ORGANOMETALLICS

Role of the X Coligands in Cyclometalated [Ni(Phbpy)X] Complexes (HPhbpy = 6-Phenyl-2,2'-bipyridine)

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ABSTRACT: The coligand X was varied in the organonickel complexes [Ni(Phbpy)X] (X = F, Cl, Br, I, C_6F_5) carrying the anionic tridentate C^N^N ligand 6-(phen-2-ide)-2,2'-bipyridine (Phbpy⁻) to study its effect on electronic structures of these complexes and their activity in Negishi-like C–C cross-coupling catalysis. The complexes were synthesized from the precursor [Ni(COD)₂] (COD = 1,5-cyclooctadiene) by chelate-assisted oxidative addition into the phenyl C–X bond of the protoligand 6-(2-halidophenyl)-2,2'-bipyridine) and were obtained as red powders. Protoligands X–Phbpy carrying the halide surrogates X = OMe, OTf (triflate) failed in this reaction. Single-crystal XRD allowed us to add the structures of [Ni(Phbpy)Cl] and [Ni(Phbpy)I] to the previously reported Br derivative. Cyclic voltammetry showed reversible reductions for X = C_6F_5 , F, Cl, while for Br



and I the reversibility is reduced through rapid splitting of X^- after reduction (EC mechanism). UV–vis spectroelectrochemistry confirmed the decreasing degree of reversibility along the series $C_6F_5 > F > Cl \gg Br > I$, which parallels the "leaving group character" of the X coligands. This method also revealed mainly bpy centered reduction and essentially Ni(II)/Ni(III) oxidations, as corroborated by DFT calculations. The rather X-invariant long-wavelength UV–vis absorptions and excited states were analyzed in detail using TD-DFT and were consistent with predominant metal to ligand charge transfer (MLCT) character. Initial catalytic tests under Negishi-like conditions showed the complexes to be active as catalysts in C–C cross-coupling reactions but did not display marked differences along the series from Ni–F to Ni–I.

INTRODUCTION

Cyclometalated complexes for the noble transition metals Ru, Rh, Ir, Pd, Pt, and Au carrying the anionic tridentate (Phbpy⁻) ligand have been synthesized and investigated since the early 1990s.^{1–24} Most of them were accessed through a chelateassisted C–H activation reaction, presumably after N[^]N precoordination. Corresponding complexes of the base metal nickel were first reported in 2014.^{24–26} Initially, the parent [Ni(Phbpy)Br] complex (Chart 1, top) was generated in high





yields by introduction of a bromo substituent to the 2-position of the phenyl unit and follow-up treatment with $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene), affording the desired complex by a chelation-mediated oxidative addition.²⁵ This reaction has been successfully carried out also for derivatives of Phbpy.²⁶ The $[Ni(Phbpy)(CF_3)]$ complex was synthesized from [Ni(Phbpy)-Br] through a transmetalation from $CF_3(SiMe_3)$.²⁵ More recently we have obtained the parent complex [Ni(Phbpy)Br]through an alternative pathway involving base-assisted direct C-H nickelation starting from HPhbpy and NiBr₂.²⁷ In this context we also isolated the precoordinated species $[Ni(\kappa^2-N,N-HPhbpy)Br_2]_2$.²⁷ In addition, the NCN derivatives [Ni-(PyPhPy)X] (X = Cl, Br, I, OAc) were obtained recently in good yields through similar methods.²⁸

In this contribution we synthetically widen the [Ni(Phbpy)X]motif by introducing the coligands F, Cl, I, and C₆F₅. With the (2-halidophenyl)-2,2'-bipyridines XPhbpy (X = F, Cl, Br, I,

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OMe, OTf) and $[Ni(COD)_2]$ at hand, we successfully adapted the oxidative addition method with $[Ni(COD)_2]$ (Chart 1, top). Alternatively, a transmetalation reaction with XMgBr opens up a general diversification pathway to [Ni(Phbpy)X], as exemplified here with $X = C_6F_5$ (Chart 1, bottom).

With this series of complexes we cover a broad range in electronegativity (EN) of the X coligands and expect marked differences in their contributions to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). We probed the frontier orbitals using UV-vis absorption spectroscopy and (spectro)electrochemical experiments combined with quantum chemical calculations based on density functional theory. Ready and variable access to the complex family [Ni(Phbpy)X] allowed the study of electronic effects of X substitution on the catalytic activity in nickeldependent C-C coupling. Both terpy Ni(II) complexes²⁹ (terpy = 2,2';6',2''-terpyridine) and complexes of the type $[Ni(II)(N^N)(aryl)Br]$ $(N^N = \alpha$ -diimine)³⁴⁻³⁷ have been well-studied in the context of C-C coupling reactions. Here we investigate the electronic properties and catalytic activities of nickel complexes bearing the carbanionic Phbpy⁻ for comparison. In particular, we expected that, alongside decreasing EN, the leaving-group character of the X coligands should also markedly increase. Consequently, the complexes with X = Br, I might be better precatalysts in Negishi-type C-C coupling reactions over the X = Cl, F, C_6F_5 derivatives.

RESULTS AND DISCUSSION

Preparation and Characterization of Ligands and **Complexes.** The protoligands X–Phbpy are readily accessible via the Kroehnke pyridine synthesis^{26,27,38} and have been synthesized from 2-acetylpyridine and 2'-halidoacetophenones. X-Phbpy derivatives were characterized using NMR spectroscopy and mass spectrometry, which both confirmed the successful preparation of the products and their purity (details are given in the Supporting Information). The complexes [Ni(Phbpy)X] were prepared from the protoligands X–Phbpy and $[Ni(COD)_2]$ by performing a chelation-assisted oxidative addition into the C-X bond. For X = Cl, Br the red products were immediately observed, while the blue or violet intermediates observed for X = F, I likely correspond to [Ni(X–Phbpy)(COD)].^{25,26} The latter is counterintuitive, since the C-I bond should be the most reactive for oxidative addition in the halide series. These Ni(0) intermediates were also observed for X = OMe, OTf, where the oxidative addition reaction leading to the target [Ni(Phbpy)X] complexes could not be initiated, even when the reaction mixture was heated under reflux (THF). This is remarkable in view of the recent reports of the successful nickelation of two closely related 4-(tBu)-2-(1,10-phenanthrolin-2-yl)phenol derivatives RO-(tBu)Phphen (R = triflate, pivalyl) using the same method at ambient temperature.^{39,40} Presumably, the more rigid phenanthroline vs bipyridine precoordination and the *t*Bu group which probably stratifies the phenol group to the coordination plane in conjunction with its electron-releasing property are responsible for this success.

This is in keeping with the recently reported nickelation of a phenolate-based semirigid N^{\circ}C^{\wedge}N^{\circ}O ligand using Ni(OAc)₂ under reflux in HOAc/HCCl₃ (9/1).⁴¹

MS, elemental analysis, and single-crystal XRD confirmed the successful preparation of [Ni(Phbpy)X] with X = F (82%), Cl (87%), Br (74%), I (58% yield). [Ni(Phbpy)(C₆F₅)] was synthesized by a transmetalation reaction²⁵ of (C₆F₅)MgBr with

[Ni(Phbpy)Br] in an excellent yield (98%). The new complexes were red solids, as was the parent [Ni(Phbpy)Br]. Standing for longer times in protic solvents leads to hydrolysis and formation of green paramagnetic solutions and materials which indicate nonorganometallic octahedral Ni(II) species.³⁷ The C₆F₅ complex undergoes rapid decomposition reactions in solution. The main reaction is a reductive elimination, yielding C₆F₅– Phbpy and Ni(0) species (see below).

Single-Crystal XRD. In addition to the already well-known crystal structure of [Ni(Phbpy)Br],²⁵ single crystals suitable for X-ray diffraction were obtained from a saturated CH_2Cl_2 solution of [Ni(Phbpy)Cl] and from a THF solution of [Ni(Phbpy)I].

The complex [Ni(Phbpy)Cl] crystallizes in the monoclinic space group $P2_1/n$ (isotypic with [Ni(Phbpy)Br])²⁵ containing four asymmetric units per unit cell and allowing the discrimination between N2 and C1 on the periphery of the Phbpy ligand. The structure of [Ni(Phbpy)I] was initially solved in the monoclinic space group C2/c containing a rotation axis in the middle of the molecule. N2 and C1 were refined assuming a 1/1 disorder. The failure to discriminate between C and N can be caused by the diffuse electron density of heavier atoms such as iodine, which has already been reported for an analogous Pd(II) complex.²³ To be able to define N2 and C1, we thus embarked on solving the structure in the triclinic space group $P\overline{1}$ (details are given in the Supporting Information), while no solution in the isotypic monoclinic $P2_1/n$ (found for X = Cl, Br) was obtained from the data set.

The crystal-packing structure (Figure 1, left) and the molecular structure (Figure 1, right) of [Ni(Phbpy)Cl] are



Figure 1. Crystal structure of [Ni(Phbpy)Cl] viewed along the crystallographic *a* axis (left) and molecular structure (right) with thermal ellipsoids at 50% probability. Protons are omitted for clarity.

very similar to those of the previously reported [Ni(Phbpy)Br]. Now having the series Cl–Br–I in hand, we found that in the crystal structures the completely planar complexes with X = Cl, Br, I all show head to tail stacking (Figure 1, left; more figures are given in the Supporting Information).

The Ni–X distances in the molecules increased as expected from the increasing covalent radii of the X atoms (Table 1).⁴² The Ni–N1 bond *trans* to the coligands X is rather invariant; no *trans* influence was found. All three complexes were square-planar with the sum of *cis* angles amounting to $360 \pm 1^{\circ}$ (Table 1).

In comparison with the N^CN-coordinated complexes [Ni(PyPhPy)X],^{28,41} the central Ni–N1 bond of the Phbpy (C^NN^AN coordinated) is not much longer than the central Ni–C bond (+0.01–0.02 Å) in the PyPhPy derivatives, as the stronger σ -donating power of the carbanionic phenide moiety vs pyridine would suggest. Also the Ni–X bond lengths were only about 4% longer for the PyPhPy derivatives.²⁸ Obviously, the

Table 1. Selected Atom Distances, Angles, and Dihedral Angles of [Ni(Phbpy)X] (X = Cl, Br, I) from Single-Crystal XRD^{*a*}

		X = Cl	$X = Br^{b}$	X = I				
		Distances/Å						
	Ni1-C1	1.917(3)	1.947(5)	1.967(3)				
	Ni1-N1	1.838(2)	1.848(5)	1.847(3)				
	Ni1-N2	1.973(2)	1.969(5)	1.964(3)				
	Ni1-X1	2.169(1)	2.301(1)	2.490(1)				
	Angles/deg							
	C1-Ni1-N1	83.2(1)	82.8(2)	82.4(1)				
	N1-Ni1-N2	82.3(1)	82.6(2)	82.7(1)				
	C1-Ni1-X1	97.3(1)	96.9(1)	97.6(1)				
	N2-Ni1-X1	97.3(1)	97.7(1)	97.3(1)				
	C1-Ni1-N2	165.5(1)	165.4(2)	165.1(1)				
	N1-Ni1-X1	179.2(1)	A 1.947(5) $1.9671.848(5)$ $1.8471.969(5)$ $1.9642.301(1)$ $2.490g82.8(2)$ $82.4(82.6(2)$ $82.7(96.9(1)$ $97.6(97.7(1)$ $97.3(165.4(2)$ $165.1178.7(1)$ $180.0s/deg0.49(1)$ $0.9(0.17(1)$ $1.4(s/deg360.0(1)$ $360((16 N 13 \overline{D} \overline{b} \overline{b}$	180.0(1)				
		1–N11–X1 1/9.2(1) 1/8./(1) 180.0(1) Dihedral Angles/deg						
	C1-C6-C20-N1	0.41(1)	0.49(1)	0.9(4)				
	N1-C24-C30-N2	0.21(1)	0.17(1)	1.4(1)				
	Sums of Angles/deg							
		360.1(1)	360.0(1)	360(1)				
-		W CID : Da /	1 6 17	\overline{h}				

^aStructure solution for X = Cl, Br in $P2_1/n$ and for X = I in P1. ^bFrom ref 25.

perfect match to all three donor atoms of both tridentate ligands partially overrules the stronger *trans* influence of the carbanionic phenide in comparison with pyridine.

Due to the high tendency of $[Ni(Phbpy)(C_6F_5)]$ to decompose via reductive eliminations in solution at ambient temperature, no single crystals could be obtained. Attempts to crystallize this complex at low temperatures were not successful. From a batch containing $[Ni(Phbpy)(C_6F_5)]$ and unconverted [Ni(Phbpy)Br] (from NMR analysis), we obtained single crystals of reasonable quality of the compound [Ni(κ^2 -N,N- C_6F_5Phbpy)Br₂]·THF containing a κ^2 -N,N-bound C_6F_5 -Phbpy ligand (data and figures are given in the Supporting Information). This ligand is the expected product of the reductive elimination together with zerovalent Ni. Indeed, we found Ni nanoparticles alongside this C₆F₅–Phbpy ligand as the main components in decomposed solutions of [Ni(Phbpy)- (C_6F_5)]. The peculiar product $[Ni^{II}(\kappa^2-N_1N-C_6F_5Phbpy)Br_2]$ was only obtained in the presence of the [Ni(Phbpy)Br] component in this crystallization batch, explaining the Ni +II oxidation state and the bromide ligands in this compound.

Electrochemical Experiments and Frontier MO Pattern. Akin to the parent complex [Ni(Phbpy)Br]²⁵ in THF solutions the F, Cl, and C₆F₅ derivatives show a fully reversible first reduction slightly positive of -2 V, while for [Ni(Phbpy)I]an irreversible wave is observed (Figure 2 and Table 2; further plots are given in the Supporting Information).



Figure 2. Cyclic voltammograms of [Ni(Phbpy)Cl (left) and [Ni(Phbpy)I] (right) in 0.1 M *n*Bu₄NPF₆/THF. Scan rate: 100 mV/s.

Table 2. Electrochemical Data of	[Ni((Phbpy)X	^a
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Х	$E_{1/2}(Ox1)$	$E_{1/2}(\text{Red1})$	$E_{1/2}(\text{Red2})$	$\Delta E(Ox1 - Red1)$
C_6F_5	0.32 irr ^b	-1.90	-2.59	2.22
F	0.07 irr	-1.92	-2.52	1.99
Cl	0.04	-1.93	-2.58	1.97
Br	0.08	-1.90	-2.52	1.98
Ι	0.15 irr	-1.93 irr	-2.62	2.08
^a Potentials	s in V vs	ferrocene/fer	rocenium. r	ecorded in 0.1 M

*n*Bu₄NPF₆/THF, half-wave potentials $E_{1/2}$ for reversible waves, E_{pa} = anodic peak potential or E_{pc} = cathodic peak potential for irreversible (irr) waves, scan rate 100 mV/s. ^bFurther oxidation at E_{pa} = 0.64 V.

By a decrease in the scan rate from the standard 100 to 20 mV/s, the reversibility of the Cl and the Br complexes also decreased while the waves for the F and C_6F_5 complexes remained fully reversible. This is in line with the EC mechanism already reported for the [Ni(Phbpy)Br] complex.^{25,26} After the electrochemical one-electron reduction (E) the bromide ligand is cleaved (C). Within our series of complexes, the rate of the cleavage goes with the trend of the EN and the "leaving group character" of X: $C_6F_5 \approx F < Cl \ll Br \ll I$.

Akin to previous work on the Ni(II) complexes of the metalated N^CN congener,²⁸ the coligand X in [Ni(Phbpy)X] has only a very mild effect on the reduction process, both quantitatively and qualitatively: in particular the potentials crowd at E(Red1) = -1.92 V, pointing to a ligand-centered reduction process.

Density functional theory methods corroborate this conclusion (Figure 3; computational details are given in the



Figure 3. DFT-derived frontier molecular orbitals of [Ni(Phbpy)X](X = Cl, Br, I): blue, occupied; red, virtual. Plots for X = F, C_6F_5 are given in Figures S20 and S24 in the Supporting Information.

Experimental Section). Computed metrics have been calibrated with experimental data, and an excellent match is generally observed (Table S6 in the Supporting Information). The elongated Ni–N bond located *trans* to the Ni–C bond is an artifact of the computation, as recently shown.⁴⁰ Structures constrained to the experimental metrics are isoenergetic. The π -ligand-borne character of the virtual frontier MOs is conserved along the series [Ni(Phbpy)X], as is the energy of the essentially bpy-localized lowest unoccupied molecular orbital (LUMO). Very similar results have been recently also received with Ni complexes of related phenanthroline-derived C[^]N[^]N ligands.⁴⁰ An excellent linear correlation of computed LUMO energies and experimental reduction potentials exists across a series of 17

planar Ni(II) complexes (Figure S28 in the Supporting Information; additional data are from refs 28 and 40).

For the complexes with X = F, Cl, C_6F_5 further reversible reduction waves were observed at around -2.6 V. For the substitutionally labile Br and I complexes, intermediate reduction waves were observed at around -2.3 V at slow scans for X = Br and normal scans for X = I (Figure 2), likely representing the reduction of the halide-stripped radical complex [Ni(Phbpy)(THF)]^{•.25,26}

In an allusion to the MO diagrams in Figure 3 (plots for X = F, C_6F_5 are given in Figures S20 and S24 in the Supporting Information), the three highest occupied frontier MOs are clearly metal-borne (if they are superimposed with π -interacting contributions of X and/or phenide). While our DFT settings identify the nonbonding d_{z^2} as the highest occupied molecular orbitals (HOMOs) in all cases, this assignment may well be method dependent, given the narrow clustering of the HOMO to HOMO-2 levels within <100 meV. The contribution of π^* antibonding X-ligand p orbitals to HOMO-2 becomes increasingly sizable along the series F < Cl < Br < I (Figures S20-S23 in the Supporting Information). Mulliken spin densities of doublet cations [Ni(Phbpy)X]⁺ obtained from preliminary DFT calculations indeed indicated an ever-growing localization of spin density on X along the series $F \ll Cl < Br < I$. Nevertheless, the first oxidation event in CV must be associated with the Ni(II/III) couple. Furthermore, the energies of the HOMO vary only slightly with a variation of X so that conserved oxidation potentials should prevail. Accordingly, [Ni(Phbpy)-Cl] showed a reversible one-electron-oxidation wave at around 0 V, as was likewise observed for the parent bromido complex and assigned to a Ni(II/III) couple.^{25,26} For X = F, C_6F_5 , I, irreversible oxidation waves were observed. For C₆F₅ we assume that oxidation induces the notorious reductive elimination, as was also found for the CF_3 derivative previously.²⁵ For X = F we have evidence from EI-MS for a similar oxidatively induced reductive elimination forming F-Phbpy (Figure S5 in the Supporting Information), in line with our failure to obtain single crystals of this complex. For X = iodide we believe that the iodide ligand is the final "hole acceptor" (electron donor),⁴³ after initial oxidation of the Ni(II) center.

The electrochemical band gap is conserved at about 2 V for X = F, Cl, Br, I, in keeping with the small variations of the LUMO and HOMO energies almost compensating each other (Figure 3). The slightly higher value of 2.2 V for $X = C_6F_5$ very probably reflects the essentially covalent Ni–C bond of the C_6F_5 coligand in comparison with the ionic Ni–X bonds.

UV–Vis Absorption Spectroscopy and TD-DFT Calculations. The nature and energy span of the frontier MOs of the entire complex series suggests the existence of optical transitions with MLCT character in the visible spectral range. Indeed, the optical spectra of the complexes all feature significant absorption bands across the visible range up to 600 nm (THF solution; Figure 4 and Table 3).

In agreement with the largely X invariant redox chemistry and the conserved MO pattern, the five complexes show very similar spectral features. Four sets of absorption bands are found in all spectra, peaking at around 520 nm (λ_1), 410 nm (λ_2), 360 nm (λ_3), and 280 nm (λ_4). The partially structured long-wavelength envelope between 450 and 600 nm (2000 < ε_{max} (L mol⁻¹ cm⁻¹) < 5000) is in line with the visually observed red color. While the energies of the main maxima are almost identical, the intensities vary markedly. The same is true for the bands at around 400 nm and the two UV bands at 350 and 280 nm (Table 3).



Figure 4. Experimental UV–vis absorption spectra of [Ni(Phbpy)X](X = C₆F₅, F, Cl, Br, I) in THF (top). TD-DFT derived convoluted and line spectra of [Ni(Phbpy)X] (bottom).

In order to receive insights into the character of the underlying individual optical transitions, the spectra were modeled with TD-DFT methods. A very satisfying match of the experimental band energies and intensities was obtained with TPSSh/QZVP settings (bottom in Figure 4), which are well suited to model planar Ni(II) complexes.^{28,39,40,44,45}

With a view to the intensity ($\varepsilon \gg 1000 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) an assignment of the leading transitions as ligand field (d–d) absorption bands can be ruled out. While the three expected d–d transitions of planar d⁸ nickel(II), that is, {}^{1}A_{1g} \rightarrow {}^{1}B_{1g}, ${}^{1}A_{1g} \rightarrow {}^{1}B_{3g}$, and ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$, 46 certainly contribute, TD-DFT results for [Ni(Phbpy)Br] and derivatives with substituted Phbpy²⁶ had rather pointed to an interpretation in terms of metal to ligand charge transfer bands (MLCT; $d_{Ni} - \pi^*_{bpy}$).

In keeping with this, the present TD-DFT difference densities derived of diagnostic transitions of [Ni(Phbpy)Br] reveal predominant MLCT character for the low-energy band (Figure 5; plots for for X = F, Cl, I are given in Figures S25–S27 in the Supporting Information). It is noted that for X = Cl, Br, I the HOMO \rightarrow LUMO transition has vanishing intensity; this is a recurrent finding for this class of compounds. The energies of the leading vis transitions decrease along the series C₆F₅ > F > Cl = Br > I, which is consistent with the EN of the halides. Toward

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	$X = C_6 F_5$	X = F	X = Cl	X = Br	X = I
$\lambda_1\left(arepsilon ight)^a$	$496^{b}(1.60)$	$504^{c}(2.10)$	506 (3.47)	509 (2.81)	513 (3.11)
$\lambda_2 (\varepsilon)^a$	402 (2.10)	401 (4.03)	391 (2.67)	392 (3.28)	401 (2.68)
$\lambda_{3}\left(arepsilon ight)^{a}$	351 (7.45)	353 (12.0)	354 (15.3)	355 (11.0)	352 (10.3)
$\lambda_{4}\left(arepsilon ight)^{a}$	277 (14.7)	277 (23.9)	281 (26.7)	282 (20.2)	276 (34.0)
spectral onset ^d	2.50	2.46	2.45	2.44	2.42

Table 3. Absorption Maxima of the [Ni(Phbpy)X] (X = C₆F₅, F, Cl, Br, I) Complexes

^{*a*}Measured in THF, with absorption maxima λ in nm and molar absorption coefficients ε in 1000 L mol⁻¹ cm⁻¹. ^{*b*}Long-wavelength shoulder at 560 nm. ^{*c*}The band extends up to 540 nm. ^{*d*}In eV.



Figure 5. TD-DFT derived difference densities of diagnostic vis and near-UV transitions: orange, source; blue, sink.

the UV regime the transitions are of mixed MLCT/L'LCT character ($\pi_{Ph}-\pi^*_{bpy}$ with minor contributions of X; Figure 5).

UV-Vis Spectroelectrochemistry (SEC). SEC measurements were carried out on the complex [Ni(Phbpy)Cl] (Figure 6) to probe for the corresponding orbitals and the overall

Figure 6. UV–vis absorption spectra recorded during electrochemical reductions of [Ni(Phbpy)Cl] in in 0.1 M *n*Bu₄NPF₆/THF, in 0.1 V steps.

reversibility of the redox processes. During the first reduction, structured long-wavelength bands appear in the ranges 700–1000 and 480–600 nm. Together with the intense band at 380 nm, they are typical for a bpy-centered reduction, as was expected on the basis of the CV discussion and the MO pattern (see above).

Similar spectra were observed previously in the parent complex [Ni(Phbpy)Br] and also in the noncyclometalated complexes [Ni(bpy)(Mes)Br] and $[Ni(bpy)Mes)_2]$ (Mes =

2,4,6-trimethylphenyl).^{25,26,34–36} Upon further reduction, the band system at 700–1000 nm shifts to 650–800 nm, while the 480–600 nm band system undergoes a slight red shift and the 380 nm band massively intensifies concomitant with a red shift to 420 nm. This is typical for 2-fold-reduced Ni(II) complexes of bpy.^{25,35} In a return to the initial potential after the first reduction, the original spectrum could not be restored. Although in the CV experiment the reduction is reversible, the far slower SEC experiment reveals chemical irreversibility, most probably due to the Ni–Cl scission after reduction (EC), which was discussed above.

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The same behavior was observed for the [Ni(Phbpy)F] and $[Ni(Phbpy)(C_6F_5)]$ derivatives (Figure S16 and S17 in the Supporting Information). During oxidation, the three longwavelength bands are markedly bleached, while a band at about 320 nm grows in (Figure \$19 in the Supporting Information). The disappearance or marked blue shift of the long-wavelength bands is in line with the MLCT character of these bands. Removal of an electron from a metal-borne orbital necessarily results in stabilization of this orbital (blue shift) and a loss of intensity. At the same time, in the EI-MS(+) spectra of [Ni(Phbpy)X] the $[M]^+$ signature of the C–C coupled ligand 2,2'-bis((2,2'-bipyridin)-6-yl)-1,1'-biphenyl ($C_{32}H_{22}N_4$) is observed alongside the [Ni(Phbpy)]⁺ and [Phbpy]⁺ fragments (see the Experimental Section). This C-C coupling is consistent with a mechanism that involves removal of one electron from the Ni-C bond, leaving oxidized Ni(III) and a bpyPh[•] radical intermediate. For the $X = F_{1}, C_{6}F_{5}$ derivatives a very similar bleaching of the long-wavelength band was observed upon oxidation (Figures S16 and S17 in the Supporting Information). The remaining bands lie markedly below 300 nm, indicating the presence of the protoligands XPhbpy (X = F, C_6F_5). They were presumably produced by a reductive elimination after oxidation. In contrast to this, after exhaustive oxidation of the chlorido complex [Ni(Phbpy)Cl] intense UV bands at 320 nm very probably represent the C-C coupled bpyPh–Phbpy (Figure S18).

Negishi-Type C–C Cross-Coupling Catalysis. Mechanistically, the reduction of the Ni(II) precatalyst and the cleavage of halide coligands play an important role in Negishi-type C–C cross-coupling reactions.^{29–35} The four halogenido complexes [Ni(Phbpy)X] (X = F, Cl, Br. I) were submitted to two typical test reactions (Scheme 1) to probe for the effect of the X coligand.

After a 12 h reaction time, the mixtures were studied using GC-MS with hexamethylbenzene as an internal standard. In addition to the starting materials, the targeted C–C cross products 4-pentyltoluene and 4-(2-(1,3-dioxan-2-yl)ethyl)-toluene were observed alongside the homocoupling products *n*-decane (homoalkyl coupling), 4,4'-bis-toluene, and bis((1,3-dioxan-2-yl)ethan-1yl) (homoaryl coupling). The cumulative

Scheme 1. C–C Coupling Reactions under Negishi Conditions a

^{*a*}Conditions: 5 mol % of [Ni(Phbpy)X] precatalysts (X = F, Cl, Br, I), 12 h, stirring at ambient *T*, in THF.

yields increased from 47 to 61% along the series X = I < Br < Cl < F for reaction I (Figure 7).

Figure 7. Yields of the C–C cross coupling, homo aryl and homo alkyl coupling, and accumulated yields for reaction I (left) and reaction II (right) using the complexes [Ni(Phbpy)X] (X = F, Cl, Br, I) as precatalysts.

To exclude the presence of Pd particles in the precatalyst material, ICP-OES measurements with a detection limit of 3 ppb were carried out on a number of [Ni(R-Phbpy)Br] derivatives, including the parent complex [Ni(Phbpy)Br], and on the Ni precursor $[Ni(acac)_2]$ for the $[Ni(COD)_2]$. In none of the materials did we find Pd.

The yields of the targeted C–C cross product 4-pentyltoluene vary only slightly from 40 to 45% with no correlation with the EN or leaving-group character of the X coligand. In addition, the product selectivity, measured as the heterocoupling/homocoupling product ratio, is very similar for the complexes with X = F, Cl, Br (ratio 2.3–3.4, Table S7 in the Supporting Information). Strikingly, however, the iodido complex exhibited a markedly higher ratio (11/1). Quite clearly, the selectivity in the hetero/homo ratios is inversely coupled to the cumulative yields, but even if the ratio is corrected through the cumulated yields, the iodide complex is still markedly more selective.

For reaction II the cumulative yields are in the same range as for reaction I with, once more, the iodido complex showing the lowest yield. Generally, the product selectivity for reaction II was markedly lower than for reaction I (Table S8). In keeping with the leaving-group hypothesis, however, the complexes with X =Br, I still reach a hetero/homo ratio of about 1, while for X = Cl, F the homocoupling products are prevalent.

We tentatively ascribe the huge difference in terms of selectivity for reaction I vs reaction II to the possibility for Zn to form a chelate binding using the dioxane function in reaction II, thus tuning its reactivity. Similar phenomena have been reported previously.^{47–49} Further, the role of the different halides might go beyond that of being a more or less suitable leaving group. Salt byproducts are known to play a critical role in Negishi cross-coupling reactions.^{50,51}

For comparison we tested some of the previously reported complexes [Ni((R)Phbpy)Br] (H-(R)Ph(R')bpy = substituted 6-phenyl-2,2'-bipyridine; Figure 8). For reaction I the accumulated yields range from 25 to 56%, thus being somewhat

Figure 8. Yields of the C–C cross coupling, homo aryl and homo alkyl coupling, and accumulated yields for reaction I (left) and II (right) using the complexes [Ni(R-Phbpy)Br] as precatalysts.

lower in comparison with that for the unsubstituted [Ni-(Phbpy)Br] (57%). For reaction II the yields are markedly higher, ranging from 38 to 72%. The best catalyst for both reactions in terms of selectivity is the complex [Ni(Ph(4'-(3-MeOPh)bpy)Br] with a 3-MeO-substituted 4'-bpy ligand, while the complex [Ni((3-MeOPh)bpy)Br] shows the highest total yields (Tables S9 and S10). Unfortunately, the small number of samples in view of the largely varying yields and selectivities preclude a structure–activity correlation at this stage.

CONCLUSIONS

Nickel-driven C-C coupling schemes imply redox-dependent labilization of the coordination sphere. Herein we have addressed this hypothesis through the synthetic variation of potentially labile, anionic coligands X in planar nickel(II) platforms, [Ni(Phbpy)X] (with X = F, Cl, Br, I, C₆F₅). The complexes with X = F, Cl, Br, I were synthesized in good (58%) to excellent (87%) yields from $[Ni(COD)_2]$ (COD = 1,5cyclooctadiene) by chelate-assisted oxidative addition into the phenyl C-X bond of the protoligand 6-(2-halidophenyl)-2,2'bipyridine, whereas the $[Ni(Phbpy)(C_6F_5)]$ derivative was accessible in excellent yield using the $(C_6F_5)MgBr$ Grignard reagent. Their use in hetero-C-C coupling revealed the entire series of complexes to be good catalysts under Negishi-type conditions. A comparison of precatalysts with varying X coligands and with R substituents on the Phbpy ligand indeed indicated a selectivity-steering influence of X, $I \gg Br > Cl \approx F$, which appears to scale inversely with the overall turnover. In contrast to this, the derivatives [Ni(R-Phbpy)Br] were highly sensitive to the nature of the R substituent on the phenyl core.

An interpretation in terms of a combined effect of varied electronegativity and leaving-group character of the coligand X is corroborated by DFT-augmented (spectro-)electrochemical investigations. That is, the reversibility of the reduction and oxidation waves of the Phbpy complexes is massively altered with varying X coligands, while the potentials are rather conserved. Variable mixing of Ph and X contributions to the essentially Ni centered highest occupied molecular orbitals (HOMO) compensates for the variation in X, in complete agreement with the invariant electrochemical data, $E_{1/2}(Ox1)$, and the likewise X-invariant long-wavelength UV-vis absorptions. The corresponding excitations were analyzed in detail using TD-DFT and were consistent with metal to ligand charge transfer (MLCT) character. The scan-rate-dependent electrochemical reduction of [Ni(Phbpy)X] increasingly gained irreversible character for X = Br, I, whereas reduction remained fully reversible for $X = F_1 C_6 F_5$, even at the lowest scan rates. The redox-dependent lability of the Ni-X bond clearly shows up in

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the lack of reversibility in spectroelectrochemical reduction– reoxidation cycles. Reduction potentials could be linearly correlated with DFT-derived LUMO energies. This assignment allows us to make a clear distinction between complexes derived from isomeric metalating ligands: that is, C^N^N and N^C^N. When the C^N^N-coordinated [Ni(Phbpy)X] complexes are compared with the N^C^N-coordinated derivatives [Ni-(PyPhPy)X], the different location of the carbanionic phenide group causes a great difference in the long-wavelength absorption energies (-0.4 eV) and the reduction potentials (-0.4 V), which clearly shows the superior π -accepting capacity of the bpy moiety in Phbpy in comparison with the two electronically "isolated" pyridines in PyPhPy. Interestingly, the bonding of X coligands is much less affected by this location. We will embark on further catalytic tests to assess this parameter.

EXPERIMENTAL SECTION

Instrumentation. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker Avance II 300 MHz (¹H, 300 MHz; ¹³C, 75 MHz; ¹⁹F, 282 MHz) double-resonance (BBFO) 5 mm observation probehead with a z-gradient coil spectrometer. Chemical shifts were relative to TMS. UV-vis absorption spectra were recorded on a Varian Cary 05E spectrophotometer. Elemental analyses were obtained using a HEKAtech CHNS EuroEA 3000 analyzer. EI-MS(+) spectra were measured with a Finnigan MAT 95 instrument. Simulations were performed using ISOPRO 3.0. Electrochemical measurements were carried out in 0.1 M *n*Bu₄NPF₆ solution in THF using a three-electrode configuration (glassy-carbon electrode, Pt counter electrode, Ag/AgCl reference) and a Metrohm Autolab PGSTAT30 potentiostat and function generator. The potentials were referenced against the ferrocene/ferrocenium redox couple as an internal standard. UV-vis spectroelectrochemical measurements (in 0.1 M nBu₄NPF₆ solution in THF) were performed using an optically transparent thin-layer electrode (OTTLE) cell^{52,53} at room temperature. For single-crystal structure analyses (XRD), crystals were obtained from CH₂Cl₂ solutions layered carefully with dry hexane. Measurements were performed at 170(2) K using an IPDS IIT (STOE and Cie) diffractometer, all with Mo K α radiation ($\lambda = 0.71073$ Å) employing the $\omega - \varphi - 2\theta$ scan technique. The structure was solved by direct methods using SIR 2014,⁵⁴ and refinement was carried out with SHELXL 2016 by employing full-matrix least-squares methods on $F_0^2 \ge$ $2\sigma(F_0^{-2})$.⁵⁵ The numerical absorption corrections (X-RED; Stoe and Cie, 2006) were performed after optimizing the crystal shapes using X-SHAPE (Stoe and Cie, 2006).⁵⁶ The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The hydrogen atoms were included by using appropriate riding models. Data of the structure solutions and refinements for [Ni(Phbpy)Cl] (CCDC 1484145), [Ni(Phbpy)I] (1821672), and [Ni(F₅C₆Phbpy)-Br₂]·THF (1484538) can be obtained free of charge at https:// summary.ccdc.cam.ac.uk/structure-summary-form or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ UK (fax + 44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

Computational Calculations (DFT). Electronic structure calculations on the complexes have been performed through density functional theory (DFT) methods using the ORCA program package.⁵⁷ For all optimizations triple- ξ -valence TZVP⁵⁸ basis sets were used with the generalized gradient approximated functional BP86.⁵⁹ Pertinent metrical data are arranged in Table S6 in the Supporting Information alongside experimental data, showing good agreement of calculated and experimental metrics. Molecular orbitals and electronic properties were extracted from single-point calculations in the optimized positions with the global hybrid functional TPSSh⁶⁰ and quadruple- ξ -valence QZVP basis sets. Grimme's third-generation D3 correction of dispersion was used;^{61,62} medium effects were approximated in a dielectric continuum approach (COSMO), parametrized for THF.⁶³ Coordinates of the computed structures are assembled in the COORDINATES file in the Supporting Information; frontier orbital landscapes are shown in Figure 3 and Figures S20–S24 in the Supporting Information. For each

complex the 70–90 lowest optical electronic transitions (Figure 5 and Figures S25–S27 in the Supporting Information) were assessed with ORCA implemented TD-DFT methods within the Tamm–Dancoff approximation.

Materials. Commercially available chemicals were purchased from Sigma-Aldrich, Acros, ABCR, or Fisher-Scientific and were used without further purification. Dry THF was obtained from distillation over sodium/potassium alloy.

Preparation of the XPhbpy (X = F, Cl, Br, I, OH, OMe, OTf) Protoligands and [Ni(COD)₂]. The preparation is described in the Supporting Information.

Preparation of the Complexes [Ni(Phbpy)X]: General Procedure. Under an inert atmosphere the corresponding 6-(2-halidophenyl)-2,2'-bipyridine derivative (1.0 mmol) was dissolved in 8 mL of dry THF. A 2 mL portion of a freshly prepared 0.5 M suspension of $[Ni(COD)_2]$ in dry THF was added to the solution. The mixture turned dark red, and a red precipitate formed. After 22 h of stirring at ambient temperature the solution was decanted. The solid was washed with 10 mL of dry pentane and dried under vacuum.

[*Ni*(*Phbpy*)*F*]. Yield: 3 g (13.2 mmol, 82%). Anal. Found (calcd) for C₁₆H₁₁N₂NiF (M = 308.97 g mol⁻¹): C, 62.09 (62.20); H, 3.55 (3.59); N, 9.02 (9.07). ¹H NMR (600 MHz, CD₂Cl₂): δ 8.74 (s, 1H, H6'), 8.03 (m, 1H, H4'), 7.85 (m, 1H, H3'), 7.79 (m, 1H, H3), 7.59 (m, 1H, H4), 7.42–7.37 (m, 2H, Ha, H5'), 7.32 (m, 1H, H5'), 7.13–7.06 (m, 3H, Hc, Hd, Hb) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ –180.7 ppm. EI-MS(+): m/z 308 [M]⁺, 289 [M − F]⁺, 250 [FPhbpy]⁺, 462 [bpyPh–Phbpy]⁺. In solution, this complex readily undergoes a decomposition reaction. In one of them, a reductive elimination yields F−Phbpy comparable to what has been observed for the CF₃ complex [Ni(Phbpy)(CF₃)].²⁵ Data for F−Phbpy are given in the Supporting Information.

[Ni(Phbpy)Cl]. Yield: 3.7 (13.9 mmol, 87%). Anal. Found (calcd) for C₁₆H₁₁N₂NiCl (M = 325.42 g mol⁻¹): C, 59.02 (59.05); H, 3.45 (3.41); N, 8.66 (8.61). ¹H NMR (600 MHz, CD₂Cl₂): δ 8.99 (d, 1H, H6'), 8.03 (m, 1H, H4'), 7.90 (m, 1H, H3'), 7.87 (m, 1H, H3), 7.56 (m, 1H, H4), 7.53–7.50 (m, 3H, Ha, H5, H5'), 7.33 (m, 1H, Hc), 7.09 (m, 2H, Hd, Hb) ppm. EI-MS(+): m/z 324 (100%), 326 (72%) [M]⁺, 289 [M – Cl]⁺, 462 [bpyPh–Phbpy]⁺,266 [ClPhbpy]⁺.

[*Ni(Phbpy)Br*]. Yield: 3.7 g (11.8 mmol, 74%). Anal. Found (calcd) for $C_{16}H_{11}N_2NiBr$ (M = 369.87 g mol⁻¹): C, 51.92 (51.96); H, 3.01 (3.00); N, 7.61 (7.57). ¹H NMR (300 MHz, CD₂Cl₂): δ 9.20 (s, 1H, H6'), 7.98 (m, 1H, H4'), 7.89 (m, 1H, H3), 7.84 (m, 1H, H3'), 7.77 (m, 1H, Ha), 7.53 (m, 1H, H4), 7.48 (m, 1H, H5'), 7.42 (m, 1H, H5), 7.29 (m, 1H, Hc), 7.05 (m, 1H, Hd), 7.01 (m, 1H, Hb) ppm. EI-MS(+): m/z 370 (100%), 368 (72%) [M]⁺, 289 [M – Br]⁺.

[*Ni(Phbpy)I*]. Yield: 3.7 g (9.3 mmol, 58%). Anal. Found (calcd) for $C_{16}H_{11}N_2NiI$ (M = 416.87 g mol⁻¹): C, 46.12 (46.10); H, 2.71 (2.66); N, 6.74 (6.72). ¹H NMR (300 MHz, CDCl₃): δ 8.69 (dd, J = 4.8, 0.8 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.41 (dd, J = 7.9, 0.8 Hz, 1H), 7.95–7.63 (m, 4H), 7.53–7.48 (m, 1H), 7.43–7.27 (m, 3H) ppm. EI-MS(+): m/z 370 (100%), 368 (72%) [M]⁺, 289 [M – I]⁺, 358 [IPhbpy]⁺, 462 [bpyPh–Phbpy]⁺.

Preparation of [Ni(Phbpy)(C₆F₅)]. Under an inert atmosphere 185 mg of [Ni(Phbpy)Br] (0.5 mmol) was dissolved in THF. At 0 °C 0.5 mmol of freshly prepared C₆F₅MgBr solution in THF was added dropwise to the solution. After 18 h of stirring at room temperature, the mixture was filtered under an argon atmosphere before the solvent was removed under reduced pressure. The resulting dark red solid was washed with 10 mL of dry pentane. Yield: 224 mg (0.49 mmol, 98%). Anal. Found (calcd) for $C_{22}H_{11}F_5N_2Ni$ (*M* = 457.02 g mol⁻¹): C, 57.72 (57.82); H, 2.42 (2.43); N, 6.14 (6.13). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.95 (dt, 1H, J = 7.70, 1.54 Hz), 7.86 (t, 2H, J = 7.86 Hz), 7.76 (d, 1H, *J* = 5.31 Hz), 7.57 (d, 2H, *J* = 11.98 Hz), 7.54 (d, 2H, *J* = 12.16 Hz), 7.34 (dt, 2H, J = 10.25, 1.37 Hz), 7.00 (dt, 1H, J = 7.42, 1.23 Hz), 6.88 (dt, 1H, J = 7.41, 1.43 Hz), 6.31 (d, 1H, J = 7.35 Hz) ppm. ¹⁹F NMR (282) MHz, CD₂Cl₂): δ –164.3 (m, 2F, 3,5-F), –162.2 (tt, 1F, J = 19.57, 2.21 Hz, 4-F), -116.0 (m 2F, 2,6-F) ppm. EI-MS(+): *m*/*z* 456 [M]⁺, 289 $[M - C_6F_5]^+$. In solution, this complex readily undergoes reductive elimination, yielding F₅C₆–Phbpy data (¹H NMR (300 MHz, CD₂Cl₂) δ 8.62 (d, 1H, J = 4.11 Hz), 8.35 (d, 1H, J = 7.86 Hz), 7.98 (d, 1H, J =

8.01 Hz), 7.84 (dd, 1H, *J* = 7.47 Hz), 7.75 (dt, 1H, *J* = 1.67, 7.74 Hz), 7.66 (dt, 1H, *J* = 7.51, 1.37 Hz), 7.59 (dt, 1H, *J* = 1.38, 7.47 Hz), 7.47 (dd 1H, *J* = 6.39 Hz), 7.30 (dd, 1H, *J* = 12.25, 0.93 Hz), 7.27 (dd, 1H, *J* = 2.49, 0.99 Hz) ppm; ¹⁹F NMR (282 MHz, CD₂Cl₂) δ –164.3 (m, 2F, 3,5-F), -157.49 (t, 1F, *J* = 20.78 Hz, 4-F), -141.72 (m, 2F, *J* = 23.23, 7.96 Hz, 2,6-F) ppm; EI-MS(+) *m*/*z* 398) comparable to those observed for the CF₃ complex [Ni(Phbpy)(CF₃)].²⁵

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00237.

Details on the synthesis of the new complexes and the C– H activation reactions, NMR spectra, further pictures of the crystals, and molecular structures with tables of all parameters (PDF)

Cartesian coordinates of the calculated structures (PDF)

Accession Codes

CCDC 1484145, 1484538, and 1821672 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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