Organometallic Ni(II), Ni(III), and Ni(IV) Complexes Relevant to Carbon-Carbon and Carbon-Oxygen Bond Formation Reactions

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Herein, the pyridinophane tetradentate ligand 3,6,9-trimethyl-3,6,9,15-Tetraazabicyclo[9.3.1]pentadeca-1(15),11,13-triene, $PyNMe_3$, is used to isolate and structurally characterize well-defined organometallic Ni(II) and Ni(III) complexes bearing the cycloneophyl fragment, an alkyl/aryl C-donor ligand. Furthermore, spectroscopic and cryo-mass spectrometry studies suggest the formation of a transient Ni(IV) organometallic complex, and its relevance to C-C and C-O bond formation reactivity studies is discussed.

Introduction

The formation of new C-C and C-heteroatom bonds through transition-metal catalyzed cross-coupling reactions (i.e., Suzuki, Kumada, and Negishi reactions) is currently one of the most powerful tools in organic chemistry.[1-3] In this context, noble metal-based systems are the more commonly used catalysts for these transformations, due to their widely known mechanistic understanding.[4-7] For example, Pd-catalyzed reactions usually occur via Pd^0/Pd^{II} catalytic cycles and mostly involve diamagnetic intermediate species, which makes their characterization more feasible.[8] In contrast, the mechanisms of Ni-catalyzed cross-coupling reactions are far less understood since this first-row transition-metal can easily undergo both one- and two-electron redox processes, often involving paramagnetic intermediate species that lead to more complex mechanistic pathways.[9-11] Although traditionally Ni-catalyzed cross-coupling reactions have been proposed to involve Ni^0, Ni^I and Ni^{II} intermediates,[12-14] recent studies suggest that high-valent Ni^{III} and Ni^{IV} species are key intermediates in the C-C/C-heteroatom bond-forming step.[15-24]

Pyridinophane tetradentate ligands have been shown to stabilize uncommon high-valent organometallic nickel complexes. Indeed, in the past several years, Mirica and co-workers have employed a series of tetradentate pyridinophane ligands with different amine N-substituents ($^RN4$ ligands, R = Me, Ts, ^{i}Pr, ^{t}Bu, Np) as well as the tridentate 1,4,7-trimethyl-1,4,7-triazacyclononane ligand (Me_3tacn) to stabilize $Ni^{III/IV}$ complexes (Fig. 1a), as well as $Pd^{II/IV}$ complexes, that undergo C-C/C-heteroatom bond formation reactions.[25-40] Recently, a macrocyclic N-based tetradentate ligand $PyNMe_3$ has been employed by Costas, Company and co-workers to stabilize high-valent intermediate species and has proved successful to trap $Fe^{IV/V}$-oxo species (Fig. 1b) and dinuclear Cu^{II} side-on peroxo species.[41-45] However, the use of the $PyNMe_3$ ligand has

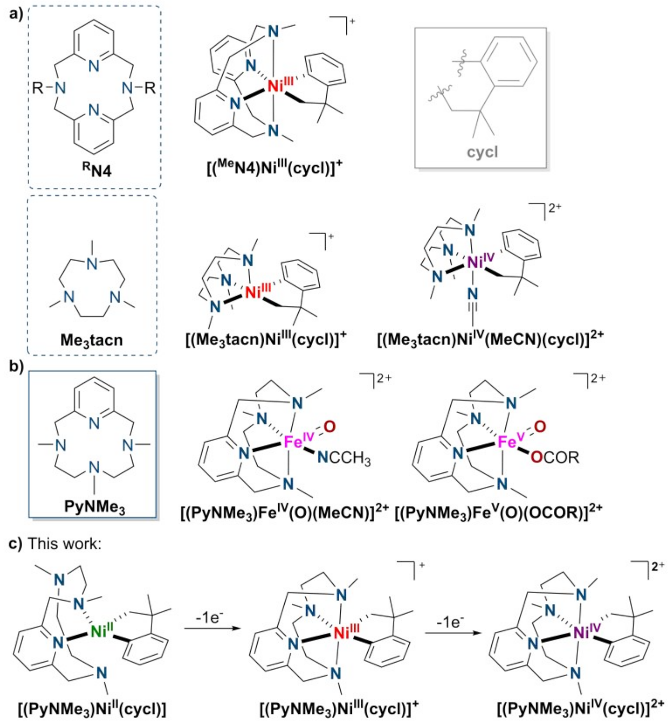

Fig. 1 a) Isolated organometallic nickel complexes bearing tridentate or tetradentate *N*-donor ligands and cycloneophyl as the C-donor ligand; b) Spectroscopically characterized high-valent iron-oxo intermediate species relevant for O_2 activation chemistry bearing the tetradentate *N*-based $PyNMe_3$ ligand, and c) Synthesis of well-defined organometallic nickel complexes bearing the $PyNMe_3$ and the cycloneophyl ligands and their C-C and C-O bond formation reactivity.

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never been employed to explore the reactivity of organometallic Ni complexes.

Herein we report the synthesis, characterization, and initial reactivity studies of a series of organometallic Ni^{II}, Ni^{III} and Ni^{IV} complexes supported by the $PyNMe_3$ ligand and containing the cycloneophyl fragment, an alkyl/aryl C-donor ligand (Fig. 1c). The cycloneophyl ligand was developed by Carmona *et al.* as an ancillary ligand to isolate organonickel complexes, since the resulting Ni(cycloneophyl) complexes are less prone to reductive elimination or β-hydride elimination.[46-48] In addition, the cycloneophyl moiety has been widely and successfully employed together with N-based ligands independently by Sanford and Mirica in order to study C-C and C-heteroatom bond forming reactions.[31-33, 49-54] The current study reports the reactivity of the isolated $(PyNMe_3)Ni^{II}(cycl)$ complex with oxidants to promote C-C or C-O reductive elimination through Ni^{IV} intermediate species is described.

Results and Discussion

Our first attempt to isolate organometallic nickel complexes bearing the $PyNMe_3$ ligand consisted of the *in situ* oxidative addition of 1-bromo-4-fluorobenzene using $Ni(cod)_2$. The putative $[(PyNMe_3)Ni^{II}(p\text{F-Ph})(Br)]$ complex could not be isolated due to fast decomposition and rapid ligand exchange that leads to the formation of 0.5 equiv $(PyNMe_3)Ni^{II}Br_2$ (**1-Br**) and 0.5 equiv $[(PyNMe_3)Ni^{II}(p\text{F-Ph})_2]$. The latter di-aryl complex then undergoes reductive elimination to afford the homocoupled product *p*F-Ph-Ph-*p*F (as detected via GC-MS), free ligand and Ni(0) (Fig. 2a). In addition, reaction of $[(PyNMe_3)Ni^{II}(Cl)_2]$ (**1-Cl**) with MeMgCl in THF at -50ºC led to an intractable mixture due to fast decomposition of the desired nickel(II)-dimethyl complex (Fig. 2b). Nonetheless, the putative $[(PyNMe_3)Ni^{II}(Me)_2]$ species could only be detected via ^{1}H NMR, which revealed two singlets below 0 ppm that integrated to three protons each and presumably correspond to the two inequivalent methyl groups directly attached to the Ni center (Figure S1).

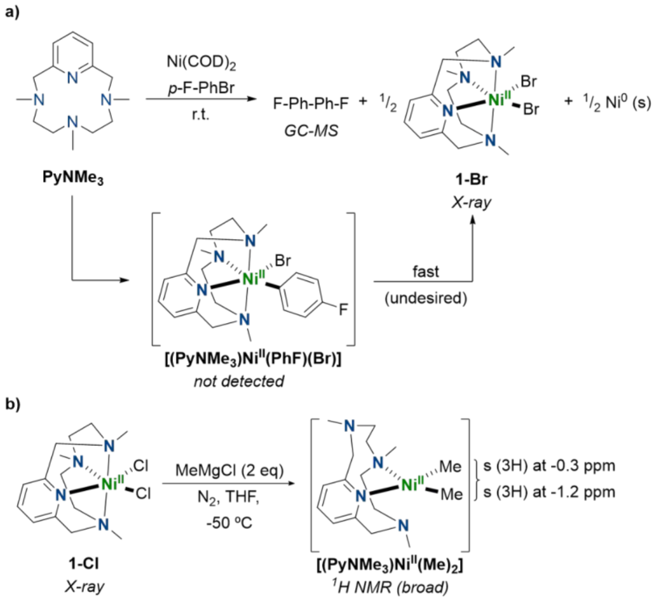


Fig. 2 a) Attempt to synthesize $[(PyNMe_3)Ni^{II}(PhF)(Br)]$ via oxidative addition at nickel(0), and b) Attempt to synthesize $[(PyNMe_3)Ni^{II}(Me)_2]$ via transmetallation at the nickel(II)-chloride precursor, **1-Cl**.

Gratifyingly, the combination of $PyNMe_3$ and cycloneophyl (-CH_2CMe_2-*o*-C_6H_4-, or cycl) as ligands allows the stabilization and isolation of complex $[(PyNMe_3)Ni^{II}(cycl)]$ (**2**) in 67 % yield. The complex was synthesized via ligand exchange of the Ni(II) precursor $(py)_2Ni^{II}(cycl)$ with an equimolar amount of $PyNMe_3$ in 1:1 toluene/pentane, for 16 hours at room temperature under a nitrogen atmosphere (Fig. 3a). The X-ray structure revealed a square planar geometry around the Ni(II) center, with the $PyNMe_3$ ligand coordinated in a bidentate fashion (Fig. 3b). This new system allows for the observation the *trans* influence of the ligands. Interestingly, $PyNMe_3$ ligand coordinates to the Ni(II) center through the pyridine moiety which is *trans* to the alkyl ligand, and one of the adjacent amines *trans* to the phenyl group. This type of coordination could not be observed with the previously reported systems bearing symmetric pyridinophane type ligands (^{R}N4). In addition, the ^{1}H-NMR spectrum confirms that **2** is a low-spin diamagnetic Ni(II) complex. Detailed NMR experiments were used to assign all proton and carbon peaks for **2** (Figures S2-S9). The broadness of the peaks, especially the methylene protons on the $PyNMe_3$ ligand, is likely due to rapid ligand exchange of the four types of N donors. Furthermore, the unusual Ni(II) structure allows for an anagostic interaction of the methylene protons vicinal to the tertiary amine and the Ni metal center, with a Ni···H distance of 2.40 Å and a Ni···H-C9 angle of 170º. The cyclic voltammogram (CV) of **2** in 0.1 M $(n\text{Bu}_4\text{N})PF_6$/MeCN reveals a quasi-reversible redox event at $E_{1/2}$ = 250 mV vs ferrocene (Fc), followed by another quasi-reversible oxidation at $E_{1/2}$ = 630 mV (Fig. 3c). These observed pseudo-reversible oxidations are presumably assigned to the $Ni^{III/II}$ and $Ni^{IV/III}$ redox couples, respectively. This result suggests accessible Ni(III) and Ni(IV) species, likely due to the stabilizing effect of the two anionic chelating C donors from the cycloneophyl ligand, as well as the tetradentate $PyNMe_3$ ligand, as reported previously for high-valent iron-oxo species.[27, 33, 37]

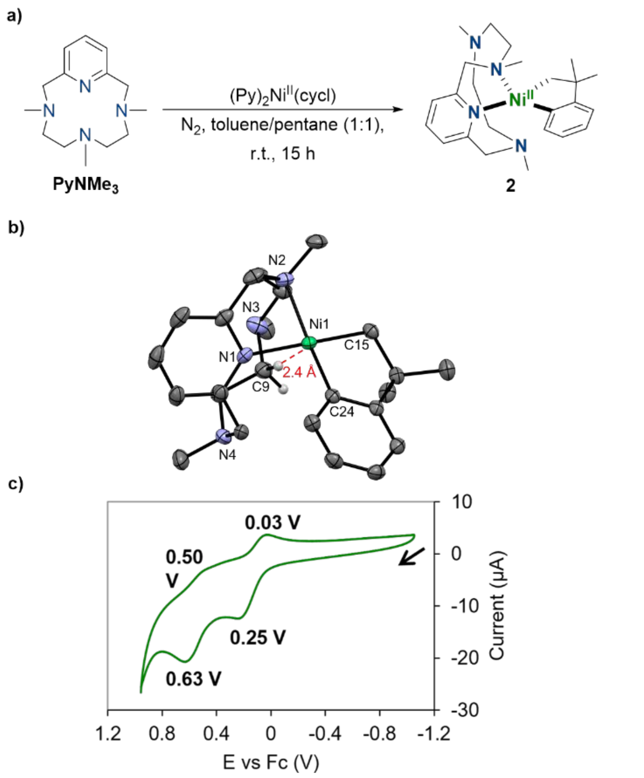


Fig. 3 a) Synthesis and characterization of complex $[(PyNMe_3)Ni^{II}(cycl)]$, **2**; b) ORTEP representation of **2** (50% probability thermal ellipsoids; hydrogen atoms have been omitted for clarity; selected distances (Å): Ni-C24, 1.888(2); Ni-C15, 1.932(2); Ni-N2, 2.0535(19); Ni-N1, 1.9923(19), and c) CV of **2** in 0.1 M $NBu_4(PF_6)$/MeCN at a scan rate of 100 mV/s (Ag wire as reference electrode).

In fact, **2** was rapidly oxidized with 1 equiv of ferrocenium hexafluorophosphate ($FcPF_6$) in MeCN at -35 ºC to yield the reddish product $[(PyNMe_3)Ni^{III}(cycl)](PF_6)$, **3** (Fig. 4a). The EPR spectrum of **3** in 1:3 MeCN/PrCN is consistent with a Ni (III) d^7 complex and exhibits a pseudoaxial signal with superhyperfine coupling to two nitrogen atoms in the g_z direction (A_{2N} = 13.7 G), indicating that two I = 1 nitrogen atoms, presumably from the ligand and/or solvent, coordinate to the Ni(III) center (Fig. 4b). Luckily, complex **3** was stable and isolated at low temperature in a 73 % yield.

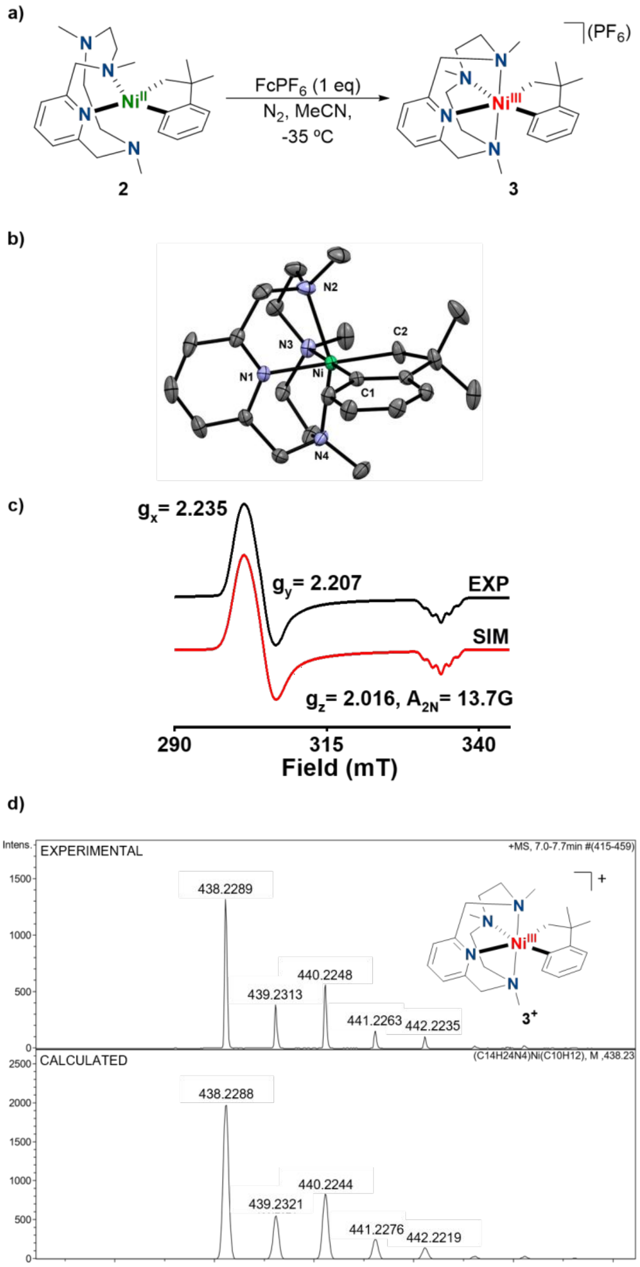


Fig. 4 a) Synthesis and characterization of complex $[(PyNMe_3)Ni^{III}(cycl)](PF_6)$, **3**; b) EPR spectra of complex **3** at 77 K 1:3 MeCN/PrCN (black: experimental; red: simulated); c) ORTEP representation of **3** (50% probability thermal ellipsoids; hydrogen atoms have been omitted for clarity; selected distances (Å): Ni-C1, 1.9492 (12); Ni-C2, 1.9693 (14); Ni-N1, 1.9944 (11); Ni-N2, 2.2543 (13); Ni-N3, 2.1463 (12); Ni-N4, 2.2470 (12), and d) Cryo-HR-MS of **3** showing the monocationic peak (3^+) at m/z = 438.2289 (top) and simulation of its isotopic pattern (bottom).

The single crystal X-ray structure of **3** confirmed the six-coordinate Ni(III) center in a distorted octahedral geometry where the 6 coordination positions are occupied by the $PyNMe_3$ and cycloneophyl ligands, thus confirming the EPR data (Fig.4c). Intriguingly, both the Ni-N and Ni-C distances in **3** are longer than those in **2**, as previously observed for similar complexes, and likely due to the change in the coordination number from 4 to 6 upon oxidation.[33, 37] Moreover, cryo-ESI-mass spectrometry at -40 ºC was performed to further characterize this Ni(III) complex. The MS spectrum showed a major monocharged peak with a m/z = 438.2289 and an isotopic pattern fully consistent with the calculated values for 3^+, $[(C_{14}H_{24}N_4)Ni^{III}(C_{10}H_{12})]^+$ (Fig. 4d).

Attempts to synthetize the corresponding Ni(IV) complex were conducted through a stepwise oxidation of **2**. The oxidation of **2** to obtain **3** was monitored by low-temperature UV/vis spectroscopy (Fig. 5a and b). This experiment was performed at -40 ºC using a 0.5 mM solution of **2** in MeCN. An initial spectrum was recorded for the starting Ni(II) complex, which exhibited an absorption band with λ_{max} = 462 nm. For the one-electron oxidation of each complex monitored by low-temperature UV/vis, $NO(SbF_6)$ was used as oxidant in order to obtain a cleaner spectrum, since Fc^+ exhibits two absorption bands at 325 nm and 440 nm that could interfere with the detection of new species. Thus, addition of 1 equiv of NO^+ to **2** immediately yields **3**, which exhibits an absorption band with λ_{max} = 513 nm. Afterwards, another equivalent of the same oxidant was added to generate the new Ni(IV) complex, **4**. Upon addition of the second equivalent of oxidant the UV/vis spectrum instantly changed and showed the formation of two absorption bands with λ_{max} of 384 nm and 470 nm, and a shoulder at 620 nm (Fig. 5b). Subsequent injection of an aliquot into cryo-ESI-mass spectrometer confirmed the generation of species **4** with a dicationic major peak with a mass value of m/z = 219.1120 and an isotopic pattern fully consistent with the calculated value for $[(C_{14}H_{24}N_4)Ni^{IV}(C_{10}H_{12})]^{2+}$ (Fig. 5c). This novel complex was further characterized by NMR spectroscopy, where a stepwise injection of 2 equiv NO^+ resulted in the observation of a new Ni(IV) species (Figures S10-S11).

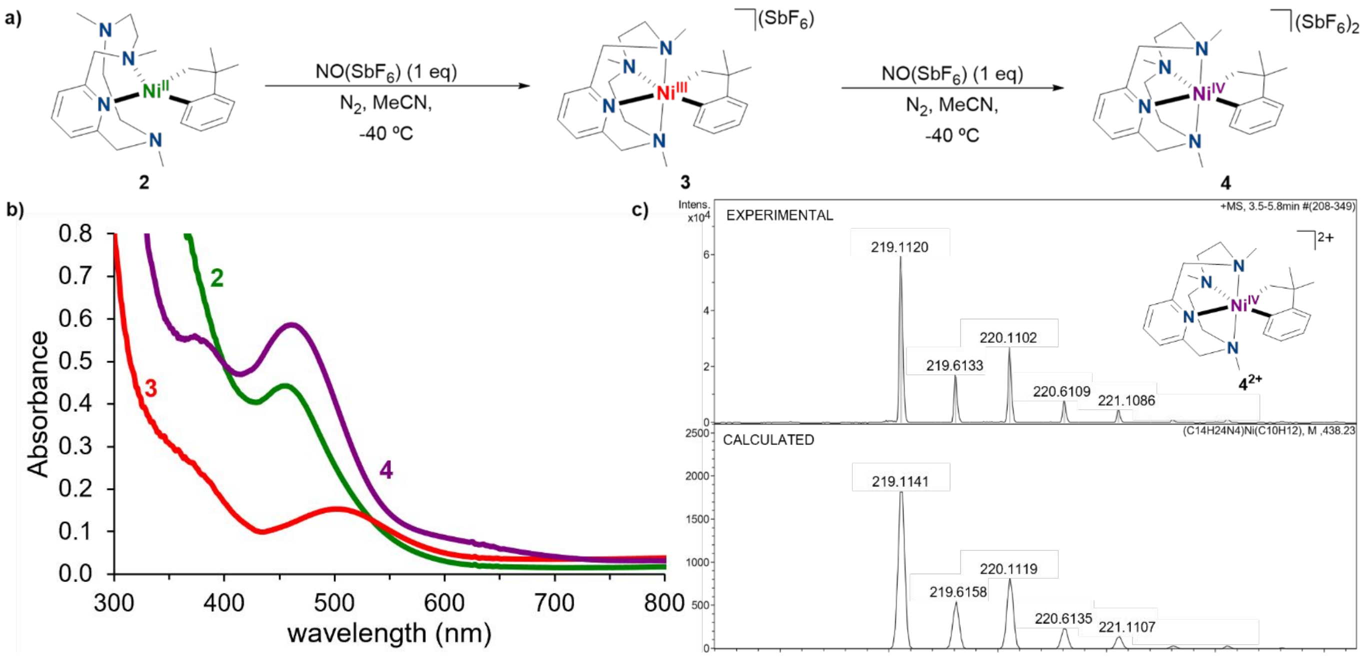
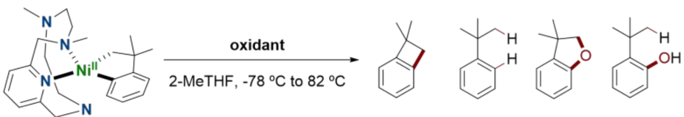


Fig. 5 a) Step-wise one-electron oxidation to nickel(IV) from 2 using NO(SbF_6) as oxidant; b) UV-vis characterization of complexes **2**, **3** and **4** obtained by consecutive one-electron oxidation of **2** with NO(SbF_6), respectively, and c) Cryo-HR-MS of **4** showing the dicationic peak ($\mathbf{4^{2+}}$) at m/z = 219.1120 (top) and simulation of its isotopic pattern (bottom).

In line with the UV-vis results, monitoring the oxidation by NMR provided complementary information. A color change from orange to red-pink was observed upon the addition of 1 equiv of oxidant in CD_3CN at -35 ºC, while the obtained paramagnetic NMR spectrum supports the formation of a Ni(III) species. To no surprise, a second equivalent of oxidant allowed the formation of a new diamagnetic species, tentatively assigned as a Ni(IV) complex. The inherent broadness of the NMR spectrum of the putative Ni(IV) species is likely caused by the residual Ni(III), which made peak assignment difficult. However, the obtained Ni(IV) spectrum closely resembles those of the recently reported Ni^{IV}-cycloneophyl complexes supported by the *N*-based macrocycles pyridinophane (^{Me}N4) and triazacyclononane (^{Me}tacn).[32, 37] Due to the highly electrophilic nature of the Ni(IV) species, a key structural feature observed in both ^{Me}N4 and ^{Me}tacn Ni^{IV}-cyclonephyl systems is a large shift of the Ni^{IV}-CH_2- protons from ~2.10 ppm in their Ni^{II}-CH_2- counterparts to 5.33 ppm and 5.50 ppm, respectively. A similar shift was observed with **4**, in which the Ni^{IV}-CH_2- protons shifted to 5.29 ppm, similar to what was observed for (^{Me}tacn)Ni^{IV}(cycl).[32]

Next, we focused on the reactivity of **3** and **4** in C-C or C-O bond formation reactions. First, we exposed the Ni^{III} species **3** to high temperatures (80 ºC) to evaluate its stability, and it was found that the compound decomposed to an intractable mixture, which contains ~15% of the protodemetalation product t-butylbenzene, yet no reductive elimination products were obtained. Then, since the Ni(IV), **4**, was metastable, we studied its reactivity by generating it *in situ* through oxidation of **2** with a variety of two-electron oxidants such as XeF_2, 1-fluoro-2,4,6-trimethylpyridinium triflate (NFTPT), and $PhI(OAc)_2$, yet no appreciable amount of any reductive elimination products were observed. On the contrary, promising results were obtained when exploring its reactivity with green oxidants such as O_2, H_2O_2, and ^{t}BuOOH (Fig. 6).

In these reactions, only trace amounts (<1%) of protodemetalation product t-butylbenzene, **B**, was observed in GC-MS, indicating a nearly full conversion of **2** into corresponding Ni^{III}/Ni^{IV} species. The reaction of **2** with 2 equiv H_2O_2 in 2-MeTHF results in the formation of 11% **C** and 9% **A** as the primary organic products. The reaction of **2** with ^{t}BuOOH shows similar distribution of products. On the other hand, the reaction of **2** with dioxygen generated up to 59% of C-C coupled product **A**, exhibiting an appreciable C-C bond formation reactivity, which is proposed to occur via the intermediacy of the Ni(IV) species **4**. It is important to note that this tetradentate $PyNMe_3$ ligand system displays a different reactivity from the structurally related pyridinophane ^{R}N4 system,[33] where C-O reductive elimination was greatly enhanced. In that case, it is likely that a Ni^{IV}-hydroxo transient, yet metastable intermediate was generated and led to competing C-C/C-O reductive elimination steps, which has been observed for M^{IV} complexes (M = Pt, Pd) bearing ligands that are prone



2

Entry	Oxidant	A	B	C	D
1	O_2	59 %	0 %	6 %	2 %
2	H_2O_2	9 %	1 %	11 %	2 %
3	^{t}BuO_2H	3 %	1 %	8 %	3 %

GC-MS

Fig. 6 Reactivity studies of **2** in front different two-electron oxidants, and the quantification of the respective organic products by GC-MS.

to reductive elimination.[32,33] By contrast, the $[(PyNMe_3)Ni(cycl)]$ system seems to favor the C-C bond formation reactivity over the formation of any oxygen-containing products, possibly because the $PyNMe_3$ ligand is flexible enough to strongly bind to the Ni(IV) species and complete the octahedral coordination geometry, without allowing the coordination of any additional oxidant-derived, O-donor ligand.

Conclusion

In summary, we have been able to explore the rich organometallic redox chemistry of Ni by characterizing spectroscopically Ni^{II} (**2**), Ni^{III} (**3**) and Ni^{IV} (**4**) complexes supported by the tetradentate N-donor ligand $PyNMe_3$. **2** features a square-planar geometry with two pendant aliphatic amine moieties, which enter into the coordination sphere of the metal upon oxidation to a Ni(III), **3**, that features a distorted octahedral geometry. Further reaction of **3** with another equivalent of oxidant affords the putative Ni(IV), **4**. Reactivity studies indicate that the in situ formed Ni(IV) complex, $[(PyNMe_3)Ni^{IV}(cycl)](SbF_6)_2$ (**4**), promotes C-C coupling over C-O coupling despite the use of of O-based oxidants, in contrast to the related pyridinophane $^{R}N4$ systems.[33] Overall, this new $PyNMe_3$ ligand system provides important insight in understanding at a molecular level the electronic properties of dissymmetric macrocyclic ligands on well-defined Ni^{II} (**2**), Ni^{III} (**3**) and Ni^{IV} (**4**) organometallic complexes and their role in C-C and C-O bond formation transformations.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ CCDC 2118410 (**1-Br**), 2118413 (**1-Cl**), 2118411 (**2**), 2118412 (**3**) contains 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. The Supporting Information also provides additional information.

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