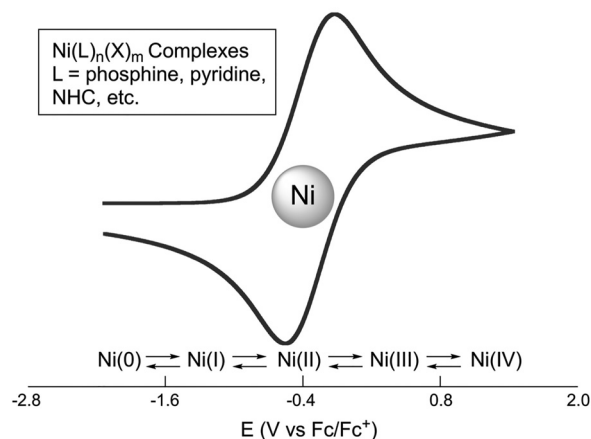


Experimental Electrochemical Potentials of Nickel Complexes

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Published as part of the Cluster
 Modern Nickel-Catalyzed Reactions



Received: 21.07.2021

Accepted after revision: 10.08.2021

Published online: 26.08.2021

DOI: 10.1055/s-0040-1719829; Art ID: st-2021-k0259-nt

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.

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

1 Introduction

1.1 Scope

In recent years, nickel-catalyzed cross-coupling,¹ photoredox-dual catalysis,² and electrocatalytic³ 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 ($\Delta G^\circ = -nFE^\circ$).

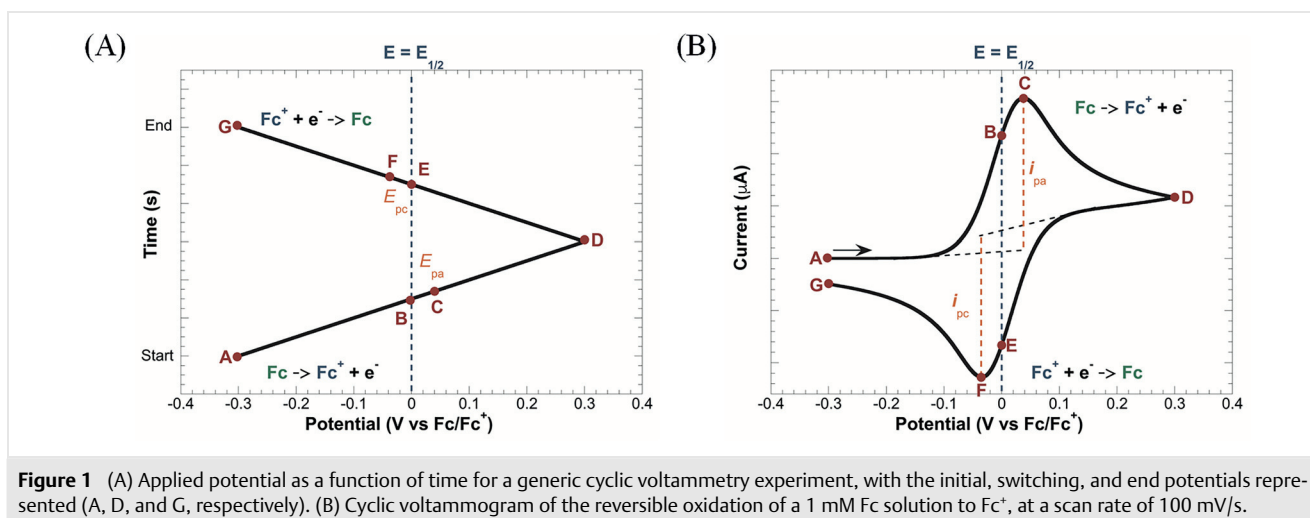
A formal potential, sometimes referred to as a conditional potential, is the reduction potential that applies to a half reaction under a specific set of conditions, as opposed to the standard-state conditions.⁴ Nicewicz and co-workers measured and summarized the formal potentials of organic molecules with common functional groups.⁵ 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⁻ to 4⁺,⁶ 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.^{7,8} 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⁺) on the electrode surface. The higher the oxidation potential applied to the electrode, the higher the current and higher ratio of [Fc⁺]/[Fc] till the electrode potential reaches point B, whose potential is $E_{1/2}$, where $[Fc] = [Fc^+]$. 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⁺] 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.⁹ 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 $E^{0'}$.⁸ 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 $E^{0'}$.⁵ $E_{p/2}$ values must be considered in the context of the detailed conditions at which the CVs are measured.⁵ 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⁺ couple, as recommended by IUPAC.¹⁰ 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.¹¹ Table 1 summarizes potentials of the Fc/Fc⁺ couple, measured in different solvents and with supporting electrolytes.¹² 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^a

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

^a 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⁺ based on Table 1 or the Fc/Fc⁺ 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⁺ is sensitive to the experimental conditions, such as electrolytes and their concentration, solvent, etc.¹³ Thus, it is strongly recommended to specify solvent and electrolyte conditions when reporting CV data against Fc/Fc⁺.¹²

2 Redox Potentials of Nickel Complexes

2.1 Redox Potentials of (Phosphine)Ni Complexes

Most phosphine ligands applied to support nickel complexes are strong σ -donors.²⁰ 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⁻(CH₂PⁱPr₂)₃]Ni **4** and **6**, with a borate on the ligand, have E[Ni(I/0)] as negative as -1.95 V, whereas (B₂P₂)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(PⁱPr₂)₂]₂NiX₂ (X = NO₃ **7**, ClO₄ **9**, BF₄ **10**) are almost identical. Generally, Ni(I)-aryl and halide complexes exhibit significantly more negative redox potentials than Ni(diphosphine)₂ complexes.

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

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

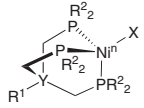
Complex	Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc ⁺)
(dppv) ₂ Ni(BF ₄) ₂ ³⁴	Ni(I) → Ni(0)	MeCN	Et ₄ NBF ₄ (0.3)	Fc/Fc ⁺	-0.83
(B ₂ P ₂)Ni ³⁵	Ni(0) → Ni(I)	MeCN	TBAPF ₆ (0.1)	Fc/Fc ⁺	0.06

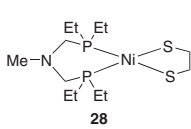
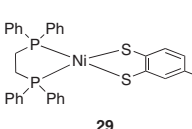
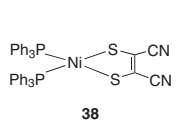
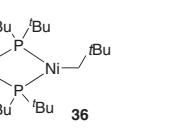
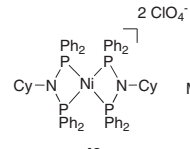
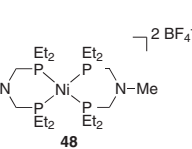
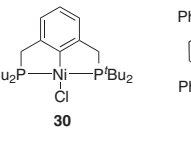
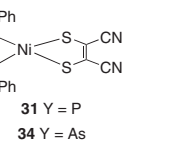
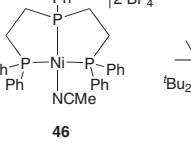
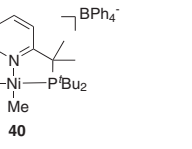
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Table 3 Formal Potentials of the Ni(II)/Ni(I) Transformation for (Phosphine)Ni Complexes

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

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

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

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

^a Fc = 0.46 V vs Ag/Ag⁺ 0.1 M LiCl in DCM (DCM/TBAClO₄).³⁸

^b Fc = 0.69 V vs NHE (MeCN/TBAPF₆).³⁹

^c E⁰ for Sp isomer.

^d Fc = 0.33 V vs Ag/AgCl (DCM/TBAPF₆).⁴²

^e E⁰ for Td isomer.

^f Fc = 0.46 V vs SCE (DCM/TBAPF₆).¹²

^g Fc = 0.176 V vs Ag/0.01 M AgNO₃ (THF/TBAPF₆).⁴⁹

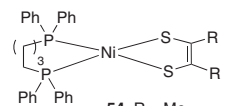
^h Fc = 0.40 V vs SCE (MeCN/Et₄NBF₄).³²

ⁱ Fc = 0.38 V vs SCE (MeCN/Et₄NClO₄).⁴⁸

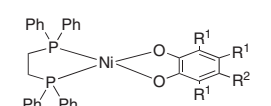
Table 4 Formal Potentials of the Ni(III)/Ni(II) and Ni(IV)/Ni(III) Transformations for Selected (Phosphine)Ni Complexes

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

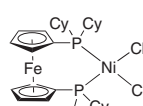
Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc^+)	
$[o-C_6H_4(PMe_2)_2]_2NiBr_2$ ⁵²	58	Ni(III) → Ni(IV)	MeCN	Et_4NClO_4	SCE	0.84 ^c
$[o-C_6H_4(AsMe_2)_2]_2NiCl_2$ ⁵²	69	Ni(III) → Ni(IV)	MeCN	Et_4NClO_4	SCE	0.91 ^c
$[o-C_6F_4(PMe_2)_2]_2NiCl_2$ ⁵²	57	Ni(III) → Ni(IV)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



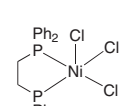
54 R = Me
55 = C₆H₄-p-OMe



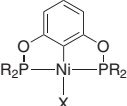
53 R¹ = H R² = ^tBu
59 = Cl = Cl



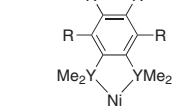
60



62



61 R = ^tBu X = H
63 = ⁱPr = OAc
64 = Ph = OAc
65 = ^tBu = Cl
66 = ^tBu = Br
67 = Ph = OTf
68 = ⁱPr = OTf



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

^a $Fc = 0.46$ V vs Ag/Ag^+ 0.1 M LiCl in DCM (DCM/TBAClO₄).³⁸

^b $Fc = 0.39$ V vs SCE (MeCN/TBAPF₆).¹⁴

^c $Fc = 0.38$ V vs SCE (MeCN/ Et_4NClO_4).⁴⁸

^d 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).^{6,58} N-

ligands are π -acceptors and generally stronger σ -donors than phosphines.⁵⁹ The redox activity of π -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^+)	
$[(-)-i-Pr-pybox]Ni(Ph)B(Ar^f)_4$ ⁶⁰	70	Ni(I) → Ni(0)	THF	TBAPF ₆	Fc/Fc^+	-2.36
$(dtbbpy)(C^{prop2}C)Ni(PF_6)_2$ ⁶¹	71	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-2.06
$(bpy)(C^{prop2}C)Ni(PF_6)_2$ ⁶¹	72	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-2.00
$(P^i\text{bimiiql})Ni(PF_6)_2$ ⁶²	73	Ni(I) → Ni(0)	MeCN	TBAPF ₆	SCE	-1.60 ^a
$(6,6'-Mebpy)NiBr_2$ ⁶³	74	Ni(I) → Ni(0)	MeCN	TBAPF ₆	SCE	-1.56 ^b
$(DippBIAN)NiCl_2$ ⁶⁴	75	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.52
$(DippBIAN)NiBr_2$ ⁶⁴	76	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.47
$(DippBIAN)NiI_2$ ⁶⁴	77	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.46
$(DippBIAN)Ni(NCMe)_4(BF_4)_2$ ⁶⁴	78	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.45
$(DippN^PyN^DippN)NiCl_2$ ⁶⁵	79	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.23
$(DippN^PyN^DippN)NiBr_2$ ⁶⁵	80	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.22
$(bpy)Ni(cod)$ ³⁰	81	Ni(0) → Ni(I)	THF	TBAPF ₆	Fc/Fc^+	-1.17
$(2-Ome-Ph-Me_2DAB)(Cp)NiBF_4$ ⁶⁶	82	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.17
$(Ph-Me_2DAB)(Cp)NiBF_4$ ⁶⁶	83	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-1.05
$(2-CF_3-Ph-Me_2DAB)(Cp)NiBF_4$ ⁶⁶	84	Ni(I) → Ni(0)	MeCN	TBAPF ₆	Fc/Fc^+	-0.80

Complex	Process	Solvent	Electrolyte (0.1 M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc ⁺)
	2^+ 2PF_6^-				
70	71 R = ^t Bu 72 R = H				81
	79 X = Cl 80 X = Br				
	75 X = Cl 76 X = Br 77 X = I				
	2^+ 2BF_4^-				82 R = <i>o</i> -OMe 83 R = H 84 R = <i>o</i> -CF ₃

^a Fc = 0.40 V vs SCE (MeCN/TBAPF₆).¹²

^b Fc = 0.38 V vs SCE (MeCN/TBABF₄).⁶³

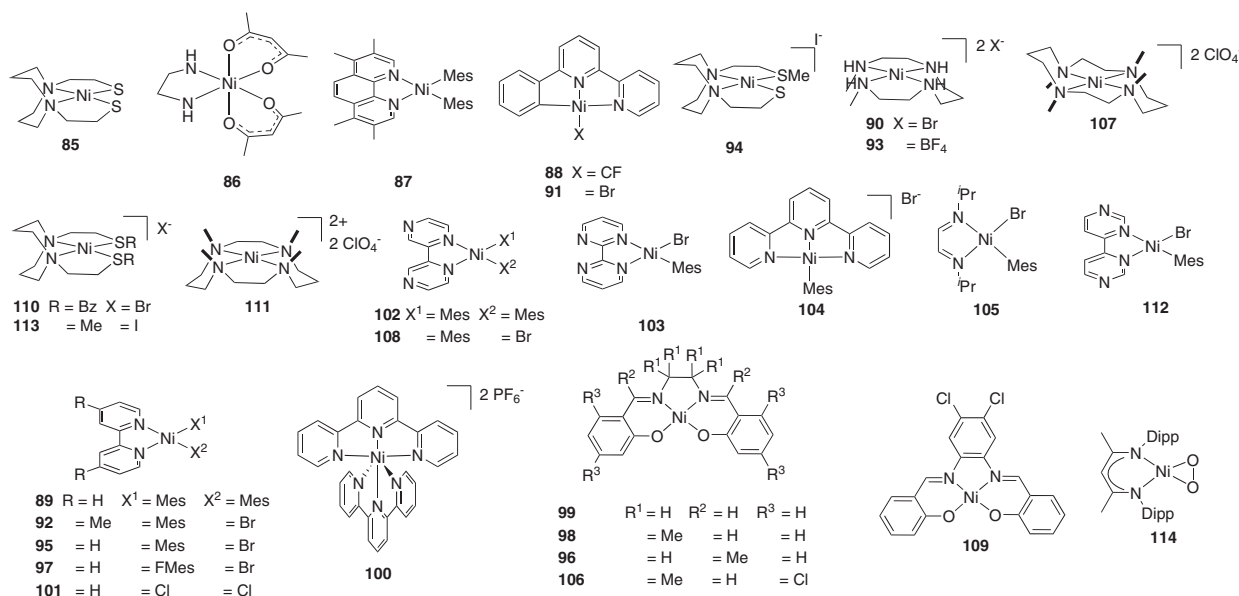
The electronic effect of ligands on the redox potential is evident by comparing a series of (4,4'-Mebpy)Ni (4,4'-Mebpy = **92**), (bpy)Ni (bpy = **95**), and DAB(Ni) (DAB = **105**) complexes (Table 6). The first reduction of Ni(II) complexes can be ligand centered, depending on the coordination number, geometry, and the ligand. For example, the first electron reduction of (dtbbpy)(C^{Prop2}C)Ni(PF₆)₂ **71** and (bpy)(C^{Prop2}C)Ni(PF₆)₂

72 is ligand centered, and the second electron reduction is metal centered.⁶¹ 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.⁶⁹

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

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



^a Fc = 0.64 V vs NHE (MeCN/TBAPF₆).¹²

^b Fc = 0.47 V vs SCE (DMF/TBAClO₄).¹²

^c Fc = 0.38 V vs SCE (MeCN/TBAClO₄).¹²

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

^e Fc = 0.037 V vs Ag/0.1 M AgNO₃ (MeCN/TBAPF₆).⁷⁷

^f Fc = 0.40 V vs SCE (MeCN/TBAPF₆).¹²

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–NH₂ **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[(T^tBuP)Ni **132**] < E[(TⁱPrP)Ni **133**] < E[(T^{Et}PrP)Ni **134**] < E[(T^tBuP)Ni **137**] < E[(TPP)Ni **138**].⁸⁶

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

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

135 X = BF ₄ 136 = ClO ₄	141	143	119 X = Cl 125 = NO ₃ 144 = Br	128	129
132 R = CMe ₃ 133 = CHMe ₂ 134 = CHEt ₂ 137 = CH ₂ CHMe ₂ 138 = Ph	120 R = H 124 = Me	140	130 R = Me 131 = H	139	
117 R = NH ₂ 121 = OMe 123 = H 126 = Cl 127 = Ac	115 Y = C R ¹ = ^t Bu R ² = NCMe R ³ = NCMe 116 = C = ^t Bu = NCMe = Br 118 = N = ^t Bu = Cl = <i>p</i> -F-Ph 122 = N = ^t Bu = Br = <i>p</i> -F-Ph 142 = N = Me = Me = Me				

^a Fc = 0.87 V vs Ag/AgI (0.4 M TBAClO₄ and 0.05 M TBAI in DCM) (DCM/TBAPF₆).⁷⁹

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

^c Fc = 0.037 V vs Ag/Ag⁺ 0.1 M AgNO₃ (MeCN/TBAPF₆).⁷⁷

^d Fc = 0.64 V vs NHE (MeCN/TBAPF₆).¹²

^e Fc = 0.50 V vs SCE (PhCN/TBAClO₄).¹⁹

^f Fc = 0.38 V vs SCE (MeCN/TBAClO₄).¹²

^g Fc = 0.40 V vs SCE (MeCN/TBAPF₆).¹²

2.3 Redox Potentials of (NHC)Ni Complexes

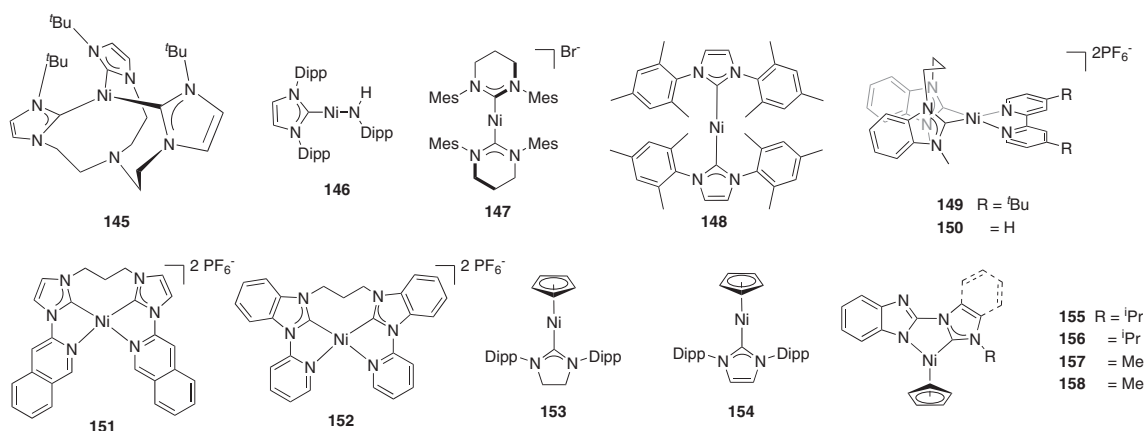
The use of *N*-heterocyclic carbenes (NHC) in homogeneous nickel catalysis has dramatically expanded over the past two decades as a modular, strongly σ -donating, and nonlabile alternative to phosphines.²⁰ (NHC)Ni complexes have found a wide range of applications in cross-coupling reactions, in which nickel is stabilized in both open and closed-shell electron configurations.^{20,92} 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 σ -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 σ -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⁺ 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.

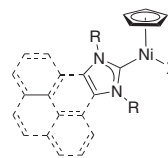
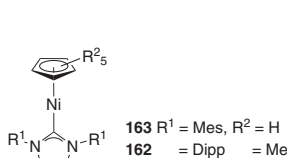
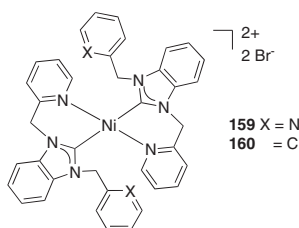
Table 8 Formal Potentials of the Ni(I)/Ni(0) Transformation for Selected (NHC)Ni Complexes

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

^a Fc = 0.80 V vs NHE (THF/TBAPF₆).¹²^b Fc = 0.40 V vs SCE (MeCN/TBAPF₆).¹²**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 ⁺)
[(benzo)I(CH ₂ Py) ₂] ₂ NiBr ₂ ¹⁰⁰	159	Ni(II) → Ni(I)	DMF	TBAPF ₆	Ag/AgCl	-1.56 ^a
(^{Me} C ^{Prop} C ^{Me})Ni(dtbbpy)(PF ₆) ₂ ⁶¹	149	Ni(II) → Ni(I)	MeCN	TBAPF ₆	Fc/Fc ⁺	-1.54
[(benzo)I(CH ₂ Py)(Bz)] ₂ NiBr ₂ ⁹⁹	160	Ni(II) → Ni(I)	DMF	TBAPF ₆	Ag/AgCl	-1.51 ^a
(IMes)(Cp)NiCl ¹⁰⁰	161	Ni(II) → Ni(I)	MeCN	TBAPF ₄	NHE	-1.51 ^b
(^{Me} C ^{Prop} C ^{Me})Ni(bpy)(PF ₆) ₂ ⁶¹	150	Ni(II) → Ni(I)	MeCN	TBAPF ₆	Fc/Fc ⁺	-1.42
(^{Pr} bimiqI)Ni(PF ₆) ₂ ⁶²	151	Ni(II) → Ni(I)	MeCN	TBAPF ₆	SCE	-1.32 ^c
(IPr)Ni(Cp [*]) ¹⁰¹	162	Ni(I) → Ni(II)	THF	TBAPF ₆	Fc/Fc ⁺	-1.18
(^{Pr} bzbimpy)Ni(PF ₆) ₂ ⁶²	152	Ni(II) → Ni(I)	MeCN	TBAPF ₆	SCE	-1.03 ^c
(TIMEN ^{tBu})Ni ⁹⁴	145	Ni(I) → Ni(II)	THF	TBAClO ₄	Fc/Fc ⁺	-1.09

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



^a Fc = 0.51 V vs Ag/AgCl (DMF/TBAPF₆).¹⁰⁰

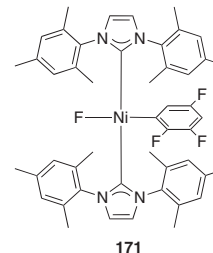
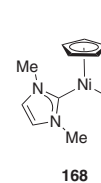
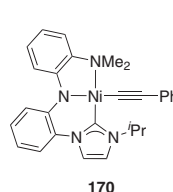
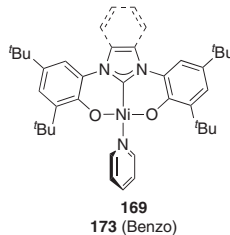
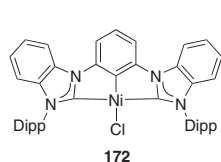
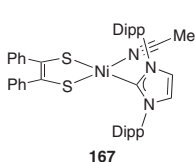
^b Fc = 0.69 V vs NHE (MeCN/TBAPF₆).¹⁰¹

^c Fc = 0.40 V vs SCE (MeCN/TBAPF₆).¹²

^d Fc = 0.44 V vs SCE (DCM/TBAPF₆).¹⁰³

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 ⁺)
(IPr)Ni(S ₂ C ₂ Ph ₂)(MeCN) ¹⁰³	167 Ni(II) → Ni(III)	DCM	TBAPF ₆	Fc/Fc ⁺	-0.13
(IMe)(Cp)Ni ¹⁰¹	168 Ni(II) → Ni(III)	MeCN	TBAPF ₆	NHE	-0.13 ^a
(IMes)(Cp)NiCl ¹⁰¹	161 Ni(II) → Ni(III)	MeCN	TBAPF ₆	NHE	0.03 ^a
[l(2-oxy-3,5- ⁱ Bu ₂ Ph)]Ni(Py) ¹⁰⁴	169 Ni(II) → Ni(III)	DCM	TBAPF ₆	Fc/Fc ⁺	0.10
(ⁱ PrC ₂ NN)Ni(CCPH) ¹⁰⁵	170 Ni(II) → Ni(III)	DCM	TBAPF ₆	Fc/Fc ⁺	0.21
<i>trans</i> -[(IMes) ₂ NiF(2,3,5-F-Ph)] ⁹⁷	171 Ni(II) → Ni(III)	MeCN	TBAPF ₆	Fc/Fc ⁺	0.40
(^{DIPP} CCC)NiCl ¹⁰⁶	172 Ni(II) → Ni(III)	DCM	TBAPF ₆	Fc/Fc ⁺	0.57
[(benzo)l(2-oxy-3,5- ⁱ Bu ₂ Ph)]Ni(Py) ¹⁰⁵	173 Ni(II) → Ni(III)	DCM	TBAPF ₆	Fc/Fc ⁺	0.71
[l(2-oxy-3,5- ⁱ Bu ₂ Ph)]Ni(Py) ¹⁰⁵	169 Ni(III) → Ni(IV)	DCM	TBAPF ₆	Fc/Fc ⁺	0.70
[(benzo)l(2-oxy-3,5- ⁱ Bu ₂ Ph)]Ni(Py) ¹⁰⁵	173 Ni(III) → Ni(IV)	DCM	TBAPF ₆	Fc/Fc ⁺	1.30



^a Fc = 0.69 V vs NHE (MeCN/TBAPF₆).¹⁰¹

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

This work was supported by the National Science Foundation under Award Number CHE-1654483.

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