H} NMR (C_6D_6, 25 ºC, 100 MHz) δ 18.0 (s, *C*H$_3$), 19.1 (s, *C*H$_3$), 24.8 (vt, J^{*}_{CP} = 11.0 Hz *C*H), 30.8 (vt, J^{*}_{CP} = 11.9 Hz, *C*H$_2$), 121.2 (c, J^{*}_{CF} = 318.7 Hz, *C*F$_3$), 123.5 (vt, J^{*}_{CP} = 10.5 Hz, $C_{ar}H_m$), 125.9 (s, $C_{ar}H_p$), 149.5 (t, $^{2}J_{CP}$ = 11.2 Hz, C_{ar-i}), 151.1 (vt, J^{*}_{CP} = 10.3 Hz, C_{ar-o}) .^{31}P{^{1}H} NMR (C_6D_6, 25 ºC, 161 MHz) δ 63.2 ppm. Anal. Calcd. for $C_{21}H_{35}F_3OP_2PdS$: C, 42.54; H, 5.95; S, 5.41 ; found: C, 42.50; H, 5.78; S, 5.14. IR (Nujol mull) ν(SO_3) 1314 , 1203 , 1161 cm^{-1}.

Synthesis of [($^{i\text{Pr}}$PCP)Ni-H and [($^{i\text{Pr}}$PCP)Pd-H]: The synthesis of these two compounds involves a protocol for the consecutive generation of the amides [$^{i\text{Pr}}$(PCP)M-NH_2],[5b,c] and methoxides [$^{i\text{Pr}}$(PCP)M-OMe],[5b,c] which are then reacted with trimethoxysilane. The intermediate complexes have been reported before,[5] except for the palladium amide derivative. Due to its thermal instability, this compound was characterized by NMR only, and data are reported below.

a) Generation of amide complexes [$^{i\text{Pr}}$(PCP)M-NH_2]: A solution of [($^{i\text{Pr}}$PCP)Pd-Cl] (1.59 g, 3.3 mmol) or [($^{i\text{Pr}}$PCP)Ni-Br] (1.57 g, 3.3 mmol) in THF (60 mL) was transferred to a flask charged with $NaNH_2$ (1.29 g, 33.2 mmol), and the

resulting suspension sonicated for 2 h. The initially colourless solution turned red. $NaNH_2$ in excess was eliminated by centrifugation. For NMR characterization, the solution containing [(^{iPr}PCP)Pd-NH_2] was taken to dryness and dissolved in C_6D_6: ^{1}H NMR (C_6D_6, 25 ºC, 400 MHz) δ -0.42 (s, 2H, NH2.), 0.93 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx$ 6.9 Hz, CH_3), 1.27 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx$ 7.6 Hz, CH_3), 1,89 (m, 4H, C*H*), 2.95 (vt, 4H, J^*_{HP} = 3.8 Hz, CH_2), 7.09 (m, 3H, 2×C$_{ar}H_m$, C$_{ar}H_p$). ^{13}C{^{1}H} NMR (C_6D_6, 25 ºC, 100 MHz) δ 18.1 (s, *C*H$_3$), 19.1 (s, *C*H$_3$), 24.1 (vt, J^*_{CP} = 10.6 Hz, *C*H), 35.9 (vt, J^*_{CP} = 12.0 Hz, *C*H$_2$), 122.0 (vt, J^*_{CP} = 10.1 Hz, $C_{ar}H_m$), 124.0 (s, $C_{ar}H_p$), 149.7 (vt, J^*_{CP} = 10.9 Hz, $C_{ar\text{-}o}$), 164.4 (s, $C_{ar\text{-}i}$). ^{31}P{^{1}H} NMR (C_6D_6, 25 ºC, 161 MHz) δ 58.8 ppm.

b) Generation of methoxide complexes complexes [^{iPr}(PCP)M-OMe]: After removal of NaH_2, THF solutions of the amido complexes were treated with 0.20 mL of methanol (5 mmol) at room temperaure. The resulting solutions were taken to dryness and the residue was taken up in 20 mL THF or hexane and used for the synthesis of the hydrides as follows.

c) Reaction of methoxide complexes with triethoxysilane: A solution of the appropriate methoxide complex in THF (Ni) or hexane (Pd), prepared as indicated above, was cooled to 0 ºC and treated with an excess of triethoxysilane (0.9 mL, 5 mmol). The mixture was allowed to warm at room temperature and the volatiles were removed under vacuum. The nickel hydride [(^{iPr}PCP)Ni-H] was obtained as yellow needles after recrystallization from pentane at -30 ºC. Yield, 60 %. ^{1}H NMR (C_6D_6, 25 ºC, 400 MHz) δ −9.92 (t, $^2J_{HP}$ = 55.4 Hz, 1H, Ni-H) 0.96 (dvt, 12H, $^3J_{HH} \approx J^*_{HP}$ ≈ 6.9 Hz, CH_3), 1.20 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx$ 7.6 Hz, CH_3), 1,92 (m, 4H, C*H*), 3.15 (vt, 4H, J^*_{HP} = 3.9 Hz, CH_2), 7.24 (m, 3H, 2×C$_{ar}H_m$, C$_{ar}H_p$). ^{13}C{^{1}H} NMR (C_6D_6, 25 ºC, 100 MHz) δ 18.4 (s, *C*H$_3$), 19.5 (s, *C*H$_3$), 24.6 (vt, J^*_{CP} = 11.9 Hz, *C*H), 37.5 (vt, J^*_{CP} = 12.3 Hz, *C*H$_2$), 121.0 (vt, J^*_{CP} = 10.1 Hz, $C_{ar}H_m$), 124.7 (s, $C_{ar}H_p$), 151.3 (vt, J^*_{CP} = 13.7 Hz, $C_{ar\text{-}o}$), 178.1 (t, $^2J_{CP}$ = 11.1 Hz, $C_{ar\text{-}i}$). ^{31}P{^{1}H} NMR (C_6D_6, 25 ºC, 161 MHz) δ 76.9 ppm. IR (Nujol mull) = 1761 and 1743 cm^{-1} (ν Ni-H); IR (C_6D_6 solution) ν_{max} (cm^{-1}): 1735 (ν Ni-H); Anal calcd for $C_{20}H_{36}P_2Ni$: C, 60.49; H, 9.14; found: C, 60.21; H, 9.01. [(^{iPr}PCP)Pd-H]: Colorless solid, 90 % yield. ^{1}H NMR (C_6D_6, 300 MHz, 25 ºC): δ −3.77 (t, 1H, $^2J_{HP}$ = 17.0 Hz, Pd−H), 0.91 (dvt, $^3J_{HH}$ = 7.2 Hz, J^*_{HP} = 7.2 Hz, 12H, CH_3), 1.17 (dvt, $^3J_{HH}$ = 7.8 Hz, J^*_{HP} = 7.8 Hz, 12H, CH_3), 1.88 (m, 4H, C*H*), 3.24 (vt, J^*_{HP} = 4.1 Hz, 4H, CH_2), 7.23 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C$_{ar}H$), 7.28 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C$_{ar}H$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 25 ºC): δ 18.7 (*C*H$_3$), 20.1 (vt, J^*_{CP} = 3.4 Hz, *C*H$_3$), 25.3 (vt, J^*_{CP} = 11.6 Hz, *C*H), 39.8 (tv, J^*_{CP} = 11.7 Hz, *C*H$_2$), 121.4 (tv, J^*_{CP} = 9.6 Hz, C$_{ar}H_m$), 125.0 (C$_{ar}H_p$), 150.3 (vt, J^*_{CP} = 10.7 Hz, C$_{ar–o}$), 179.7 (t, $^2J_{CP}$ = 3.8 Hz, C$_{ar–i}$). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) = δ 71.7; IR (Nujol mull) = 1787 and 1763 cm^{-1} (ν Pd-H); IR (C_6D_6 solution) ν_{max} (cm^{-1}): 1721 (ν Pd-H); Anal calcd for $C_{20}H_{36}P_2Pd$: C, 54.00; H, 8.16; found: C, 53.49; H, 8.24.

[(^{iPr}PCP)Ni-F]: *a) From [(^{iPr}PCP)Ni-Br]:* A solution of the nickel bromide complex (0.381 g, 0.8 mmol) in THF (20 mL) was added to a suspension of AgF (0.203 g, 1.6 mmol) in toluene (10 mL) and the resulting suspension was sonicated for 12 h. The solvent was removed under reduced pressure and the residue extracted with hexane (3 × 25 mL). The combined extracts were centrifugued,concentrated and cooled −30ºC, affording the product as yellow crystals in 80% yield. *b) From [(^{iPr}PCP)Ni-Me]:* A solution of TREAT-HF in THF (0.25 M, 6.0 mL, 1.5 mmol) was added to a solution of [(^{iPr}PCP)Ni-Me] (1.23 g, 3 mmol) in THF (80 mL) at −78 °C. The reaction mixture was allowed to reach room temperature. The $Et_3N{\cdot}3HF$ excess was eliminated transferring the solution to a flask charged with CaH_2 (2.0 g) and the suspension resulting was stirred for 24 h. The reaction mixture was centrifuged and filtered to afford a yellow solution. The solvent was evaporated under reduced pressure, the residue extracted with hexane (3 × 50 mL), and the solution taken to dryness. Yield 62%. ^{1}H NMR (CD_2Cl_2, 25 ºC, 300MHz) δ 1.28

(dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx$ 7.0 Hz, CH_3), 1.43 (dvt, 12H, $^3J_{HH} \approx J^*_{HP} \approx$ 7.7 Hz, CH_3), 2.19 (m, 4H, CH), 2.99 (vt, 4H, J^*_{HP} = 5.1 Hz, CH_2), 6.73 (d, 2H, $^3J_{HH}$ =6.9 Hz, $C_{ar}H_m$), 6.78 (t, 1H, $^3J_{HH}$ =6.6 Hz, $C_{ar}H_p$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 ºC, 75 MHz) δ 18.2 (s, CH_3), 18.9 (s, CH_3), 23.3 (vt, J^*_{CP} = 9.7 Hz, CH), 30.7 (vt, J^*_{CP} = 12.9 Hz, CH_2), 122.2 (vt, J^*_{CP} = 8.7 Hz, $C_{ar}H_m$), 124.7 (s, $C_{ar}H_p$), 152.1 (bs, C_{ar-i}), 153.3 (t, $^2J_{CP}$ = 10.9 Hz, C_{ar-o}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 ºC, 121 MHz) δ 54.3 ppm (d, $^2J_{FP}$= 36.7 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 25 ºC, 376 MHz) δ −287.0 ppm. Anal. Calcd. for $C_{20}H_{35}FNiP_2$: C, 57.86; H, 8.50; found: C, 57.99; H, 8.48.

[(*i*^{Pr}PCP)Pd-F]: *a) From [(*^{iPr}*PCP)Pd-I] and AgF:* A solution of the palladium iodide complex (0.457 g, 0.8 mmol) in THF (20 mL) was added to flask charged with AgF (0.203 g, 1.6 mmol) and the resulting suspension was sonicated for 12 h. The solvent was removed under reduced pressure and the residue was extracted with hexane (3 × 25 mL). The complex [(*i*^{Pr}PCP)Pd-F] was obtained as a colourless solid after cooling to −30ºC. *b) From [(*^{iPr}*PCP)Pd-Me and TREAT-HF.* For the success of this method, the correct adjustment of the reagents ratio is essential. Since the weighting of TREAT-HF may involve significant error, we used a standard solution of this reagent in THF. The TREAT-HF content of this solution was estimated by reacting a sample of this solution with half the required amount of [(iPrPCP)Pd-Me] at 50 ºC for 2 h, and then analyzing the ratio product : starting material by $^{31}P\{^1H\}$ NMR. Once the concentration of the TREAT-HF is accurately known, the synthesis can be carried out as follows: A solution of TREAT-HF in THF (0.1 M, 3.4 mL, 0.34 mmol) was added to a solution of [(*i*^{Pr}PCP)Pd-CH_3] (0,467 g, 1.02 mmol) in THF (10 mL) at room temperature. The resulting mixture was heated at 50ºC for 2 h. The solvent was evaporated under reduce pressure and the residue extracted with hexane (3 × 25 mL). The complex [(*i*^{Pr}PCP)Pd-F] was obtained as a colourless solid after cooling to −30ºC. Yield: 42%. ^1H NMR (C_6D_6, 25 ºC, 300 MHz): δ 1.00 (dvt, $^3J_{HH} \approx J^*_{HP} \approx$ 7.2 Hz, 12H, CH_3), 1.34 (dvt, $^3J_{HH} \approx J^*_{HP} \approx$ 7.9 Hz, 12H, CH_3), 1.96 (m, 4H, CH), 2.75 (vt, J^*_{HP} = 4.0 Hz, 4H, CH_2), 6.91 (d, $^3J_{HH}$ = 7.4 Hz, 2H, $C_{ar}H_m$), 7.00 (t, $^3J_{HH}$ = 7.4 Hz, 1H, $C_{ar}H_p$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 ºC, 100 MHz): δ 18.2 (s, CH_3), 19.0 (s, CH_3), 24.1 (vt, J^*_{CP} = 10.4 Hz, CH), 32.4 (vt, J^*_{CP} = 10.3 Hz, CH_2), 122.8 (vt, J^*_{CP} = 10.3 Hz, $C_{ar}H_m$), 124.6 (s, $C_{ar}H_p$), 151.2 (vt, J^*_{CP} = 10.9 Hz, C_{ar-o}), 155.2 (d, $^2J_{CF}$ = 48.2 Hz, C_{ar-i}). $^{31}P\{1H\}$ NMR (C_6D_6, 121 MHz): δ 57.5 (d, $^2J_{FP}$ = 5.9 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 25 ºC, 376 MHz) δ −245.3 ppm Anal calcd for $C_{20}H_{35}FP_2Pd$: C, 51.90; H, 7.62; found C, 51.52, H, 7.72.

Reactions of Fluoride Complexes with LiOMe.

To a solution of [(*i*^{Pr}PCP)Ni-F] (0.66 g, 1.6 mmol, see below) or [(*i*^{Pr}PCP)Pd-F] (0.74, 1.6 mmol, see below) in THF (25 mL) was added a solution of MeOLi (2.4 mmol) in THF (20 mL) at −78 ºC. The resulting mixture was allowed to warm at room temperature and stirred for 20 min. According to the $^{31}P\{^1H\}$ spectra of the reaction mixtures, the fluoride complexes were cleanly and quantitatively converted in the corresponding methoxides. Lithium fluoride was removed by centrifugation, the solvent evaporated under reduced pressure and the residue extracted with hexane. The complexes [(*i*^{Pr}PCP)Pd-OMe][5c] and [(*i*^{Pr}PCP)Ni-OMe][5b] were obtained after concentration and cooling to −30 ºC.

Reaction of Halide Complexes with Dodecyl Iodide.

Solutions of the halide complexes [(^{iPr}PCP)Ni-Br], [(^{iPr}PCP)Ni-I], [(^{iPr}PCP)Ni-F], [(^{iPr}PCP)Pd-I] or [(^{iPr}PCP)Pd-Cl] (0.02 mmol) and *n*-iododecane (50 μL, 0.2 mmol) in C_6D_6 (0.6 mL) containing a small amount of *p*-cymene as internal standard for ^{1}H integration were transferred to NMR tubes capped with J. Young® valves and placed in a pre-heated oil bath at 100 ºC. The course of the reactions was monitored by ^{1}H and ^{31}P{^{1}H} NMR. The reaction of [(^{iPr}PCP)Pd-F] with dodecyl iodide was studied directly in the NMR probe at the same temperature.

Catalytic fluorination of Dodecyl Iodide.

To a suspension of AgF (0.065 g, 0.52 mmol) in toluene (1 mL) was added a solution of [(^{iPr}PCP)Ni-Br], [(^{iPr}PCP)Ni-I], [(^{iPr}PCP)Ni-F], [(^{iPr}PCP)Pd-I] or [(^{iPr}PCP)Pd-F] (0.035 mmol) in toluene (2 mL). The resulting suspension was stirred for 3 h at 100 ºC. Aliquots were taken out for GC analysis. Yields and conversions were calculated by GC using *p*-cymene as internal standard.

X-ray structure analysis for [(iPrPCP)Ni-F], [(iPrPCP)Ni-H], [(iPrPCP)Ni-Me], [(iPrPCP)Ni-Ph] and [iPr(P(O)C(Me)P(O)]·H2O.

A summary of crystallographic data and structure refinement results for these new crystalline compounds is given in the Table 3. Crystals coated with dry perfluoropolyether were mounted on glass fibers and fixed in a cold nitrogen stream (T = 100 or 120 K). Intensity data were collected on a Bruker SMART CCD diffractometer operating with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), except for compound [(iPrPCP)Ni-Me] whose intensity data were collected on an Enraf-Nonius FR590-Kappa CCD 2000 diffractometer equipped with a graded multilayer mirror providing monochromated Cu-Kα radiation (λ = 1.54178 Å). For the Bruker diffractometer the data were reduced by SAINT[37] while for the Enraf-Nonius diffractometer the data were reduced by HKL-Denzo and Scalepak.[38] The data were in all cases corrected for absorption effects by the multi-scan method (SADABS).[36] The structures were solved by direct methods (SIR-2002, SHELXS)[39,40] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[37] minimizing $w[F_o^2-F_c^2]^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the attached carbon atoms with the isotropic temperature factors (*U*iso values) fixed at 1.2 times (1.5 times for the methyl groups) those *U*eq values of the corresponding carbon atoms.

Table 3. Summary of crystallographic data and structure refinement results for [(^{iPr}PCP)Ni-F], [(^{iPr}PCP)Ni-H], [(^{iPr}rPCP)Ni-Me], [(^{iPr}PCP)Ni-Ph] and [^{iPr}(P(O)C(Me)P(O)]·H_2O

Compound	[(iPrPCP)Ni-F]	[(iPrPCP)Ni-H]	[(iPrPCP)Ni-Me]	[(iPrPCP)Ni-Ph]	[iPr(P(O)C(Me)P(O)]·H_2O
Chemical formula	$C_{20}H_{35}FNiP_2$	$C_{20}H_{36}NiP_2$	$C_{21}H_{38}NiP_2$	$C_{26}H_{40}NiP_2$	$C_{21}H_{38}O_2P_2$•H_2O
Formula Mass	415.13	397.14	411.16	473.23	402.47

Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
a/Å	18.316(1)	18.038(4)	10.998(9)	10.4777(10)	13.5036(11)
b/Å	19.001(2)	18.938(5)	13.794(9)	13.9169(14)	12.3747(11)
c/Å	19.963(2)	20.036(5)	28.90(3)	18.1873(18)	14.2276(12)
α/°	90.00	90.00	90.00	81.963(2)	90.00
β/°	113.933(2)	113.393(4)	96.038(14)	76.658(1)	107.045(2)
γ/°	90.00	90.00	90.00	77.812(2)	90.00
Unit cell volume/Å^3	6350.2(10)	6282(3)	4360(6)	2510.7(4)	2273.0(3)
Temperature/K	100(2)	100(2)	120(2)	100(2)	100(2)
Space group	*P2(1)/n*	*P2(1)/n*	*P2(1)/n*	$P\bar{1}$	*P2(1)/c*
No. of formula units per unit cell, *Z*	12	12	8	4	4
Radiation type	MoK_α	MoK_α	CuK_α	MoK_α	MoK_α
Absorption coefficient, *μ*/mm^{-1}	1.076	1.078	2.648	0.910	0.208
No. of reflections measured	41108	39578	36997	30622	14665
No. of independent reflections	15961	15516	6775	12620	5757
R_{int}	0.0863	0.0937	0.0788	0.0379	0.0546
Final R_1[a] values [$F^2>2\sigma(F^2)$]	0.0679	0.0728	0.0476	0.0383	0.0470
Final $wR_2(F^2)$ [b] values [$F^2>2\sigma(F^2)$]	0.1428	0.1637	0.1159	0.0708	0.0687
Final R_1[a] values (all data)	0.1168	0.1359	0.0586	0.0560	0.0787
Final $wR(F^2)$ [b] values (all data)	0.1647	0.1939	0.1224	0.0745	0.0743
Goodness of fit on F^2, S[c]	1.003	0.993	0.997	0.835	0.980

[a] $R_1(F) = \sum||F_0|-|F_c|| / \sum|F_0|$. [b] $wR_2(F^2) = \left\{\sum\left[w(F_o^2 - F_c^2)^2\right] / \sum(F_0^2)^2\right\}^{1/2}$. [c] $S = \left\{\sum\left[w(F_o^2 - F_c^2)^2\right] / (n-p)\right\}^{1/2}$ (n = number of reflections, p = number of parameters).

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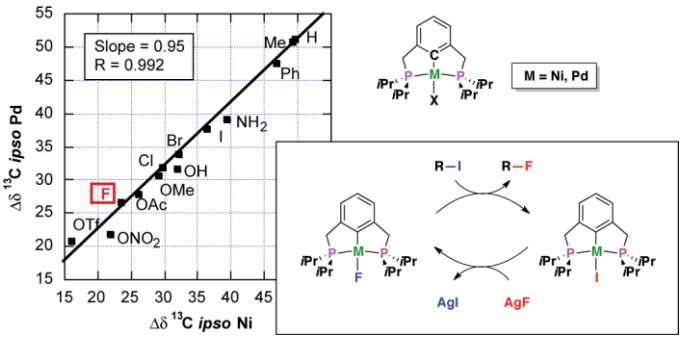
FOR TABLE OF CONTENTS ONLY

Synthesis and Reactivity of Nickel an Palladium Fluoride Complexes with PCP Pincer Ligands. A NMR-Based Assessment of Electron-Donating Properties of Fluoride and Other Monoanionic Ligands.

Luis Miguel Martínez-Prieto, Cristóbal Melero, Diego del Río, Pilar Palma, Juan Cámpora* and Eleuterio Álvarez.



The electronic properties of the fluoride ligand were assessed on the basis of a survey of ^{13}C NMR data for a series of ^{1Pr}PCP pincer complexes containing various monoanionic ligands. The complexes [(^{iPr}PCP)M-F] are highly nucleophilic and undergo fluoride exchange reactions.