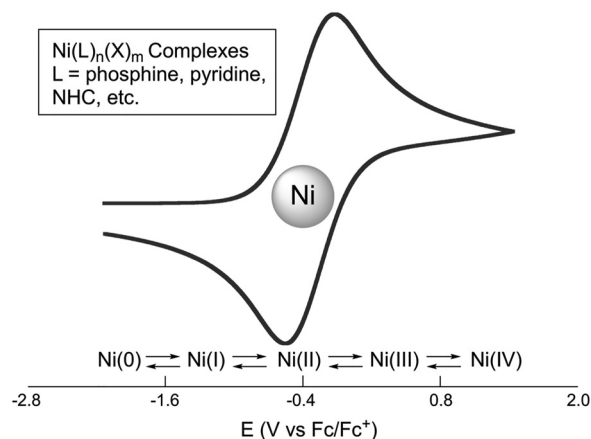


# Experimental Electrochemical Potentials of Nickel Complexes

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**Abstract** Nickel-catalyzed cross-coupling and photoredox catalytic reactions has found widespread utilities in organic synthesis. Redox processes are key intermediate steps in many catalytic cycles. As a result, it is pertinent to measure and document the redox potentials of various nickel species as precatalysts, catalysts, and intermediates. The redox potentials of a transition-metal complex are governed by its oxidation state, ligand, and the solvent environment. This article tabulates experimentally measured redox potentials of nickel complexes supported on common ligands under various conditions. This review article serves as a versatile tool to help synthetic organic and organometallic chemists evaluate the feasibility and kinetics of redox events occurring at the nickel center, when designing catalytic reactions and preparing nickel complexes.

- 1 Introduction
  - 1.1 Scope
  - 1.2 Measurement of Formal Redox Potentials
  - 1.3 Redox Potentials in Nonaqueous Solution
- 2 Redox Potentials of Nickel Complexes
  - 2.1 Redox Potentials of (Phosphine)Ni Complexes
  - 2.2 Redox Potentials of (Nitrogen)Ni Complexes
  - 2.3 Redox Potentials of (NHC)Ni Complexes

**Key words** redox potentials, nickel, cyclic voltammetry, reduction, oxidation

## 1 Introduction

### 1.1 Scope

In recent years, nickel-catalyzed cross-coupling,<sup>1</sup> photoredox-dual catalysis,<sup>2</sup> and electrocatalytic<sup>3</sup> reactions have emerged as versatile tools to enable challenging transformations and construct organic molecules. Reaction development is dependent on delicate design and intricate arrangement of redox-active organonickel species to accom-

plish the catalytic cycle. A proper selection of the nickel catalyst and the corresponding organic substrates delivers selective electron-transfer processes. The thermodynamic driving force of an outer-sphere electron-transfer event is often estimated by the Gibbs free energy change, which can be calculated by the standard potentials of the donor and the acceptor ( $\Delta G^\circ = -nFE^\circ$ ).

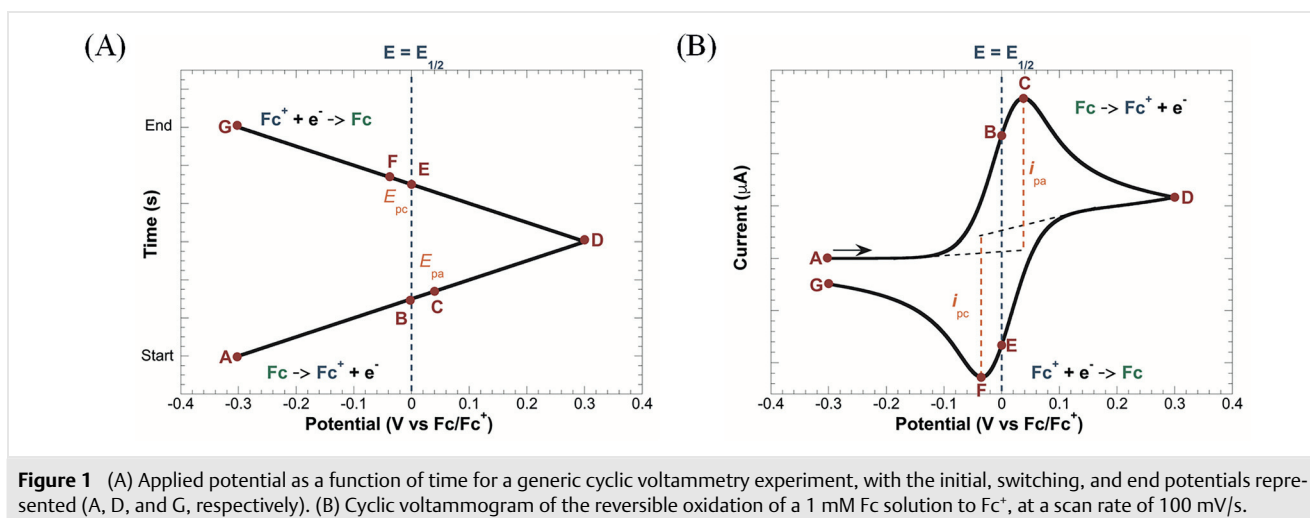
A formal potential, sometimes referred to as a conditional potential, is the reduction potential that applies to a half reaction under a specific set of conditions, as opposed to the standard-state conditions.<sup>4</sup> Nicewicz and co-workers measured and summarized the formal potentials of organic molecules with common functional groups.<sup>5</sup> In this review article, we tabulate the redox potentials of nickel complexes that have been reported in the literature. Since nickel can accommodate oxidation states ranging from 1<sup>-</sup> to 4<sup>+</sup>,<sup>6</sup> more than one redox processes can occur at a certain nickel center. We organize nickel complexes according to their isolated oxidation states and indicate the directions of the redox transformations in the 'process' column.

### 1.2 Measurement of Formal Redox Potentials

Cyclic voltammetry (CV) is a common tool for determining the formal potential for a redox-active compound.<sup>7,8</sup> As described by the Nernst equation, the electrode potential (E) is determined by the formal potential ( $E^{0'}$ ) and the concentrations of the oxidized and reduced analyte, where R is the gas constant, T is the temperature, F is the Faraday's constant, n is the number of electrons transferred, and [ox] and [red] are the concentrations of the oxidized and reduced species, respectively (Equation 1).

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{[\text{ox}]}{[\text{red}]}$$

Equation 1



For example, in the CV scan of ferrocene (Fc), an electric potential is applied linearly to the sample (Figure 1A). The line in the voltammogram is the current passed-per-unit time (Figure 1B). Current is dependent on the concentration of the substrate at the electrode per unit time, which is determined by the rate of diffusion, caused by the concentration gradient near the electrode. As the potential is scanned in a positive direction, current starts to build and increases from point A to point C, due to the increasingly faster diffusion of Fc to the electrode, as Fc is oxidized to ferrocenium (Fc<sup>+</sup>) on the electrode surface. The higher the oxidation potential applied to the electrode, the higher the current and higher ratio of [Fc<sup>+</sup>]/[Fc] till the electrode potential reaches point B, whose potential is  $E_{1/2}$ , where [Fc] = [Fc<sup>+</sup>]. The diffusion rate continues to grow until arriving point C, where the current reaches maximum at point C ( $E_p$ ). When the applied potential travels from point C to D, [Fc] far away from the electrode starts to deplete and [Fc<sup>+</sup>] far away from the electrode increases. The current decreases, as the electrooxidation becomes diffusion controlled. At point D, the current converges to the value of 'diffusion-limited current'.

The same process occurs when scanning Fc in a negative direction, resulting in a reduction peak.<sup>9</sup> For an electrochemically reversible process,  $E_{1/2}$  is determined as the midpoint of anodic and cathodic peak potentials and is typically regarded as the formal potential  $E^{0'}$ .<sup>8</sup> For an irreversible CV, when the reverse peak is not observed, the half-peak potential  $E_{p/2}$ , defined as the potential at the half-peak current, is used as an alternative to estimate  $E^{0'}$ .<sup>5</sup>  $E_{p/2}$  values must be considered in the context of the detailed conditions at which the CVs are measured.<sup>5</sup> In this review, we focus on nickel complexes with available  $E_{1/2}$  data.

### 1.3 Redox Potentials in Nonaqueous Solution

Formal potentials ( $E^{0'}$ ) estimated by averaging the forward and backward peak potentials from reversible redox-active species are documented in this review vs. the Fc/Fc<sup>+</sup> couple, as recommended by IUPAC.<sup>10</sup> Aqueous reference electrodes such as saturated calomel electrode (SCE) or saturated Ag/AgCl could cause the generation of liquid junction potentials, a potential difference built up due to the tendency of electrolytes to diffuse between two different solutions, when applied to the organic media. The resulting liquid junction potentials could shift the observed potential from the inherent redox potential to various extents according to the solvent.<sup>11</sup> Table 1 summarizes potentials of the Fc/Fc<sup>+</sup> couple, measured in different solvents and with supporting electrolytes.<sup>12</sup> Given the good reproducibility of SCE in nonaqueous solutions, Table 1 can be used to calibrate potentials measured in different solvents and using different electrolytes.

**Table 1** Formal Potentials (V) of the Ferrocene/Ferrocenium Redox Couple vs SCE with Selected Electrolytes<sup>a</sup>

Solvent	TBABF <sub>4</sub>	TBAPF <sub>6</sub>	TBAClO <sub>4</sub>	Et <sub>4</sub> NPF <sub>6</sub>	Et <sub>4</sub> NClO <sub>4</sub>	Et <sub>4</sub> NBF <sub>4</sub>
MeCN	0.39 <sup>14</sup>	0.40	0.38	0.38	0.39 <sup>15</sup>	
DCM	0.46 <sup>16</sup>	0.46	0.48		0.49 <sup>26</sup>	0.59 <sup>17</sup>
THF		0.56	0.53			
DMF	0.55 <sup>18</sup>	0.45	0.47	0.46		
Acetone		0.48	0.50	0.46		
PhCN			0.50 <sup>19</sup>		0.47 <sup>19</sup>	

<sup>a</sup> Supporting electrolyte concentration, 0.1 M. Data are extracted from ref. 12 unless specified otherwise.

In this article, we extract CV data from the literature and convert the potential values of a certain reference electrode into Fc/Fc<sup>+</sup> based on Table 1 or the Fc/Fc<sup>+</sup> potentials reported in the original paper; the parameters used for the conversion are listed underneath each table. In this regard, we unify the redox potentials to the same reference for direct comparison. As shown in Table 1, the potential of Fc/Fc<sup>+</sup> is sensitive to the experimental conditions, such as electrolytes and their concentration, solvent, etc.<sup>13</sup> Thus, it is strongly recommended to specify solvent and electrolyte conditions when reporting CV data against Fc/Fc<sup>+</sup>.<sup>12</sup>

## 2 Redox Potentials of Nickel Complexes

### 2.1 Redox Potentials of (Phosphine)Ni Complexes

Most phosphine ligands applied to support nickel complexes are strong  $\sigma$ -donors.<sup>20</sup> Table 2 summarizes the one-

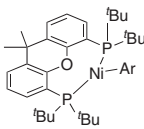
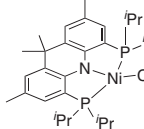
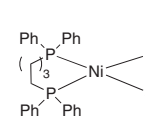
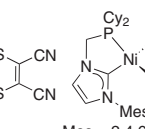
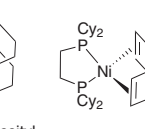
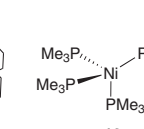
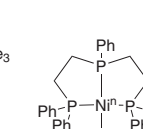
electron oxidation potentials of (phosphine)Ni(0) or the one-electron reduction of (phosphine)Ni(I) complexes. Redox potentials are directly related to the valence orbitals, sensitive to both the identity of the ligands and the molecular geometry. In general, electron-rich substituents on the ligand framework shift the redox potentials to the negative direction. For example, [PhB<sup>-</sup>(CH<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>]Ni **4** and **6**, with a borate on the ligand, have E[Ni(I/0)] as negative as -1.95 V, whereas (B<sub>2</sub>P<sub>2</sub>)Ni **27**, a complex supported on an electron-deficient borane ligand, has the most positive E[Ni(I/0)] in Table 2. Outer-sphere counterions, on the other hand, only have subtle impact on the redox potentials. The E[Ni(I/0)] of [HN(P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]<sub>2</sub>NiX<sub>2</sub> (X = NO<sub>3</sub> **7**, ClO<sub>4</sub> **9**, BF<sub>4</sub> **10**) are almost identical. Generally, Ni(I)-aryl and halide complexes exhibit significantly more negative redox potentials than Ni(diphosphine)<sub>2</sub> complexes.

**Table 2** Formal Potentials of the Ni(I)/Ni(0) Transformation for (Phosphine)Ni Complexes

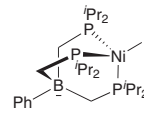
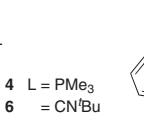
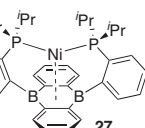
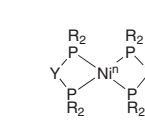
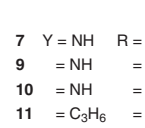
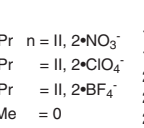
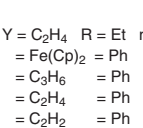
Complex	Process	Solvent	Electrolyte (M)	Potential reference	E <sub>1/2</sub> (V vs. Fc/Fc <sup>+</sup> )
( <sup>t</sup> BuXantphos)Ni(2,4-xylene) <sup>21</sup>	<b>1</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.4)	Fc/Fc <sup>+</sup>	-2.78
( <sup>t</sup> BuXantphos)Ni(o-Tol) <sup>21</sup>	<b>2</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.4)	Fc/Fc <sup>+</sup>	-2.70
(dppb)Ni[(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>40</sup>	<b>3</b> Ni(I) → Ni(0)	DMF	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	-2.22
[PhB <sup>-</sup> (CH <sub>2</sub> P <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> ]Ni(PMe <sub>3</sub> ) <sup>22</sup>	<b>4</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.95
( <sup>ac</sup> riPNP)Ni(CO) <sup>23</sup>	<b>5</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.3)	Fc/Fc <sup>+</sup>	-1.87
[PhB <sup>-</sup> (CH <sub>2</sub> P <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> ]Ni(CN <sup>t</sup> Bu) <sup>22</sup>	<b>6</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.85
[HN(P <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(NO <sub>3</sub> ) <sup>24</sup>	<b>7</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.53
Ni(PCy <sub>2</sub> N <sup>t</sup> Bu) <sub>2</sub> <sup>25</sup>	<b>8</b> Ni(0) → Ni(I)	PhCN	TBAPF <sub>6</sub> (0.2)	Fc/Fc <sup>+</sup>	-1.49
[HN(P <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(ClO <sub>4</sub> ) <sup>24</sup>	<b>9</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.49
[HN(P <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(BF <sub>4</sub> ) <sup>24</sup>	<b>10</b> Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.45
Ni(dmpp) <sub>2</sub> <sup>26</sup>	<b>11</b> Ni(0) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-1.33
Ni(PMe <sub>3</sub> ) <sub>4</sub> <sup>27</sup>	<b>12</b> Ni(0) → Ni(I)	1,2-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.31
(P <sup>Me</sup> <sub>2</sub> N <sup>Ph</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sup>28</sup>	<b>13</b> Ni(I) → Ni(0)	PhCN	TBAPF <sub>6</sub> (0.2)	Fc/Fc <sup>+</sup>	-1.30
Ni(depe) <sub>2</sub> <sup>26</sup>	<b>14</b> Ni(0) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-1.29
(P <sup>Ph</sup> <sub>2</sub> N <sup>Me(CH)Ph</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sup>29</sup>	<b>15</b> Ni(I) → Ni(0)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.27
Ni(NHC <sup>Me</sup> -CH <sub>2</sub> P <sup>Cy</sup> )(cod) <sup>30</sup>	<b>16</b> Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.26
Ni(dppf) <sub>2</sub> <sup>31</sup>	<b>17</b> Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub> (0.2)	Fc/Fc <sup>+</sup>	-1.18
(P <sup>Ph</sup> <sub>2</sub> N <sup>Ph(CH)Ph</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sup>29</sup>	<b>18</b> Ni(I) → Ni(0)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.14
(P <sup>Ph</sup> <sub>2</sub> N <sup>Bn</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sup>29</sup>	<b>19</b> Ni(I) → Ni(0)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.13
(P <sup>Ph</sup> <sub>2</sub> N <sup>p-Tol</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sup>29</sup>	<b>20</b> Ni(I) → Ni(0)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.08
(triphos)(PEt <sub>3</sub> )Ni(BF <sub>4</sub> ) <sup>32</sup>	<b>21</b> Ni(I) → Ni(0)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.2)	SCE	-1.05 <sup>a</sup>
Ni(dcype)(cod) <sup>30</sup>	<b>22</b> Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-0.95
Ni(dppp) <sub>2</sub> <sup>26</sup>	<b>23</b> Ni(0) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.91
(triphos)Ni(PPh <sub>3</sub> ) <sup>33</sup>	<b>24</b> Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	NHE	-0.90 <sup>b</sup>
Ni(dppe) <sub>2</sub> <sup>26</sup>	<b>25</b> Ni(0) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.88

Complex	Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
(dppv) <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>34</sup>	Ni(I) → Ni(0)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.83
(B <sub>2</sub> P <sub>2</sub> )Ni <sup>35</sup>	Ni(0) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	0.06



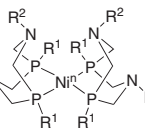
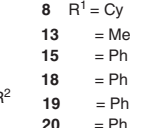
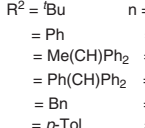
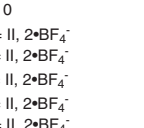
  

						
1 Ar = 2,4-xylene	5	3	16 Mes = 2,4,6-mesityl	22	12	21 n = II, 2•BF <sub>4</sub> <sup>-</sup>
2 = <i>o</i> -tol						24 n = 0

						
4 L = PMe <sub>3</sub>	6 L = CN <sup>t</sup> Bu	27	7 Y = NH R = <sup>t</sup> Pr n = II, 2•NO <sub>3</sub> <sup>-</sup>	9 = NH = <sup>t</sup> Pr = II, 2•ClO <sub>4</sub> <sup>-</sup>	10 = NH = <sup>t</sup> Pr = II, 2•BF <sub>4</sub> <sup>-</sup>	11 = C <sub>3</sub> H <sub>6</sub> = Me = 0
			14 Y = C <sub>2</sub> H <sub>4</sub> R = Et n = 0	17 = Fe(Cp) <sub>2</sub> = Ph = 0	23 = C <sub>3</sub> H <sub>6</sub> = Ph = 0	25 = C <sub>2</sub> H <sub>4</sub> = Ph = 0
			26 = C <sub>2</sub> H <sub>2</sub> = Ph = 2, 2•BF <sub>4</sub> <sup>-</sup>			

					
8 R <sup>1</sup> = Cy	13 = Me	15 = Ph	18 = Ph	19 = Ph	20 = Ph

<sup>a</sup> Fc = 0.40 V vs SCE (MeCN/Et<sub>4</sub>NBF<sub>4</sub>).<sup>32</sup>

<sup>b</sup> Fc = 0.56 V vs SCE (THF/TBAPF<sub>6</sub>).<sup>1,2</sup> Converted into NHE by adding 0.24 V.

Complexes with halide ligands generally do not have reversible reduction CV, due to the fast dissociation of halides. Monodentate phosphine ligands can be labile and may result in geometry reorganization upon oxidation or reduction.<sup>36</sup> The one-electron oxidation of Ni(PMe<sub>3</sub>)<sub>4</sub> **12** shows a reversible CV, whereas the following oxidation to Ni(II) is electrochemically quasireversible, reflecting a change of geometry from tetrahedral to square planar.<sup>27</sup> The synthesis of a series of Ni(I) complexes has enabled the measurement of redox potentials starting from the +1 oxidation state. A (<sup>t</sup>BuXantphos)Ni(I)-aryl complex **1** exhibits a very negative reversible reduction peak at -2.78 V.<sup>21</sup> In contrast, Ni(I)-bromide and Ni(I)-chloride complexes, supported on an isopropyl phosphine ligand with a dibenzofuran backbone, give irreversible reduction peaks due to the fast halide dissociation.<sup>37</sup>

[(Cy)N(Ph<sub>2</sub>P)<sub>2</sub>]Ni(ClO<sub>4</sub>)<sub>2</sub> **43** exists as an equilibrium between the tetrahedral and square planar geometries in acetonitrile. Two E[Ni(II/I)] peaks are observed at -0.97 V and -1.77 V, responding to the tetrahedral and the square planar isomers, respectively. This data is consistent with the lower-energy LUMO in a tetrahedral field. Sometimes, the CV data of certain complexes cannot be used to estimate the potentials of their analogues. Bis(diphosphine)Ni com-

plexes exhibit a wide range of redox potentials, from -1.16 V of Ni(depe)<sub>2</sub> **14** to -0.19 V of Ni(dppv)<sub>2</sub> **23**, responding to the substituents and the chain length between the two phosphines. Dithiolate and catecholate are good electron-donating ligands. E[Ni(II/I)] of [(Me)N(Et<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>]Ni(C<sub>2</sub>H<sub>4</sub>S<sub>2</sub>) **28** is -2.34 V (Table 3), whereas that of [(Me)N(Et<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>]Ni(BF<sub>4</sub>)<sub>2</sub> **48** is -0.64 V. With the same spectator ligand, varying the halide down the group shifts the potential to a more positive direction (E[Ni-Cl] < E[Ni-Br] < E[Ni-I], E[Ni-OR] < E[Ni-SR] < [Ni-SeR]).

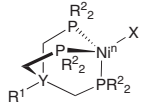
The two-electron reduction, E[Ni(II/0)], is also observed, in some cases, due to the overlap of two redox events.<sup>50</sup> (Triphos)(P(OMe)<sub>3</sub>)Ni(BF<sub>4</sub>)<sub>2</sub> shows a two-electron reduction peak at -0.85 V, while its analogue (triphos)(PEt<sub>3</sub>)Ni(BF<sub>4</sub>)<sub>2</sub> **21** gives two sequential one-electron reductions at -0.77 V and -1.05 V.<sup>32</sup> Theoretically, the half-peak separation, |E<sub>pa</sub> - E<sub>pc</sub>|/2, of the two-electron redox processes should be 30 mV, narrower than that of a one-electron event, 60 mV. Since peak separation is also dependent on kinetics and the resistance, the peak-to-peak separation alone is indefinite for determining the electron stoichiometry for redox events.<sup>51</sup> Formal potentials for high-valence (phosphines)Ni mostly are obtained via oxidation of isolated Ni(II) complexes (Table 4).

**Table 3** Formal Potentials of the Ni(II)/Ni(I) Transformation for (Phosphine)Ni Complexes

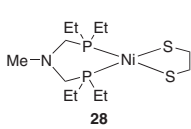
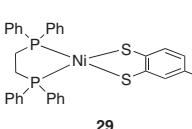
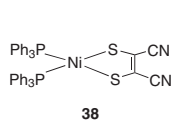
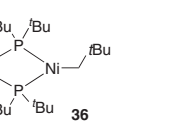
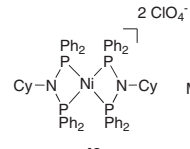
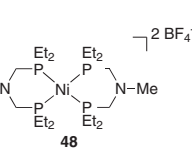
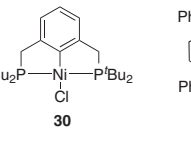
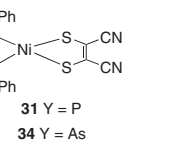
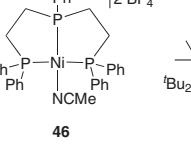
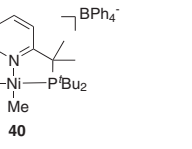
Complex		Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
[(Me)N(Et <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ]Ni(C <sub>2</sub> H <sub>4</sub> S <sub>2</sub> ) <sup>47</sup>	<b>28</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-2.34
(dppe)Ni(3,4-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> S <sub>2</sub> ) <sup>38</sup>	<b>29</b>	Ni(II) → Ni(I)	DCM	TBAClO <sub>4</sub> (0.1)	Ag/AgCl	-2.05 <sup>a</sup>
[2,6-( <sup>t</sup> Bu <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]NiCl <sup>39</sup>	<b>30</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.1)	NHE	-1.88 <sup>b</sup>
[(cyclohexyl)N(Ph <sub>2</sub> P) <sub>2</sub> ] <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>44</sup>	<b>43</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.45)	Fc/Fc <sup>+</sup>	-1.77 <sup>c</sup>
(dppe)Ni[(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>38</sup>	<b>31</b>	Ni(II) → Ni(I)	DCM	TBAClO <sub>4</sub> (0.1)	Ag/AgCl	-1.66 <sup>a</sup>
( <sup>t</sup> BuXantphos)Ni(2,4-xylene) <sup>21</sup>	<b>1</b>	Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub> (0.4)	Fc/Fc <sup>+</sup>	-1.59
( <sup>t</sup> BuXantphos)Ni(o-Tol) <sup>21</sup>	<b>2</b>	Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub> (0.4)	Fc/Fc <sup>+</sup>	-1.51
[PhB <sup>-</sup> (CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]Ni(OSiPh <sub>3</sub> ) <sup>22</sup>	<b>32</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.47
[PhB <sup>-</sup> (CH <sub>2</sub> PPr <sub>2</sub> ) <sub>3</sub> ]NiCl <sup>22</sup>	<b>33</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.44
(dae)Ni[(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>38</sup>	<b>34</b>	Ni(II) → Ni(I)	DCM	TBAClO <sub>4</sub> (0.1)	Ag/AgCl	-1.44 <sup>a</sup>
(dppb)Ni[(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>40</sup>	<b>3</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.43
[PhB <sup>-</sup> (CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]Ni(O- <i>p</i> - <sup>t</sup> Bu-Ph) <sup>22</sup>	<b>35</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.36
(d <sup>t</sup> bpe)Ni(CH <sub>2</sub> CMe <sub>3</sub> ) <sup>41</sup>	<b>36</b>	Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub> (0.4)	Fc/Fc <sup>+</sup>	-1.25
( <sup>ac</sup> riPNP)Ni(CO) <sup>23</sup>	<b>5</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.3)	Fc/Fc <sup>+</sup>	-1.20
[PhB <sup>-</sup> (CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]NiCl <sup>22</sup>	<b>37</b>	Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.20
(PPh <sub>3</sub> ) <sub>2</sub> Ni[(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>38</sup>	<b>38</b>	Ni(II) → Ni(I)	DCM	TBAClO <sub>4</sub> (0.1)	Ag/AgCl	-1.20 <sup>a</sup>
[ <sup>n</sup> Bu)N(Ph <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ]NiCl <sub>2</sub> <sup>42</sup>	<b>39</b>	Ni(II) → Ni(I)	DCM	TBAPF <sub>6</sub> (0.1)	Ag/AgCl	-1.18 <sup>d</sup>
Ni(depe) <sub>2</sub> <sup>26</sup>	<b>14</b>	Ni(I) → Ni(II)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-1.16
[(Me <sub>4</sub> PNP <sup>t</sup> Bu)NiMe](BPh <sub>4</sub> ) <sup>43</sup>	<b>40</b>	Ni(I) → Ni(II)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.14
[PhB <sup>-</sup> (CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]Ni <sup>22</sup>	<b>41</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.12
[PhB <sup>-</sup> (CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]Ni(S- <i>p</i> - <sup>t</sup> Bu-Ph) <sup>22</sup>	<b>42</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.35)	Fc/Fc <sup>+</sup>	-1.12
[HN(P <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(NO <sub>3</sub> ) <sub>2</sub> <sup>24</sup>	<b>7</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.06
(P <sup>Me</sup> <sub>2</sub> N <sup>Ph</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>28</sup>	<b>13</b>	Ni(II) → Ni(I)	PhCN	TBAPF <sub>6</sub> (0.2)	Fc/Fc <sup>+</sup>	-1.01
[HN(P <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>24</sup>	<b>8</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-1.01
[(cyclohexyl)N(Ph <sub>2</sub> P) <sub>2</sub> ] <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>44</sup>	<b>43'</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.45)	Fc/Fc <sup>+</sup>	-0.97 <sup>e</sup>
[HN(P <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>24</sup>	<b>10</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-0.97
(P <sup>Ph</sup> <sub>2</sub> N <sup>Me(CH)Ph</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>29</sup>	<b>15</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-0.93
(tdppme)Ni(S <sup>t</sup> Bu) <sup>45</sup>	<b>44</b>	Ni(I) → Ni(II)	DCM	TBAPF <sub>6</sub> (0.1)	SCE	-0.93 <sup>f</sup>
Ni(dmpp) <sub>2</sub> <sup>26</sup>	<b>11</b>	Ni(I) → Ni(II)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.89
(dppp)NiBr <sub>2</sub> <sup>46</sup>	<b>45</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub> (0.1)	Ag/AgNO <sub>3</sub>	-0.89 <sup>g</sup>
(triphos)(MeCN)Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>32</sup>	<b>46</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.2)	SCE	-0.88 <sup>h</sup>
Ni(PCy <sub>2</sub> N <sup>t</sup> Bu) <sub>2</sub> <sup>25</sup>	<b>9</b>	Ni(I) → Ni(II)	PhCN	TBAPF <sub>6</sub> (0.2)	Fc/Fc <sup>+</sup>	-0.87
(P <sup>Ph</sup> <sub>2</sub> N <sup>p-Tol</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>29</sup>	<b>20</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-0.83
(triphos)(PEt <sub>3</sub> )Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>32</sup>	<b>21</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.2)	SCE	-0.77 <sup>h</sup>
(tdppme)Ni(S <sup>Ph</sup> ) <sup>45</sup>	<b>47</b>	Ni(I) → Ni(II)	DCM	TBAPF <sub>6</sub> (0.1)	SCE	-0.75 <sup>f</sup>
(P <sup>Ph</sup> <sub>2</sub> N <sup>Ph(CH)Ph</sup> ) <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>29</sup>	<b>18</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-0.72
Ni(dppe) <sub>2</sub> <sup>26</sup>	<b>25</b>	Ni(I) → Ni(II)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.70
[(Me)N(Et <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>47</sup>	<b>48</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.64
(tdppme)Ni(Se <sup>Ph</sup> ) <sup>45</sup>	<b>49</b>	Ni(I) → Ni(II)	DCM	TBAPF <sub>6</sub> (0.1)	SCE	-0.64 <sup>f</sup>
(tdppme)NiCl(ClO <sub>4</sub> ) <sup>48</sup>	<b>50</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NClO <sub>4</sub> (0.1)	SCE	-0.63 <sup>i</sup>
(tdppme)NiBr(ClO <sub>4</sub> ) <sup>48</sup>	<b>51</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NClO <sub>4</sub> (0.1)	SCE	-0.57 <sup>i</sup>
(dppp) <sub>2</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>34</sup>	<b>26</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.52
(tdppme)Ni(ClO <sub>4</sub> ) <sup>48</sup>	<b>52</b>	Ni(II) → Ni(I)	MeCN	Et <sub>4</sub> NClO <sub>4</sub> (0.1)	SCE	-0.47 <sup>i</sup>

Complex	Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )	
Ni(PMe <sub>3</sub> ) <sub>4</sub> <sup>27</sup>	<b>12</b>	Ni(I) → Ni(II)	1,2-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	-0.33
Ni(dppp) <sub>2</sub> <sup>26</sup>	<b>23</b>	Ni(I) → Ni(II)	MeCN	Et <sub>4</sub> NBF <sub>4</sub> (0.3)	Fc/Fc <sup>+</sup>	-0.19

Complex	Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
					
<b>32</b> Y = B <sup>c</sup> R <sup>1</sup> = Ph R <sup>2</sup> = Ph X = OSiPh <sub>3</sub> n = II					
<b>33</b> = B <sup>c</sup> = Ph = <sup>i</sup> Pr = Cl = II					
<b>35</b> = B <sup>c</sup> = Ph = Ph = O- <i>p</i> - <sup>t</sup> Bu-Ph = II					
<b>37</b> = B <sup>c</sup> = Ph = Ph = Cl = II					
<b>41</b> = B <sup>c</sup> = Ph = Ph = I = II					
<b>42</b> = B <sup>c</sup> = Ph = Ph = S- <i>p</i> - <sup>t</sup> Bu-Ph = II					
<b>44</b> = C = Me = Ph = S <sup>t</sup> Bu = I					
<b>47</b> = C = Me = Ph = SPh = I					
<b>49</b> = C = Me = Ph = SePh = I					
<b>50</b> = C = Me = Ph = Cl = II, ClO <sub>4</sub> <sup>-</sup>					
<b>51</b> = C = Me = Ph = Br = II, ClO <sub>4</sub> <sup>-</sup>					
<b>52</b> = C = Me = Ph = I = II, ClO <sub>4</sub> <sup>-</sup>					

Complex	Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
					
<b>28</b>					
					
<b>29</b>					
					
<b>38</b>					
					
<b>36</b>					
					
<b>43</b>					
					
<b>48</b>					
					
<b>30</b>					
					
<b>31</b> Y = P					
<b>34</b> Y = As					
					
<b>46</b>					
					
<b>40</b>					

<sup>a</sup> Fc = 0.46 V vs Ag/Ag<sup>+</sup> 0.1 M LiCl in DCM (DCM/TBAClO<sub>4</sub>).<sup>38</sup>

<sup>b</sup> Fc = 0.69 V vs NHE (MeCN/TBAPF<sub>6</sub>).<sup>39</sup>

<sup>c</sup> E<sup>0</sup> for Sp isomer.

<sup>d</sup> Fc = 0.33 V vs Ag/AgCl (DCM/TBAPF<sub>6</sub>).<sup>42</sup>

<sup>e</sup> E<sup>0</sup> for Td isomer.

<sup>f</sup> Fc = 0.46 V vs SCE (DCM/TBAPF<sub>6</sub>).<sup>12</sup>

<sup>g</sup> Fc = 0.176 V vs Ag/0.01 M AgNO<sub>3</sub> (THF/TBAPF<sub>6</sub>).<sup>49</sup>

<sup>h</sup> Fc = 0.40 V vs SCE (MeCN/Et<sub>4</sub>NBF<sub>4</sub>).<sup>32</sup>

<sup>i</sup> Fc = 0.38 V vs SCE (MeCN/Et<sub>4</sub>NClO<sub>4</sub>).<sup>48</sup>

**Table 4** Formal Potentials of the Ni(III)/Ni(II) and Ni(IV)/Ni(III) Transformations for Selected (Phosphine)Ni Complexes

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )	
(dppe)Ni(3,4- <sup>t</sup> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O <sub>2</sub> ) <sup>38</sup>	<b>53</b>	Ni(II) → Ni(III)	DCM	TBAClO <sub>4</sub>	Ag/AgCl	-0.25 <sup>a</sup>
(dppb)Ni[(Me) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>40</sup>	<b>54</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.20
(dppb)Ni[(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>40</sup>	<b>55</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.15
[ <i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> NiCl <sub>2</sub> <sup>52</sup>	<b>56</b>	Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub>	SCE	-0.03 <sup>b</sup>
[ <i>o</i> -C <sub>6</sub> F <sub>4</sub> (PMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> NiCl <sub>2</sub> <sup>52</sup>	<b>57</b>	Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub>	SCE	0.08 <sup>b</sup>
[ <i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> NiBr <sub>2</sub> <sup>52</sup>	<b>58</b>	Ni(II) → Ni(III)	MeCN	Et <sub>4</sub> NClO <sub>4</sub>	SCE	0.10 <sup>c</sup>
(dppe)Ni( <i>o</i> -C <sub>6</sub> Cl <sub>4</sub> O <sub>2</sub> ) <sup>38</sup>	<b>59</b>	Ni(II) → Ni(III)	DCM	TBAClO <sub>4</sub>	Ag/AgCl	0.25 <sup>a</sup>
(dcpf)NiCl <sub>2</sub> <sup>53</sup>	<b>60</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.30
[2,6-( <sup>t</sup> Bu <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> NiH <sup>54</sup>	<b>61</b>	Ni(II) → Ni(III)	MeCN-THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.33
(dppe)NiCl <sub>3</sub> <sup>55</sup>	<b>62</b>	Ni(III) → Ni(II)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.40
[2,6-( <sup>i</sup> Pr <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> Ni(OAc) <sup>56</sup>	<b>63</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.43
[2,6-(Ph <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> Ni(OAc) <sup>56</sup>	<b>64</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.55
[( <sup>t</sup> Bu <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> NiCl <sub>3</sub> <sup>54</sup>	<b>65</b>	Ni(II) → Ni(III)	MeCN-THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.72
[2,6-( <sup>t</sup> Bu <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> NiBr <sub>3</sub> <sup>57</sup>	<b>66</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.75
[2,6-(Ph <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> Ni(OTf) <sup>56</sup>	<b>67</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.81
[2,6-( <sup>i</sup> Pr <sub>2</sub> PO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> Ni(OTf) <sup>56</sup>	<b>68</b>	Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.98
(dppb)Ni[(Me) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>40</sup>	<b>54</b>	Ni(III) → Ni(IV)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.50 <sup>d</sup>
(dppb)Ni[(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> ] <sup>40</sup>	<b>55</b>	Ni(III) → Ni(IV)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.44
[ <i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> NiCl <sub>2</sub> <sup>52</sup>	<b>56</b>	Ni(III) → Ni(IV)	MeCN	TBAPF <sub>6</sub>	SCE	0.79 <sup>b</sup>

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. $Fc/Fc^+$ )	
$[o-C_6H_4(PMe_2)_2]_2NiBr_2$ <sup>52</sup>	<b>58</b>	Ni(III) → Ni(IV)	MeCN	$Et_4NClO_4$	SCE	0.84 <sup>c</sup>
$[o-C_6H_4(AsMe_2)_2]_2NiCl_2$ <sup>52</sup>	<b>69</b>	Ni(III) → Ni(IV)	MeCN	$Et_4NClO_4$	SCE	0.91 <sup>c</sup>
$[o-C_6F_4(PMe_2)_2]_2NiCl_2$ <sup>52</sup>	<b>57</b>	Ni(III) → Ni(IV)	MeCN	TBAPF <sub>6</sub>	SCE	1.01 <sup>b</sup>

**54** R = Me  
**55** = C<sub>6</sub>H<sub>4</sub>-p-OMe

**53** R<sup>1</sup> = H R<sup>2</sup> = <sup>t</sup>Bu  
= Cl = Cl

**60**

**62**

**61** R = <sup>t</sup>Bu X = H  
**63** = <sup>i</sup>Pr = OAc  
**64** = Ph = OAc  
**65** = <sup>t</sup>Bu = Cl  
**66** = <sup>t</sup>Bu = Br  
**67** = Ph = OTf  
**68** = <sup>i</sup>Pr = OTf

**56** Y = P R = H X = Cl  
**57** = P = F = Cl  
**58** = P = H = Br  
**69** = As = H = Cl

<sup>a</sup>  $Fc = 0.46$  V vs  $Ag/Ag^+$  0.1 M LiCl in DCM (DCM/TBAClO<sub>4</sub>).<sup>38</sup>

<sup>b</sup>  $Fc = 0.39$  V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>14</sup>

<sup>c</sup>  $Fc = 0.38$  V vs SCE (MeCN/ $Et_4NClO_4$ ).<sup>48</sup>

<sup>d</sup> Potentials estimated from differential pulse voltammetry by width-at-half-height analysis.

## 2.2 Redox Potentials of (Nitrogen)Ni Complexes

Ni-catalyzed cross-coupling reactions proceeding through radical pathways has benefited from various bidentate and tridentate N-ligands, including bipyridine (bpy), bioxazoline (biOx), terpyridine (terpy), pyridine-oxazoline (pyox), and pyridine-bioxazoline (pybox).<sup>6,58</sup> N-

Ligands are  $\pi$ -acceptors and generally stronger  $\sigma$ -donors than phosphines.<sup>59</sup> The redox activity of  $\pi$ -acceptor ligands greatly contributes to the stability of radical complexes. Redox processes may occur on the ligand rather than the metal center. Data in Table 5 and Table 6 refer to the formal oxidation state of the nickel complexes, but do not distinguish the change of oxidation state due to ligand redox activity.

**Table 5** Formal Potentials of the Ni(I)/Ni(0) Transformation for Selected Ni/Nitrogen Complexes

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. $Fc/Fc^+$ )	
$[(-)-i\text{-Pr-pybox}]Ni(Ph)B(Ar^f)_4$ <sup>60</sup>	<b>70</b>	Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub>	$Fc/Fc^+$	-2.36
$(dtbbpy)(C^{prop2}C)Ni(PF_6)_2$ <sup>61</sup>	<b>71</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-2.06
$(bpy)(C^{prop2}C)Ni(PF_6)_2$ <sup>61</sup>	<b>72</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-2.00
$(P^i\text{bimiiql})Ni(PF_6)_2$ <sup>62</sup>	<b>73</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	SCE	-1.60 <sup>a</sup>
$(6,6'\text{-Mebpy})NiBr_2$ <sup>63</sup>	<b>74</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	SCE	-1.56 <sup>b</sup>
$(DippBIAN)NiCl_2$ <sup>64</sup>	<b>75</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.52
$(DippBIAN)NiBr_2$ <sup>64</sup>	<b>76</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.47
$(DippBIAN)NiI_2$ <sup>64</sup>	<b>77</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.46
$(DippBIAN)Ni(NCMe)_4(BF_4)_2$ <sup>64</sup>	<b>78</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.45
$(DippN^PyN^DippN)NiCl_2$ <sup>65</sup>	<b>79</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.23
$(DippN^PyN^DippN)NiBr_2$ <sup>65</sup>	<b>80</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.22
$(bpy)Ni(cod)$ <sup>30</sup>	<b>81</b>	Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.17
$(2\text{-Ome-Ph-Me}_2\text{DAB})(Cp)NiBF_4$ <sup>66</sup>	<b>82</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.17
$(Ph\text{-Me}_2\text{DAB})(Cp)NiBF_4$ <sup>66</sup>	<b>83</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-1.05
$(2\text{-CF}_3\text{-Ph-Me}_2\text{DAB})(Cp)NiBF_4$ <sup>66</sup>	<b>84</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	$Fc/Fc^+$	-0.80

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
	$2+ / 2 PF_6^-$				
	$71$ R = <sup>t</sup> Bu $72$ R = H				
	$75$ X = Cl $76$ X = Br $77$ X = I				
	$79$ X = Cl $80$ X = Br				
	$82$ R = <i>o</i> -OMe $83$ R = H $84$ R = <i>o</i> -CF <sub>3</sub>				

<sup>a</sup> Fc = 0.40 V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>

<sup>b</sup> Fc = 0.38 V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>63</sup>

The electronic effect of ligands on the redox potential is evident by comparing a series of (4,4'-Mebpy)Ni (4,4'-Mebpy = **92**), (bpy)Ni (bpy = **95**), and DAB(Ni) (DAB = **105**) complexes (Table 6). The first reduction of Ni(II) complexes can be ligand centered, depending on the coordination number, geometry, and the ligand. For example, the first electron reduction of (dtbbpy)(C<sup>Prop2</sup>C)Ni(PF<sub>6</sub>)<sub>2</sub> **71** and (bpy)(C<sup>Prop2</sup>C)Ni(PF<sub>6</sub>)<sub>2</sub>

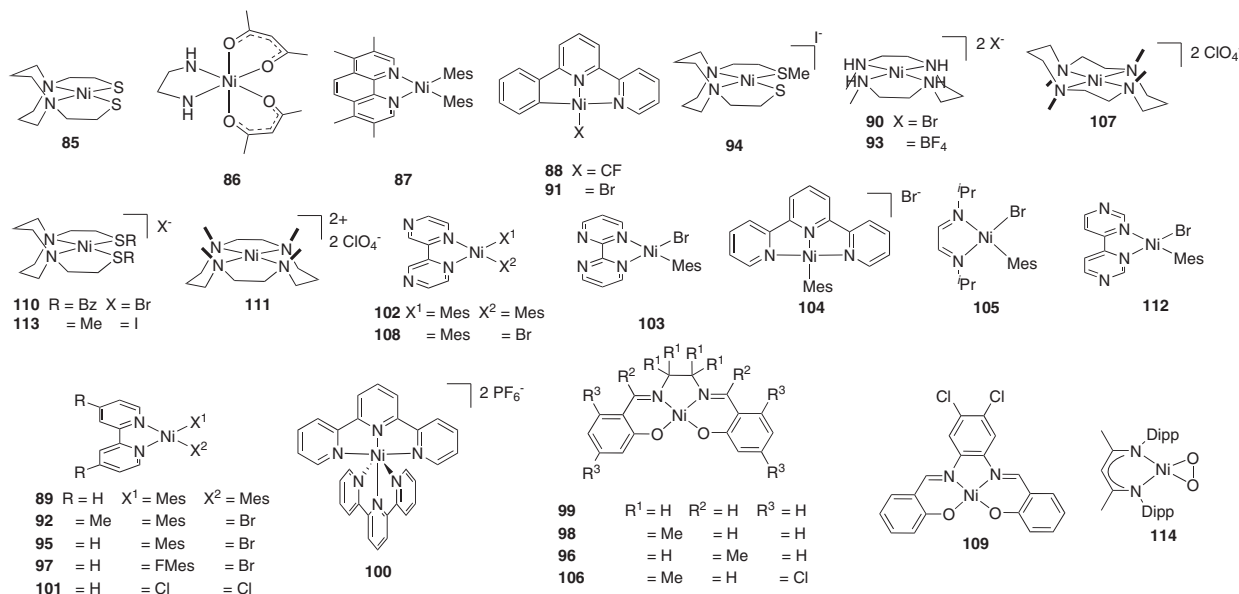
**72** is ligand centered, and the second electron reduction is metal centered.<sup>61</sup> The nature of ligands can affect the reversibility of CV. Halides can easily dissociate upon reduction and give rise to irreversible CVs. Terpy complex **104** shows a reversible CV at room temperature, but the CVs of bidentate nitrogen-ligated Ni(Mes)Br complexes in Table 6 were measured at -60 °C to prevent bromide dissociation.<sup>69</sup>

**Table 6** Formal Potentials of the Ni(II)/Ni(I) Transformation for (Nitrogen)Ni Complexes

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )	
(bme-daco)Ni <sup>67</sup>	<b>85</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	NHE	-2.58 <sup>a</sup>
(en)Ni(acac) <sub>2</sub> <sup>68</sup>	<b>86</b>	Ni(II) → Ni(I)	DMF	TBAClO <sub>4</sub>	SCE	-2.57 <sup>b</sup>
(3,4,7,8-tmphen)Ni(Mes) <sub>2</sub> <sup>69</sup>	<b>87</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-2.22
(Phbpy)Ni(CF <sub>3</sub> ) <sub>2</sub> <sup>70</sup>	<b>88</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-2.04
(bpy)Ni(Mes) <sub>2</sub> <sup>69</sup>	<b>89</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-2.02
(cyclam)NiBr <sub>2</sub> <sup>71</sup>	<b>90</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-2.00
(Phbpy)NiBr <sup>70</sup>	<b>91</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.90
(4,4'-Mebpy)Ni(Mes)Br <sup>69</sup>	<b>92</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.87
(cyclam)Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>71</sup>	<b>93</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.85
(Me-bme-daco)Ni <sup>67</sup>	<b>94</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	NHE	-1.84 <sup>a</sup>
(bpy)Ni(Mes)Br <sup>69</sup>	<b>95</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.79
( $\alpha,\alpha'$ -Me <sub>2</sub> salen)Ni <sup>72</sup>	<b>96</b>	Ni(II) → Ni(I)	DMF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-1.71
(bpy)Ni(Fmes)Br <sup>69</sup>	<b>97</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.68
(saltMe)Ni <sup>72</sup>	<b>98</b>	Ni(II) → Ni(I)	DMF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-1.67
(salen)Ni <sup>72</sup>	<b>99</b>	Ni(II) → Ni(I)	DMF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-1.60
(dtbbpy)(C <sup>Prop2</sup> C)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>61</sup>	<b>71</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.59
(terpy) <sub>2</sub> Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>73</sup>	<b>100</b>	Ni(II) → Ni(I)	MeCN	TBAClO <sub>4</sub>	SCE	-1.58 <sup>c</sup>
(bpy)NiCl <sub>2</sub> <sup>74</sup>	<b>101</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Ag/AgCl	-1.52 <sup>d</sup>
(bpy)(C <sup>Prop2</sup> C)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>61</sup>	<b>72</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.50
(bpz)Ni(Mes) <sub>2</sub> <sup>69</sup>	<b>102</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.48



Complex		Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
(bpym)Ni(Mes)Br <sup>69</sup>	<b>103</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.47
(terpy)Ni(Mes)Br <sup>69</sup>	<b>104</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.45
[(-)- <i>i</i> -Pr-pybox]Ni(Ph)B(Ar <sup>F</sup> ) <sub>4</sub> <sup>60</sup>	<b>70</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.37
( <i>i</i> -Pr-DAB)Ni(Mes)Br <sup>69</sup>	<b>105</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.37
(Cl <sub>2</sub> -saltMe)Ni <sup>72</sup>	<b>106</b>	Ni(II) → Ni(I)	DMF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-1.37
( <i>trans</i> -III-Me <sub>4</sub> -cyclam)Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>75</sup>	<b>107</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Ag/AgNO <sub>3</sub>	-1.36 <sup>e</sup>
(bpz)Ni(Mes)Br <sup>69</sup>	<b>108</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.34
(Bz <sub>2</sub> -bme-daco)NiBr <sub>2</sub> <sup>67</sup>	<b>110</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	NHE	-1.31 <sup>a</sup>
(saloph-Cl <sub>2</sub> )Ni <sup>72</sup>	<b>109</b>	Ni(II) → Ni(I)	DMF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-1.30
(6,6'-Mebpy)NiBr <sub>2</sub> <sup>63</sup>	<b>74</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	SCE	-1.26
( <i>trans</i> -I-Me <sub>4</sub> -cyclam)Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>75</sup>	<b>111</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Ag/AgNO <sub>3</sub>	-1.23 <sup>e</sup>
(bpm)Ni(Mes)Br <sup>69</sup>	<b>112</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.20
(P <sup>+</sup> bimiiql)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>62</sup>	<b>73</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	SCE	-1.14 <sup>f</sup>
(Me <sub>2</sub> -bme-daco)NiI <sub>2</sub> <sup>67</sup>	<b>113</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	NHE	-1.12 <sup>a</sup>
(DippBDI)Ni(η <sup>2</sup> -O <sub>2</sub> ) <sup>76</sup>	<b>114</b>	Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.98
(DippBIAN)NiCl <sub>2</sub> <sup>64</sup>	<b>75</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.97
(DippNPyN <sup>Dipp</sup> N)NiCl <sub>2</sub> <sup>65</sup>	<b>79</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.86
(DippBIAN)NiBr <sub>2</sub> <sup>64</sup>	<b>76</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.81
(DippBIAN)NiI <sub>2</sub> <sup>64</sup>	<b>77</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.80
(DippBIAN)Ni(NCMe) <sub>4</sub> (BF <sub>4</sub> ) <sub>2</sub> <sup>64</sup>	<b>78</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.77
(bpy)Ni(cod) <sup>30</sup>	<b>81</b>	Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.76
(DippNPyN <sup>Dipp</sup> N)NiBr <sub>2</sub> <sup>65</sup>	<b>80</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.68



<sup>a</sup> Fc = 0.64 V vs NHE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>

<sup>b</sup> Fc = 0.47 V vs SCE (DMF/TBAClO<sub>4</sub>).<sup>12</sup>

<sup>c</sup> Fc = 0.38 V vs SCE (MeCN/TBAClO<sub>4</sub>).<sup>12</sup>

<sup>d</sup> Fc = 0.50 V vs Ag/0.1 M NaCl (DMF).<sup>72</sup>

<sup>e</sup> Fc = 0.037 V vs Ag/0.1 M AgNO<sub>3</sub> (MeCN/TBAPF<sub>6</sub>).<sup>77</sup>

<sup>f</sup> Fc = 0.40 V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>

Ligand effects in the oxidation of Ni(II) to Ni(III) states follow the typical trend: electron-withdrawing *para* substituents of the NCN pincer ligand shift the oxidation potential to the positive direction: E[Ni–NH<sub>2</sub> **117**] < E[Ni–OMe **121**] < E[Ni–H **123**] < E[Ni–Cl **126**] < E[Ni–Ac **127**] (Table 7).

The reduction potentials of (porphyrin)Ni(III) complexes also reflect the electronic trend of the ligands. Reduction requires a more negative potential for complexes with electron-donating substitutions: E[(<sup>t</sup>BuP)Ni **132**] < E[(<sup>t</sup>PrP)Ni **133**] < E[(<sup>t</sup>EtPrP)Ni **134**] < E[(<sup>t</sup>BuP)Ni **137**] < E[(TPP)Ni **138**].<sup>86</sup>

**Table 7** Formal Potentials of Ni(III)/Ni(II) and Ni(IV)/Ni(III) Transformations for Selected (Nitrogen)Ni Complexes

Complex	Process	Solvent	Electrolyte (M)	Potential reference	E <sub>1/2</sub> (V vs. Fc/Fc <sup>+</sup> )
(N <sup>i</sup> Bu <sub>2</sub> PyPh)Ni(MeCN) <sub>2</sub> PF <sub>6</sub> <sup>78</sup>	<b>115</b> Ni(II) → Ni(III)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.66
(N <sup>i</sup> Bu <sub>2</sub> PyPh)NiBr(MeCN)PF <sub>6</sub> <sup>78</sup>	<b>116</b> Ni(III) → Ni(II)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.65
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> -(4-NH <sub>2</sub> )C <sub>6</sub> H <sub>3</sub> ]NiBr <sup>79</sup>	<b>117</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Ag/AgCl	−0.45 <sup>a</sup>
(N <sup>i</sup> Bu <sub>2</sub> Py <sub>2</sub> )Ni( <i>p</i> -F-Ph)Cl <sup>80</sup>	<b>118</b> Ni(II) → Ni(III)	MeCN	TBAClO <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.45
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]NiCl <sub>2</sub> <sup>81</sup>	<b>119</b> Ni(III) → Ni(II)	Acetone	TBACl (0.1)	Ag/AgCl	−0.44 <sup>b</sup>
(Tp)(Cp)Ni(PF <sub>6</sub> ) <sup>82</sup>	<b>120</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.42
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> -(4-OMe)C <sub>6</sub> H <sub>2</sub> ]NiBr <sup>79</sup>	<b>121</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Ag/AgCl	−0.40 <sup>a</sup>
(N <sup>i</sup> Bu <sub>2</sub> Py <sub>2</sub> )Ni( <i>p</i> -F-Ph)Br <sup>80</sup>	<b>122</b> Ni(II) → Ni(III)	MeCN	TBAClO <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.40
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]NiBr <sup>79</sup>	<b>123</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Ag/AgCl	−0.39 <sup>a</sup>
(Tp)(Cp <sup>*</sup> )Ni(PF <sub>6</sub> ) <sup>82</sup>	<b>124</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.39
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]Ni(NO <sub>3</sub> ) <sub>2</sub> <sup>81</sup>	<b>125</b> Ni(III) → Ni(II)	Acetone	TBACl (0.1)	Ag/AgCl	−0.38 <sup>b</sup>
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> -(4-Cl)C <sub>6</sub> H <sub>2</sub> ]NiBr <sup>79</sup>	<b>126</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Ag/AgCl	−0.33 <sup>a</sup>
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> -(4-Ac)C <sub>6</sub> H <sub>2</sub> ]NiBr <sup>79</sup>	<b>127</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Ag/AgCl	−0.32 <sup>a</sup>
(Phbpy)Ni(CF <sub>3</sub> ) <sub>2</sub> <sup>70</sup>	<b>88</b> Ni(II) → Ni(III)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.08
(dtbbpy)Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>83</sup>	<b>128</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.02
(Phbpy)NiBr <sup>70</sup>	<b>91</b> Ni(II) → Ni(III)	THF	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	0.08
(TACN) <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>3</sub> <sup>84</sup>	<b>129</b> Ni(III) → Ni(II)	MeCN	TBAClO <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	0.56
(Me <sub>2</sub> Ac <sub>2</sub> Me <sub>2</sub> malen)Ni <sup>85</sup>	<b>130</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	Ag/AgNO <sub>3</sub>	0.57 <sup>c</sup>
(Me <sub>2</sub> Ac <sub>2</sub> H <sub>2</sub> malen)Ni <sup>85</sup>	<b>131</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	Ag/AgNO <sub>3</sub>	0.68 <sup>c</sup>
(bpy)Ni(Fmes)Br <sup>69</sup>	<b>97</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	0.81
(Bz <sub>2</sub> -bme-daco)NiBr <sub>2</sub> <sup>67</sup>	<b>109</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	NHE	0.93 <sup>d</sup>
(Me <sub>2</sub> -bme-daco)NiI <sub>2</sub> <sup>67</sup>	<b>113</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	NHE	0.93 <sup>d</sup>
( <sup>t</sup> BuP)Ni <sup>86</sup>	<b>132</b> Ni(II) → Ni(III)	PhCN	TBAClO <sub>4</sub> (0.1)	SCE	1.08 <sup>e</sup>
( <sup>t</sup> PrP)Ni <sup>86</sup>	<b>133</b> Ni(II) → Ni(III)	PhCN	TBAClO <sub>4</sub> (0.1)	SCE	1.14 <sup>e</sup>
( <i>trans</i> -III-Me <sub>4</sub> -cyclam)Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>75</sup>	<b>107</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	Ag/AgNO <sub>3</sub>	1.18 <sup>c</sup>
( <i>trans</i> -I-Me <sub>4</sub> -cyclam)Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>75</sup>	<b>111</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	Ag/AgNO <sub>3</sub>	1.23 <sup>c</sup>
( <sup>t</sup> EtPrP)Ni <sup>86</sup>	<b>134</b> Ni(II) → Ni(III)	PhCN	TBAPF <sub>6</sub> (0.1)	SCE	1.23 <sup>e</sup>
(bpy) <sub>3</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>87</sup>	<b>135</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	1.23
(terpy) <sub>2</sub> Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>73</sup>	<b>100</b> Ni(II) → Ni(III)	MeCN	TBAClO <sub>4</sub> (0.1)	SCE	1.27 <sup>f</sup>
(bpy) <sub>3</sub> Ni(ClO <sub>4</sub> ) <sub>2</sub> <sup>88</sup>	<b>136</b> Ni(II) → Ni(III)	MeCN	TBAClO <sub>4</sub> (0.2)	SCE	1.30 <sup>f</sup>
( <sup>t</sup> BuP)Ni <sup>86</sup>	<b>137</b> Ni(II) → Ni(III)	PhCN	TBAClO <sub>4</sub> (0.1)	SCE	1.32 <sup>e</sup>
(TPP)Ni <sup>86</sup>	<b>138</b> Ni(II) → Ni(III)	PhCN	TBAClO <sub>4</sub> (0.1)	SCE	1.33 <sup>e</sup>
(bpy) <sub>2</sub> Ni <sup>88</sup>	<b>139</b> Ni(II) → Ni(III)	MeCN	TBAClO <sub>4</sub> (0.2)	SCE	1.34 <sup>f</sup>
(OEP)Ni <sup>86</sup>	<b>140</b> Ni(II) → Ni(III)	PhCN	TBAClO <sub>4</sub> (0.1)	SCE	1.38 <sup>e</sup>
(Tp)Ni(CF <sub>3</sub> ) <sub>3</sub> <sup>89</sup>	<b>141</b> Ni(IV) → Ni(III)	MeCN	TBAPF <sub>6</sub> (0.1)	SCE	−0.80 <sup>g</sup>
(N <sup>Me</sup> <sub>2</sub> Py <sub>2</sub> )NiMe <sub>2</sub> (PF <sub>6</sub> ) <sup>90</sup>	<b>142</b> Ni(III) → Ni(IV)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	−0.03
(N <sup>Me</sup> <sub>2</sub> Py <sub>2</sub> )Ni(cycloneophyl)(PF <sub>6</sub> ) <sup>90</sup>	<b>143</b> Ni(III) → Ni(IV)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	0.21

Complex	Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
(Tp)(Cp)Ni(PF <sub>6</sub> ) <sup>82</sup>	<b>120</b> Ni(III) → Ni(IV)	DCM	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	0.44
[2,6-(Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]NiBr <sub>2</sub> <sup>91</sup>	<b>144</b> Ni(III) → Ni(IV)	MeCN	TBAPF <sub>6</sub> (0.1)	Fc/Fc <sup>+</sup>	0.69
(dtbbpy)Ni(C <sub>4</sub> F <sub>3</sub> ) <sup>83</sup>	<b>128</b> Ni(III) → Ni(IV)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	1.16
(bpy) <sub>3</sub> Ni(BF <sub>4</sub> ) <sub>2</sub> <sup>87</sup>	<b>135</b> Ni(III) → Ni(IV)	MeCN	TBABF <sub>4</sub> (0.1)	Fc/Fc <sup>+</sup>	1.98

<b>135</b> X = BF <sub>4</sub> <b>136</b> = ClO <sub>4</sub>	<b>141</b>	<b>143</b>	<b>119</b> X = Cl <b>125</b> = NO <sub>3</sub> <b>144</b> = Br	<b>128</b>	<b>129</b>
<b>132</b> R = CMe <sub>3</sub> <b>133</b> = CHMe <sub>2</sub> <b>134</b> = CHEt <sub>2</sub> <b>137</b> = CH <sub>2</sub> CHMe <sub>2</sub> <b>138</b> = Ph	<b>120</b> R = H <b>124</b> = Me				<b>139</b>
<b>117</b> R = NH <sub>2</sub> <b>121</b> = OMe <b>123</b> = H <b>126</b> = Cl <b>127</b> = Ac					
	<b>115</b> Y = C R <sup>1</sup> = <sup>t</sup> Bu R <sup>2</sup> = NCMe R <sup>3</sup> = NCMe <b>116</b> = C = <sup>t</sup> Bu = NCMe = Br <b>118</b> = N = <sup>t</sup> Bu = Cl = <i>p</i> -F-Ph <b>122</b> = N = <sup>t</sup> Bu = Br = <i>p</i> -F-Ph <b>142</b> = N = Me = Me = Me				

<sup>a</sup> Fc = 0.87 V vs Ag/AgI (0.4 M TBAClO<sub>4</sub> and 0.05 M TBAI in DCM) (DCM/TBAPF<sub>6</sub>).<sup>79</sup>

<sup>b</sup> Fc = 0.63 V vs Ag/Ag<sup>+</sup> 0.1 M LiCl in acetone (acetone/TBACl).<sup>81</sup>

<sup>c</sup> Fc = 0.037 V vs Ag/Ag<sup>+</sup> 0.1 M AgNO<sub>3</sub> (MeCN/TBAPF<sub>6</sub>).<sup>77</sup>

<sup>d</sup> Fc = 0.64 V vs NHE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>

<sup>e</sup> Fc = 0.50 V vs SCE (PhCN/TBAClO<sub>4</sub>).<sup>19</sup>

<sup>f</sup> Fc = 0.38 V vs SCE (MeCN/TBAClO<sub>4</sub>).<sup>12</sup>

<sup>g</sup> Fc = 0.40 V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>

### 2.3 Redox Potentials of (NHC)Ni Complexes

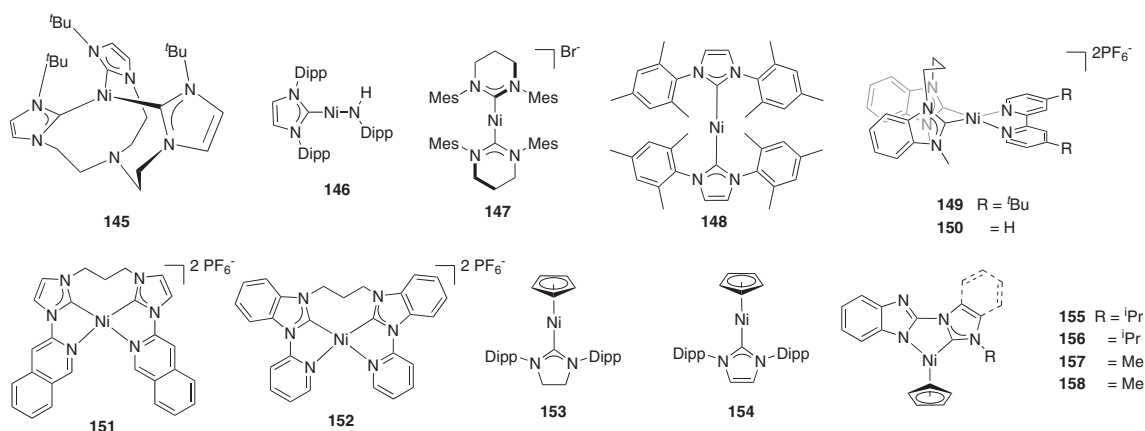
The use of *N*-heterocyclic carbenes (NHC) in homogeneous nickel catalysis has dramatically expanded over the past two decades as a modular, strongly  $\sigma$ -donating, and nonlabile alternative to phosphines.<sup>20</sup> (NHC)Ni complexes have found a wide range of applications in cross-coupling reactions, in which nickel is stabilized in both open and closed-shell electron configurations.<sup>20,92</sup> A wide range of oxidation states can be supported on (NHC)Ni complexes. Data collected in Table 8, Table 9, and Table 10 cover single-electron transformations from Ni(0) up to Ni(IV). As a strong  $\sigma$ -donor, NHC drastically shifts the redox potentials of nickel complexes to the negative direction.  $E[\text{Ni}(I/0)]$  of **145** is as negative as  $-2.50$  V. Nickel(0) complexes carrying

more NHC ligands, or electron-donating substituents, are oxidized at a more negative potential (Table 8). The better  $\sigma$ -donor (SIPr)Ni(0) **153** is oxidized at a more negative potential relative to (IPr)Ni(0) **154**.

In summary, we tabulate the redox potentials of nickel complexes experimentally measured by CV and convert data to a unified Fc/Fc<sup>+</sup> reference electrode for direct comparison. The redox potentials are clearly determined by the oxidation state, the electronic effect of the ligand, the coordination geometry, the solvent, and the electrolyte conditions. This article is meant to assist synthetic organic and organometallic chemists to evaluate the feasibility and kinetics of redox events occurring at the nickel center, when designing catalytic reactions and preparing nickel complexes.

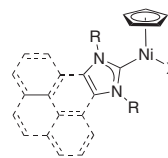
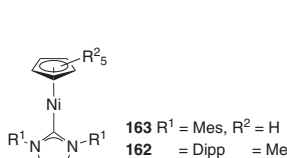
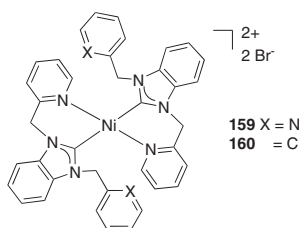
**Table 8** Formal Potentials of the Ni(I)/Ni(0) Transformation for Selected (NHC)Ni Complexes

Complex		Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
(TIMEN <sup>tBu</sup> )Ni <sup>93</sup>	<b>145</b>	Ni(0) → Ni(I)	THF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-2.50
(IPr)Ni(NHDipp) <sup>94</sup>	<b>146</b>	Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-2.41
(SPMes) <sub>2</sub> NiBr <sup>95</sup>	<b>147</b>	Ni(I) → Ni(0)	THF	TBAPF <sub>6</sub>	NHE	-2.12 <sup>a</sup>
(IMes) <sub>2</sub> Ni <sup>96</sup>	<b>148</b>	Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.90
( <sup>Me</sup> C <sup>Prop</sup> C <sup>Me</sup> )Ni(dtbbpy)(PF <sub>6</sub> ) <sub>2</sub> <sup>61</sup>	<b>149</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.85
( <sup>Me</sup> C <sup>Prop</sup> C <sup>Me</sup> )Ni(bpy)(PF <sub>6</sub> ) <sub>2</sub> <sup>61</sup>	<b>150</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.79
( <sup>Pr</sup> bimiqI)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>62</sup>	<b>151</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	SCE	-1.78 <sup>b</sup>
( <sup>Pr</sup> bzbimpy)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>62</sup>	<b>152</b>	Ni(I) → Ni(0)	MeCN	TBAPF <sub>6</sub>	SCE	-1.62 <sup>b</sup>
(SiPr)Ni(Cp) <sup>97</sup>	<b>153</b>	Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.75
(IPr)Ni(Cp) <sup>98</sup>	<b>154</b>	Ni(0) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.66
<sup>i</sup> Pr(bzim)Ni(Cp) <sup>98</sup>	<b>155</b>	Ni(0) → Ni(I)	DCM	TBA[B(Ar <sup>f</sup> ) <sub>4</sub> ]	Fc/Fc <sup>+</sup>	0.22
(benzo) <sup>i</sup> Pr(bzim)Ni(Cp) <sup>99</sup>	<b>156</b>	Ni(0) → Ni(I)	DCM	TBA[B(Ar <sup>f</sup> ) <sub>4</sub> ]	Fc/Fc <sup>+</sup>	0.27
IMe(bzim)Ni(Cp) <sup>99</sup>	<b>157</b>	Ni(0) → Ni(I)	DCM	TBA[B(Ar <sup>f</sup> ) <sub>4</sub> ]	Fc/Fc <sup>+</sup>	0.32
(benzo)IMe(bzim)Ni(Cp) <sup>99</sup>	<b>158</b>	Ni(0) → Ni(I)	DCM	TBA[B(Ar <sup>f</sup> ) <sub>4</sub> ]	Fc/Fc <sup>+</sup>	0.40

<sup>a</sup> Fc = 0.80 V vs NHE (THF/TBAPF<sub>6</sub>).<sup>12</sup><sup>b</sup> Fc = 0.40 V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>**Table 9** Formal Potentials of the Ni(II)/Ni(I) Transformation for Selected (NHC)Ni Complexes

Complex		Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
[(benzo)I(CH <sub>2</sub> Py) <sub>2</sub> ] <sub>2</sub> NiBr <sub>2</sub> <sup>100</sup>	<b>159</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Ag/AgCl	-1.56 <sup>a</sup>
( <sup>Me</sup> C <sup>Prop</sup> C <sup>Me</sup> )Ni(dtbbpy)(PF <sub>6</sub> ) <sub>2</sub> <sup>61</sup>	<b>149</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.54
[(benzo)I(CH <sub>2</sub> Py)(Bz)] <sub>2</sub> NiBr <sub>2</sub> <sup>99</sup>	<b>160</b>	Ni(II) → Ni(I)	DMF	TBAPF <sub>6</sub>	Ag/AgCl	-1.51 <sup>a</sup>
(IMes)(Cp)NiCl <sup>100</sup>	<b>161</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>4</sub>	NHE	-1.51 <sup>b</sup>
( <sup>Me</sup> C <sup>Prop</sup> C <sup>Me</sup> )Ni(bpy)(PF <sub>6</sub> ) <sub>2</sub> <sup>61</sup>	<b>150</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.42
( <sup>Pr</sup> bimiqI)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>62</sup>	<b>151</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	SCE	-1.32 <sup>c</sup>
(IPr)Ni(Cp <sup>*</sup> ) <sup>101</sup>	<b>162</b>	Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.18
( <sup>Pr</sup> bzbimpy)Ni(PF <sub>6</sub> ) <sub>2</sub> <sup>62</sup>	<b>152</b>	Ni(II) → Ni(I)	MeCN	TBAPF <sub>6</sub>	SCE	-1.03 <sup>c</sup>
(TIMEN <sup>tBu</sup> )Ni <sup>94</sup>	<b>145</b>	Ni(I) → Ni(II)	THF	TBAClO <sub>4</sub>	Fc/Fc <sup>+</sup>	-1.09

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
(IMes)Ni(Cp) <sup>102</sup>	<b>163</b> Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.06
(IPr)Ni(Cp) <sup>102</sup>	<b>154</b> Ni(I) → Ni(II)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-1.02
(IPr)Ni(NHDipp) <sup>95</sup>	<b>146</b> Ni(II) → Ni(I)	THF	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.84
( <sup>t</sup> Bu)(Cp)NiBr <sup>102</sup>	<b>164</b> Ni(II) → Ni(I)	DCM	TBAPF <sub>6</sub>	SCE	0.22 <sup>d</sup>
(pyrene- <sup>t</sup> Bu)(Cp)NiBr <sup>103</sup>	<b>165</b> Ni(II) → Ni(I)	DCM	TBAPF <sub>6</sub>	SCE	0.22 <sup>d</sup>
(benzo- <sup>t</sup> Bu)(Cp)NiBr <sup>103</sup>	<b>166</b> Ni(II) → Ni(I)	DCM	TBAPF <sub>6</sub>	SCE	0.24 <sup>d</sup>



<sup>a</sup> Fc = 0.51 V vs Ag/AgCl (DMF/TBAPF<sub>6</sub>).<sup>100</sup>

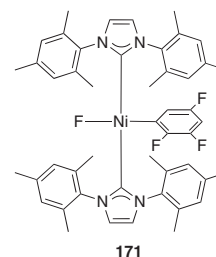
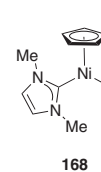
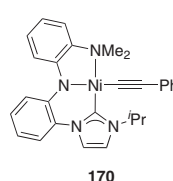
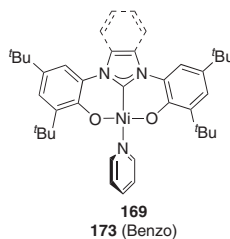
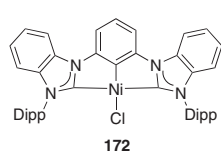
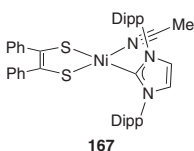
<sup>b</sup> Fc = 0.69 V vs NHE (MeCN/TBAPF<sub>6</sub>).<sup>101</sup>

<sup>c</sup> Fc = 0.40 V vs SCE (MeCN/TBAPF<sub>6</sub>).<sup>12</sup>

<sup>d</sup> Fc = 0.44 V vs SCE (DCM/TBAPF<sub>6</sub>).<sup>103</sup>

**Table 10** Formal Potentials of the Ni(III)/Ni(II) and Ni(IV)/Ni(III) Transformations for Selected (NHC)Ni Complexes

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc <sup>+</sup> )
(IPr)Ni(S <sub>2</sub> C <sub>2</sub> Ph <sub>2</sub> )(MeCN) <sup>103</sup>	<b>167</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	-0.13
(IMe)(Cp)Ni <sup>101</sup>	<b>168</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub>	NHE	-0.13 <sup>a</sup>
(IMes)(Cp)NiCl <sup>101</sup>	<b>161</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub>	NHE	0.03 <sup>a</sup>
[l(2-oxy-3,5- <sup>t</sup> Bu <sub>2</sub> Ph)]Ni(Py) <sup>104</sup>	<b>169</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.10
( <sup>ipr</sup> CNN)Ni(CCPH) <sup>105</sup>	<b>170</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.21
<i>trans</i> -[(IMes) <sub>2</sub> NiF(2,3,5-F-Ph)] <sup>97</sup>	<b>171</b> Ni(II) → Ni(III)	MeCN	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.40
( <sup>DIPP</sup> CCC)NiCl <sup>106</sup>	<b>172</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.57
[(benzo)l(2-oxy-3,5- <sup>t</sup> Bu <sub>2</sub> Ph)]Ni(Py) <sup>105</sup>	<b>173</b> Ni(II) → Ni(III)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.71
[l(2-oxy-3,5- <sup>t</sup> Bu <sub>2</sub> Ph)]Ni(Py) <sup>105</sup>	<b>169</b> Ni(III) → Ni(IV)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	0.70
[(benzo)l(2-oxy-3,5- <sup>t</sup> Bu <sub>2</sub> Ph)]Ni(Py) <sup>105</sup>	<b>173</b> Ni(III) → Ni(IV)	DCM	TBAPF <sub>6</sub>	Fc/Fc <sup>+</sup>	1.30



<sup>a</sup> Fc = 0.69 V vs NHE (MeCN/TBAPF<sub>6</sub>).<sup>101</sup>

## Conflict of Interest

The authors declare no conflict of interest.

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