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### Stable M(II)-Radicals and Nickel(III) Complexes of a Bis(phenol) **N-Heterocyclic Carbene Chelated to Group 10 Metal Ions**

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**S** Supporting Information

ABSTRACT: The tetradentate ligand based on (1-imidazolium-3,5-ditertbutylphenol) units was prepared and chelated to group 10 metal ions (Ni(II), Pd(II), and Pt(II)), affording complexes 1, 2, and 3, respectively. The X-ray crystal structures of 1-3 show a square planar metal ion coordinated to two Nheterocyclic carbenes and two phenolate moieties. The cyclic voltammetry curves of complexes 1-3 show two reversible oxidation waves in the range 0.11-0.21 V  $(E_{1/2}^{-1})$  and 0.55–0.65 V  $(E_{1/2}^{-2})$  vs Fc<sup>+</sup>/Fc, which are assigned to the successive oxidations of the phenolate moieties. One-electron oxidation affords mononuclear (S = 1/2) systems. Complex  $1^+ \cdot \text{SbF}_6^-$  was remarkably stable, and its structure was characterized. The coordination sphere is slightly dissymmetric, while the typical patterns of phenoxyl radicals were observed within the ligand framework. Complex  $1^+$  exhibits a rhombic signal at g = 2.087, 2.016, and 1.992, confirming its predominant phenoxyl radical character. The g-values are slightly smaller for 2<sup>+</sup> (2.021, 2.008, and 1.983) and larger for 3<sup>+</sup> (2.140, 1.999, and



1.885) yet consistent with phenoxyl radical species. The electronic spectra of  $1^+-3^+$  display an intervalence charge-transfer (IVCT) transition at 2396, 2600, and 2294 nm, respectively. Its intensity supports the description of cations  $1^+$  and  $3^+$  as mixedvalent (Class II/III) compounds according to the Robin Day classification. Complex 2<sup>+</sup> behaves as a mixed-valent class II radical compound. In the presence of pyridine, radical species  $1^+$  is successively converted into stable mono and bis(adducts), which are both Ni(III) complexes. Dications  $1^{+2}-3^{+2}$  were prepared electrochemically. They are electron paramagnetic resonance (EPR)-silent and do not show IVCT transition in their NIR spectra, consistent with a bis(radical) formulation. The proposed electronic structures are fully supported by density functional theory calculations.

#### 1. INTRODUCTION

The interplay between high-valent metal centers and radical ligands is essential in biocatalysis by the metalloenzymes cytochrome P450,<sup>1-5</sup> galactose oxidase,<sup>6-17</sup> and glyoxal oxidase.<sup>15,18,19</sup> The multiredox stability of the metal center allows it to shuttle between reduced and oxidized states. The stabilization of low oxidation states is a prerequisite for a fast reduction (activation) of dioxygen. Conversely, under its oxidized form the metal center is a strong oxidant that is prone to transiently storing an oxo group for oxygen atom transfer, as in cytochrome P450.<sup>1,2,4,5</sup> The porphyrinyl or tyrosyl radicals are generated during turnovers of the above enzymes. They play crucial role in the H atom abstraction and thereby contribute to the activation of the substrate.<sup>20</sup> This original reactivity has stimulated the design of biomimetic radical complexes, for instance directed toward alcohol oxidation.<sup>12,21-23</sup> Pro-radical ligands are currently more widely used for the development of coordination complexes capable of promoting a broader range of chemical transformations.<sup>24–26</sup> Recent representative examples are reductive cyclization,<sup>27,28</sup> cross coupling reactions,<sup>29</sup> C–H amina-tion,<sup>30,31</sup> water oxidation,<sup>32–34</sup> hydrogen evolution,<sup>35,36</sup> and trifluoromethylation.<sup>37</sup> While elegant, this approach based on redox-active ligands is however limited by the control over the

oxidation site and the elucidation of the electronic structure of the precatalyst.<sup>38,39</sup>

Electron-rich di-tert-butylphenolate is a precursor of persistent phenoxyl radical species that has been used for designing model compounds for galactose oxidase (Chart 1). 40-42 This hard donor is also capable in some instances of stabilizing metal ions under unusual high-valent oxidation states, such as  $Cu(III)^{43}$  (as in the case of  $[Cu(L^{chex})]^+$ , Chart 1), while it does not easily accommodate low-valent copper.<sup>44</sup> In order to overcome this latter limitation and to design robust and multi-redox-stable systems, we recently focused our attention on redox-active ligands incorporating N-heterocyclic carbenes (NHCs, Chart 2).45 While examples of redox-active NHC are yet rare, 46-58 these moieties are well-known to easily accommodate electron-rich metals and hence are widely used in organocatalysis for this purpose.<sup>47</sup> In addition, their strong  $\sigma$ -donating capability means that they form stronger M-L bonds than neutral ligands (like imines found in most of the galactose oxidase mimics), which is beneficial to catalysis. Counterintuitively, there is recent evidence that these units can also coordinate high valent metal ions (V<sup>V</sup>, Co<sup>IV</sup>, Cu<sup>III</sup>, Mo<sup>IV</sup>

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#### Chart 1. Structure of Representative Complexes Involving Redox-Active Ligands









Nb<sup>V</sup>) when they are functionalized with aryloxide groups.<sup>59–63</sup> Thus, we envision that neutral NHCs connected to sterically hindered phenolates could form a unique family of NHCs ligands, which are potentially precursors of either high-valent metal complexes or phenoxyl radical species, both of which are scarce in literature. Provided that such high-valent species are effectively readily accessible, it should be possible, in theory, to orientate the electronic structure toward one of these two valence tautomers with a rational ligand design. Surprisingly, only few ligands associating these two units have been described. The most representative one is pincer ligand  $H_2L^{OCO}$  (Chart 2).<sup>45,64–66</sup> Its coordination chemistry has been reported for various transition metals, as well as its catalytic scope, but its oxidative chemistry is limited to cobalt and nickel  $([Ni(L^{OCO})(Pyr)]$  in Chart 2). The mono-phenolate–NHC derivative HL<sup>CO</sup> has received less attention, 67-73 while the tetradentate version is not yet described. In this article, we report the synthesis of proligand  $H_4L^{C_2O_2}Br_2$  as well as its complexes with group 10 metal ions M(II) (M = Ni, Pd, Pt; Chart 2). The intrinsic diamagnetism of these metal ions allow for fine assignment of the electronic structure of the oxidized species. We establish via combined spectroscopic and theoretical approaches that this ligand can either act as redoxnon-innocent (M = Ni, Pd, Pt) or stabilize a high-valent metal ion (Ni). The structure of  $1^+$  could be solved, showing a phenoxyl radical coordinated to the Ni(II) center. Most importantly, we unambiguously show that the nickel ion can be stabilized under an unprecedented (+III) oxidation state once engaged in coordination with NHCs in coordinating solvents.

#### 2. EXPERIMENTAL SECTION

2.1. Materials and Instruments. The solvents were HPLC-grade and used without further purification. The electrochemical experiments were performed with anhydrous CH2Cl2 (dried over molecular sieves) (Aldrich) under inert atmosphere. The X-band electron paramagnetic resonance (EPR) spectra were recorded on a BRUKER EMX Plus spectrometer controlled with the Xenon software and equipped with a Bruker teslameter. A Bruker nitrogen flow cryostat connected to a high-sensitivity resonant cavity was used. The spectrum was simulated by using the Easyspin software.<sup>74</sup> NMR spectra were recorded using an Avance III 400 Brüker spectrometer at 293 K at 400 MHz. The UV/vis spectra were recorded on a Perkin– Elmer Lambda 1050 or Cary Varian 50 spectrophotometer with Hellma quartz cells of 1.000 mm path length. Cyclic voltammetry (CV) curves were recorded on a CHI 620 potentiostat in a standard three-electrode cell under argon atmosphere. The electrolytic medium is anhydrous CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. The cell volume is 8 mL, with both the counter and reference electrodes being compartmentalized to avoid diffusion of the analyte at the platinum wire or in the AgNO<sub>3</sub>/Ag (0.01 M) compartment (in CH<sub>3</sub>CN TBAP 0.1 M). All the potentials given in the text are referred to the regular Fc<sup>+</sup>/Fc redox couple used as external reference. A vitreous carbon disc electrode (5 mm diameter) polished with 1 mm diamond paste was used as working electrode. Electrolysis was performed at 233 K with a Biologic SP300 potentiostat by using a carbon foam working electrode and was monitored by coulometry and rotating-disk electrode voltammetry. The integrity of the oxidized products was also accessed by recording CV curves after the first and second oxidation and ensuring that they match with that of the unoxidized sample.

**2.2.** Synthesis. 2.2.1. Preparation of Proligand  $H_4 L^{C_2 O_2} Br_2$ . 2.2.1.1. 2,4-Di-tert-butyl-6-nitro-phenol. First, 1.5 mL of 65% nitric acid (49.5 mmol) was added dropwise to a solution of 2,4-di-tertbutylphenol (10.08 g (48.9 mmol) in 100 mL of acetic acid and cooled down with an ice/water bath. The red mixture was stirred for 2 h, then quenched with addition of 60 mL of H<sub>2</sub>O and saturated NaHCO3 solution until pH 5 was reached. The resulting red precipitate is then collected and rinsed with water, solubilized in 250 mL of CH<sub>2</sub>Cl<sub>2</sub>, and washed with 150 mL of H<sub>2</sub>O and 150 mL of brine (2 times), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated (12.26 g, 99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32 (s, 9H, t-Bu), 1.45 (s, 9H, t-Bu), 7.64 (s, 1H, aryl-H), 7.96 (s, 1H, aryl-H), 11.45 (s, 1H, OH). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  29.53, 31.25, 34.66, 35.87, 119.00, 132.73, 133.81, 140.00, 142.10, 153.15. MS (HRMS): m/z= 250.14  $[M - H]^{-}$ . Anal. Calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>3</sub>: C, 66.89; H, 8.44; N, 5.57. Found: C, 66.01; H, 9.05; N, 5.38.

2.2.1.2. 1,5-Di-tert-butyl-2-methoxy-3-nitro-benzene. First, 13.482 g (97.5 mmol) of potassium carbonate and 29 g (204 mmol) of iodomethane are added to a solution of 12.26 g (48.8 mmol) of 2,4-di-tert-butyl-6-nitro-phenol in 210 mL of acetone. The mixture is heated at 70 °C and stirred for 20 h, and the potassium carbonate is filtered. The crude mixture is evaporated then resolubilized in 250 mL of CH<sub>2</sub>Cl<sub>2</sub>, washed with 150 mL of H<sub>2</sub>O and 150 mL of brine (2 times), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated to obtain 1,5-di-tert-butyl-2-methoxy-3-nitro-benzene as an orange oil (12.42 g, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.32 (s, 9H, t-Bu), 1.41 (s, 9H, t-Bu), 3.79 (s, 3H, O–CH<sub>3</sub>), 7.55 (d, 1H, aryl–H, 2.50 Hz), 7.59 (d, 1H, aryl–H, 2.5 Hz). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  30.67, 31.32, 34.90, 35.95, 61.43, 120.49, 128.64, 143.93, 144.55, 145.90, 150.96. MS (HRMS): m/z= 266.18 [M + H]<sup>+</sup>. Anal. Calcd for C<sub>15</sub>H<sub>23</sub>NO<sub>3</sub>: C, 67.88; H, 8.75; N, 5.28. Found: C, 68.13; H, 8.97; N, 5.17.

2.2.1.3. 3,5-Di-tert-butyl-2-methoxy-aniline. First, 12.42 g (46.8 m mol) of 1,5-di-tert-butyl-2-methoxy-3-nitro-benzene was solubilized in 200 mL of EtOH, and 1.25 g of 10% mol palladium on charcoal is added. The mixture is then vigorously stirred under H<sub>2</sub> atmosphere for 3 days at room temperature. The catalyst is filtered over Celite, and the filtrate was evaporated, affording 3,5-di-tert-butyl-2-methoxy-aniline as an orange solid (10.83 g, 98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.27 (s, 9H, t-Bu), 1.39 (s, 9H, t-Bu), 3.60 (s, 2H, NH<sub>2</sub>), 3.79 (s, 3H, O-CH<sub>3</sub>), 6.67 (s, 1H, aryl-H), 6.76 (s, 1H, aryl-H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  31.25, 31.64, 34.58, 35.34, 59.20, 112.36, 114.50, 139.73, 142.02, 144.82, 146.41. MS (HRMS): *m*/z= 236.30 [M + H]<sup>+</sup>. Anal. Calcd for C<sub>15</sub>H<sub>25</sub>NO: C, 76.53; H, 10.73; N, 5.95. Found: C, 76.63; H, 10.76; N, 4.94.

2.2.1.4. 1-(3,5-Di-tert-butyl-2-methoxy-phenyl)imidazole. First, 0.52 mL (4.55 mmol) of glyoxal 10 wt % in H<sub>2</sub>O was added to a solution of 1.06 g (4.51 mmol) of 3,5-di-tert-butyl-2-methoxy-aniline in 25 mL of EtOH. The mixture is stirred overnight at room temperature before adding 482 mg (9.01 mmol) of ammonium chloride and 0.68 mL of formaldehyde 37 wt % in H<sub>2</sub>O. The mixture is heated to reflux for 2 h, and 0.74 mL of  $H_3PO_4$  85 wt % in  $H_2O$  was added. The mixture is maintained at reflux for a further 12 h. The crude mixture is evaporated and treated with a potassium hydroxide solution (40% in water) until pH 9 is reached. The aqueous phase is extracted with  $CH_2Cl_2$  (3 × 30 mL), and the combined organic phases are washed with  $H_2O$  (50 mL) and brine (2 × 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The crude brown solid is purified on silica chromatography with a pentane/ethyl acetate 40/60 eluent affording 1-(3,5-di-tert-butyl-2-methoxy-phenyl)imidazole as a pale white solid (788 mg, 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.32 (s, 9H, t-Bu), 1.41 (s, 9H, t-Bu), 3.20 (s, 3H, O-CH<sub>3</sub>), 7.11 (d, 1H, aryl-H, 2.36 Hz), 7.22 (s, 1H, aryl-H), 7.23 (s, 1H, aryl-H) 7.37 (d, 1H, aryl-H, 2.32 Hz), 7.76 (s, 1H, aryl-H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  30.78, 31.51, 34.77, 35.66, 59.72, 120.42, 121.60, 123.95, 129.72, 130.52, 137.71, 143.74, 146.58, 151.07. MS (HRMS): *m*/*z* = 287.21  $[M + H]^+$ . Anal. Calcd for  $C_{18}H_{26}N_2O$ : C, 75.47; H, 9.17; N, 9.78. Found: C, 74.20; H, 9.86; N, 9.78.

2.2.1.5.  $H_4L^{OMe}Br_2$ . A mixture of 1 mL (14.25 mmol) of dibromomethane and 103.1 mg (0.36 mmol) of 1-(3,5-di-*tert*-butyl-2-methoxy-phenyl)imidazole is sealed in a tube and stirred overnight at 100 °C. The resulting white precipitate is collected and washed with cold acetone giving the pure product as a white solid (88.0 mg, 65%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  1.31 (s, 18H, *t*-Bu), 1.42 (s, 18H, *t*-Bu), 3.35 (s, 6H, O-CH<sub>3</sub>), 6.90 (s, 2H, CH<sub>2</sub>), 7.47 (d, 2H, aryl-H, 2.00 Hz) 7.54 (d, 2H, aryl-H, 2.08 Hz), 8.26 (s, 2H, aryl-H) 8.34 (s, 2H, aryl-H), 9.96 (s, 2H, aryl-H). <sup>13</sup>C NMR (500 MHz, DMSO- $d_6$ )  $\delta$  30.51, 30.97, 34.62, 35.27, 58.72, 61.04, 121.95, 122.62, 124.10, 125.86, 128.20, 139.04, 143.57, 146.81, 150.21. MS (HRMS):  $m/z = 293.21 [M - 2Br]^{2+}$ . Anal. Calcd for C<sub>37</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>.2Br: C, 59.51; H, 7.30; N, 7.50. Found: C, 59.30; H, 7.71; N, 7.21.

2.2.1.6.  $H_4L^{C_2O}Br_2$ . First, 0.36 mL (3.54 mmol) of boron tribomide is added dropwise to a solution of 434.2 mg (0.58 mmol) of  $H_4L^{OMe}Br_2$  in 15 mL of dry  $CH_2Cl_2$  under argon atmosphere. The solution is stirred overnight then quenched by successive additions and evaporations of MeOH (4 × 20 mL). The resulting white solid is collected and washed with cold acetone (377.6 mg, 90%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  1.29 (s, 18H, t-Bu), 1.42 (s, 18H, t-Bu), 6.93 (s, 2H, CH<sub>2</sub>), 7.32 (d, 2H, aryl-H, 2.40 Hz) 7.45 (d, 2H, aryl-H, 2.35 Hz), 8.14 (t, 2H, aryl-H, 1.77 Hz) 8.27 (t, 2H, aryl-H, 1.72 Hz), 9.19 (s, 2H, aryl-H), 9.89 (s, 2H, aryl-H). <sup>13</sup>C NMR (500 MHz, DMSO- $d_6$ )  $\delta$  29.54, 31.10, 34.22, 35.19, 58.08, 121.09, 122.28, 124.37, 124.92, 125.58, 139.10, 139.81, 142.67, 146.94. MS (HRMS):  $m/z = 279.20 [M - 2Br]^{2+}$ . Anal. Calcd for C<sub>35</sub>H<sub>50</sub>N<sub>4</sub>O<sub>2</sub>·2Br: C, 58.49; H, 7.03; N, 7.80. Found: C, 57.31; H, 7.26; N, 7.23. 2.2.2. Preparation of the Complexes. 2.2.2.1. Complex 1. First, 0.12 mL (0.86 mmol) of triethylamine was added to a solution of 80.1 mg (0.111 mmol) of  $H_4L^{C_2O_2}Br_2$  and 28.6 mg (0.115 mmol) of nickel(II) acetate tetrahydrate in 10 mL of MeOH under argon atmosphere. The mixture is heated at 55 °C and stirred overnight, and the precipitated pale yellow powder is collected and washed with MeOH (49.7 mg, 73%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  1.29 (s, 18H, t-Bu), 1.43 (s, 18H, t-Bu), 6.13 (s, 2H, CH<sub>2</sub>), 7.00 (d, 2H, aryl-Hx or aryl-Hy, 2.12 Hz) 7.39 (d, 2H, aryl-Hx or aryl-Hy, 2.04 Hz), 7.74 (s, 2H, aryl-Hx or aryl-Hy, 1.96 Hz) 8.34 (s, 2H, aryl-Hx or aryl-Hy, 2.04 Hz). <sup>13</sup>C NMR (500 MHz, DMSO- $d_6$ )  $\delta$  30.16, 31.68, 33.82, 35.61, 60.44, 111.88, 118.11, 119.96, 121.45, 124.27, 133.21, 138.77, 152.09, 153.65. MS (HRMS): m/z = 612.30 [NiL]<sup>+</sup>. Anal. Calcd for C<sub>35</sub>H<sub>46</sub>NiN<sub>4</sub>O<sub>2</sub> 1/3 CH<sub>3</sub>OH: C, 67.99; H, 7.64; N, 8.98. Found: C, 67.56; H, 7.81; N, 9.13.

2.2.2.2 Complex 2. First, 65 μL (0.46 mmol) of triethyl amine was added to a solution of 81.5 mg (0.113 mmol) of  $H_4L^{C_2O_2}Br_2$  and 25.6 mg (0.115 mmol) of palladium(II) acetate in 10 mL of MeOH under argon atmosphere. The mixture is heated at 60 °C and stirred for 4 h, and the precipitated pale gray powder is collected and washed with MeOH (42.5 mg, 57%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  1.30 (s, 18H, *t*-Bu), 1.48 (s, 18H, *t*-Bu), 6.33 (s, 2H, CH<sub>2</sub>), 7.08 (d, 2H, aryl-H, 1.60 Hz) 7.40 (s, 2H, aryl-H), 7.81 (d, 2H, aryl-H, 1.64 Hz) 8.39 (d, 2H, aryl-H, 1.84 Hz). <sup>13</sup>C NMR (500 MHz, DMSO- $d_6$ )  $\delta$  29.90, 31.69, 33.83, 35.77, 62.15, 113.51, 118.07, 120.79, 121.25, 125.04, 132.98, 139.61, 153.84, 154.52. MS (HRMS): m/z= 661.27 [PdL + H]<sup>+</sup>. Anal. Calcd for C<sub>35</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub>Pd: C, 63.57; H,7.03; N, 8.47. Found: C, 63.18; H, 6.84; N, 8.03.

2.2.2.3. Complex **3**. First, 0.06 mL (0.43 mmol) of triethyl amine was added to a solution of 76.0 mg (0.106 mmol) of  $H_4L^{C_3O_3}Br_2$  and 48.8 mg (0.116 mmol) of *cis*-dichlorobis(dimethyl sulfoxide)-platinum(II) in 12 mL of EtOH under argon atmosphere. The mixture is heated at 100 °C and stirred for 5 h then overnight at 60 °C. The precipitated white powder is collected and washed with cold EtOH (58.0 mg, 73%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  1.30 (s, 18H, *t*-Bu), 1.48 (s, 18H, *t*-Bu), 6.28 (s, 2H, CH<sub>2</sub>), 7.11 (s, 2H, aryl-H) 7.43 (s, 2H, aryl-H), 7.68 (s, 2H, aryl-H) 8.37 (s, 2H, aryl-H). <sup>13</sup>C NMR (500 MHz, DMSO- $d_6$ )  $\delta$  29.94, 31.66, 33.90, 35.88, 62.07, 113.24, 116.74, 120.46, 120.87, 125.34, 134.29, 139.50, 140.04, 151.76. MS (HRMS): m/z = 749.33 [PdL]<sup>+</sup>. Anal. Calcd for C<sub>35</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub>Pt·1/3CH<sub>3</sub>OH: C, 55.80; H, 6.27; N, 7.37. Found: C, 55.40; H, 6.64; N, 7.39.

2.3. Crystal Structure Analysis. Single crystals of 1, 2, 3, and 1<sup>+</sup>.  $SbF_6^-$  were coated with perfluoropolyether, picked up with nylon loops, and mounted in the nitrogen cold stream of the diffractometer. Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) from a Mo-target rotating-anode Xray source equipped with INCOATEC Helios mirror optics was used. Final cell constants were obtained from least-squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the program SADABS.<sup>75</sup> The structures were readily solved by charge-flipping methods and subsequent difference Fourier techniques. The OLEX software<sup>76</sup> was used for the refinement. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. CCDC 1886567-1886569 and 1897863 contain the crystallographic data for 1, 2, 3, and  $1^+ \cdot \text{SbF}_6^-$ ; these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html.

**2.4. Computational Details.** Full geometry optimizations were performed with the Gaussian 9 program,<sup>77</sup> by using the B3LYP,<sup>78,79</sup> B3LYP-D3,<sup>80</sup> or CAM-B3LYP<sup>81</sup> functionals. The 6-31g\* basis set<sup>82</sup> was used for the C, H, N, and O atoms. For the metal ion in 1<sup>+</sup>, we tested both the 6-31g\* basis set and a pseudo-potential based on the LANL2Dz basis set.<sup>83</sup> For 2<sup>+</sup> and 3<sup>+</sup>, we used only the pseudo-potential for the metal center. Frequency calculations were systematically performed in order to ensure that the optimized structure corresponds to a minimum and not a saddle point. Optical properties were computed by using time-dependent density functional theory (TD-DFT)<sup>84</sup> with the same basis set as for optimization. The solvent



Figure 1. Synthetic route toward proligand  $H_4 L^{C_2 O_2} Br_2$ .

was taken in account by using a polarized continuum model (PCM).<sup>85</sup> The 30 lowest energy excited states were calculated. The calculations of the EPR parameters of  $1^+$  were carried out using the ORCA program package.<sup>86</sup> The EPR parameters were computed using the B3LYP functional<sup>78,87</sup> with D3 dispersion correction with Becke–Johnson damping. The Def2-TZV/P basis set<sup>88,89</sup> was used for all atoms except the metal. A softer basis set ("CP(PPP)") was used for the metal ion. The integration grid was Grid 6 in the orca convention, with a special radial integration accuracy set to 5.67 for the metal ion. A complete mean field approach was used to calculate the SOC, with Coulomb terms via RI. The magnetic exchange was calculated by using the Yamaguchi approach.<sup>90</sup>

#### 3. RESULTS AND DISCUSSION

**3.1. Synthesis of the Proligand and Complexes.** Proligand  $H_4L^{C_2O_2}Br_2$  was prepared in 33% yield following a six-step sequence starting from inexpensive 2,4-di-*tert*butylphenol (Figure 1). First, the starting material was quantitatively nitrated in a HNO<sub>3</sub>/CH<sub>3</sub>COOH medium. Then, the phenol protecting group was added by reaction with MeI under basic K<sub>2</sub>CO<sub>3</sub> condition following a classical procedure. The imidazole was constructed according to van der Donk et al.<sup>47</sup> by a treatment with glyoxal, followed by ammonium chloride, formaldehyde, and a strong acid. The coupling reaction between the aryl-substituted imidazole and dibromomethane was conducted under reflux and afforded the bis(imidazolium) salt as a white precipitate. Finally, deprotection of the phenol moieties was performed with BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> to yield the targeted ligand  $H_4L^{C_2O_2}Br_2$ .

The synthesis of nickel complex 1 was performed by mixing equimolar amounts of the bis(imidazolium) proligand  $H_4L^{C_2O_2}Br_2$  and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O under an argon atmosphere at refluxing EtOH in the presence of 4 equiv of Et<sub>3</sub>N. The same procedure was used for 2 and 3 except that the metal salt was Pd(OAc)<sub>2</sub> or Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>, respectively, in these cases.

**3.2. Structures of Complexes 1, 2, and 3.** The structure of 1 is depicted in Figure 2a; those of 2 and 3 are shown in the Supporting Information. The complexes are isostructural and show a mostly square planar metal center coordinated to two phenolate oxygens (O1) and two carbons of both NHC units



Figure 2. X-ray crystal structures of (a) 1 and (b)  $1^+ \cdot \text{SbF}_6^-$ .

(C7). Within 1, the Ni–O1 and Ni–C7 bond distances are 1.881 and 1.843 Å, respectively. The tetrahedral distortion at the metal center is marginal since the angle between the opposite mean planes O1–Ni–C7 and O1\*–Ni–C7\* is only  $5^{\circ}$ . The ligand is almost planar, with the two NHC units being coplanar within  $3^{\circ}$ , and the phenolate rings are coplanar with the neighboring NHC units within  $9^{\circ}$ . Geometry optimization by using the B3LYP-D3/6-31g\* functional accurately predict the structure of 1, with calculated Ni–C bond distances at 1.843 Å and Ni–O bond distances at 1.878 and 1.888 Å. For palladium and platinum derivatives 2 and 3, the same global arrangement is observed, with larger coordination bond distances due to the increased ionic radius of the metal center (Table 1, Supporting Information).

**3.3. Electrochemistry of the Proligand and Complexes.** The electrochemical behavior of proligand  $H_4L^{C_2O_2}Br_2$ and metal complexes 1–3 has been investigated by CV in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP (Figure 3 and the Supporting Information). The CV curve of the ligand (Supporting Information) displays irreversible oxidation waves at substantially low potentials, 0.31 and 0.63 V vs Fc<sup>+</sup>/Fc. The

Table 1. Coordination Bond Distances in 1–3 and 1<sup>+</sup> (Å) as well as the Nickel Complex from the Pincer Carbene Ligand  $H_2L^{OCO}$  (Chart 2)

complex	M-01	M-02 <sup><i>a</i></sup>	М-С7	M–X <sup><i>a</i>,<i>b</i></sup>
1	1.881(2)		1.843(2)	
2	2.021(2)		1.927(3)	
3	2.028(5)		1.918(7)	
[Ni(L <sup>OCO</sup> )(Pyr)]	1.835(2)	1.847(2)	1.793(4)	1.953(3)
1+	1.840(5)	1.854(5)	1.847(8)	1.850(8)
$[Ni(L^{OCO})(Pyr)]^+$	1.774(5)	1.785(7)	1.825(9)	1.985(10)

<sup>*a*</sup>For 1–3, the second half of the complex is generated by a symmetry operation. <sup>*b*</sup>X = C17 (1<sup>+</sup>) or  $N_{pyridine}$  ([Ni(L<sup>OCO</sup>)(Pyr)] and associated cation).



**Figure 3.** CV curve of a 0.5 mM CH<sub>2</sub>Cl<sub>2</sub> solution of 1, containing 0.1 M TBAP. T = 298 K, vitreous carbon working electrode. The potentials are given versus the Fc<sup>+</sup>/Fc reference.

irreversibility complicates the assignment of these redox processes; however, it is reasonable to assume that they are due to phenol oxidation. Complexes 1, 2, and 3 exhibit two oxidation waves in their CV curve. Both coulometry and rotating-disk electrode voltammetry demonstrate two successive monoelectronic processes. The oxidation waves are reversible, indicating that the oxidized products are stable on the CV time scale and that the reorganization upon oxidation is small. These results argue for ligand-centered redox processes, which produce phenoxyl radical species (see below). The potentials of the oxidation waves (all vs  $Fc^+/$ Fc) are  $E_{1/2}^{1} = 0.11$  and  $E_{1/2}^{2} = 0.60$  V (1),  $E_{1/2}^{1} = 0.21$  V and  $E_{1/2}^{2} = 0.55$  V (2), and  $E_{1/2}^{1} = 0.21$  and  $E_{1/2}^{2} = 0.65$  V (3) (Table 2). The  $E_{1/2}$  values are only slightly affected by the nature of the metal ion, reinforcing the idea that the phenolate groups undergo sequential oxidations. The potential values are in general smaller than those reported for group 10 metal(II)-N,N'-bis(3,5-ditert-butylsalicylidene)-1,2-cyclohexanediamine complexes, consistent with an increased thermodynamic

Table 2. Electrochemical Data for the Neutral Complexes<sup>a</sup>

complex	$E_{1/2}^{1}$	$\Delta E_{ m p}^{-1}$	$E_{1/2}^{2}$	$\Delta E_{\rm p}^{\ 2}$	$E_{1/2}{}^2 - E_{1/2}{}^1$	$K_{c}^{b}$
1 <sup>c</sup>	0.11	0.09	0.60	0.09	0.49	$2.7 \times 10^8$
2 <sup><i>c</i></sup>	0.21	0.06	0.55	0.07	0.34	$7 \times 10^{5}$
3 <sup>c</sup>	0.21	0.06	0.65	0.08	0.44	$3.7 \times 10^{7}$

"The potentials are given at 298 K and referenced to the Fc<sup>+</sup>/Fc redox couple (0.19 V vs Ag/AgNO<sub>3</sub> 0.01 M and  $\Delta E_p = 0.08$  V under our experimental conditions). "Comproportionation constant. Calculated according to  $K_c = \exp^{[(E_{1/2}^2 - E_{1/2}^1)F]/[RT]}$ . "In CH<sub>2</sub>Cl<sub>2</sub> (+ 0.1 M TBAP).

stabilization of high oxidation states with the present bis(phenol) NHC ligand.<sup>91,92</sup> It is also remarkable that the  $E_{1/2}^{1}$  value of 1 is similar to that reported for  $[Ni(L^{OCO})(Pyr)]$ (Chart 2, also assigned to the phenoxyl/phenolate couple). The large difference in Ni-O bond lengths between 1 and  $[Ni(L^{O\check{C}O})(Pyr)]$  therefore appears that it either is not a determinant for the first oxidation event within these series or is compensated by geometrical effects. The  $\Delta E_{1/2}$  value, which corresponds to the difference  $E_{1/2}^2 - E_{1/2}^{-1}$ , is usually taken as a measure of the electrochemical communication between two redox-active centers.<sup>92</sup>  $\Delta E_{1/2}$  is similar between 1 and [Ni(Salcn)] (0.49 vs 0.48 V), as well as between 2 and [Pd(Salcn)] (0.34 vs 0.35 V), showing that the influence of the spacer on the coupling is marginal. In contrast, the  $\Delta E_{1/2}$ differs substantially between 1 and [Ni(L<sup>OCO</sup>)(Pyr)] (0.60 V), suggesting that the denticity of the ligand and subsequent orientation of the phenolate groups with respect to each other plays important role. Finally, it must be emphasized that the  $\Delta E_{1/2}$  and subsequent comproportionation constant of **2** is the lowest of the series. Assuming that the two oxidative processes are centered on the ligand, this points to a weaker electronic communication between the redox active units in the palladium complex.

3.4. Oxidation Protocol and Structure of  $1^+$ ·SbF<sub>6</sub><sup>-</sup>. The cations were generated quantitatively either by exhaustive electrolysis at +0.25 V or by addition of 1.2 equiv of silver hexafluoroantimonate to a CH2Cl2 solution of the neutral precursor. Both methods gave the same results, with a successful oxidation that is verified by a color change from pale to dark green. Cation  $1^+$  was remarkably stable in CH<sub>2</sub>Cl<sub>2</sub> solution as no decomposition was observed after 2 weeks. Electrogenerated cations  $2^+$  and  $3^+$  were comparatively less stable, since an appreciable decomposition is observed within a couple of hours at room temperature. The lower stability of the phenoxyl radical complexes of palladium in comparison to that of nickel analogs was already noticed for one-electron-oxidized salen species.<sup>91</sup> It is therefore attributed to a particular reactivity of the phenoxyl ring rather than an effect of the carbene ligation. For cation  $1^+$ , a slow diffusion of pentane (2 days) into a concentrated solution of the chemically generated complex affords dark single crystals of 1+·SbF<sub>6</sub> of X-ray diffraction quality. The structure of 1+·SbF<sub>6</sub><sup>-</sup> shows a fourcoordinated nickel ion in a slightly dissymmetric environment. The Ni-O1, Ni-O2, Ni-C7, and Ni-C17 bond distances are 1.840, 1.855, 1.846, and 1.849 Å, respectively, disclosing a contraction of the coordination sphere upon oxidation. The angle between the mean planes O1-Ni-C2 and O2-Ni-C1 is 9°, indicative of a main square planar geometry as for 1. Interestingly, one phenolato ring (which comprises the C17 atom) is coplanar with the neighboring NHC unit, whereas the angle between the opposite phenolate (which comprises the C7 atom) and NHC rings is 20°. In line with this geometrical feature, the C-C bond connecting the NHC and phenolate rings is shorter when the latter rings are coplanar (1.402 vs 1.427 Å), suggesting an extended conjugation. The C1-O1 bond distance is 1.329 Å, which compares fairly well with that of 1, while the C11–O2 bond length is markedly shorter, 1.284 Å. This latter value falls in the range of that reported for phenoxyl radical rings.<sup>93–99</sup> Thus, the present data unequivocally show that oxidation has occurred on the organic framework in 1. The fact that a significant difference of bond lengths is observed between C1-O1 and C11-O2 whereas the difference does not reach such an extent regarding the Ni–

functional complex	B3LYP 1 <sup>+a</sup>	B3LYP-D3 1 <sup>+a</sup>	CAM-B3LYP 1 <sup>+a</sup>	B3LYP 1 <sup>+b</sup>	B3LYP-D3 1 <sup>+b</sup>	exp 1 <sup>+</sup>	B3LYP-D3 1 <sup>2+a</sup>
Ni-O1	1.839	1.840	1.811	1.871	1.872	1.840(5)	1.877
Ni-O2	1.852	1.851	1.863	1.886	1.884	1.854(5)	1.894
Ni-C1	1.840	1.848	1.822	1.864	1.871	1.847(8)	1.846
Ni-C2	1.833	1.844	1.840	1.859	1.869	1.850(8)	1.841
a 21 a* basis set on	all stome b6 2	1 of having not on t	ba C H N O and	I and 2D7 ECD	on Ni		

Table 3. Calculated Coordination Bond Distances in 1<sup>+</sup> (Å)

'6-31 g\* basis set on all atoms. '6-31 g\* basis set on the C, H, N, O, and LanL2DZ ECP on Ni.

O1 and Ni-O2 bond distances suggests partial localization of the ligand radical at the solid state. Accordingly,  $1^+$  can be classified as a borderline II/III mixed-valent radical compound, similar to one-electron-oxidized nickel(II) salophen complexes.98 Finally, it must be stressed that the oxidation is accompanied by a slight contraction of the coordination sphere. As already noticed in salen complexes, the removal of an electron from an antibonding ligand-centered orbital results in increased back-donation and further contraction of the coordination sphere.93

3.5. DFT Calculations of the Cations and Dications. The electronic structure of the complexes has been investigated by density functional theory (DFT). For that purpose we used the popular hybrid functional B3LYP, which gave excellent results for [Ni(L<sup>OCO</sup>)(Py)]<sup>+,45</sup> as well as the B3LYP-D3 and CAM-B3LYP which both include corrections for long-range dispersion interactions. The latter proved to be superior to B3LYP for describing one-electron-oxidized nickel salen complexes featuring di-tert-butyl groups.<sup>100</sup> Both fullelectron and effective core potentials were used for the metal center in the case of  $1^+$  (and its pyridine adducts) and  $1^{2+}$ , while effective core potentials only were used for the heavier metal center in the cases of  $2^+$ ,  $3^+$ , and  $2^{2+}$ . The bonding parameters for the neutral complexes are summarized in the Supporting Information.

The B3LYP functional in combination with a full-electron basis set leads to optimized structures wherein the coordination bonds are within 0.015 Å of the experiment for  $1^+$  (Table 3). The coordination sphere is slightly dissymmetric, with a Ni–O1 bond that is 0.013 Å shorter than the Ni–O2 one. The contraction of the coordination sphere upon oxidation of 1 to  $1^+$  is nicely predicted. As expected, the use of a pseudopotential for the metal center is detrimental to the accuracy of the optimization. The B3LYP-D3 functional affords an optimized structure that is mostly similar to that obtained with the B3LYP functional, with somewhat better agreement with experiment regarding the Ni-C bonds. CAM-B3LYP predicts an exceedingly dissymmetric coordination sphere (Ni-O bonds of 1.811 and 1.863 Å, Table 3), with large differences in C-O bond distances: 1.321 vs 1.278 Å. For all the functionals and basis sets tested, the spin density is mainly found on the O and both C<sub>ortho</sub> and C<sub>para</sub> atoms of the peripheral ring(s), without any appreciable density at the carbene moieties. As an example, the spin density plot for 1<sup>+</sup> with the B3LYP-D3 functional is depicted in Figure 4 (see the Supporting Information for those of  $2^+$  and  $3^+$ ). This confirms the main phenoxyl radical character of the cations. The extent of delocalization is largely influenced by the functional. Both the B3LYP and B3LYP-D3 predicts large delocalization of the spin density over both peripheral rings in the cations, whereas the CAM-B3LYP predicts localization on one peripheral ring. As will be shown below, large delocalization is observed by spectroscopy for 1<sup>+</sup>, suggesting that the B3LYP-D3 functional is more appropriate for describing these complexes. Interest-



Figure 4. Spin density plot of  $1^+$ , including the Mulliken spin populations (B3LYP-D3/6-31g\*).

ingly, the Mulliken spin population is not zero on the nickel atom, but 0.17 (B3LYP and B3LYP-D3) or 0.10 (CAM-B3LYP). This small but sizable spin population results from the interaction between an out-of-plane d orbital and the  $\pi$ orbital of the phenoxyl moieties, as already noticed in a few nickel radical complexes.<sup>41,101</sup> It has to be emphasized that the calculations do not predict significant changes in Mulliken spin population on the organic framework along the series Ni, Pd, and Pt, further supporting homogeneity in the electronic structure of the cations.

On going from cation  $1^+$  (or  $2^+$ ) to dication  $1^{2+}$  (or  $2^{2+}$ ), the calculations predict an elongation of the M-O bonds of ca. 0.04 Å, with a coordination sphere that remains slightly dissymmetric. For 1<sup>2+</sup>, the predicted Ni-O1 and Ni-O2 bond distances are indeed 1.894 and 1.877 Å with the B3LYP-D3 functional. In contrast, the M–C bonds are mostly unaffected by the change in oxidation state of the complexes (1.841 and 1.846 Å for  $1^{2+}$ ). Similar to the cations, the complex is bowlshaped, but the effect is more pronounced in this case. The energetic analysis shows that the broken symmetry solution lies lower in energy than the triplet state for the dication. The genuine singlet was located 9 kcal/mol above the triplet. Its wave function has an internal instability, and collapses to the broken symmetry solution upon reoptimization. The distribution of the spin density in the broken symmetry singlet is mostly similar to that observed in the cation except that it is twice as large (in magnitude), positive on one phenoxyl ring, and negative on the opposite one. In other terms, the dications are antiferromagnetically exchanged bis(phenoxyl) diradical species. The magnetic exchanges estimated by using the Yamaguchi formula are -215 and -102 cm<sup>-1</sup> for  $1^{2+}$  and  $2^{2+}$ , respectively (see the Supporting Information). These large values are comparable to those calculated for bis-(iminosemiquinone)<sup>38</sup> and bis(phenoxyl)<sup>102</sup> radical systems and consistent with the absence of EPR signal for the dications.

**3.6. UV–Vis–NIR Spectroscopy in CH<sub>2</sub>Cl<sub>2</sub>.** The CH<sub>2</sub>Cl<sub>2</sub> solutions of complexes 1-3 show a pale green color. Their UV-vis spectra (Figure 5, Table 4, and the Supporting Information) show a band in the range of 360–377 nm, which is assigned to a  $d-\pi$ (phenolate)  $\rightarrow d-\pi^*$ (carbene) transition



**Figure 5.** UV–vis–NIR spectra of **1** (black), (1<sup>+</sup>) (red), and (1<sup>2+</sup>) (blue) in CH<sub>2</sub>Cl<sub>2</sub> solutions containing 0.1 M TBAP. The NIR feature in the spectrum of  $1^{2+}$  arises from its decomposition into  $1^{2+}$ . T = 298 K (neutral) and 253 K (cation and dication).

Table 4. UV-Vis-NIR Data for the Metal Complexes<sup>*a,b*</sup>

complex	$\lambda_{ m max} \; [ m nm] \; (arepsilon \; [ m M^{-1} \;  m cm^{-1}])$
1	348 (9788), 377 (5451), 460 (446, br)
1+	332 (14146), 881 (4308), 1094 (6014), 2390 (19291)
1 <sup>2+c</sup>	291 (19810), 309 (18397), 399 (7088), 708 (3185, sh), 906 (7700), 1107 (4485, sh), 2388 (2595)
$1_{py}^{+d}$	401 (7807), 728 (2820), 1775 (1149)
$1_{py2}^{+d}$	341 (10873), 395 (7831), 707 (656)
2	341 (6100), 360 (4939, sh)
<b>2</b> <sup>+</sup>	318 (13017), 395 (3642, sh), 410 (3271, sh), 528 (2029), 1700 (2366, sh), 2600 (2930, br)
2 <sup>2+</sup>	310 (18339), 416 (5266), 516 (3985), 766 (2449)
3	312 (6396), 348 (6766), 367 (7214)
3+	322 (12635), 400 (3968, sh), 532 (1185), 622 (1479), 822 (2888), 962 (3404), 2294 (16037)
a	

<sup>*a*</sup>In CH<sub>2</sub>Cl<sub>2</sub> solutions containing 0.1 M TBAP. Sh: shoulder; Br: broad. <sup>*b*</sup>The dication 3<sup>2+</sup> was proved to be significantly less stable than the other ones. It quickly evolves toward the cation (see the Supporting Information). <sup>*c*</sup>Due to the instability of the dication it was not possible to avoid the presence of a small amount of 1<sup>+</sup> as contaminant (ca. 15%), which gives rise to the band at around 2400 nm. The molar extinction coefficients are calculated based on the initial concentration of complex (before electrolysis). <sup>*d*</sup>Data of 1<sub>py2</sub><sup>+</sup> were taken from spectra recorded in 0.4 M pyridine. The data of 1<sub>py</sub><sup>+</sup> are taken from the fitted spectrum.

on the basis of TD-DFT calculations ( $\lambda_{calc} = 392 \text{ nm}$ ,  $f_{osc} = 0.1357$  for 1, see the Supporting Information). A broad band of lower intensity is observed at 500 nm, which corresponds to the  $d_{z^2} \rightarrow d_{x^2-y^2}$  transition ( $\lambda_{calc} = 449 \text{ nm}$ ,  $f_{osc} = 0.0158$ ).

The monocations exhibit a rich vis-NIR spectrum, in contrast to the neutral precursors (Figure 5 and Supporting Information). The most salient feature is a band of moderate to high intensity at 2396 nm (4174 cm<sup>-1</sup>), 2600 nm (broad, 3850 cm<sup>-1</sup>), and 2294 nm (4359 cm<sup>-1</sup>) for 1<sup>+</sup>, 2<sup>+</sup>, and 3<sup>+</sup>, respectively (Table 4). Additional bands are observed in the range 800-1100 nm. Fully delocalized class III mixed-valent and borderline class II/III species (according to the Robin Day classification)<sup>106</sup> usually exhibit a sharp and intense chargetransfer transition at low energy. Accordingly, the shape of the most prominent NIR band was analyzed by using the Marcus-Hush equation.<sup>105</sup> As summarized in Table 5, the calculated  $\Delta v_{1/2}$  is larger than the experimental values for 1<sup>+</sup> and 3<sup>+</sup>, indicative of substantial delocalization of the electronic hole over both peripheral rings. This high extent of delocalization is also supported by the fact that the  $2H_{AB}/\lambda$  ratio is close to one for 1<sup>+</sup>, hence at the limit of class III mixed valent systems.<sup>103</sup> The low intensity and relatively important line width of the lowest energy band of  $2^+$  suggests that this complex is the least delocalized of the series.<sup>107</sup> This observation is consistent with the above electrochemical data, which disclose a weaker electronic communication between the peripheral rings in the palladium complex.

Dications  $1^{2+}$  and  $2^{2+}$  were found to be stable enough at 253 K for allowing spectroscopic characterization. Unfortunately, complex  $3^{2+}$  decomposes significantly at this temperature into  $3^+$  (Supporting Information) precluding any detailed investigation; hence, the oxidation of the cations to corresponding dications  $1^{2+}$  and  $2^{2+}$  is accompanied by a strong decrease of the characteristic band above 2000 nm, which is no more present in the second case. Interestingly, the features in the 500–1000 nm region are still present but shifted and with distinct ratio of intensity (Table 4). In the case of  $1^{2+}$ , it is observed as a main band at 906 nm together with shoulders appearing on either side of the predominant band.

In order to gain insight on the electronic excitations involved in the transitions, we conducted TD-TFT calculations. For all the cations, the calculations with the B3LYP-D3 functional predict an intense NIR band in the 4281–5081 cm<sup>-1</sup> region (Table 6), in agreement with experiment. As an example, the band predicted at 5081 cm<sup>-1</sup> ( $f_{osc} = 0.173$ ) for 1<sup>+</sup> is assigned to the experimental band at 4174 cm<sup>-1</sup>. It corresponds to  $\beta$ -HOMO  $\rightarrow \beta$ -LUMO, with both the donor and acceptor orbitals being developed over both peripheral rings (Table 6, Figure 6). It is therefore assigned to an intervalence chargetransfer (IVCT) transition. The calculations also predict two electronic excitations of moderate intensity in the range 800–

Table 5. Band Shape Analysis of the Lowest Energy NIR Transition in the Monoradical Complexes

complex <sup>a</sup>	$\lambda = \nu_{\rm max} \ ({\rm cm}^{-1})$	$\varepsilon ~(\mathrm{M^{-1}~cm^{-1}})$	calcd $\Delta  u_{1/2}~({ m cm}^{-1})$	$\exp  \Delta \nu_{1/2}  \left( \mathrm{cm}^{-1} \right)^{\boldsymbol{b}}$	$\% \Delta \nu_{\rm HTL}^{c}$	$H_{\rm AB}~({\rm cm}^{-1})^d$	$2H_{ m AB}/\lambda$
1+	4184	19291	684	2778	25%	1915 <sup>e</sup>	0.916
2+				n.d. <sup>f</sup>			
3+	4359	16037	800	2835	28%	1764 <sup>g</sup>	0.809

<sup>*a*</sup>Electrochemically generated in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup>Calculated in the high-temperature limit (htl) at 293 K according to  $\Delta \nu_{1/2} = (16 \ln 2 RT \nu_{max})^{1/2}$ . <sup>*c*</sup>Calculated from %  $\Delta \nu_{HTL} = (\text{calcd } \Delta \nu_{1/2}/\text{exp } \Delta \nu_{1/2}) \times 100$ . <sup>*d*</sup>Electronic coupling matrix element was calculated according to refs 103–105:

$$H_{\rm AB} = 2.06 \times 10^{-2} \times \frac{\sqrt{\varepsilon_{\rm max}} \ \Delta \nu_{1/2}}{r_{\rm CT}}$$

<sup>e</sup>With  $r_{\rm CT} = r_{\rm O1-O2}$  distance (2.527 Å) from the crystallographic structure of 1<sup>+</sup>. <sup>f</sup>Not determined due to the lack of precision regarding the estimation of large line width. <sup>g</sup>With  $r_{\rm CT} = r_{\rm O1-O2}$  distance (2.762 Å) from the crystallographic structure of 3.

			energy	(cm <sup>-1</sup> )	
complex (multiplicity)	main transition	assignment	calcd	exp	$f_{ m osc}$
	$\beta$ -HOMO $\rightarrow \beta$ -LUMO	LLCT	5081	4184	0.173
1 <sup>+</sup> (doublet)	b	MLCT/LLCT	10482	9141	0.0728
	b	MLCT/LLCT	12019	11351	0.0368
1 + (doublat)	$\beta$ -HOMO $\rightarrow \beta$ -LUMO	LMCT	7973	5634	0.0341
I <sub>py</sub> (doublet)	b	LMCT	16346	13736	0.0431
$1_{py2}^{+}$ (doublet)	b	LMCT/dd	26553	25316	0.0736
$2^{+}$ (doublat)	$\beta$ -HOMO $\rightarrow \beta$ -LUMO	LLCT	4281	3846	0.1887
2 (doublet)	$\beta$ -HOMO-5 $\rightarrow \beta$ -LUMO	MLCT/LLCT	16287	18940	0.0359
	$\beta$ -HOMO $\rightarrow \beta$ -LUMO	LLCT	4998	4359	0.2068
3 <sup>+</sup> (doublet)	$\beta$ -HOMO-1 $\rightarrow \beta$ -LUMO	LLCT	11353	10395	0.045
	$\beta$ -HOMO-2 $\rightarrow \beta$ -LUMO	LLCT	12723	1265	0.0247
$1^{2+}$ DC(1.1)	$\beta$ -HOMO $\rightarrow \beta$ -LUMO	LLCT	9963	9033	0.099
1 D3(1,1)	Ь	LLCT	11870	11038	0.0691
2 <sup>2+</sup> BS(1,1)	$\alpha$ -HOMO $\rightarrow \alpha$ -LUMO	LLCT	11500	13055	0.0600
	b	LLCT	17769	19380	0.0659

Table 6. TD-DFT Assignment of the Lowest Energy Transitions in the Radical Complexes<sup>a</sup>

<sup>a</sup>B3LYP-D3/TZVP except for Pd and Pt (LanL2DZ ECP)/PCM. <sup>b</sup>From a natural transition orbital (NTO) analysis.



**Figure 6.** TD-DFT calculated electronic excitations for 1<sup>+</sup> (B3LYP-D3/TZVP/PCM).

1100 nm (9000–12 500 cm<sup>-1</sup>) for 1<sup>+</sup> and 3<sup>+</sup>, which are blueshifted and out of the range for 2<sup>+</sup> according to experiment (Table 6). For 1<sup>+</sup> they are calculated at 10 482 cm<sup>-1</sup> ( $f_{osc} =$ 0.0728) and 12 019 cm<sup>-1</sup> ( $f_{osc} =$  0.0368) and account for the experimental bands at 9225 and 11 415 cm<sup>-1</sup>. A natural transition orbital analysis (Figure 6 and the Supporting Information) show that both are  $\pi$ -d  $\rightarrow \pi^*$  charge transfer (CT) transitions. In the case of 3<sup>+</sup>, they are calculated at 11 353 cm<sup>-1</sup> ( $\beta$ -HOMO-1  $\rightarrow \beta$ -LUMO,  $f_{\rm osc} = 0.045$ ) and 12 723 cm<sup>-1</sup> ( $\beta$ -HOMO-2  $\rightarrow \beta$ -LUMO,  $f_{\rm osc} = 0.0247$ ) and account for the experimental bands at 10 395 and 12 165 cm<sup>-1</sup>. Both are again mostly assigned to ligand-to-ligand charge transfer (LLCT) transitions, wherein the donor orbital is mainly delocalized over both the peripheral rings and carbene units and the acceptor one corresponds to the peripheral phenoxyl rings.<sup>108</sup>

For dications  $1^{2+}$  and  $2^{2+}$ , we considered the broken symmetry solutions, according to the energetic analysis. Calculations perfectly predict the absence of electronic transition below ca.  $10\,000$  cm<sup>-1</sup> (Table 6, Supporting Information). The lowest energy electronic excitations with the most significant intensity are predicted at 9963 and 11 870  $cm^{-1}$  for  $1^{2_{+}}$  and 11 500 and 17 769  $cm^{-1}$  for  $2^{2_{+}}$ . While the latter needs a NTO analysis to be described (see the Supporting Information), the first corresponds to  $\beta/\alpha$ -HOMO  $\rightarrow \beta/\alpha$ -LUMO and arises from an LLCT charge transfer (Table 6). Here the donor orbital is localized on one phenoxyl ring, while the acceptor one is localized on the opposite ring. Hence, it corresponds to a phenoxyl-to-phenoxyl CT (see the Supporting Information) that is mostly similar in nature to the intense NIR feature reported for singlet bis(iminosemiquinone) and bis(diiminosemiquinone) dirad-



**Figure 7.** X-Band EPR spectra of the electrochemically generated 1<sup>+</sup> in a)  $CH_2Cl_2$  (+ 0.1 M TBAP);  $CH_2Cl_2$  (+ 0.1 M TBAP) containing 0.4 M pyridine (conversion of 1<sup>+</sup> into 1py<sub>2</sub><sup>+</sup>). The black lines are experimental spectra; the red lines are simulation by using the parameters given in Table 7. Microwave frequency 9.43 GHz, power 1.1 mW; mod. frequency 100 kHz, amperage 0.3 mT; T = 100 K.



**Figure 8.** X-band EPR spectra of electrochemically generated  $2^+$  and  $3^+$  in frozen CH<sub>2</sub>Cl<sub>2</sub> (+ 0.1 M TBAP). The black lines are experimental spectra; the red lines are simulation by using the parameters given in Table 6. Microwave frequency 9.43 GHz; power 1.1 mW (a) or 2.2 mW (b); mod. frequency 100 kHz, amperage 0.3 mT; T = 100 K.



**Figure 9.** Vis–NIR spectra of  $1^+$  in CH<sub>2</sub>Cl<sub>2</sub> (+ 0.1 M TBAP) upon addition of pyridine (0 to 0.4 M). (a) Experimental spectra; (b) Simulated spectra for  $1^+$  (blue) and the pyridine adducts  $1_{py}^+$  (orange) and  $1_{py2}^+$  (red) giving the log  $\beta$  values listed in the text. T = 298 K.

ical complexes.<sup>38,109–111</sup> The electronic excitation leads to the phenolate-Ni-phenoxonium state.

3.7. EPR Spectroscopy in CH<sub>2</sub>Cl<sub>2</sub>. The EPR spectra of the monocations recorded in frozen CH<sub>2</sub>Cl<sub>2</sub> at 100 K are depicted in Figures 7 and 8 and the Supporting Information. The spectrum of chemically generated cation  $1^+$  consists of a single unresolved resonance at g = 2.033, which is reminiscent of an (S = 1/2) system (Figure 7). The large peak-to-peak line width (5.55 mT) suggests an unresolved anisotropy in the system, as already noticed for [Ni(L<sup>OCO</sup>)(Pyr)]<sup>+</sup>. In the presence of 0.1 M TBAP (or in the case of the electrochemically generated  $1^+$ ) the anisotropy is clearly resolved, revealing a rhombic system with principal g-tensor components at 2.087, 2.016, and 1.992  $(g_{av} 2.032)$ . Due to line broadening of the low-field component, the precision on the highest g-tensor is inferior to that of the other ones. Both in the presence and absence of electrolyte, the  $g_{average}$  values in  $CH_2Cl_2$  are indicative of a main phenoxyl radical character of 1<sup>+</sup>. However, both the anisotropy and gaverage exceed the values typically reported for genuine phenoxyl radicals ( $g_{iso} = 2.005$ ).<sup>112</sup> This behavior reflects a participation of an out-of-plane d orbital to the singly occupied molecular orbital (SOMO), as predicted by calculations (Figure 5).<sup>40,41,93,94,113</sup> It is significant that the g value of  $1^+$ is much smaller than that reported for  $[Ni(L^{OCO})(Pyr)]^+$   $(g_{iso})$ = 2.056).<sup>45</sup> The metallic character of the SOMO is therefore much less in 1, which may be inferred, at least partially, from the longer coordination bond distances. We calculated the gtensor by DFT-D3 methods. The predicted g values for  $1^+$  are  $g_z = 1.991$ ,  $g_x = 2.018$ , and  $g_y = 2.054$  (giving a  $g_{average}$  of 2.021), which agree well with experiments. It is noticeable that these

calculations perfectly reproduce the decrease in  $g_{iso/gaverage}$  between 1<sup>+</sup> and  $[Ni(L^{OCO})(Pyr)]^+$ .

The EPR spectrum of electrochemically generated  $2^+$ displays a rhombic (S = 1/2) system characterized by g values 2.021, 2.008, and 1.983 ( $g_{average} = 2.004$ ). As already noticed for salen and semiquinone systems, the  $g_{\text{average}}$  is much less than that in the corresponding nickel complexes. It falls well below those classically observed in Pd(III) complexes ( $g_{\perp}$  > 2.1),<sup>114–116</sup> confirming the radical character of  $2^+$ . Similar to 1<sup>+</sup>, we used DFT-D3 with all-electron basis sets to calculate the g-tensor. The predicted values for  $2^+$  are 2.013, 1.999, 1.992, i.e., again in reasonable agreement with experiments. The spectrum of platinum complex 3<sup>+</sup> was deconvoluted into two subspectra corresponding to the <sup>195</sup>Pt isotope (nuclear spin 1/ 2, 34%) and other isotopes with no nuclear spin (66%). The g values obtained from simulation are 2.140, 1.999, and 1.885, with hyperfine coupling (HFC) constants of 280, 160, and 150 MHz, respectively. Similar to the palladium complex, the g values of  $3^+$  span over a short-range around g = 2, pointing out the main radical character of the complex.<sup>91,92</sup> The same observation applied to the HFC constants, which are relatively small in comparison to genuine Pt(III) complexes.<sup>117–119</sup>

**3.8.** Formation of Nickel(III)–Pyridine Adducts. The UV–vis–NIR spectrum of  $1^+$  was found to be sensitive to the presence of the coordinating base pyridine.<sup>120</sup> An example of titrations conducted in CH<sub>2</sub>Cl<sub>2</sub> at 298 K is depicted in Figure 9. A clean isosbestic point is observed during the addition of the first aliquots (up to 300 equiv), indicative of a simple equilibrium between two absorbing species. The absorbance remains unchanged after several hours confirming the substantial stability of the so-formed pyridine adduct. During

the addition of pyridine (up to 300 equiv), both the bands in the 800–1200 nm and >2000 nm region decrease in intensity, while new bands appear at around 1700 and 700 nm, as well as features around 400 nm. The addition of more pyridine (up to 4000 equiv, 0.4 M pyridine) results in the total disappearance of the NIR transitions. Only a low-intensity band subsists at around 707 nm, as well as an intense band at 395 nm (Table 4).

In order to determine the binding constants with pyridine, we fitted the vis-NIR titration data by considering two equilibria involving the formation of monopyridine adduct  $\mathbf{1}_{py}$ followed by the formation of dipyridine adduct  $1_{2py}^+$ . The corresponding log  $\beta$  values are 1.3 and 2.2 M<sup>-1</sup> at 298 K, with a deconvoluted visible spectrum that shows an intense band at 728 nm for  $\mathbf{1}_{py}^+$  (Figure 9b). At lower temperatures, the formation of the pyridine adducts is facilitated, as reflected by larger log  $\beta$  values of 2.5 and 3.8 M<sup>-1</sup> at T = 233 K. This temperature dependence follows that observed for one-electron-oxidized Ni(II)-salophen complexes,<sup>113,121</sup> but all the log  $\beta$  values are remarkably lower in the present case. We interpret this trend by the strong Ni-carbene bonds in organometallic complex 1<sup>+</sup>, which disfavors the binding of axial ligands. The structures of the monopyridine and dipyridine adducts were computed by DFT-D3. For  $1_{py}^{+}$ , the metal ion lies in a square pyramidal geometry, with the pyridine bound in apical position. In the case of  $1_{py2}^+$ , the metal center lies in an elongated octahedral geometry. In the latter case, the ligand adopts an umbrella shape, while the two pyridines are tilted by ca.  $90^{\circ}$ , in order to minimize the steric clashes (see the Supporting Information). In both  $1_{py}^{+}$  and  $1_{py2}^{+}$ , the magnetic orbital is  $d_{z^2}$ , with Mulliken spin population at the nickel ion of 0.81 and 0.87, respectively. The binding of one or two pyridine molecules therefore promotes an intramolecular electron transfer that leads ultimately to Ni(III) complexes in both cases. By using TD-DFT-D3, we calculated the electronic spectra of the adducts. For  $1_{py}^{+}$ , an intense band is predicted at 612 nm ( $f_{osc} = 0.0431$ ), which is assigned to the visible band unraveled at 728 nm in the deconvoluted spectrum. A less intense NIR band is predicted at 1254 nm ( $f_{osc} = 0.0341$ ,  $\beta$ -HOMO  $\rightarrow \beta$ -LUMO), which accounts for the NIR tail experimentally detected during the titration. Both arise from LMCT transitions. Calculations on  $1_{py2}^{+}$  do not predict bands of significant intensity ( $f_{\rm osc}$  > 0.004) above 450 nm, in agreement with experiment. An intense electronic excitation (mainly LMCT) is predicted at 377 nm ( $f_{osc} = 0.0736$ ), which corresponds to the band experimentally observed at 395 nm.

In order to confirm the nature of the pyridine adducts, we recorded the EPR spectrum of 1<sup>+</sup> as a function of pyridine concentration. By using a stoichiometric amount of pyridine a rhombic signal was observed with g values of 2.233, 2.199, and 2.003 (Table 7, Supporting Information). Both the large anisotropy and the deviation of the  $g_{average}$  value from that measured for 1<sup>+</sup> demonstrate the predominant metallic character of the SOMO. On the other hand the ordering of g values suggests a  $d_{z^2}$  ground state for the complex, as expected for square pyramidal or octahedral Ni(III) complexes. Most importantly, the high-field component was hyperfine split into a three-line pattern (70 MHz). The unpaired electron thus interacts strongly with the nuclear spin of a single <sup>14</sup>N nucleus  $(I_{\rm N} = 1)$ , consistent with a square pyramidal environment of the metal center with an axially bound pyridine. In the presence of 0.4 M pyridine, the EPR spectrum of 1<sup>+</sup> displays a rhombic signal with g values of 2.191, 2.165, and 2.013 (Table

## Table 7. Spin Hamiltonian Parameters for the<br/>Monocations $^{a}$

complex <sup>a</sup>	g-tensor	gaverage	A-tensor
1+	2.087, 2.016, 1.992	2.032	
1 <sup>+b</sup>	2.054, 2.018, 1.991	2.021	
1py <sup>+</sup>	2.233, 2.199, 2.003	2.145	68, 83, 70
1py+ <sup>b</sup>	2.174, 2.142, 2.020	2.112	59, 61, 77
$1py_2^{+c}$	2.191, 2.165, 2.013	2.123	50, 50, 64 <sup>c</sup>
$1py_2^{+b}$	2.140, 2.127, 2.020	2.096	47, 48, 61
<b>2</b> <sup>+</sup>	2.021, 2.008, 1.983	2.004	
2 <sup>+b</sup>	2.013, 1.999, 1.992	2.001	
3+	2.140, 1.999, 1.885	2.008	280, 160, 150 <sup>d</sup>

<sup>*a*</sup>Electrochemically generated in CH<sub>2</sub>Cl<sub>2</sub> (+ 0.1 M TBAP). The hyperfine coupling constants are given in MHz. Values determined by spectral simulations. <sup>*b*</sup>Calculated by DFT (B3LYP-D3BJ with the TZVP basis set for C,H,O,N and CP(PPP) for the metal center). <sup>*c*</sup>In the presence of 0.5 mM pyridine (**1Py**<sup>+</sup>), or 0.4 M pyridine (**1Py**<sub>2</sub><sup>+</sup>). <sup>*d*</sup>The spectrum was simulated by considering 34% of the <sup>195</sup>Pt isotope (nuclear spin = 1/2) and 66% of isotopes with no nuclear spin.

7), which are again reminiscent of Ni(III) complexes. They are distinct from those measured for  $1_{py}^{+}$ , disclosing the formation of a different complex. In this case, a five-line pattern is observed in all three main resonances, which arises from the interaction of the electron spin with two equivalent <sup>14</sup>N nucleus. The HFC constants of 50-64 MHz are fully consistent with the fact that both <sup>14</sup>N are orientated along the  $d_{z^2}$  orbital, i.e., the magnetic orbital of a  $d^7$  Ni(III) metal ion in an elongated octahedral geometry. We further calculated the spin Hamiltonian parameters by using quantum chemistry. As shown in Table 7 the calculations predict reasonably well the experimental values, despite the anisotropy and  $g_{average}$ being slightly underestimated. This behavior is in fact not unexpected and reflects the tendency of DFT to overestimate the covalency of the coordination bonds. Most importantly, the trend in both  $g_{average}$  and g anisotropy is perfectly predicted along the series  $1^+$ ,  $1_{py}^+$ , and  $1_{2py}^+$ , as well as the trend in HFC constants. Thus, the combined EPR and DFT results corroborate the successive formation of the mono and bis(pyridine) adduct upon addition of increasing amount of pyridine to  $1^+$  and confirm the formation of a Ni(III) complex featuring NHC donors.

#### 4. CONCLUSION

In summary, we prepared the bis(phenol) NHC complexes  $[M(II)(L^{C_2O_2})]$  (M(II) = Ni, 1; Pd, 2; and Pt, 3), which feature a planar  $C_2O_2$  donor set. They could be readily oxidized into stable radical cations. Both 1<sup>+</sup> and 3<sup>+</sup> exhibit an intense NIR band (intervalence charge transfer), which reflects their class (II/III) mixed-valent radical character. In other terms, the ligand radical SOMO is delocalized over both phenoxyl moieties. This band is less intense in 2<sup>+</sup>, suggesting less delocalization. Cation 1<sup>+</sup> was crystallized and consistently shows an almost symmetrical coordination sphere with ligand radical features. Addition of pyridine induces an intramolecular electron transfer, which affords an unprecedented NHC–Ni(III) complex. The Ni(III) center lies in either a square pyramidal or octahedral geometry, depending on the amount of pyridine added.

In conclusion, we herein demonstrate with this unique ligand design that the carbene function, which is well-known for stabilizing low-valent metal ions (Ni(0), Ni(I), and Ni(II)

in particular)<sup>47</sup> could also accommodate Ni(III) or alternatively participates in the stabilization of radical complexes<sup>122</sup> having high oxidation states (Ni, Pd, and Pt), both of which being elusive or rarely described species. We envisage that these findings could open new perspectives in catalysis.<sup>47,123</sup> In addition, these results illustrate the importance of the ligand design and its denticity in controlling the electronic structure of the oxidized complexes (Chart 3). The cationic monopyridine adduct of  $H_2L^{OCO}$  is indeed mostly a radical complex,<sup>45</sup> whereas  $1_{pv}$ <sup>+</sup> is a genuine Ni(III) complex.

## Chart 3. Electronic Structures of Oxidized Bis(phenol) NHC Nickel Complexes<sup>a</sup>



<sup>a</sup>Structure of [Ni(L<sup>OCO</sup>)(Pyr)]<sup>+</sup> from ref 45.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00784.

Additional UV–vis–NIR, EPR and CV data, spin density plots for the cations and dications, xyz coordinates for all the complexes, TD-DFT and NTO analysis of the electronic excitations, and crystallographic data (PDF)

#### **Accession Codes**

CCDC 1886567–1886569 and 1897863 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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