Mononuclear Nickel(III) Complexes $[Ni^{III}(OR)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (R = Me, Ph) Containing the Terminal Alkoxide Ligand: Relevance to the Nickel Site of Oxidized-Form [NiFe] Hydrogenases

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The unprecedented nickel(III) thiolate $[Ni^{III}(OR)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ [R = Ph (1), Me (3)] containing the terminal Ni^{IIII}–OR bond, characterized by UV–vis, electron paramagnetic resonance, cyclic voltammetry, and single-crystal X-ray diffraction, were isolated from the reaction of $[Ni^{III}(CI)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ with 3 equiv of [Na][OPh] in tetrahydrofuran (THF)–CH₃CN and the reaction of complex 1 with 1 equiv of $[Bu_4N][OMe]$ in THF–CH₃OH, respectively. Interestingly, the addition of complex 1 into the THF–CH₃OH solution of $[Me_4N][OH]$ also yielded complex 3. In contrast to the inertness of complex $[Ni^{III}(CI)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ toward 1 equiv of [Na][OPh], the addition of 1 equiv of [Na][OMe] into a THF–CH₃CN solution of $[Ni^{III}(CI)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ yielded the known $[Ni^{III}(CH_2CN)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (4). At 77 K, complexes 1 and 3 exhibit a rhombic signal with *g* values of 2.31, 2.09, and 2.00 and of 2.28, 2.04, and 2.00, respectively, the characteristic *g* values of the known trigonal-bipyramidal Ni^{III} $[Ni^{III}(L)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (L = SePh, SEt, CI) complexes. Compared to complexes $[Ni^{III}(EPh)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ [E = S (2), Se] dominated by one intense absorption band at 592 and 590 nm, respectively, the electronic spectrum of complex 1 coordinated by the less electron-donating phenoxide ligand displays a red shift to 603 nm. In a comparison of the Ni^{IIII}–OMe bond length of 1.885(2) Å found in complex 3, the longer Ni^{IIII}–OPh bond distance of 1.910(3) Å found in complex 1 may be attributed to the absence of σ and π donation from the [OPh]-coordinated ligand to the Ni^{IIII} center.

Introduction

Hydrogenase, a metalloenzyme, catalyzes a reversible twoelectron oxidation of H₂ in aerobic and anaerobic microorganisms.^{1–3} Two classes of hydrogenases, [Fe]-only hydrogenases ([Fe]-only H₂ases) and [NiFe] hydrogenases ([NiFe] H₂ases), have been studied widely. The X-ray crystallographic studies of the active-site structure of [NiFe] H₂ases isolated from *Desulfovibrio gigas*, *Desulfovibrio vulgaris*, *Desulfovibrio fructosovorans*, and *Desulfovibrio desulfuricans* ATCC27774 in combination with infrared spectroscopy have revealed an active site comprised of a heterobimetallic (S_{cys})₂Ni(μ -S_{cys})₂(μ -X)Fe(CO)(CN)₂ (X = O²⁻, HO₂⁻, OH⁻) cluster.^{2,3} The bridging ligand X was proposed to be an oxide, hydroxide, or hydroperoxide in the oxidized state and was found to be absent in the reduced state. Extended X-ray absorption fine structure (EXAFS) studies of *Chromatium*

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Complexes $[Ni^{III}(OR)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (R = Me, Ph)

vinosum showed that the Ni-O distance of 1.91 Å is consistent with a hydroxy bridge (Ni-A state).² The coordination environment about Ni in the [NiFe] H₂ases is pseudo square pyramidal in the oxidized state. The Ni site has been proposed to be redox-active and changes between Ni^{III} and Ni^{II}, while the Fe site remains as Fe^{II} in all spectrally defined redox states of the enzyme.²⁻⁵ The EXAFS/electron paramagnetic resonance (EPR) studies indicate that the formal oxidation state of the Ni center is paramagnetic Ni^{III} in Ni-A, Ni-B, and Ni-C states.²⁻⁵ Also, the ENDOR experiments showed that the Ni-A form exhibits an ¹⁷O signal from a solvent-derived $(H_2^{17}O)$ species, and the signal disappears upon redox cycling to the Ni-C state.^{2g} In particular, recent X-ray absorption spectroscopy shows that the Ni site of the regulatory hydrogenase (RH) in the presence of hydrogen (RH^{+H₂}), proposed as the Ni-C state, isolated from Ralstonia eutropha is a six-coordinate $[Ni^{III}S_2(O/N)_3(H)].^4$

Despite a number of well-characterized high-valent dinuclear bis(μ -oxo)nickel(III) complexes,⁵ no mononuclear nickel(III) thiolate complexes containing the terminal alkoxide ligand were reported.⁶ Recently, we reported the isolation and characterization of the mononuclear [Ni^{III}(L)(P(C₆H₃- $3-SiMe_3-2-S_3)^{-}$ (L = 2-S-C₄H₃S, SePh, SEt, Cl).⁷ The increased electron density of the Ni center of complexes $[Ni^{III}(L)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ modulated by the monodentate ligand L and the substituted groups of the phenylthiolate rings promotes the stability of the nickel(III) thiolate complexes. The similarity of the synthesized [Ni^{III}(SR)(P(C₆H₃- $3-SiMe_3-2-S_3)^{-1}$ complexes to the nickel active-site structure of [NiFe] H₂ases has inspired the preparation of derivatives to mimic the features of the Ni-A and Ni-B states of the catalytic cycle of [NiFe] H₂ase. Herein, we report the synthesis of $[Ni^{III}(OR)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ [R = Ph (1), Me (3)] containing the terminal Ni^{III}–OPh and Ni^{III}–OMe bonds, respectively.

Results and Discussion

In contrast to the inertness of $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ toward 1 equiv of [Na][OPh] in tetrahydrofuran

Scheme 1



(THF)-CH₃CN (3:1 volume ratio) at room temperature, $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ and 3 equiv of [Na][OPh]dissolved in THF-CH₃CN (3:1 volume ratio) were stirred at ambient temperature for 12 h to yield the mononuclear $[Ni^{III}(OPh)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (1; yield 73%) after separation of the insoluble NaCl and the excess [Na][OPh] by filtration (Scheme 1a).⁷ Complex 1 is air-stable in the solid state and exhibits a diagnostic ¹H NMR spectrum with phenyl proton resonances well removed from the diamagnetic region. The proton resonances [δ 15.8 (br), 10.4 (br), 9.4 (br), -5.3 (br) ppm] were assigned to $[OPh]^-$ and $[P(C_6H_3-$ 3-SiMe₃-2-S)₃]³⁻ ligands. Compared to the rhombic signal with g values of 2.31, 2.09, and 2.00 (4.2 K) observed in $[Ni^{III}(SePh)(P(o-C_6H_3-2-S)_3)]^{-}$,^{7a} complex 1 displays a rhombic signal with g values of 2.31, 2.04, and 1.99 [THF-CH₃CN (3:1 volume ratio)] at 77 K and g values of 2.28, 2.09, and 2.02 in a powdered sample EPR spectrum (Figure 1). The effective magnetic moment was 1.73 $\mu_{\rm B}$ for complex 1. These results are consistent with the central Ni^{III} possessing a d7 electronic configuration in a trigonalbipyramidal ligand field.⁷

In contrast, upon the addition of 1 equiv of a [Na][SPh] to the THF–CH₃CN (3:1 volume ratio) solution of [Ni^{III}(Cl)-(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻, a pronounced color change from dark green to blue green occurs at ambient temperature. The UV–vis, EPR, and single-crystal X-ray diffraction studies confirmed the formation of [Ni^{III}(SPh)(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻ (**2**; Figure 2). Presumably, the stronger σ - and π -electron-donating nature of phenylthiolate [SPh]⁻, compared to phenoxide [OPh]⁻, rendering the Ni^{III} center of the [Ni^{III}(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻ motif in the more electron-rich functionality to promote the stability of complex **2** is responsible for the facile formation of complex **2** when [Ni^{III}(Cl)(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻ was reacted with 1 equiv of [Na][SPh] in THF–CH₃CN. In comparison with complex

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Figure 1. (a) X-band frozen-solution [THF-CH₃CN (3:1 volume ratio)] EPR spectrum of complex **1** with *g* values of 2.31, 2.04, and 1.99 recorded at 77 K and (b) X-band powdered sample EPR spectrum of complex **1** with *g* values of 2.28, 2.09, and 2.02.



Figure 2. ORTEP drawing and labeling scheme of complex 2 with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ni(1)–S(4) 2.2459(9), Ni(1)–S(1) 2.2986(8), Ni(1)–S(2) 2.2698(9), Ni(1)–S(3) 2.2133(8), Ni(1)–P(1) 2.1375(8); S(4)–Ni(1)–P(1) 176.82(3), S(4)–Ni(1)–S(1)93.16(3), S(4)–Ni(1)–S(2)90.38(4), S(4)–Ni(1)–S(3) 96.11(3), S(1)–Ni(1)–S(2)1.6.92(3), S(2)–Ni(1)–S(3) 123.94(4), S(1)–Ni(1)–S(3) 128.06(4).

2 and $[Ni^{III}(SePh)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ dominated by one intense absorption band at 592 and 590 nm, respectively, the electronic spectrum of complex **1** coordinated by the less electron-donating phenoxide ligand displays a red shift to 603 nm (Figure 3).

To further examine the effect of electronic modulations of the monodentate ligand [OR]⁻ on the stability and



Figure 3. UV-vis spectrum (in THF) of complex 1.

reactivity of [Ni^{III}(OR)(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻ complexes, complex $[Ni^{III}(OMe)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (3) containing the terminal methoxide ligand was synthesized by adopting complex 1 serving as a precursor. In contrast to the reaction of $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ and [Na][OPh] yielding complex 1 as shown in Scheme 1a, the addition of 1 equiv of [Na][OMe] into a THF-CH₃CN solution of [Ni^{III}(Cl)(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻ produced the known Ni^{III} complex [Ni^{III}(CH₂- $CN(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (4) characterized by the UV-vis spectrum [characteristic absorptions (543 and 648 nm) for (CH₃CN); Scheme 1b]. These results implicate the electrondeficient [NiPS₃] core induced by the elimination of a NaCl salt from the reaction of $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^{-1}$ and [Na][OMe] may promote coordination of CH₃CN to the [NiPS₃] core to yield the proposed $[Ni^{III}(NCCH_3)(P(C_6H_3 3-SiMe_3-2-S_3$] intermediate. The stronger base [OMe]⁻, compared to [OPh]⁻, may then trigger deprotonation of the coordinated CH₃CN of the proposed [Ni^{III}(NCCH₃)(P(C₆H₃-3-SiMe₃-2-S)₃] intermediate, and the subsequent coordination of the [CH₂CN]⁻ carbanion to Ni^{III} yields the thermally stable complex $4.^7$

Upon slow injection of 1 equiv of [n-Bu₄N][OMe] in MeOH into the THF-MeOH solution of complex 1 and after stirring overnight at room temperature, the anionic 3 was isolated as a dark green solid and characterized by singlecrystal X-ray diffraction (Scheme 1c). The conversion of complex 1 to complex 3 was monitored by UV-vis spectrometry; the intense absorption bands at 603 and 743 nm disappeared, accompanied by the formation of absorption bands at 599 and 749 nm. The frozen-solution EPR spectrum of complex 3 in THF-CH₃OH (3:1 volume ratio) at 77 K, essentially indistinguishable from those of the 77 K EPR spectra of complexes 1 and 2 (g = 2.31, 2.04, and 1.99 in THF-CH₃CN (3:1 volume ratio) at 77 K), exhibits high rhombicities with three principal g values of 2.28, 2.04, and 2.00 (Figure 4). Compared to complex 2 ($E_{1/2} = -1.09$ V) and $[Ni^{III}(ER)(P(C_6H_3-3-SiMe_3-2-S)_3)]^ (E_{1/2} = -1.32$ V for ER = SEt and $E_{1/2} = -1.26$ V for ER = SePh), complexes 1 and 3 with the coordinated $[OPh]^-$ and $[OMe]^-$ ligands reveal one reversible Ni^{III/II} redox process at -1.08 V [$E_{1/2}$ (CH_3CN)] and -0.96 V $[E_{1/2}$ (MeOH)] (vs Cp₂Fe/Cp₂Fe⁺), respectively (Figure 5). The more anodic redox potential of complexes 1 and 3, compared to those of complexes 2 and $[Ni^{III}(SEt)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$, is ascribed to the weaker electron-donating ability of the coordinated $[OR]^-$ (R = Ph,

Complexes $[Ni^{III}(OR)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ (R = Me, Ph)



Figure 4. X-band frozen-solution [THF–MeOH (3:1 volume ratio)] EPR spectrum of complex **3** with *g* values of 2.28, 2.04, and 2.00 recorded at 77 K.



Figure 5. Cyclic voltammograms of (a) a 2.0 mM CH₃CN solution of complex **2**, (b) a 2.0 mM CH₃CN solution of complex **1**, and (c) a 2.0 mM MeOH solution of complex **3** in 0.1 M [n-Bu₄N][PF₆] with a glassy carbon working electrode. [Potentials were measured at 298 K vs a Ag/AgCl reference electrode by using a glassy carbon working electrode. Under the conditions employed, the potential (V) of the ferrocinium/ferrocene couple was 0.39 (CH₂Cl₂)].

Me) ligand compared to [SEt]⁻ and implies the existence of the metastable [Ni^{II}(OR)(P(C₆H₃-3-SiMe₃-2-S)₃)]²⁻. Reduction of complex **1** by 1 equiv of [PPN][BH₄] in THF– CH₃CN under N₂ at ambient temperature yielded the proposed [Ni^{II}(OPh)(P(C₆H₃-3-SiMe₃-2-S)₃)]²⁻ [UV–vis: 447 and 792 nm (Figure 6)], the analogue of the known [Ni^{II}(PPh₃)(P(C₆H₄-2-S)₃)]^{-,7b} and then the thermally unstable [Ni^{II}(OPh)(P(C₆H₃-3-SiMe₃-2-S)₃)]²⁻ converted into the known [Ni^{II}₂(P(C₆H₃-3-SiMe₃-2-S)₃)]²⁻ characterized by UV–vis and single-crystal X-ray diffraction.^{7d}

It has been known that the reactivity of $[Ni^{III}(L)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ may be tailored by ligand L.⁷ To further explore the nickel(III) thiolate complexes containing the terminal Ni^{III}-OH bond, we repeated the reaction of complex 1 and $[Me_4N][OH]$ in THF-CH₃OH. On the basis of the UV-vis spectrum and single-crystal X-ray diffraction, complex 3 was isolated after the reaction solution of complex 1 and 1 equiv of $[Me_4N][OH]$ was stirred for 3 h and the insoluble solid was removed.



Figure 6. UV-vis spectrum (in THF-CH₃CN) of the proposed [Ni^{II}(OPh)(P(C₆H₃-3-SiMe₃-2-S)₃)]^{2-,7b}



Figure 7. ORTEP drawing and labeling scheme of complex 1 with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ni(1)-O(1) 1.910(3), Ni(1)-S(1) 2.2603(11), Ni(1)-S(2) 2.3191(11), Ni(1)-S(3) 2.2254(11), Ni(1)-P(1) 2.1313(11); O(1)-Ni(1)-P(1) 177.25(10), O(1)-Ni(1)-S(1) 90.39(9), O(1)-Ni(1)-S(2) 97.20(9), O(1)-Ni(1)-S(3) 94.35(8), S(1)-Ni(1)-S(2) 106.04(4), S(2)-Ni(1)-S(3) 122.29(4), S(1)-Ni(1)-S(3) 130.25(5).

Compared to the reported dinuclear $bis(\mu-oxo)nickel(III)$ complexes [(PhTtⁱBu)Ni]₂(µ-O)₂, [Tp^{Me3}Ni(µ-O)NiTp^{Me3}], and $[Ni_2(\mu-O)(Me_3-tpa)_2]^{2+}$,⁵ complexes 1 and 3 are the first examples of mononuclear nickel(III) thiolate complexes containing a terminal phenoxide/alkoxide ligand, characterized by single-crystal X-ray diffraction. Single-crystal X-ray structures of complexes 1 and 3 are shown in Figures 7 and 8, respectively, and selected bond lengths and bond angles are collected in the figure captions. The geometry of the Ni center in complex 3 is a distorted trigonal bipyramid, with O(1) and P(1) occupying the axial positions. The Ni-O(R)distances of 1.910(3) and 1.885(2) Å in complexes 1 and 3, respectively, are comparable to the Ni-O(H) bond distance (1.91 Å) observed in the active-site structure of the oxidized form [NiFe] H₂ase,^{2e-g} and similar to the corresponding metrics for dinuclear $bis(\mu$ -oxo)nickel(III) complexes established by single-crystal X-ray analysis.⁵ The shortening of the Ni–OMe bond distance [1.885(2) Å] in complex 3, compared to the Ni-OPh bond length of 1.910(3) Å in complex 1, is presumably caused by the stronger electrondonating methoxide ligand coordinating to the electrondeficient Ni^{III} core to stabilize complex 3. Of importance, in contrast to the Ni-OPh and Ni-OMe bond distances of 1.910(3) and 1.885(2) Å found in **1** and **3**, respectively, the shorter Ni-SPh distance of 2.246(1) Å observed in complex



Figure 8. ORTEP drawing and labeling scheme of complex **3** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ni(1)-O(1) 1.885(2), Ni(1)-S(1) 2.2591(10), Ni(1)-S(2) 2.2988(10), Ni(1)-S(3) 2.2794(10), Ni(1)-P(1) 2.1162(10); O(1)-Ni(1)-P(1) 176.65(8), O(1)-Ni(1)-S(1) 91.35(8), O(1)-Ni(1)-S(2) 100.97(9), O(1)-Ni(1)-S(3) 96.18(9), S(1)-Ni(1)-S(2) 136.15(4), S(2)-Ni(1)-S(3) 105.84(4), S(1)-Ni(1)-S(3) 114.51(4).

Table 1. Selected Bond Length (Å) and Angle (deg) for Complexes 1-3, $[Ni^{III}(SePh)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$, and $[Ni^{III}(SEt)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$

	Ni $-$ ER (E =		
	O, S, Se; R		
compound	= Ph, Et)	Ni-S _{ave}	Ni-P
1	1.910(3)	2.268(1)	2.131(1)
3	1.885(2)	2.279(1)	2.116(1)
2	2.246(1)	2.261(1)	2.138(1)
$[Ni^{III}(SEt)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$	2.273(1)	2.253(1)	2.135(1)
$[Ni^{III}(SePh)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$	2.347(1)	2.263(1)	2.132(1)

2, compared to the Ni–SEt distance of 2.273(1) Å observed in $[Ni^{III}(SEt)(P(C_6H_3-3-SiMe_3-2-S)_3)]^{-,7}$ may implicate the significant σ and π donation from [SPh] to Ni^{III} (Table 1).⁸ Presumably, the tunable electron-donating functionalities of the tetradentate ligand $[P(C_6H_3-3-SiMe_3-2-S)_3]^{3-}$ of $[Ni^{III}(L)-(P(C_6H_3-3-SiMe_3-2-S)_3)]^{-}$ modulated by the monodentate ligand L may reimburse the electronic deficiency of the Ni center induced by the less electron-donating ability of the $[OR]^{-}$ ligand to stabilize the $[Ni^{III}-OR]$ motif.

Conclusion and Comments

Mononuclear **1** containing a terminal [OPh]-coordinated ligand, characterized by UV-vis, EPR, CV, and singlecrystal X-ray diffraction, was synthesized from the reaction of $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ with 3 equiv of [Na][OPh] in THF-CH₃CN (3:1 volume ratio) at room temperature. In the synthesis of mononuclear $[Ni^{III}(OMe)-(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ containing a terminal $[OMe]^-$ ligand, methoxide $[n-Bu_4N][OMe]$ triggers ligand substitution of complex **1** to yield complex **3**, in contrast to the addition of $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ into [Na][OMe] producing the known **4** in THF-CH₃CN. These results show that the reaction pathways [ligand-displacement reaction yielding complex **1** (Scheme 1a) vs deprotonation reaction yielding complex **4** (Scheme 1b)] upon the reaction of $[Ni^{III}(Cl)(P(C_6H_3-3-SiMe_3-2-S)_3)]^-$ and nucleophiles ([Na][OR], R = Ph, Me) in THF-CH₃CN may be regulated by nucleophiles.

At 77 K, complexes 1 and 3 exhibit a rhombic signal with g values of 2.31, 2.09, and 2.00 and of 2.28, 2.04, and 2.00, respectively, the characteristic g values of the trigonalbipyramidal low-spin d⁷ Ni^{III} complexes [Ni^{III}(L)(P(C₆H₃- $3-SiMe_3-2-S_3)^{-1}$ (L = SEt, SePh, Cl, CH₂CN).⁷ In contrast to the Ni^{III}-SPh and Ni^{III}-SEt bond distances of 2.246(1) and 2.273(1) Å found in $[Ni^{III}(SR)(P(C_6H_3-3-SiMe_3-2-S)_3)]^{-1}$ (R = Ph, Et), respectively, the longer terminal Ni^{III}-OPh bond distance of 1.910(3) Å observed in complex 1, compared to the $Ni^{III}\text{-}OMe$ bond length of 1.885(2) Å found in complex 3, may implicate the absence of the significant σ and π donation from [OPh] to Ni^{III.8} Presumably, the electron-rich functionalities of the Ni^{III} center derived from $[P(C_6H_3-3-SiMe_3-2-S)_3]^{3-}$ acting as a strong σ - and π -donating group in complexes 1 and 3 are responsible for the stabilization of the Ni^{III} state to prevent the reduction of Ni^{III} by the monodentate $[OR]^-$ (R = Ph, Me) ligand. This study unambiguously illustrates the aspect of how the coordinated ligands ($[OR]^-$ and $[P(C_6H_3-3-SiMe_3-2-S)_3]^{3-}$) of the mononuclear [Ni^{III}(OR)(P(C₆H₃-3-SiMe₃-2-S)₃)]⁻ function cooperatively to reach an optimum electronic condition to stabilize the nickel(III) thiolate alkoxide complexes.

Experimental Section

Manipulations, reactions, and transfers were conducted under N2 according to Schlenk techniques or in a glovebox. Solvents were distilled under N2 from appropriate drying agents (diethyl ether from CaH₂; acetonitrile from CaH₂-P₂O₅; methylene chloride from CaH₂; hexane and THF from sodium benzophenone) and stored in dried, N₂-filled flasks over 4 Å molecular sieves. N₂ was purged through these solvents before use. Solvent was transferred to the reaction vessel via a stainless cannula under a positive pressure of N₂. The reagents [Na][OC₆H₅], [*n*-Bu₄N][OCH₃], bis(triphenylphosphoranylidene)ammonium chloride ([PPN][Cl]; Fluka), diphenyl disulfide, nickel(II) dichloride, [(CH₃)₄N][OH], and [Na][OMe] were used as received. Compound [PPN][Ni(Cl)(P(o-C₆H₃-3-SiMe₃-2-S)₃)] was synthesized by published procedures.^{7c} UV-vis spectra were recorded on a GBC Cintra 10e. ¹H NMR spectra were obtained on a Varian Unity-500 spectrometer. Electrochemical measurements were performed with CHI model 421 potentionstat (CH Instrument) instrumentation. Cyclic voltammograms were obtained from 2.0 mM analyte concentration in THF using 0.1 M [n-Bu₄N][PF₆] as the supporting electrolyte. Potentials were measured at 298 K vs a Ag/AgCl reference electrode by using a glassy carbon working electrode. Under the conditions employed, the potential (V) of the ferrocinium/ferrocene couple was 0.39 (CH₂Cl₂). Analyses of C, H, and N were obtained with a CHN analyzer (Heraeus).

Preparation of [PPN][Ni(OC₆H₅)P(C₆H₃-3-SiMe₃-2-S)₃] (1). Compounds [PPN][Ni(Cl)P(C₆H₃-3-SiMe₃-2-S)₃] (0.242 g, 0.2 mmol) and [Na][OC₆H₅] (0.070 g, 0.6 mmol) were dissolved in 5 mL of a THF-CH₃CN (volume ratio 3:1) mixture solution in a Schlenk tube under N₂. The reaction solution was stirred for 12 h at ambient temperature, and a solution color change from yellow green to deep green was observed. The blue-shift absorptions from 430 and 620 nm ([PPN][Ni(Cl)P(C₆H₃-3-SiMe₃-2-S)₃]) to 411 and 603 nm implicated the formation of **1**. The mixture solution was

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filtered through Celite to remove the insoluble NaCl and the excess [Na][OC₆H₅]. Diethyl ether (20 mL) was then added to precipitate the deep-green solid **1** (yield 0.181 g, 73%). Crystals suitable for X-ray diffraction were obtained by layering of a THF–CH₃CN solution of complex **1** and diethyl ether at ambient temperature for 6 days. ¹H NMR (C₄D₈O): δ 15.8 (br), 10.4 (br), 9.4 (br), -5.3 (br) ppm ([OC₆H₅]⁻ and [P(C₆H₃-3-SiMe₃-2-S)₃]³⁻). Absorption spectrum (THF) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)]: 411 (6700), 603 (2900), 743 (1550), 910 (1100). Anal. Calcd for C₆₉H₇₁P₃NiOS₃Si₃: C, 65.65; H, 5.67. Found: C, 65.15; H, 5.70.

Preparation of [PPN][Ni(SC₆H₅)P(C₆H₃-3-SiMe₃-2-S)₃] (2). Compounds [PPN][Ni(Cl)P(C₆H₃-3-SiMe₃-2-S)₃] (0.242 g, 0.2 mmol) and [Na][SC₆H₅] (0.027 g, 0.2 mmol) were loaded into a 20 mL Schlenk tube and dissolved in 5 mL of a THF–CH₃CN (volume ratio 4:1) mixture solution under N₂. The reaction solution was stirred for 4 h at ambient temperature, and then the mixture solution was filtered through Celite to remove the insoluble NaCl. Diethyl ether (20 mL) was then added to precipitate the green solid 2 (yield 0.175 g, 70%). Crystals suitable for X-ray diffraction were obtained by layering of a THF–CH₃CN solution of complex **2** and diethyl ether at ambient temperature for 6 days. ¹H NMR (C₃D₆O): δ 14.8 (br), 10.5 (br), 8.3 (br), -4.0 (br) ppm ([SC₆H₅]⁻ and [P(C₆H₃-3-SiMe₃-2-S)₃]³⁻). Absorption spectrum (MeCN) [λ_{max}, nm (ε, M⁻¹ cm⁻¹)]: 357 (7350), 592 (1650), 949 (700). Anal. Calcd for C₆₉H₇₁P₃NiS₄Si₃: C, 64.82; H, 5.60. Found: C, 64.49; H, 5.69.

Preparation of [PPN][Ni(OCH₃)P(C₆H₃-3-SiMe₃-2-S)₃] (3). Complex 1 (0.248 g, 0.2 mmol) was loaded into a 30 mL Schlenk tube, followed by the addition of 5 mL of a THF-CH₃OH (volume ratio 9:1) mixture solvent by a cannula under positive N₂ pressure. A portion of [n-Bu₄N][OCH₃] [0.32 mL (20% in CH₃OH solution)] was then added into the THF-CH₃OH solution of complex 1 by syringe. The mixture solution was stirred overnight at room temperature. The mixture solution was filtered through Celite to remove the insoluble $[Bu_4N][OC_6H_5]$, and diethyl ether (20 mL) was then added to precipitate the dark-green solid [PPN]-[Ni(OCH₃)P(C₆H₃-3-SiMe₃-2-S)₃] (3) (yield 0.127 g, 54%). Darkgreen crystals suitable for X-ray diffraction analysis were obtained by layering of the THF-CH₃OH solution of complex **3** and diethyl ether at ambient temperature for 6 days. ¹H NMR (C₃D₆O): δ 15.4 (br), 10.4 (br), 9.3 (br), -4.9 (br) ppm ([OCH₃]⁻ and [P(C₆H₃-3-SiMe₃-2-S)₃]³⁻). Absorption spectrum (CH₃OH) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)]: 418 (3750), 599 (1400), 749 (800). Anal. Calcd for C₆₄H₆₉-P₃NiOS₃Si₃: C, 64.80; H, 5.86. Found: C, 64.07; H, 5.76.

Reaction of [PPN][Ni(Cl)(P(C₆H₃-3-SiMe₃-2-S)₃)] and [Na]-[OCH₃]. Complexes [PPN][Ni(Cl)(P(C₆H₃-3-SiMe₃-2-S)₃)] (0.242 g, 0.2 mmol) and [Na][OCH₃] (0.011 g, 0.2 mmol) were dissolved in a THF–CH₃CN [5 mL (volume ratio 3:1)] mixture solution under N₂, and the solution was stirred for 3 h at ambient temperature. The solution color changing from yellow-green to purple was observed. The reaction solution was monitored by UV–vis, and the electronic absorptions (543, 648, and 925 nm) implicated the formation of the known 4.^{7c} The resulting purple solution was filtered through Celite to remove the insoluble NaCl. The filtrate was concentrated under vacuum, and diethyl ether was then added to precipitate the known dark-purple solid 4 (yield 0.186 g, 72%) characterized by UV–vis.^{7c} **Reaction of Complex 1 and [(CH₃)₄N][OH] in THF–CH₃OH.** The CH₃OH solution of [(CH₃)₄N][OH] (0.018 g, 0.2 mmol) was added to the THF–CH₃OH solution [5 mL (volume ratio 3:1)] of complex **1** (0.248 g, 0.2 mmol) under N₂. The mixture solution was stirred for 3 h at ambient temperature, and the solution color change from deep green to dark green was observed. The reaction solution was monitored by UV–vis, and the electronic absorptions (418, 599, and 749 nm) implicated the formation of the complex **3**. The resulting dark-green solution was filtered through Celite to remove the insoluble [(CH₃)₄N][OPh]. The filtrate was concentrated under vacuum, and diethyl ether was then added to precipitate the dark-green solid complex **3** (yield 0.186 g, 72%) characterized by UV–vis and X-ray diffraction analysis.

Crystallography. Crystallographic data of complexes 1-3 are summarized in Tables S2-S4 in the Supporting Information, respectively. The crystals chosen for X-ray diffraction studies measured 0.30 \times 0.18 \times 0.07 mm for complex 1, 0.48 \times 0.38 \times 0.20 mm for complex 2, and $0.42 \times 0.30 \times 0.15$ mm for complex 3, respectively. Each crystal was mounted on a glass fiber and quickly coated in an epoxy resin. Unit-cell parameters were obtained by least-squares refinement. Diffraction measurements for complexes 1-3 were carried out on a SMART CCD (Nonius Kappa CCD) diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.7107$ Å) and between 2.08 and 25.34° for complex 1, between 2.08 and 25.34° for complex 2, and between 2.08 and 25.36° for complex 3. Least-squares refinement of the positional and anisotropic thermal parameters of all non-H atoms and fixed H atoms were based on F^2 . A SADABS absorption correction was made.⁹ The SHELXTL structure refinement program was employed.10

EPR Measurements. EPR measurements were performed at the X band using a Bruker EMX spectrometer equipped with a Bruker TE102 cavity. The microwave frequency was measured with a Hewlett-Packard 5246 L electronic counter. X-band EPR spectra of complex 1 in THF–CH₃CN were obtained with a microwave power of 19.78 mW (20.02 mW for complex 3), a frequency at 9.604 GHz (9.636 GHz for complex 3), and a modulation amplitude of 0.80 G at 100 kHz.

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Supporting Information Available: X-ray crystallographic file in CIF format and tables of crystallographic data for the structure determinations of 1-3. This material is available free of charge via the Internet at http://pubs.acs.org.

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