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[(dcpp)Ni(η^2 -Arene)] Precursors: Synthesis, Reactivity and Catalytic Application to the Suzuki-Miyaura Reaction.

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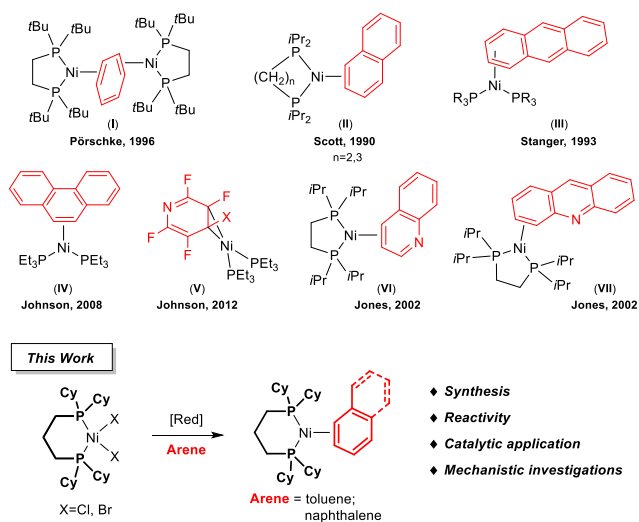
Supporting Information Placeholder

ABSTRACT: The complexes $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\eta^2\text{-arene})$ (arene = toluene, naphthalene) (**3**) and (**4**) have been synthesized and studied in detail. Displacement reactions of the toluene ligand afford the complexes $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\eta^2\text{-styrene})$ (**5**), $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\text{PhCN})$ (**6**), $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\text{CO})_2$ (**7**), $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\text{PPh}_3)$ (**8**), $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\text{PCy}_3)$ (**9**), $\{(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}\}_2(\mu\text{-H})_2$ (**10**), $(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}(\eta^2\text{-CO}_2)$ (**11**) and $[(\text{Cy}_2\text{PC}_3\text{H}_6\text{PCy}_2)\text{Ni}]_2\mu\text{-}\eta^2(1,5\text{-COD})$ (**12**). The relative rates of ArCl oxidative addition at Ni complexes (**3**), (**4**), (**6**), (**8**) and (**12**) has been evaluated experimentally and the mechanism calculated by DFT. Complexes (**3**) and (**4**) are efficient catalysts for the Suzuki-Miyaura reaction between chloroarenes and $\text{Ar}^*\text{B}(\text{OH})_2$.

■ INTRODUCTION

The Suzuki-Miyaura Reaction (SMR) represents an undeniable synthetic tool to build C–C bonds for both academic and industrial purposes,^[1] and typically involves Pd(o)/Pd(II) redox scenarios. While this chemistry is largely developed for palladium complexes, the use of nickel catalysts is simultaneously mechanistically intriguing^[2] and highly desirable due to its higher abundance, economic issues and essential properties.^[3] In recent years, important improvements were achieved in terms of substrate scope^[4] and catalyst loadings.^[5] In turn, several reaction pathways are plausible when dealing with nickel catalysis and precisely designed studies are essential to discern the operative mechanism.^[2,3] In this sense, the generation of electron-rich yet unsaturated metal fragments seems to be crucial facilitating reactivity at a metal centre, and thus entering into the catalytic loop.^[6] A common strategy relies on the stabilization of the desired fragment by a weakly coordinating ligand, readily displaced under mild conditions. In 1974, Jonas reported the synthesis of $[(\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2)\text{Ni}(\eta^2\text{-arene})]$ ($n = 2, 3$) complexes by the stoichiometric reduction of the halide bridged Ni(I) dimers.^[7–9] In this seminal work, the formation of these complexes were exclusively proved by elemental analyses,^[8] and it was stated that arenes were readily displaced by several two electron donors such as alkenes or PPh_3 , without further evidence.^[7]

Chart 1. Representative examples of stable low-valent $[\text{P}_2\text{Ni}(\text{o})-(\eta^2\text{-arene})]$ fragments.



Two decades later, a family of related complexes has been isolated with different electron rich phosphines (platforms **I**,^[10,11] **II**^[12,13] and **III**^[14–16] in Chart 1).^[10–16] The group of Pörschke has particularly studied the chemistry of the $[(\text{tBu}_2\text{P}(\text{CH}_2)_2\text{PtBu}_2)\text{Ni}(\eta^2\text{-benzene})]$ complex for which they obtained structural information and showed that the arene

acts as a weak two electron donor in an η^2 -coordination mode, for either one or two Ni centers.^[10,11] Accordingly, Ni(I)-hydride species could be obtained upon treatment of the benzene complex with H₂ as documented by Jonas and Wilke,^[7] with the Cy₂P(CH₂)_nPCy₂ (n = 2, 3) systems, and by Pörschke with **I**.^[11]

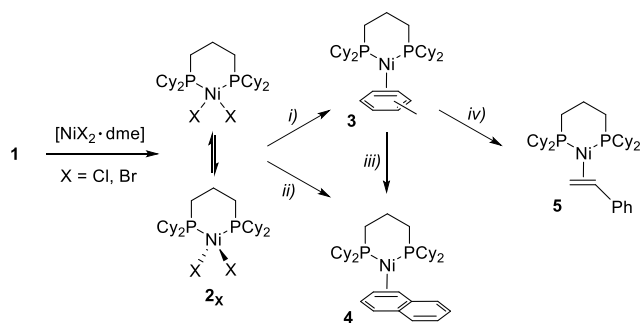
After *ca* 2 decades of latency, Johnson and Jones independently expanded the range of arenes that are able to stabilize low-valent P₂Ni(o) fragments.^[17–20] In an elegant approach, Johnson proved the easy replacement of the anthracene ligand from complexes of type **III**^[17] and **IV**^[18] to achieve the low temperature NMR identification of **V**,^[19] which displays η^2 -coordination of the fluorinated pyridines prior to the C–X bond activation (X = H, F). In 2002, Jones isolated complexes **VI** and **VII** stabilized by quinolines and acridines, that are involved in the selective cleavage of Ar–CN bonds.^[20] In addition, Love has recently demonstrated the ability of Pörschke’s complex **I** to promote original C–heteroatom bond activations of epoxides, oxaziridines and (thio)esters.^[21]

Over the last five decades, this chemistry was almost exclusively developed with monodentate phosphines and/or chelating bis-dialkylphosphines (mostly focusing on the “ethylene” bridged ones). In light of the impact of the bite angle on the reactivity at the metal center,^[22] we decided to focus on the bidentate ligand featuring a propyl bridge between the two phosphorus moieties, Cy₂P(CH₂)₃PCy₂ (dcpp; **1**), and report here the synthesis and full characterization by multinuclear NMR and X-ray analysis of [(Cy₂P(CH₂)₃PCy₂)Ni(η^2 -arene)] complexes **3** and **4** (arene = toluene or naphthalene, respectively). In this contribution, we describe several displacement reactions of the aromatic ligand to yield the corresponding Ni(o) complexes **5–12**. Among the results presented, we show that complexes **3** and **4** are excellent precursors for the synthesis of rare [(dcpp)Ni(L)] species, where L = phosphine, 1,5-cyclooctadiene (COD), acetonitrile or CO₂. We provide an experimental comparative study of several [(dcpp)Ni(L)] complexes for the oxidative addition of 4-chlorobenzotrifluoride at the nickel center, associated to a DFT study of the mechanism. Finally, the use of complex **4** as efficient catalyst for the SMR is evidenced, and mechanistic investigations *via* stoichiometric experiments demonstrated the viability of a Ni(o)/Ni(II) catalytic cycle for this transformation.

RESULTS AND DISCUSSION

Complexes **2x** (X = Cl or Br) were readily synthesized by the stoichiometric reaction of [NiX₂·dme] with **1** in THF at room temperature. The reactions of the nickel precursors with **1** did not present new signals in ³¹P NMR, suggesting the formation of complexes **2x** with tetrahedral (Td) geometries in THF. Complexes **2x** were crystallized in excellent yields (from 93 to 97%). Note that when dissolved in CH₂Cl₂ crystals of **2x** are diamagnetic while they are still paramagnetic in THF, pointing a solvent induced equilibrium in solution. The structure of **2c1** is represented in Figure 1a (see data for **2c1** in ESI). Both complexes **2x** display a square planar (SP) geometry in the solid state as shown by the Σ_{angles} of 360.0° for **2c1**. This feature already points to an increased flexibility of the bidentate ligand compared to the related diphosphinoethylene type ligands, for which only the SP complexes are observed in solution by NMR and in the solid state by X-ray diffraction analysis.

The 2 *e*[−] reduction of complexes **2x** was subsequently studied using mono-electronic reductants such as KC₈ or Na/naphthalene at low temperatures (Scheme 1). Note that the reduction of complex **2c1** by 2 equiv of Na sand in toluene was studied by Nobile.^[23]



Scheme 1. Synthesis of complexes **2x**, further reduction to [(dcpp)Ni(η^2 -arene)] species **3–4**, and styrene coordination. Reaction conditions: *i*) 2 equiv of KC₈ in toluene at -40°C , and slow warming up to r.t. overnight; *ii*) 2 equiv of Na/naphthalene in THF at -80°C , and slow warming up to r.t. overnight; *iii*) 1 equiv of naphthalene in toluene at r.t.; and *iv*) 1 equiv of styrene in toluene at r.t.

We found out that the reduction of **2x** with KC₈ leads to the formation of two novel species characterized by two singlets with a ratio of *ca* 85/15 ratio, at 15.4 ppm and 25.1 ppm in the ³¹P{¹H} NMR spectrum. Luckily, the minor species is much more soluble than the major compound which allowed their efficient separation. The minor species is the dihydride dimer **11** (*vide infra* in Scheme 3), as shown by the characteristic hydride shift at -10.8 ppm in the ¹H NMR spectrum. Complex **11** is likely obtained because of the formation of small amounts of H₂ when KC₈ is suspended in toluene (although toluene was first dried using a commercial purification system followed by distillation over Na, < 10 ppm H₂O *via* Karl Fisher titration). Optimization of the yield of **3** (83% isolated yield) can be achieved using a very concentrated medium which favors its precipitation upon formation. After elimination of the soluble dihydride complex **11**, **3** can be extracted in toluene allowing elimination of both the KX salts and the graphite. Complex **3** is reminiscent of the one reported by Jonas, [(dcpp)Ni(η^2 -benzene)], obtained in 37% yield from the reduction of the corresponding Ni(I) precursor in benzene, itself obtained by the comproportionation of a “(dcpp)Ni(II)” precursor and [(dcpp)Ni(η^2 -ethylene)].^[8] After isolation, **3** was characterized with multinuclear NMR spectroscopy. However, in contrast to the [(*t*Bu₂P(CH₂)₃P*t*Bu₂)Ni]₂(μ^2 - η^2 : η^2 -C₆H₆)] system **I** studied by Pörschke for which a slow exchange of benzene by C₆D₆ was observed at room temperature,^[10] the toluene ligand in **3** was rapidly exchanged by C₆D₆ even at 0°C. Nevertheless, integration of the ¹H signals of toluene *vs* dcpp proved the coordination of one toluene per Ni fragment, showing that the toluene does not act as a bridging ligand in the present case. Moreover, the ³¹P NMR spectrum shows only one signal at 15.4 ppm in toluene, for apparent equivalent chemical environments of the phosphorus atoms, although the coordination of the toluene should lead to a differentiation. Low temperature NMR experiments were carried out in toluene-d⁸ (down to -80°C) but the fast equilibration process could not be frozen or even slowed down. Crystallization of **3** was successful upon cooling a concentrated solution of the complex in toluene. The X-ray structure is represented in Figure 1b. One of the main information is the confirmation

of the η^2 -coordination of the toluene ligand. It can be noted that the coordinating bond of toluene is only slightly elongated, (1.424(6) Å, compared to about 1.39 Å for free toluene) indicating a weak donation of the nickel in the carbon-carbon bond, thus accounting for its poor coordination.

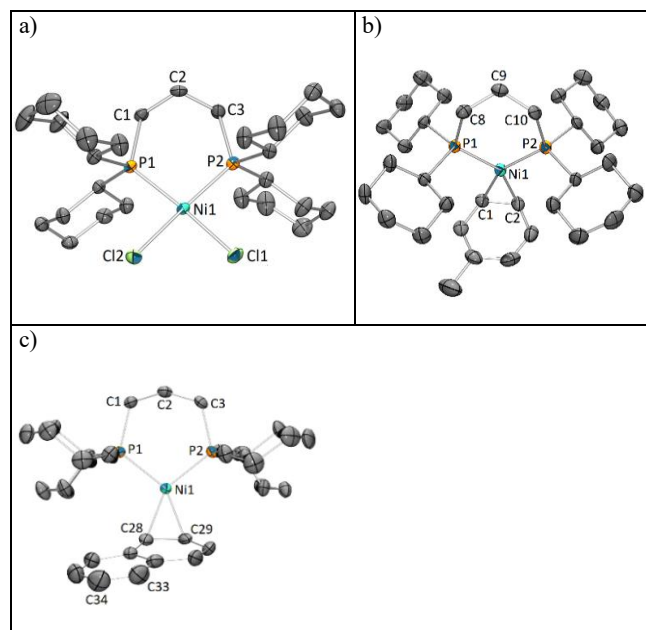
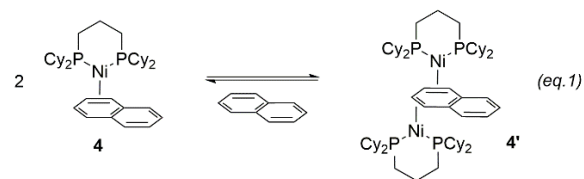


Figure 1. Molecular views of **2ci** (a), **3** (b) and **4** (c). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for: **2ci**, Ni₁-P₁ 2.192(1), Ni₁-P₂ 2.191(1), Ni₁-Cl₁ 2.217(1), Ni₁-Cl₂ 2.219(1), P₁-Ni₁-P₂ 97.50(3), Cl₁-Ni₁-Cl₂ 91.12(3), P₁-Ni₁-Cl₁ 176.44(3), P₂-Ni₁-Cl₂ 175.96(3); **3**, Ni₁-P₁ 2.147(1), Ni₁-P₂ 2.156(1), Ni₁-C₁ 2.001(4), Ni₁-C₂ 1.993(4), C₁-C₂ 1.424(6), P₁-Ni₁-P₂ 104.09(4), C₂-Ni₁-C₁ 41.77(16); **4**, Ni₁-P₁ 2.151(1), Ni₁-P₂ 2.163(1), Ni₁-C₂₈ 2.001(2), Ni₁-C₂₉ 1.980(2), C₂₈-C₂₉ 1.435(4), C₃₃-C₃₄ 1.378(5), P₁-Ni₁-P₂ 103.31(3), C₂₈-Ni₁-P₁ 107.10(8), C₂₈-Ni₁-C₂₉ 42.27(10), C₂₉-Ni₁-P₂ 107.45(8).

An alternative entry to the “(dcp)Ni(arene)” platform was achieved by reacting **2Br** with 2 equiv of freshly prepared Na/naphthalenide. After dropwise addition of the reducing agent at -78 °C and subsequent stirring at room temperature overnight, the reaction turned from green to deep yellow, and was accompanied by abundant precipitation of a yellow solid containing a mixture of NaBr and “(dcp)Ni(o)” species. ³¹P NMR of the reaction mixture evidenced the reduction of **2Br** and displayed two broad signals resonating at 15.3 and 21.0 ppm at room temperature. Satisfyingly, these signals resolved into two doublets appearing at 15.2 and 20.9 ppm ($J_{P,P} = 37.2$ Hz) upon cooling at -60 °C, thus manifesting the presence of a dynamic phenomenon in solution (see ESI).^[13,15,16] ¹H NMR of isolated **4** displays the presence of free naphthalene in solution despite abundant washing of **4** with diethyl ether. Integration of the signals attributed to the free naphthalene vs complexed naphthalene vs the “(dcp)Ni(o)” fragment gave approximately an 1:1:2 molar ratio, thus suggesting an equilibrium between the expected monometallic complex **4** and the dimer structure **4'** in solution. The atom connectivity in **4** was definitively confirmed by X-ray diffraction of single crystals obtained from a concentrated solution of **4** in toluene (see Figure 1c). As expected, **4** crystallizes in a trigonal planar geometry around the Ni center ($\Sigma_{\text{angles}} = 360.13^\circ$). The structure shows the η^2 coordination of the naphthalene ligand

through C₂₈ and C₂₉ displaying a significantly elongated C₂₈-C₂₉ bond distance of 1.435(4) Å, and a P₁-Ni₁-P₂ angle of 103.31(3)° much larger than the one observed in **2ci** (97.50(3)°).



Scheme 2. Equilibrium between (dcp)Ni(naphthalene) **4** and the dimer **4'**.

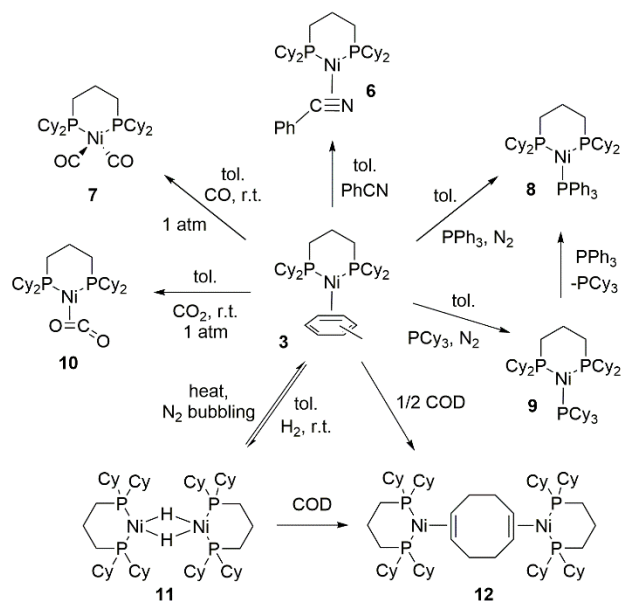
To explore the relevance of complexes **3** and **4** as entries into a SMR catalytic cycle, classical two electron donors such as alkenes (styrene and COD are presented here as representative examples),^[24,25] CO,^[26–28] or phosphines were reacted with complexes **3** or **4**. Not surprisingly, and in accord with statements by Jonas and Wilke, the 16 electron Ni(o) complex **5** was obtained nearly quantitatively upon addition of one equivalent of styrene (92% yield; Scheme 1). The complex presents the expected two doublets in the ³¹P{¹H} NMR spectrum ($\delta = 28.2$ ppm and $\delta = 19.1$ ppm, $^2J_{P,P} = 25.4$ Hz). The change in chemical shifts in the ¹H NMR spectrum for the alkene protons is significant ($\Delta\delta = -2.51$ ppm for PhCHCH₂, $\Delta\delta = -3.12$ ppm and -2.79 ppm for PhCHCH₂), revealing a strong back donation upon coordination.

Further displacement reactions were evaluated with complex **3** (Scheme 3). Mixing equimolar amounts of **3** and benzonitrile in toluene for 1 h at room temperature allowed for the isolation of **6** as a pale yellow powder in 89% yield. ³¹P{¹H} NMR characterization of **6** shows two distinct signals at 38.1 and 19.0 ppm resonating as doublets ($^2J_{P,P} = 27.9$ Hz), thus indicating a desymmetrization of the “dcpNi(o)” fragment by π -coordination of the benzonitrile. Single crystals of **6** were grown at -25 °C by slow diffusion of pentane into a concentrated solution of **6** in THF. X-ray diffraction analysis confirmed the trigonal planar geometry around the Ni center for **6** with a measured P₁-Ni₁-P₂ angle of 103.05(2)°, and shows the typical η^2 -coordination mode of the nitrile moiety (elongated Ni₁-C₁ bond distance of 1.223(3) Å, and Ni₁-C₁-C₂ angle of 137.8(2)°; Figure 2a).

The 18 electron complex **7** was obtained after bubbling CO into a solution of complex **3** at room temperature. This complex was characterized by NMR spectroscopy showing one triplet at 204.4 ppm for the CO moiety in the ¹³C NMR spectrum, with a $^2J_{PC} = 2.3$ Hz. The IR spectrum showed two bands at 1918 and 1980 cm⁻¹ as expected for the presence of two CO in a Td environment. No loss of CO from this complex could be observed even under prolonged vacuum. Single crystals were grown from a well-concentrated THF solution of **7** at -25 °C (see Figure 2b). X-ray diffraction analysis proved the atom connectivity and the distorted Td environment around Ni-centre with slightly elongated C–O bond distances of 1.151(5) Å and 1.145(5) Å compared to free carbon monoxide (1.128 Å).^[29]

The coordination of phosphines was more interesting as examples of ML₃ complexes featuring three phosphines are very rare and usually unstable.^[30] The complex [Ni(PPh₃)₃] has been synthesized by Tolman and co-workers by the Zn reduction of NiCl₂ in the presence of PPh₃.^[31] It is however described as very unstable, and its characterization was particularly difficult. In fact, it was later shown that such

reduction forms the $[\text{Ni}(\text{PPh}_3)_4]$ complex which dissociates significantly to $[\text{Ni}(\text{PPh}_3)_3]$ and free PPh_3 in solution, engaged in rapid exchange.^[32] Following a different synthetic approach, *i.e.* the disproportionation of the bimetallic complex $[(\text{Et}_2\text{N})_3\text{Ti}(\mu\text{-PCy}_2)\text{Ni}(\text{PPh}_3)]$, Stephan and co-workers were able to characterize this complex by X-ray analysis.^[33] A last example was given in 2013 by Lu and colleagues, using the tridentate ligand $\text{N}(o\text{-(NHCH}_2\text{P}i\text{Pr}_2)\text{C}_6\text{H}_4)_3$.^[34] To date, no X-ray structures for other $[\text{Ni}(\text{PR}_3)_3]$ are known. Moreover, Waterman and Hillhouse have shown that the $[\text{Ni}(t\text{Bu}_2\text{P}(\text{CH}_2)_3\text{PtBu}_2)(\text{PPh}_3)(\text{N}_2)]$ complex of pseudo Td geometry was obtained from the $[(t\text{Bu}_2\text{P}(\text{CH}_2)_3\text{PtBu}_2)\text{Ni}]_2(\mu,\eta^2\text{-C}_6\text{H}_6)$ complex upon addition of PPh_3 under N_2 .^[35]



Scheme 3. Reactivity of **3** with $2 e^-$ donor ligands.

When one equivalent of PPh_3 was added to **3** under N_2 , the color changed instantaneously from yellow to deep red. Two sets of signals were observed in the ^{31}P NMR spectrum, a triplet at 30.5 ppm ($^2J_{\text{PP}} = 85.1$ Hz) and a doublet at 11.7 ppm, corroborating the formation of a single new species, **8**. The complex, isolated in excellent 91% yield, was therefore postulated to be a rare example of a NiL_3 complex ($\text{L} = \text{phosphine}$). Further addition of one equivalent of PPh_3 did not lead to the formation of an 18 electron complex, as shown by the presence of a sharp signal for free PPh_3 in the ^{31}P spectrum. The ML_3 trigonal planar geometry was definitely proved by an X-ray diffraction study on monocrystals obtained upon cooling a concentrated solution of **8** (see structure in Figure 2c). The sum of the angles of 359.91° was measured around the Ni-center. The geometry is slightly distorted as the $\text{P}_3\text{-Ni}_1\text{-P}_1$ and $\text{P}_3\text{-Ni}_1\text{-P}_2$ angles are different ($129.98(2)^\circ$ and $123.52(2)^\circ$ respectively). The increase of the bite angle provided by the propyl bridge is shown by the $\text{P}_1\text{-Ni}_1\text{-P}_2$ angle of $106.42(2)^\circ$, which is much larger than in the related dtbpe complex reported by Waterman and Hillhouse ($93.62(2)^\circ$).^[35] This increase in the bite angle is therefore the determining factor for the observation of the NiL_3 geometry, rather than the $[\text{NiL}_3(\text{N}_2)]$ complex. The similar reaction conducted with PCy_3 , was also leading to the formation of a single complex **9** featuring the expected triplet and doublet patterns (at 38.3 ppm and at 6.0 ppm respectively, with $^2J_{\text{P-P}} = 85.1$ Hz), pointing to a similar trigonal planar geometry. This complex, featuring only alkylphosphine ligands proved

much more soluble than complex **8** and was reluctant to crystallization. Competitive coordination experiments between PPh_3 and PCy_3 were conducted. Mixing **3** with one equiv of each phosphine resulted in the appearance of the signal of complex **8** in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum together with free PCy_3 . Moreover, PCy_3 from complex **9** was quantitatively displaced by PPh_3 to form **8** in toluene.

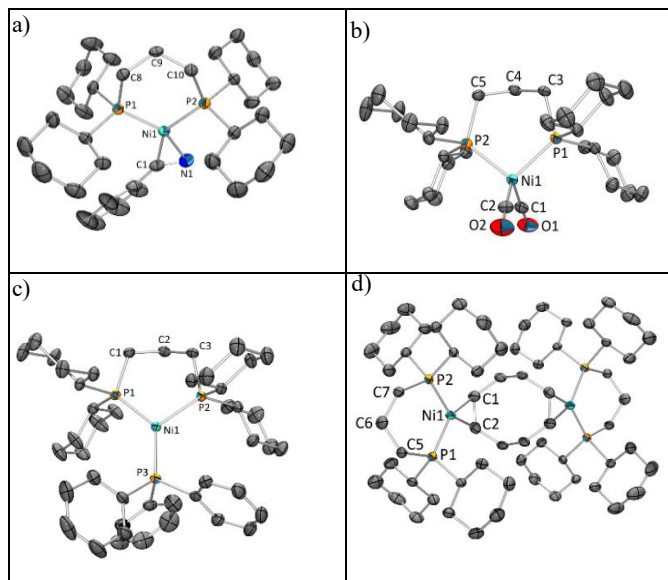
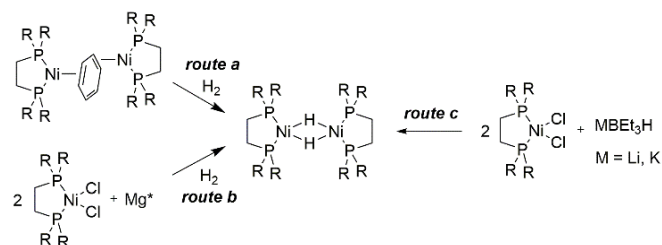


Figure 2. Molecular structures of **6** (a), **7** (b), **8** (c), and **12** (d). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for: **6**, Ni₁-P₁ 2.147(1), Ni₁-P₂ 2.169(1), Ni₁-C₁ 1.866(2), Ni₁-N₁ 1.919(2), N₁-C₁ 1.223(3), P₁-Ni₁-P₂ 103.05(2), C₁-Ni₁-N₁ 37.67(10), N₁-C₁-C₂ 137.8(2); **7**, Ni₁-P₁ 2.219(1), Ni₁-P₂ 2.220(1), Ni₁-C₁ 1.768(4), Ni₁-C₂ 1.768(4), C₁-O₁ 1.151(5), C₂-O₂ 1.145(5), P₁-Ni₁-P₂ 101.82(4), C₁-Ni₁-C₂ 111.65(18); **8**, Ni₁-P₁ 2.145(1), Ni₁-P₂ 2.152(1), Ni₁-P₃ 2.113(1), P₃-Ni₁-P₁ 129.98(2), P₃-Ni₁-P₂ 123.52(2), P₁-Ni₁-P₂ 106.42(2); **12**, Ni₁-P₁ 2.143(1), Ni₁-P₂ 2.142(1), Ni₁-C₁ 1.990(4), Ni₁-C₂ 1.992(4), C₁-C₂ 1.439(5), P₂-Ni₁-P₁ 103.79(4), C₁-Ni₁-P₂ 107.83(11), C₂-Ni₁-P₁ 105.77(11), C₁-Ni₁-C₂ 42.36(14).

From another standpoint, a reactivity similar to the one of “(diphosphine)Ni” $14 e^-$ fragments may in some instances be observed from the bimetallic Ni(I) bridging dihydride complexes. These complexes were shown to eliminate H_2 upon addition of a better two electron donor.^[36-41] In turn, these complexes have been obtained by three different routes starting typically from the readily available Ni(II) precursors (routes b and c in Scheme 4), and in one instance by the reaction of H_2 with the Ni(O)-benzene complex (Scheme 4, route a).^[11]



Scheme 4. Synthesis of bridging dihydride complexes.

Complex **11** was previously synthesized by the reduction “route c” (Scheme 4) by Jonas and Wilke,^[7] and mentioned to be synthesized by “route a” by Jonas starting from [(dcp)Ni(η^2 -benzene)].^[8] Accordingly, we obtained it quantitatively upon bubbling H₂ into a solution of complex **3** in toluene for a few minutes at room temperature. A visible color change from yellow to red was indicative of the fast reaction which was followed by ³¹P NMR showing only the appearance of the signal at 25.1 ppm for complex **11**.^[23] Proof on the lability of H₂ in complex **11** was provided by the clean formation of **12** upon addition of 1,5-cyclooctadiene (COD) under mild conditions. Alternatively, complex **12** can be prepared in excellent yield from **1** and [Ni(COD)₂] in THF (see ESI) or from **3** adding half an equivalent of COD (Scheme 3). Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of **12** in THF at -25°C, and proved the dimeric structure through double η^2 -coordination of the olefins to the “(dcp)Ni(o)” fragment (Figure 2d).

Finally, the coordination of CO₂ was studied. In fact, CO₂ has not only been shown to coordinate some Ni(o) fragments, but also to be coupled with alkynes in the coordination sphere of the metal.^[42,43] Significant results have been obtained in the recent years in the Ni catalyzed transformations of CO₂.^[44–48] However, only two examples of [(R₃P)₂Ni(η^2 -CO₂)] complexes have been structurally characterized to date, one with PCy₃ as ligand, known as Aresta’s complex,^[49] the other with P(*i*Pr)₃ as ligand reported by Johnson and co-workers.^[50] Additionally, the X-ray structure of the [(*t*Bu₂P(CH₂)₃P*t*Bu₂)Ni(CO₂)] complex was reported by Hillhouse and co-workers.^[51] Here, CO₂ was bubbled into a solution of **3** resulting in a slight change of colour from dark yellow to yellow. Evaporation to dryness resulted in the isolation of **10** in excellent 93% yield, proving the strong coordination of the CO₂ moiety. The complex was characterized in ³¹P NMR by two doublets at 43.5 ppm and 7.6 ppm (²J_{P-P} = 28.0 Hz) indicating a significantly different chemical environment. The CO₂ coordination was confirmed in the ¹³C NMR spectrum, in which a signal was observed at 193.7 ppm. An IR spectrum was performed on **10** in the solid state, giving a band at 1731 cm⁻¹, identical to the IR spectrum obtained by Nobile and co-workers, (who previously characterized this complex by EA and IR).^[52] It is interesting to note that the reaction of [(*i*Pr₂P(CH₂)₂P*i*Pr₂)Ni(μ -H)]₂ or [(*t*Bu₂P(CH₂)₂P*t*Bu₂)Ni(μ -H)]₂ with CO₂ resulted in the reduction of CO₂ into CO with the concomitant oxidation of the phosphine moiety, and thus the formation of multiple Ni(O) complexes.^[48,53] It therefore appears that the wider bite angle provided by the propylene bridge between the phosphine moieties, compared to the ethylene bridge has a significant impact on the stability of the CO₂ complex.

The arene ligand in Ni(o) complexes **3** and **4** are obviously readily displaced under mild conditions. The easy access to several Ni(o) complexes allowed us to evaluate their efficiency in the oxidative addition elementary step. We selected *p*CF₃-PhCl as substrate due to its electron-poor character, along with the very convenient presence of a CF₃-group allowing for easy ¹⁹F NMR reaction monitoring. Its reaction with complex **3** resulted in the fast formation (15 minutes at room temperature) of a single new species, complex [(dcp)NiCl(*p*CF₃-C₆H₄)] **13** isolated as a yellow powder in ca 90% yield. It is characterized by two doublets at 19.3 and 5.9 ppm (²J_{P-P} = 53.0 Hz) in ³¹P NMR and by a singlet appearing at -62.4 ppm in ¹⁹F NMR. In addition to this very diagnostic NMR pattern, the structure of **13** was definitively confirmed by X-ray diffraction of single crystals that were

obtained by cooling at -30°C a concentrated solution of **13** in a THF/Et₂O mixture of solvents. Complex **13** crystallizes in a square planar geometry around the Ni-center (see Figure 3). As may be expected, the Ni₁-P₁ bond distance of 2.255(1) Å in **13** (*trans* to the aromatic ring) is much longer than the Ni₁-P₂ bond distance (2.152(1) Å; *trans* to chloride). A moderate P₁-Ni₁-P₂ bite angle of 97.81(2)° (*vs* 104.09(4)°, 103.31(3)° and 106.42(2)° in **3**, **4** and **8**, respectively) is measured that once again illustrates the flexibility of the dcp ligand.

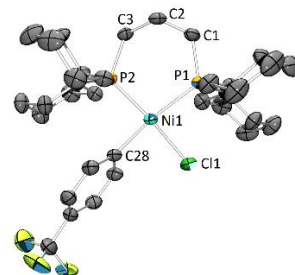
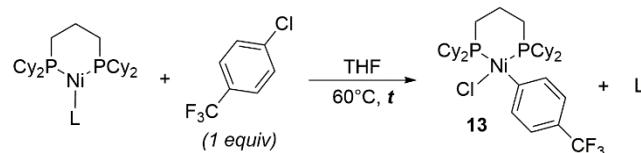


Figure 3. View of complex **13**. Thermal ellipsoids are drawn at the 50% probability level. For clarity reasons, the hydrogen and disordered atoms have not been displayed. Selected bond distances (Å) and angles (deg): Ni₁-P₁ 2.255(1), Ni₁-P₂ 2.152(1), Ni₁-C₂₈ 1.922(2), Ni₁-Cl₁ 2.219(1), P₁-Ni₁-P₂ 97.81(2), C₂₈-Ni₁-P₂ 89.19(5), C₂₈-Ni₁-Cl₁ 86.43(5), Cl₁-Ni₁-P₁ 87.52(2).

Table 1. Comparative study for the oxidative addition of 4-chlorobenzotrifluoride to complexes **3**, **4**, **6**, **8** and **12**



Entry	Complex	L Ligand	t required to reach completion
1	3	Toluene	<5 min
2	4	Naphthalene	<5 min
3	6	PhCN	60 min
4	8	PPh ₃	15 min
5	12	COD	9 days

All reactions were heated at 60°C in a J.Young NMR tube under nitrogen atmosphere starting from 19.2 μmol of the “(dcp)Ni(o)” complex, 4-chlorobenzotrifluoride (1 equiv; 19.2 μmol), and 0.6 mL of THF. Yields were determined by ¹⁹F or ³¹P NMR.

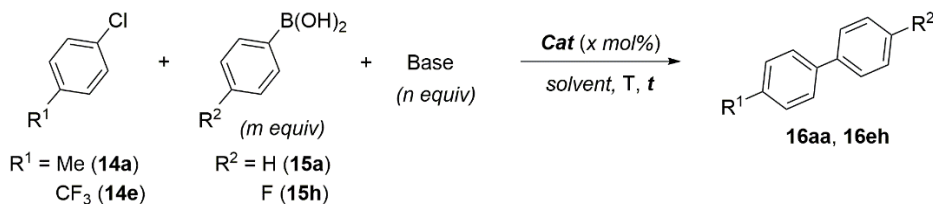
With the product complex **13** fully characterized, the oxidative addition was performed with other Ni(o) complexes: **4**, **6**, **8** and **12**. The relative rates of the oxidation reaction were compared at 60°C in THF (Table 1). The η^2 -arene Ni(o) complexes **3** and **4** produced the Ni(II) species **13** quantitatively within 5 minutes (time to record a first NMR spectrum). Complex **6** bearing the benzonitrile ligand required longer time than complex **8**, bearing PPh₃, to reach full conversion into **13** (entry 3 *vs* 4). Finally, oxidative addition from isolated complex **12** was very slow (9 days), most likely because of the extremely poor solubility of the complex, even at 60°C. It is therefore obvious that the nature of the ligand

stabilizing the 14 electron fragment [(dcp)Ni] has a very significant impact on the kinetics of the oxidative addition, and in turn will influence the overall catalytic cycle.

In line with our interest in Ni-mediated cross-coupling events, along with their associated mechanisms,^[54] we wondered whether these kinetics only depend on the strength of the Ni-L bond. In order to answer this question, the mechanism of the oxidative addition was evaluated by DFT calculations. Two mechanisms are to be envisaged for the oxidative addition of ArCl starting from a 16 electron complex [(dcp)Ni(L)], as it implies the displacement of ligand L: dissociative *vs* associative (Table 2). If the dissociative mechanism occurs, the same 14 electron intermediate [(dcp)Ni] will be formed from any complex, and the kinetics only depends on the strength of the Ni-L bond. On the other hand, in the associative mechanism, the kinetics depends on the energy of the 18 electron transition state [(dcp)Ni(L)(pCF₃-PhCl)] in which ArCl substitutes the L ligand. We thus computed the two processes starting from complexes **3**, **4**, **6**, **8** and [(dcp)Ni(C₂H₄)] as a model for complex **12** (Table 2).

It is interesting to note that the bond strength between Ni and toluene is by far the weakest ($\Delta G = 16.2$ kcal/mol *vs* 27.8 to 36.2 kcal/mol for the other ligands). In particular, it is striking that naphthalene is *ca* 11 kcal/mol more strongly bound than toluene, and closer to ethylene (27.8 *vs* 32.9). Importantly, the relative reactivity of the PPh₃ complex **8** and PhCN complex **6** cannot be rationalized only considering the Ni-L bond strength. Indeed, the Ni-PPh₃ strength is higher than the Ni-PhCN (36.2 *vs* 29.5 kcal/mol) despite leading to faster reaction. It is on the other hand consistent with the energies barrier to reach the 18 electron complexes, which is 9 kcal/mol lower for the [(dcp)Ni(PPh₃)(pCF₃-PhCl)] (**TS-X**) compared to [(dcp)Ni(PhCN)(pCF₃-PhCl)]. The highest energy barrier is found with the best acceptor of the series C₂H₄ (G = 32.9 kcal/mol). Overall, the calculations nicely reproduce the trends in the kinetics and relative rates observed for the oxidative addition. Moreover, they provide

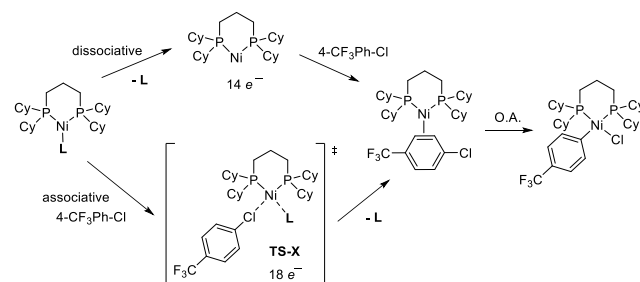
Table 3. Optimization of the reaction conditions for the “(dcp)Ni(o)”-catalyzed Suzuki-Miyaura reaction



Entry ^{a,f}	R ¹	R ²	Cat	Solvent	Base	Additive	T (°C)	t (h)	Yield (%)
1	Me (14a)	H (15a)	3	THF	3.0 K ₂ CO ₃	none	25	39.0	22 ^b
2	Me (14a)	H (15a)	3	THF	3.0 K ₂ CO ₃	none	60	87.0	73 ^b
3	Me (14a)	H (15a)	3	THF	3.0 Cs ₂ CO ₃	none	60	24.0	5 ^b
4	Me (14a)	H (15a)	3	THF	3.0 <i>t</i> BuOK	none	60	24.0	11 ^b
5	Me (14a)	H (15a)	3	THF	3.0 K ₃ PO ₄	none	60	24.0	>99 ^b
6	Me (14a)	H (15a)	3	THF	1.2 K ₃ PO ₄	none	60	24.0	41 ^b
7	CF ₃ (14e)	F (15h)	4	1,4-dioxane	3.0 K ₃ PO ₄	none	80	4.5	82 ^c
8	CF ₃ (14e)	F (15h)	4	1,4-dioxane	3.0 K ₃ PO ₄	3.0 H ₂ O	80	4.5	>99 ^c
9	Me (14a)	H (15a)	4	1,4-dioxane	3.0 K ₃ PO ₄	3.0 H ₂ O	80	16.0	>99 ^c
10	CF ₃ (14e)	F (15h)	4^d	1,4-dioxane	3.0 K ₃ PO ₄	3.0 H ₂ O	80	4.5	>99 ^c

additional insight as an associative mechanism for the oxidative addition with complexes **3**, **4** and **8** (13-23 kcal/mol) is preferred by difference with a more energetically demanding dissociative mechanism with complexes **6** and [(dcp)Ni(C₂H₄)] (> 29 kcal/mol).

Table 2. DFT evaluation of Ni-L bond strength and energies of oxidative addition in 4-chlorobenzotrifluoride



Complex	L	Ni-L bond strength (dissociative)	Energy barrier ^a (associative)
		G	G
3	Toluene	16.2	12.6
4	Naphthalene	27.8	19.3
6	PhCN	29.5	32.6
8	PPh ₃	36.2	23.1^b
Model	C ₂ H ₄	32.9	34.0

of **12**

^aCalculations at the ωB97X-D/def2-TZVPP//ωB97X-D/6-31G(d) - def2-TZVP level (see SI for details). ^bBased on a potential energy surface scan of the reaction. No TS could be located at the ωB97X-D/6-31G(d) - def2-TZVP level. Energies are given in kcal/mol.

11	CF ₃ (14e)	F (15h)	4 ^d	1,4-dioxane	3.0 K ₃ PO ₄	3.0 H ₂ O	60	2.0	80 ^c
12	CF ₃ (14e)	F (15h)	4 ^e	1,4-dioxane	3.0 K ₃ PO ₄	18.0 H ₂ O	60	2.0	60 ^c
13	CF ₃ (14e)	F (15h)	4	1,4-dioxane	1.5 KOH	1.5 H ₂ O	80	4.5	>99 ^c

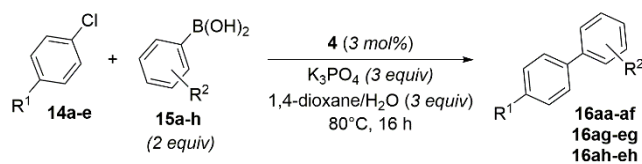
^aReactions performed in Schlenk flasks under nitrogen atmosphere using 3 mol% of catalyst loading if not otherwise specified. ^bYields determined by GC-MS analysis using *n*-decane as an internal standard. ^cYields determined by ¹⁹F NMR using 1-fluoroheptane as an internal standard. ^dCatalyst loading: 1 mol%. ^eCatalyst loading: 2 mol%. ^f1.2 equiv of the boronic acid are used in THF (entries 1-6) *vs* 2.0 equiv in 1,4-dioxane (entries 7-13).

These calculations clearly point out that both complexes **3** and **4** should be the most efficient pre-catalysts of the series for coupling processes for which oxidative additions are difficult. Accordingly, we have recently reported on the excellent catalytic activity of complex [(dcp)Ni(η^2 -toluene)] (**3**) in the Negishi type cross-coupling of aryl chlorides and ArZnCl salts.^[54b] Stoichiometric reactions and DFT-calculations allowed for the mechanism elucidation that involves a Ni(0)/Ni(II) redox scenario. We logically wondered whether this mechanism is still operative when using different transmetalating agents such as arylboronic acids, involved in the Suzuki-Miyaura Reaction (SMR).

First of all, the reaction conditions were optimized (see Table 3). With 3 mol% pre-catalyst, under nearly stoichiometric conditions (1:1.2 ArCl:Ar'B(OH)₂), the reaction requires mild heating to achieve decent yield in a rather long time (entry 2) using K₂CO₃ (3 equiv) as base. K₃PO₄ emerged as a much more efficient base (entry 5 *vs* 2-4). Most remarkably, during this optimization process the critical role of the residual amounts of water contained in the base was evidenced. In fact, the use of extensively dried K₃PO₄ in 1,4-dioxane only produced 82% of coupled product **16eh** (entry 7), whereas quantitative yield of **16eh** was reached upon addition of 3 equiv of distilled water (K₃PO₄:H₂O ratio equal to 1:1, entry 8). It even allowed reducing the catalyst charge to 1 mol% in the favorable coupling of **14e** and **15h** (entry 10 *vs* 8). However, an increase in the amount of added water had a negative effect on the reaction (compare entries 11 and 12). These observations are consistent with a recent report by Grimaud and co-workers who showed the need of residual H₂O and a base in order to gradually generate OH⁻ anions and the transmetalating [Ar-B(OH)₃]⁻ species.^[55] Finally, the coupling of **14e** and **15h** can be achieved as efficiently using 1.5 equiv of KOH and 1.5 equiv of distilled H₂O (entry 13 *vs* 8).

The scope of the SMR was then studied under the optimized conditions, *i.e.* 3 mol% catalyst **4**, 1:2:3 ratio of ArCl:Ar'B(OH)₂:K₃PO₄ at 80°C overnight in the presence of three equivalents of water (Table 4). First, 4-tolyl chloride (**14a**) was used as a model substrate and catalyst **4** proved efficient for both electron-rich (entries 1-5) and electron-poor (entries 6-8) arylboronic acids **15a-h** to produce the corresponding biaryls **16aa-ah** in excellent yields (>90%). More precisely, while electron-rich arylboronic acids **15a-e** lead to full conversion into biaryls **16aa-ae**, the introduction of electron-withdrawing substituents in the aromatic ring resulted in slightly lower yields of biaryls **16af-ah**. This phenomenon may be due to the lower nucleophilic character of fluorinated arylboronic acids and their higher propensity to undergo protodeborylation reactions.^[56,57]

Table 4. Scope of the catalytic SMR



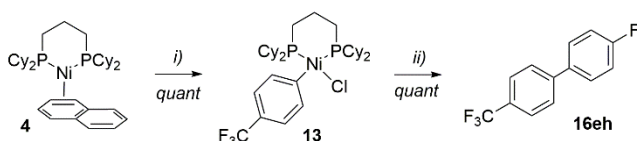
Entry ^a	R ¹	R ²	Yield (%) ^{b,c,d}
1	Me (14a)	H (15a)	>99 ^b (90)
2	Me (14a)	1-Np (15b)	>99 ^b (86)
3	Me (14a)	2-Np (15c)	>99 ^b (81)
4	Me (14a)	4-Me (15d)	>99 ^b (78)
5	Me (14a)	4-OMe (15e)	>99 ^b (90)
6	Me (14a)	4-CF ₃ (15f)	>99 ^b (95) ^e
7	Me (14a)	3,5-CF ₃ (15g)	90 ^c (68)
8	Me (14a)	4-F (15h)	95 ^c (69)
9	OMe (14b)	3,5-CF ₃ (15g)	95 ^c (26)
10	Ac (14c)	3,5-CF ₃ (15g)	90 ^c (73)
11	CO ₂ Me (14d)	3,5-CF ₃ (15g)	95 ^c (66)
12	CF ₃ (14e)	3,5-CF ₃ (15g)	95 ^c (41)
13	OMe (14b)	4-F (15h)	90 ^c (72)
14	Ac (14c)	4-F (15h)	95 ^c (45)
15	CO ₂ Me (14d)	4-F (15h)	95 ^c (96)
16	CF ₃ (14e)	4-F (15h)	95 ^c (78)

^aReactions performed in Schlenk flasks under nitrogen atmosphere starting from the appropriate aryl chloride (**14a-e**; 0.5 mmol), the corresponding arylboronic acid (**15a-h**; 1 mmol), dried K₃PO₄ (1.5 mmol), distilled water (1.5 mmol), catalyst **4** (3 mol%), and 1 mL of dry 1,4-dioxane. ^bYields determined by GC-MS analysis using *n*-decane as an internal standard. ^cYields determined by ¹⁹F NMR using 1-fluoroheptane as an internal standard. ^dIsolated yields are provided in parentheses (average of two independent runs). ^e**16af** was partially contaminated with the 4,4'-bis(trifluoromethyl)biphenyl homocoupling product.

Motivated by the recent interest for organofluorine compounds in industry,^[58] along with the important challenge of developing the SMR involving highly fluorinated arylboronic acids,^[59] our efforts were focused towards the coupling of a family of chloroarenes **14a-e** and arylboronic acids **15f-g** bearing F or CF₃-groups in the arene (see entries 6-16). Satisfyingly, **4** catalyzed the synthesis of biaryls **16af-ah**,

16bg-eg and **16bh-eh** in nearly quantitative yields (according to ^{19}F NMR analysis). The compounds were isolated in moderate to excellent yields (26–96%) after purification by flash chromatography. Finally, the scope of the transformation is not influenced by the electronic character of the substituents of the chloroaromatic and covers several functional groups such as ethers (entries 9 and 13), ketones (entries 10 and 14) and esters (entries 11 and 15).

In order to verify the plausibility of a Ni(o)/Ni(II) redox scenario during the **4**-catalyzed SMR, stoichiometric experiments were performed. As shown above, complex **4** cleanly reacts with 1 equiv of 4-chlorobenzotrifluoride (**14e**) in THF at room temperature within 2 hours to form complex **13** (Scheme 5). In agreement with Grimaud's findings,^[55] complex **13** remained unreacted in presence of K_3PO_4 (1.5 equiv) + H_2O (1.5 equiv), thus ruling out the plausible formation of a coupling-competent ArNi(II)OH key intermediate. The coupling reaction thus seems to involve the formation of the corresponding borate $[\text{Ar}-\text{B}(\text{OH})_3]^-$. Accordingly, instantaneous creation of coupled product **16eh** was achieved upon addition of 4-fluorophenylboronic acid (**15h**, 1 equiv) to the reaction mixture *via* fast transmetalation and subsequent reductive elimination. These observations provide some support for an operative catalytic loop involving Ni(o) and Ni(II) intermediates.



Scheme 5: Stoichiometric mechanistic investigations: Evidence for a Ni(o)/Ni(II) pathway. Reaction conditions: *i*) 1 equiv of 4-chlorobenzotrifluoride (**14e**) and stirring 2 hours in THF at r.t.; *ii*) 1 equiv of 4-fluorophenylboronic acid (**15h**), 1.5 equiv of K_3PO_4 + 1.5 equiv of H_2O , and stirring 2 hours in THF at r.t.

CONCLUSION

In conclusion, we have presented here an improved synthesis of complex **3** and the novel complex **4** $[(\text{Cy}_2\text{P}(\text{CH}_2)_3\text{PCy}_2)\text{Ni}(\eta^2\text{-arene})]$ (with arene = toluene and naphthalene respectively). The arene ligands in these complexes are readily displaced by stronger two electron donors. Displacement reactions with styrene, PhCN, CO, H_2 and COD (complexes **5**, **6**, **7**, **11** and **12**) were conducted with complex **3**. Moreover, rare examples of NiL_3 of the form $[(\text{diphosphine})\text{Ni}(\text{PR}_3)]$ were also isolated by this method (complexes **8** and **9**). In addition, a very rare example of $[(\text{diphosphine})\text{Ni}(\text{CO}_2)]$ complex featuring the weak ligand CO_2 has also been obtained efficiently. The capability of complexes **3** and **4** to generate under very mild conditions an equivalent of the electron rich, 14 electron “(dcpp)Ni” fragment is shown experimentally, by the oxidative addition of ArCl at Ni. Complexes **3** and **4** were therefore tested as catalysts in the coupling of chloroarenes with arylboronic acids (Suzuki-Miyaura Reaction). We evidenced the critical impact of controlled amounts of water in combination with the base in order to facilitate the transmetalation step. The optimization of the reaction conditions allowed for the preparation of a broad family of biaryls in excellent yields, including for the challenging ones bearing perfluorinated groups (F and CF_3). Preliminary stoichiometric reactions suggests the involvement of a Ni(o)/Ni(II) pathway for the SMR. The catalytic applications of complexes **3** and **4** in

other cross-coupling processes are currently undergoing in our laboratories and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The supplementary materials contain experimental and spectral details. CCDC-1960209 (**2c1**), CCDC-1960210 (**3**), CCDC-1960211 (**4**), CCDC-1960212 (**6**), CCDC-1960213 (**7**), CCDC-1960214 (**8**), CCDC-1960215 (**12**) and CCDC-1960216 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

Any additional relevant notes should be placed here.

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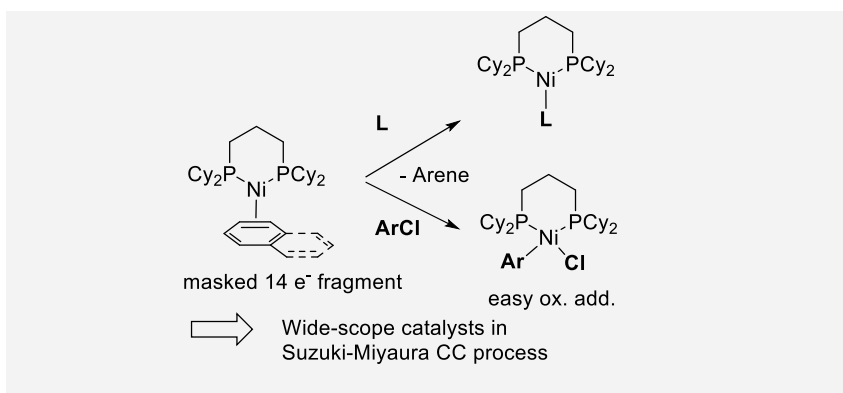
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[(dcpp)Ni(η^2 -Arene)] complexes are competent sources of the 14 electron fragment “(dcpp)Ni” as proven by easy displacement of arene by various two electron donors and fast oxidative addition in ArCl. These complexes are very efficient catalysts in the Suzuki-Miyaura cross-coupling process between ArCl and Ar²B(OH)₂.