

Accessing Pincer Bis(carbene) Ni(IV) Complexes from Ni(II) via Halogen and Halogen Surrogates

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S Supporting Information

ABSTRACT: This communication describes the two-electron oxidation of $(^{\text{DIPP}}\text{CCC})\text{NiX}$ ($^{\text{DIPP}}\text{CCC}$ = bis-(diisopropylphenyl-benzimidazol-2-ylidene)phenyl); $\text{X} = \text{Cl}$ or Br) with halogen and halogen surrogates to form $(^{\text{DIPP}}\text{CCC})\text{NiX}_3$. These complexes represent a rare oxidation state of nickel, as well as an unprecedented reaction pathway to access these species through Br_2 and halogen surrogate (benzyltrimethylammonium tribromide). The Ni^{IV} complexes have been characterized by a suite of spectroscopic techniques and can readily reduce to the Ni^{II} counterpart, allowing for cycling between the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$ oxidation states.

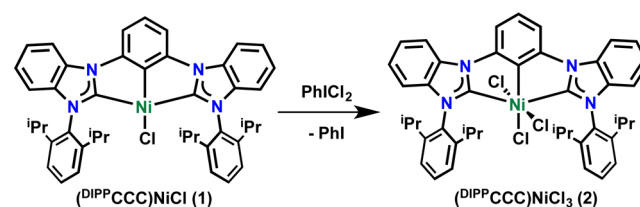
Homogenous nickel catalysis has been used for the synthesis of a variety of compounds including natural products, pharmaceuticals, and polymers. Mechanistic studies on these catalytic systems have indicated that the reactions proceed via one- or two-electron redox events to access Ni^0 , Ni^{I} , Ni^{II} , and/or Ni^{III} intermediates.^{1–5} Such studies, coupled with the recent development of well-defined $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$ catalytic cycles, which have demonstrated complementary reactivity and selectivity to their lower-valent counterparts,^{6–9} have rendered the isolation of high-valent nickel complexes an area of great interest.^{1,4} Unfortunately, despite the continued development of earth-abundant metal catalysts, isolated and well-characterized organometallic Ni^{IV} complexes are relatively rare. Reports include the isolation of octahedral Ni^{IV} species by oxidative addition of methyl iodide onto Ni^{II} acylphenolate tris(phosphine) complexes reported by Klein and co-workers,¹⁰ the pseudotetrahedral bromotris(1-norbornyl)nickel^{IV} complex isolated by Dimitrov and co-workers,¹¹ and the first isolated tetraalkyl Ni^{IV} complex reported by Turro and co-workers.¹² Most recently, Sanford and co-workers reported the isolation of octahedral Ni^{IV} complexes featuring the tris(2-pyridyl)methane and tris(pyrazolyl)borate ligand platforms, capable of reductively eliminating C–X bonds ($\text{X} = \text{O}, \text{S}, \text{N}, \text{CF}_3$).^{13,14} With the growing interest in harnessing the power of a $\text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$ redox cycle for bond-forming reactions, and given our interest in the alternate reactivity that Ni^{IV} has to offer compared to other oxidation states, we set out to investigate the viability of accessing complexes of nickel in the formal oxidation state +4 supported by a monoanionic bis(carbene) pincer platform.⁴

Previously, we reported the synthesis of Ni^{II} pincer complexes featuring the monoanionic bis(carbene) ligand platform, $^{\text{DIPP}}\text{CCC}$ ($^{\text{DIPP}}\text{CCC}$ = bis(diisopropylphenyl-benzimidazol-2-

ylidene)phenyl).¹⁵ Formation of the Ni^{II} -hydride complex, $(^{\text{DIPP}}\text{CCC})\text{NiH}$, was achieved by the oxidative addition of the ligand aryl C–H bond onto a Ni^0 starting material. The chloride derivative, $(^{\text{DIPP}}\text{CCC})\text{NiCl}$ (**1**), was synthesized in high yields from the benzimidazolium salt of the ligand $[\text{H}_3(^{\text{DIPP}}\text{CCC})]\text{Cl}_2$ and subsequent addition of $\text{LiN}(\text{SiMe}_3)_2$ and NiCl_2py_4 .¹⁵ Although **1** was previously reported by our group, the redox chemistry of this molecule was not explored. Hypothesizing that this highly donating pincer bis(carbene) ligand platform may allow us to access a high-valent Ni species, electrochemical studies were performed. Cyclic voltammetry on **1**, in dichloromethane, depicts a single reversible oxidation wave at +0.57 V versus Fc/Fc^+ , assigned to be the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ couple (Figure S1). Attempts to chemically access and isolate a Ni^{III} species by treating **1** with Ag^+ , Ph_3C^+ , or Fc^+ salts were unsuccessful and resulted in mixtures of diamagnetic products, with **1** being the main component. In addition, salt metathesis of **1** with noncoordinating anions was not successful. van Koten was able to access high-valent Ni^{III} species from the addition of CuX_2 and I_2 to a NCN pincer Ni^{II} species; similar reactions did not produce a Ni^{III} species in our system.¹⁶

Despite the failed attempts to isolate Ni^{III} complexes ligated by the $(^{\text{DIPP}}\text{CCC})$ platform, the chemical oxidation of $(^{\text{DIPP}}\text{CCC})\text{NiX}$ (**1**, $\text{X} = \text{Cl}$; **3**, $\text{X} = \text{Br}$) with two-electron oxidants was explored. Interestingly, the reaction of **1** with iodobenzene dichloride (PhICl_2) resulted in an immediate color change from orange to purple (Scheme 1). Characterization by ^1H NMR spectroscopy of the crude purple product revealed complete conversion of **1** to a new diamagnetic complex, **2**, and the concurrent formation of phenyl iodide, determined by ^1H NMR spectroscopy (7.70, 7.33 and 7.11 ppm, Figure S4). The ^1H NMR spectrum of **2** features two doublets, which integrate to 12 H each for the ^iPr methyl groups at 1.14 and 0.84 ppm (versus

Scheme 1. Synthesis of $(^{\text{DIPP}}\text{CCC})\text{NiCl}_3$ (**2**) from $(^{\text{DIPP}}\text{CCC})\text{NiCl}$ (**1**)



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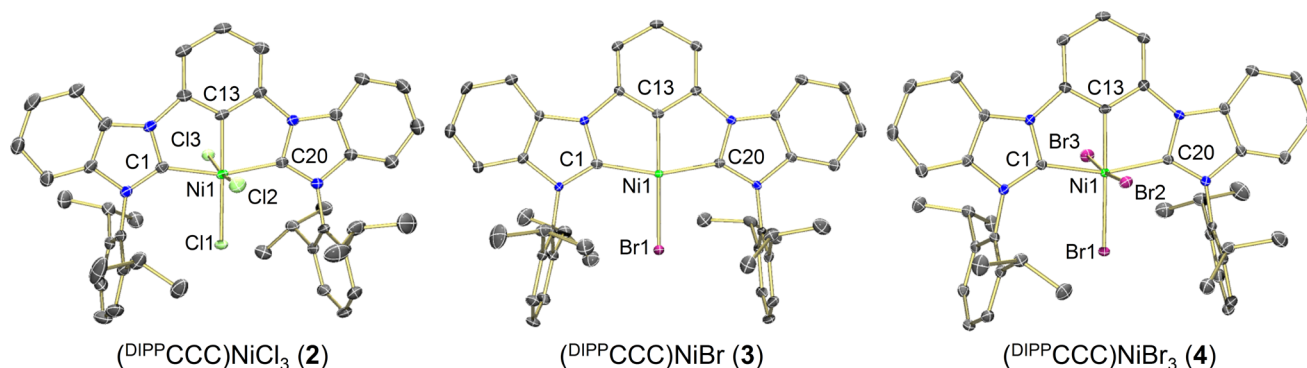


Figure 1. Molecular structures of **2**, **3**, and **4** shown with 50% probability ellipsoids. Solvent molecules and H atoms have been omitted for clarity.

Table 1. Selected Structural Parameters of Complexes 1–4

	1 (X = Cl)	2 (X = Cl)	3 (X = Br)	4 (X = Br)
Bond Distance (Å)				
Ni1–C1	1.9188(17)	1.942(3)	1.9284(19)	1.9703(14)
Ni1–C13	1.8504(16)	1.888(2)	1.8528(18)	1.8994(14)
Ni1–C20	1.9201(17)	1.936(3)	1.9328(19)	1.9788(14)
Ni1–X1	2.1879(5)	2.2682(7)	2.3365(3)	2.4102(3)
Ni1–X2		2.2192(7)		2.3511(3)
Ni1–X3		2.2106(7)		2.3675(3)
Bond Angles (deg)				
C13–Ni1–X1	175.66(5)	179.13(8)	177.17(6)	176.93(4)
C1–Ni1–C20	160.97(7)	161.96(10)	160.57(8)	160.77(6)
X2–Ni–X3		171.70(3)		173.504(10)

1.21 and 0.88 ppm of **1**), and one septet integrating to 4 H for the methine protons at 2.80 ppm (versus 2.47 ppm of **1**). The diamagnetic nature of **2** could be attributed to the formation of a dimeric complex featuring two Ni^{III} centers antiferromagnetically coupled; however, this formulation is unlikely due to the bulkiness of the diisopropylphenyl flanking groups of the ligand. The diamagnetic character of **2** could also be rationalized by a two-electron oxidation at the nickel center to form the C_{2v} symmetric, octahedral complex (DIPPPCCC)NiCl₃, which would be consistent with the number of resonances observed in the ¹H NMR spectrum of **2**. The thermal instability and diminished solubility at low-temperature of **2** precluded characterization by ¹³C NMR spectroscopy.

To elucidate the molecular structure of **2**, crystals suitable for X-ray analysis were grown by vapor diffusion of pentane into a solution of **2** in benzene/THF at –35 °C (Figure 1). Solid-state structural characterization revealed an octahedral Ni center featuring the monoanionic pincer ligand and three chloride ligands. Examination of the bond lengths in the ligand precludes the possibility of a ligand-based radical (Figure S4), thus confirming the formulation of **2** as a formal Ni^{IV} complex with the formulation (DIPPPCCC)NiCl₃ (Figure 1). Comparing the structural parameters of **2** to the Ni^{II} starting material **1** shows elongation of all the Ni–ligand bond distances in the plane of the pincer platform (Table 1). The Ni–C_{NHC} distances have elongated from 1.9188(17) and 1.9201(17) Å to 1.942(3) and 1.936(3) Å, the Ni–C_{aryl} distance has elongated from 1.8504(16) Å to 1.888(2) Å, and the Ni–Cl1 distance has elongated from 2.1879(5) Å to 2.2682(7) Å, likely due to the change in coordination at the nickel center from square planar in **1** to octahedral in **2** upon the two-electron oxidation.

Encouraged by the accessibility of Ni^{IV} via the chlorine surrogate PhICl₂, we investigated the reactivity of Ni^{II} toward

oxidation with elemental bromine in an effort to isolate (DIPPPCCC)NiBr₃. Bromine has served as a viable way to access Ni^{III} species, as shown by Zargarian^{17,18} and Nocera.¹⁹ In other examples, the halide moiety only interacts with Ni^{II} halide complexes to form trihalide anions and does not oxidize the metal center.¹⁹ Attempts to cleanly access the precursor Ni^{II}–Br species, (DIPPPCCC)NiBr (**3**), by salt metathesis of **1** with bromide salts proved to be unsuccessful; therefore, a new synthetic route to **3** was sought. Treatment of **1** with NaSPH, followed by removal of NaCl and protonation with HBr resulted in the formation of **3** with no chloride impurities. As expected, resonances in the ¹H NMR spectrum of **3** were marginally shifted from **1**. The ¹H NMR spectrum of **3** in THF-*d*₈ featured the two doublets corresponding to the ⁱPr methyl groups at 1.23 and 0.86 ppm (versus 1.21 and 0.88 ppm of **1**) and the septet corresponding to the ⁱPr methine protons at 2.46 ppm (versus 2.47 ppm of **1**) in addition to the appropriate number of aromatic proton resonances, also slightly shifted from **1**. Crystals of **3** suitable for X-ray analysis were grown by vapor diffusion of diethyl ether into a concentrated solution of **3** in THF. Complex **3** features a square-planar Ni^{II} center, with structural parameters similar to **1** and a Ni–Br distance of 2.3365(3) Å (Table 1).

Exposure of complex **3** to elemental bromine resulted in an immediate color change from orange to dark green (Figure 2). Characterization by ¹H NMR spectroscopy of the dark green product, **4**, revealed the formation of a diamagnetic species, featuring two doublets integrating to 12 H each for the ⁱPr methyl groups, and one septet integrating to four H for the ⁱPr methine protons, shifted to 1.19, 0.85, and 2.98 ppm, respectively, from the starting material **3** (Figure 2). This finding is consistent with the molecular structure of **4** being (DIPPPCCC)NiBr₃. This reaction represents a unique two electron oxidation of nickel by

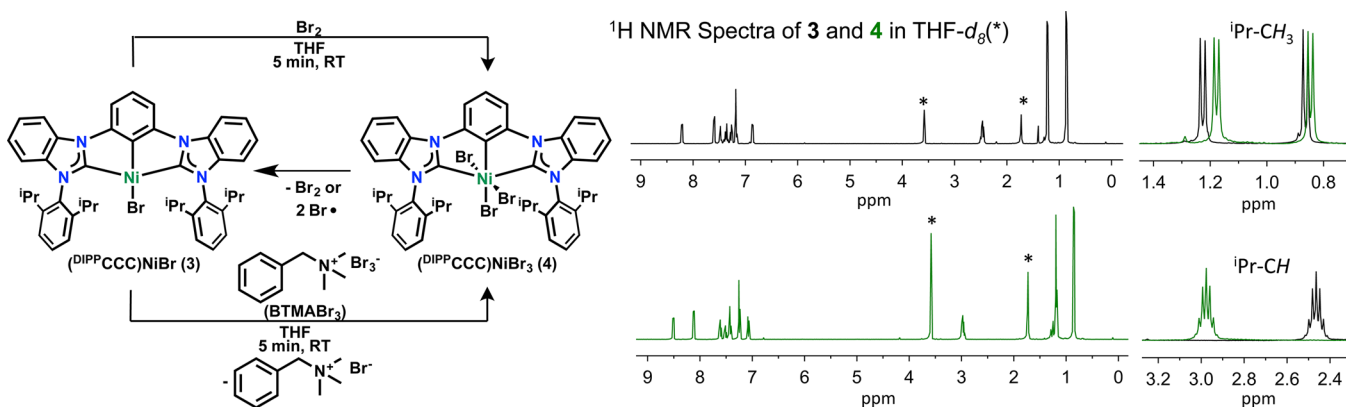


Figure 2. (Left) Reaction scheme for the synthesis of (DIPPCCC)NiBr₃ (4) from 3. (Right) Comparison of the ¹H NMR spectra of 3 (black) and 4 (green).

bromine as previous examples only resulted in the one-electron oxidized product.^{17–20}

Crystals of 4 suitable for X-ray analysis were grown by slow evaporation of a benzene solution at room temperature (Figure 1). Upon refinement, an octahedral Ni^{IV} complex with the predicted formulation (DIPPCCC)NiBr₃ was noted, similar to complex 2. In addition, the Ni–ligand bond distances in the plane of the pincer platform have elongated (Table 1), as observed in the case of the oxidation of 1 to 2. Finally, structural parameters of the ligand compared in 3 and 4 indicate there is no radical character in the ligand (Figure S9), as observed for 1 and 2. This route to access the desired Ni^{IV} complex produces complex 4 in quantitative yield (97%).

Following the isolation of Ni^{IV} by addition of elemental bromine, we explored the viability of employing the bromine surrogate benzyltrimethylammonium tribromide (BTMABr₃) as the oxidant. Upon exposure of 3 to BTMABr₃, an immediate color change from orange to dark green was noted (Figure 2) and the formation of 4 was confirmed by ¹H NMR spectroscopy. The use of BTMABr₃ is a convenient way to access complex 4 in excellent yield (96%), as it does not require weighing elemental bromine or preparing standard stock solutions. In addition, PhICl₂ and BTMABr₃ are safer alternatives to elemental halides and can be easily handled in a glovebox.


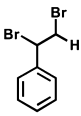








Interested in assessing the stability of the Ni^{IV} compounds, a solution of 2 in THF was analyzed after 1.5 h at room temperature by ¹H NMR spectroscopy. The spectrum revealed reduction of the trihalide to form approximately 1/3 equiv of 1. The observation of green crystals along the walls of the NMR tube suggested the remainder of the complex had formed the previously reported paramagnetic compound [H₃(DIPPCCC)]-[NiCl₄].¹⁵ This observation is consistent with the release of Cl₂ (or two •Cl), which, upon reacting with THF, forms HCl.^{21–23} Subsequent reaction of 1 with HCl results in the formation of [H₃(DIPPCCC)][NiCl₄].¹⁵ Analysis of the crude ¹H NMR spectrum was consistent with the formation of this paramagnetic species. Interestingly, it is possible to regenerate the trichloride species from 1 present in the reduced mixture upon treatment with additional PhICl₂. In contrast, a THF solution of compound 4 was found to be stable in air for over 24 h. Heating a sample of 4 in THF-*d*₈ at 50 °C for 6 h resulted in a 10% reduction of 4 to the Ni^{II} species, 3 (Figure S13). After 24 h of heating only 32% of 4 to 3 was reduced, and no other products could be observed (Figure S14).

In order to explore the possible involvement of Ni^{III} in the oxidation of 3 to 4, complex 3 was reacted with 1/2 equiv of BTMABr₃. Monitoring of the reaction by ¹H NMR spectroscopy revealed the presence of equimolar amounts of 3 and 4 with no observable paramagnetic species that would be consistent with Ni^{III} formation. This finding, as well as the clean decomposition via thermolysis, suggests a preference for oxidizing or reducing the nickel center by two electrons, respectively, as opposed to a one-electron oxidation route. This result does not rule out the possibility of the formation of a transient Ni^{III} species, which subsequently disproportionates to form 1/2 equiv of 4 and 1/2 equiv of 3, although such a pathway is unlikely.

Kraft reported the formation of a bis(carbene) palladium complex, (NHC)₂Pd^{IV}Cl₄, that was capable of chlorinating alkenes and alkynes.²⁴ Given the rather clean reduction chemistry of 2 to 1 and 4 to 3, we investigated the ability of complex 4 to transfer Br₂ (or two •Br) to an organic substrate. The addition of styrene (100 equiv) to a THF solution of 4 resulted in the formation of (1,2-dibromoethyl)benzene in 87% yield (as determined by ¹H NMR spectroscopy) suggesting the ease with which 4 can transfer halogens to a substrate (Table 2). The bromination of cyclohexene proceeded with complete conversion of 4 to 3. The brominated product was observed in 71% yield (assayed by ¹H NMR spectroscopy) concomitant with trace amounts of the corresponding halohydrin (GC–MS). Independently prepared samples of the dibrominated products confirmed the major product formation.²⁵ Reaction of 4 with 2-mesitylmagnesium bromide resulted in formation of mesityl bromide and mesitylene, as well as trace homocoupled product (GC–MS). Interestingly, the reaction of 4 with 1 equiv of lithium hexamethyldisilazide ((Me₃Si)₂NLi) resulted in the analogous formation of (Me₃Si)₂NBr and (Me₃Si)₂NH. Based on the observed reduction of 4 to 3 and subsequent transfer of halogen to substrates, we propose that the Ni^{IV} complexes are undergoing a concerted reductive elimination followed by halogenation of the alkene or other organic substrate. However, radical reactivity cannot be ruled out and further investigations are necessary and ongoing in our laboratory.

The described results confirm the ability of the electron-rich (DIPPCCC) pincer ligand to stabilize higher oxidation states at nickel. This report represents the first example of isolation of formal Ni^{IV} organometallic complexes supported by a mono-anionic bis(carbene) pincer ligand and obtained via oxidation with halogen and halogen surrogates. In addition, the coordination of halide ligands to the Ni^{IV} metal center allows

Table 2. Reactivity of **4** with Organic Substrates

Substrate	Products* (Yield)	% Conversion to 3	
	 87%	not observed	87%
100 eq. ^a			
	 71%	not observed	> 99%
100 eq. ^a			
	 50%	 33%	> 99%
1 eq. ^b			
	 50%	 50%	> 99%
1 eq. ^b			

* Product formation was determined by GC-MS and ¹H NMR spectroscopy.
^a Reaction in THF. ^b Reaction in benzene.

for possible ligand exchange to promote bond formation via reductive elimination pathways, featuring a Ni^{II}/Ni^{IV} redox couple.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12827.

Spectral data and synthesis for complexes **2–4** (PDF)
 Selected crystallographic data for complexes **2–4** (CIF)

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Notes

The authors declare no competing financial interest.

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