

Redox behavior of novel nickel and palladium complexes supported by trianionic non-innocent ligand containing β-diketiminate and phenol groups

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Dedicated to Professor Shunichi Fukuzumi on the occasion of his retirement

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ABSTRACT: A new type of nickel and palladium complexes with non-innocent β -diketiminate ligand having redox active phenol groups, 2,4-di-*tert*-butyl-6-(((1*E*,2*E*)-3-((3,5-di-*tert*-butyl-2-hydroxyphenyl) amino)-2-nitroallylidene)amino)phenol (**L**H₃, fully protonated form) have been developed, and the structure, physical properties, and reactivity of their one-electron and two-electron oxidized complexes, [$M^{II}(L^{-2-})$] and [$M^{II}(L^{-1})$]⁺ ($M = Ni^{II}$ or Pd^{II}) have been examined in detail. The two-electron oxidized forms of both complexes, [$M^{II}(L^{-1})$]⁺, exhibited hydrogen atom abstraction ability from 1,4-cyclohexadiene (CHD) comparable to its copper analog [$Cu^{II}(L^{-2-})$], was also found to oxidize CHD, whereas the nickel analog, [$Ni^{II}(L^{-2-})$], exhibited photo-induced oxidation ability of CHD.

KEYWORDS: nickel complex, palladium complex, β-diketiminate ligand, non-innocent ligand.

INTRODUCTION

Transition metal complexes supported by redox noninnocent ligands such as porphyrin and phthalocyanine derivatives have long been attracting much attention due to their relevance to enzymatic catalysis and a variety of functional materials [1, 2]. The capability of an electron release from highly conjugated π -orbitals of porphyrin and phthalocyanine are regarded as important factor to facilitate multi-electron transfer such as hydroxylation of aliphatic substrates occurring in cytochrome P450 (CYP) and its models [3–10]. Recently, phenol-containing ligand also have received much interest as an active site model of metalloenzymes containing a redox-active organic cofactor such as tyrosine or its derivatives [11–14]. Galactose oxidase is a typical example of such enzymes, which contains a copper(II)-tyrosyl (phenoxyl) radical as the key reactive intermediate for the oxidation of primary alcohols to aldehydes [15-19]. In this enzyme, the copper center is further ligated by an additional tyrosyl residue to construct a Tyr-Cu-Tyr motif. In order to mimic such an active site structure, salen-type ligands consisting with two phenol groups connected by diamine derivatives have been tested [13, 14]. In most cases, ligand effects as well as metal ion effects on the electronic structures of one-electron oxidized mix-valent systems have been investigated, but little attention has been focused on the reactivity of the phenoxyl radical transition-metal complexes. In this respect, Stack and co-workers have investigated the direct reaction between the Cu^{II}-phenoxyl radical complexes and benzyl alcohol to demonstrate the importance of substrate coordination to the metal center prior to the C-H bond activation of the substrates [20-22]. In parallel, the electronic

[◊]SPP full member in good standing

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Scheme 1. Molecular structure of the ligand

structures and chemical properties of the group 10 element complexes, Ni, Pd, and Pt, supported by salen type ligands have also been investigated in detail [23–32]. In those studies, unambiguously demonstrated are the ability of salen-type ligands modulating the multielectron redox processes of the metal center.

Recently, we have examined the reactivity of a discreet Cu^{II} -phenoxyl radical complex generated by using a new type of diphenol ligand consisting with a β -diketiminate bridging moiety as shown in Scheme 1 [33]. In this study, we have further examined the spectroscopic property and reactivity of phenoxyl radical complexes to evaluate the metal ion effects using Ni- and Pd-complexes supported by the same ligand.

RESULTS AND DISCUSSION

Synthesis and characterization

The nickel(II) and the palladium(II) complexes were prepared by treating the neutral ligand LH_3 (Scheme 1) with an equimolar amount of nickel(II) acetate or palladium(II) acetate in the presence of a base (NEt₄OH or Et₃N). The single crystals were obtained as described in the Experimental section. In the case of Pd-complex, the counter cation was exchanged from Et₃NH⁺ to Bu₄N⁺ to facilitate crystallization (see Experimental section). Figures 1(a) and 2(a) show the crystal structures of (Et_4N) $[Ni^{II}(L^{3-})]$ and $(Bu_4N)[Pd^{II}(L^{3-})]$, respectively (the counter cations are omitted for simplicity, the crystallographic data are presented in Supporting information, Table S1). In both complexes, the ligand takes the tri-anionic form (fully deprotonated form L³⁻), since there is one counter cation (R_4N^+) per one complex molecule (not shown in Fig. 1(a) and 2(a)), and the negative mode ESI-MS gave an intense peak cluster at 578.30 and 626.15, respectively, which are assignable to the molecular formula of the anionic complexes $[M^{II}(L^{3-})]^{-}$ (M = Ni and Pd) (Fig. 3). The peak distribution patterns are also consistent with those expected for the respective complexes.

The metal centers of $[Ni^{II}(L^{3-})]^{-}$ and $[Pd^{II}(L^{3-})]^{-}$ exhibited square planar geometries with the N₂O₂ donor



Fig. 1. ORTEP drawings of (a) $(Et_4N)[Ni^{II}(L^{3-})]$ and (b) $[Ni^{II}(L^{-2-})]$ showing 50% probability thermal ellipsoids. Hydrogen atoms, counter cation, and solvent molecules are omitted for clarity. For the structure of $[Ni^{II}(L^{-2-})]$, elongated bonds (more than 0.01 Å) are indicated in blue color, and shorten bonds (more than 0.01 Å) are indicated in red color

set of the ligand, where the torsion angles between the O1-M1-N1 and O2-M1-N2 planes are 2.3° and 0.4°, respectively. The bond length of Ni–O (1.841 and 1.846 Å) and Ni–N (1.855 and 1.844 Å) are slightly shorter than those of Ni^{II}-salen complex $[Ni^{II}(sal^{2-})](sal^{2-} = diphenolate$ form of salH₂, N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2cyclohexane-(1R,2R)-diamine, Ni–O, 1.852 and 1.854 Å; Ni–N, 1.852 and 1.860 Å) [35]. The Pd–O bond lengths (1.997 and 1.999 Å) are slightly longer than those of $[Pd^{II}(sal^{2-})]$ (Pd–O, 1.970 and 1.969 Å), whereas the Pd–N bond lengths (1.957 and 1.954 Å) are almost the same to those of [Pd^{II}(sal²⁻)] (Pd–N, 1.959 and 1.946 Å) [28]. Apparently, the M–O and M–N bonds of the Ni-complex are shorter than those of the Pd-complex, which is due to the difference in the ionic radius between the two metal ions; Ni(II) 0.63 Å, Pd(II) 0.78 Å.

Redox property

The redox properties of $[M^{II}(L^{3-})]^{-}$ were examined using cyclic voltammetry (CV) as shown in Fig. 4.



Fig. 2. ORTEP drawings of (a) $(Bu_4N)[Pd^{II}(L^{3-})]$ and (b) $[Pd^{II}(L^{*2-})]$ showing 50% probability thermal ellipsoids. Hydrogen atoms, counter cation, and solvent molecules are omitted for clarity. For the structure of $[Pd^{II}(L^{*2-})]$, elongated bonds (more than 0.01 Å) are indicated in blue color, and shorten bonds (more than 0.01 Å) are indicated in red color

Both complexes exhibited two reversible redox couples $(E_{1/2}^{1} \text{ and } E_{1/2}^{2})$ due to the first and second one-electron oxidation of the anionic complexes. The redox potential of the Ni^{II}- and Pd^{II}-complexes are summarized in Table 1 together with those of the Cu^{II}-complex of the same ligand [Cu^{II}(L³⁻)]⁻ and [M^{II}(sal²⁻)] (M = Cu, Ni, and Pd) for comparison (reference papers for the reported data are indicated in the table footnote).

It appears that the $E_{1/2}^{1}$ and $E_{1/2}^{2}$ values as well as the $\Delta E_{1/2}$ ($E_{1/2}^{1} - E_{1/2}^{2}$) values of all the L³⁻ complexes (M^{II} = Cu, Ni, and Pd) are fairly similar as $E_{1/2}^{1} = -0.07 \times +0.07 \text{ V}$, $E_{1/2}^{2} = +0.46 \sim +0.54 \text{ V}$ vs Ferrocene/Ferrocenium ion (Fc/Fc⁺) and $\Delta E_{1/2} = 0.47 \sim 0.50 \text{ V}$, which are largely negative as compared to those of the salen complexes. The largely negative shifts of the $E_{1/2}$ values of [M^{II}(L³⁻)]⁻ as compared to those of [M^{II}(sal²⁻)] can be attributed to the higher HOMO level of the trianionic L³⁻ as compared to that of the dianionic sal²⁻ [33].

In the salen system, it has been reported that the electronic coupling between the redox active phenolate groups correlates strongly with difference in the metal d orbital energy and ligand MO energy [20]. In the present ligand system, on the other hand, the degree of electronic coupling is independent on the metal ions as indicated by the similar $E_{1/2}$ and $\Delta E_{1/2}$ values among the three complexes (Cu, Ni, and Pd). This may be due to the conjugation between the two phenolate groups through the β -diketiminate backbone. SOMO 155a of [Cu^{II}(L²⁻)] calculated by using DFT method, which mainly consists of π -orbitals on the ligand, clearly shows that the two phenolate groups are electronically bridged by the conjugated β -diketiminate moiety [33]. In the salen system, there is no such conjugative interaction between the two phenolate groups, since the phenolate groups are connected by the saturated alkyl diamine moiety.



Fig. 3. ESI-MS (negative mode) of (a) $[Ni^{II}(L^{3-})]^{-}$ and (b) $[Pd^{II}(L^{3-})]^{-}$ in CH_2Cl_2 . Inset: expanded spectra (EXP) and their simulation spectra (SIM)



Fig. 4. Cyclic voltammograms of (a) $[Ni^{II}(L^{3-})]^-$ (5.0 × 10⁻⁴ M) and (b) $[Pd^{II}(L^{3-})]^-$ (5.0 × 10⁻⁴ M) in CH₂Cl₂ containing "Bu₄NPF₆ (0.10 M); working electrode: glassy carbon, counter electrode: Pt, reference: ferrocene, scan rate 100 mV/s

Table 1. Electrochemical data of the oxidation of $[M^{II}(L^{3-})]^{-}$ and $[M^{II}(sal^{2-})]$

Complex	$E^{1}_{1/2}, \mathrm{V}^{\mathrm{a}}$	$E_{1/2}^2, V^a$	$\Delta E_{1/2} (E_{1/2}^1 - E_{1/2}^2), \mathrm{V}$
$[Cu^{II}(L^{3-})]^{-b}$	-0.06	+0.46	0.50
$[Ni^{II}(L^{3-})]^{-}$	+0.04	+0.54	0.50
$[Pd^{II}(L^{3-})]^{-}$	+0.07	+0.54	0.47
[Cu ^{II} (sal ²⁻)] ^c	+0.45	+0.65	0.20
[Ni ^{II} (sal ²⁻)] ^d	+0.37	+0.85	0.48
[Pt ^{II} (sal ²⁻)] ^e	+0.45	+0.80	0.35

^avs Fc/Fc⁺. ^b from Ref. 15. ^c from Ref. 19. ^d from Ref. 20. ^e from Ref. 18.

Therefore, the electronic coupling can only be mediated by the metal ion (Scheme 2).

One-electron oxidation product

The one-electron oxidation products can also be generated by the chemical oxidation using an equimolar amount of $AgSbF_6$ in CH_2Cl_2 , and their single crystals suitable for X-ray crystallographic analysis were successfully obtained by recrystallization from CH₂Cl₂/ *n*-hexane. Crystal structures of the neutral complexes $[Ni^{II}(L^{\bullet 2-})]$ and $[Pd^{II}(L^{\bullet 2-})]$ are shown in Fig. 1(b) and Fig. 2(b), respectively. The crystallographic data are presented in Table S2. The crystal structure of $[Ni^{II}(L^{\bullet 2-})]$ clearly indicates that one-electron oxidation of $[Ni^{II}(L^{3-})]^{-}$ caused a distinctive structural change in the aminophenol moiety of ring A and β -diketiminate moiety. Namely, structures of the aminophenol moiety of rings A and B are nearly identical in $[Ni^{II}(L^{3-})]^{-}$ (Fig. 1(a)), whereas contribution of a quinonoid canonical form increases in the aminophenol moiety of ring A in the oxidized complex $[Ni^{II}(L^{\bullet 2-})]$ (Fig. 1(b)). The distance of Ni1-O2 (1.876 Å) increases as compared with that of Ni1–O1 (1.838 Å). In addition, such structural changes occurred on β -diketiminate moiety as well, *e.g.* the bond distances of C4-N2 and C3-C2 are shrunk from 1.423 and 1.410 to 1.390 and 1.371, respectively. These structural features of the oxidized complex are consistent with the conclusion that the one-electron oxidation takes place at the conjugated π -orbital consisting of phenolate and β -diketiminate part to give L^{•2-} rather than at the metal. One-electron oxidation product $[Pd^{II}(L^{\bullet 2-})]$ showed a similar structural features to $[Ni^{II}(L^{-2-})]$ as shown in Fig. 2(b). The notable structural change was



Scheme 2. Conjugation of π -orbital in $[M^{II}(L^{\bullet})]$ and $[M^{II}(sal^{\bullet})]^+$



Fig. 5. (a) Absorption spectra of $[Ni^{II}(\mathbf{L}^{3-})]^{-}$ (black line), $[Ni^{II}(\mathbf{L}^{*2-})]$ (blue line) and $[Ni^{II}(\mathbf{L}^{-})]^{+}$ (red line) in CH₂Cl₂ at -10°C. (b) Absorption spectra of $[Pd^{II}(\mathbf{L}^{3-})]^{-}$ (black line), $[Pd^{II}(\mathbf{L}^{*2-})]$ (blue line) and $[Pd^{III}(\mathbf{L}^{*2-})]^{+}$ (red line) in CH₂Cl₂ at 30°C

observed at the aminophenol moiety of ring A as well as the β -diketiminate moiety upon one-electron oxidation of $[Pd^{II}(L^{3-})]^{-}$.

In Fig. 5(a), the absorption spectrum of the oneelectron oxidized complex $[Ni^{II}(L^{\bullet 2-})]$ is shown in the blue line together with that of the starting material $[Ni^{II}(L^{3-})]^-$ in the black line. The λ_{max} value of the absorption band at 429 nm of $[Ni^{II}(L^{\bullet 2-})]$ is close to that of the strong absorption band at 414 nm of the starting complex $[Ni^{II}(L^{3-})]^-$, whereas the intensity of the former ($\varepsilon = 16,400 \text{ M}^{-1}.\text{cm}^{-1}$) is largely reduced as compared to that of the latter (28,100 M⁻¹.cm⁻¹). Thus, the absorption band at 429 nm together with the shoulder around 524 nm (9,860 M⁻¹.cm⁻¹) could be attributed to metal-to-phenolate charge transfer (MLCT) bands as in the case of the copper complex with the same ligand system [33].

The reduction of the intensity of this band in [Ni^{II}($L^{\cdot 2}$ ·)] is consistent with the fact that one of the phenolate rings is oxidized to the phenoxyl radical as suggested by the X-ray structure shown in Fig. 2(b). Then, the broad absorption bands at 784 nm (2,180 M⁻¹.cm⁻¹), 883 nm (2,090 M⁻¹.cm⁻¹), and 1530 nm (1,470 M⁻¹.cm⁻¹) of [Ni^{II}($L^{\cdot 2}$ ·)] in the visible to near IR (vis-NIR) region could be attributed to the phenoxyl radical moiety. Existence of such a broad absorption band at 1530 nm may be due to the expanded π -conjugation system through the β -diketiminate moiety as indicated by the X-ray structure (see Fig. 2(b)). This electronic communication between the phenoxyl radical and the phenolate rings through the expanded π -conjugated system is also suggested by the electrochemical data presented in Table 1.

The absorption spectrum of the one-electron oxidized complex $[Pd^{II}(\mathbf{L}^{*2-})]$ is also shown in the blue line together with that of the starting material $[Pd^{II}(\mathbf{L}^{3-})]^-$ in the black line in Fig. 5(b). The relatively intense absorption bands at 409 nm ($\varepsilon = 14,900 \text{ M}^{-1}.\text{cm}^{-1}$), 503 nm (14,000 M⁻¹.cm⁻¹),

and 540 nm (14,200 M⁻¹.cm⁻¹) could also be attributed to the MLCT transitions, and the broad absorption bands in the NIR region (above 800 nm) are due to the phenoxyl radical species.

5

In frozen CH₂Cl₂ at 77 K, the starting materials $[Ni^{II}(L^{3-})]^-$ and $[Pd^{II}(L^{3-})]^-$ were EPR silent (data are not shown). The ¹H-NMR spectra of $[Ni^{II}(L^{3-})]^-$ and $[Pd^{II}(L^{3-})]^-$ in CH₂Cl₂ at 298 K exhibited well-resolved proton signals in the diamagnetic region ($\delta = 0-10$ ppm) (Supporting Fig. S1). These results clearly demonstrated that the metal(II) centers have low-spin state (S = 0) in both complexes.

On the other hand, the EPR measurement of the oneelectron oxidation complexes [Ni^{II}($L^{\bullet 2}$ -)] and [Pd^{II}($L^{\bullet 2}$ -)] gave relatively broad axial signals at $g_{\perp} = 1.989$ and $g_{\parallel} =$ 1.979 ($g_{\perp} = 1.986$), and $g_{\parallel} = 2.006$ and $g_{\parallel} = 1.991$ ($g_{\infty} =$ 2.001), respectively (Figs 6(a) and 6(c)). These signals are attributed to the metal-coordinating phenoxyl radical species $L^{\bullet 2}$.

Two-electron oxidation product

Further oxidation of $[Ni^{II}(L^{•2-})]$ by $N(Ph-Br)_3 \cdot SbCl_6$ ($E_{1/2} = 0.70$ V vs Fc/Fc⁺) [36] in CH₂Cl₂ gave a twoelectron oxidized cationic complex exhibiting intense absorption bands at 460 nm (11,900 M⁻¹.cm⁻¹) and 494 nm (11,800 M⁻¹.cm⁻¹) together with a relatively weak band at 640 nm (3,800 M⁻¹.cm⁻¹) and a broad NIR band around 1525 nm (2,610 M⁻¹.cm⁻¹) (red line spectrum in Fig. 5(a)). The ESI-MS measured in the positive mode matches the chemical formulation of $[Ni^{II}(L^{-})]^+$ (Fig. 7). The EPR signals of the neutral complex of nickel, $[Ni^{II}(L^{•2-})]$ (Fig. 6(a)), were significantly weakened upon the one-electron oxidation with N(Ph-Br)₃·SbCl₆ as shown in Fig. 6(b). This clearly indicated that the *main* component of two-electron oxidized cationic complex



Fig. 6. EPR spectra of (a) $[Ni^{II}(L^{\bullet 2-})]$ (5.0 × 10⁻⁴ M), (b) $[Ni^{II}(L^{-})]^+$ (5.0 × 10⁻⁴ M), (c) $[Pd^{II}(L^{\bullet 2-})]$ (5.0 × 10⁻⁴ M), and (d) $[Pd^{III}(L^{\bullet 2-})]^+$ (5.0 × 10⁻⁴ M) at 77 K



Fig. 7. ESI-MS (positive mode) of $[Ni^{II}(L^{-})]^{+}$ in CH_2Cl_2 . Inset: expanded spectrum (EXP) and its simulation spectrum (SIM)

was an EPR-silent diamagnetic species, $[Ni^{II}(L^2)]$ (*S* = 0), where L² denotes two-electron oxidized ligand with a quinonoid canonical form.

In the case of palladium complex, oxidation of the neutral complex $[Pd^{II}(L^{\bullet 2-})]$ using N(Ph-Br)₃·SbCl₆ gave a relatively intense EPR signal at g = 2.003 (Fig. 6(d)). The result suggests formation of a triplet species (S = 1) by the oxidation of doublet neutral complex. The number of un-paired electron of the two-electron oxidized complex was estimated to be 1.66 using Evans method (Supporting Fig. S2), which is assignable to the average of singlet species (17%) and triplet species (83%) (Scheme 3) [37–39].

Thus the main locus of the second oxidation is thought to be the metal center in the palladium system to give mainly



Scheme 3. Schematic energy diagram of two-electron oxidized Pd-complex at 77 K

 $[Pd^{II}(\mathbf{L}^{\cdot 2-})]^+$ (Scheme 3). Then, the small EPR signal observed in the two-electron oxidation of the nickel system shown in Fig. 6(b) may be due to the larger contribution of singlet species $[Ni^{II}(\mathbf{L})]^+$, in which the redox locus is on the ligand moiety as discussed above [40].

Reactivity of two-electron oxidized complexes

In our previous study of the copper complexes, reactivity toward hydrogen atom donor was examined using 1,4-cyclohexadiene (CHD) as a model substrate [33]. The cationic complex $[Cu^{II}(L^{-})]^+$ (two-electron oxidized complex) underwent hydrogen atom abstraction reaction from CHD to give $[Cu^{II}(LH^{\bullet})]^+$ (protonated form of $[Cu^{II}(L^{\bullet 2^{-}})]$) and cyclohexenyl radical intermediate, the later of which further donated hydrogen atom to another molecule of $[Cu^{II}(L^{-})]^+$ to give benzene and one more $[Cu^{II}(LH^{\bullet})]^+$ (Scheme 4). Thus, the stoichiometry of the reaction was $[Cu^{II}(L^{-})]^+$:CHD = 2:1, where $[Cu^{II}(L^{-})]^+$ acted as a one-electron oxidant (Scheme 4). Addition of



Scheme 4. Reaction of [M^{II}(L²··)] with 1,4-cyclohexadiene (CHD)



Fig. 8. (a) Spectral change observed upon addition of 1,4-cyclohexadiene $(2.0 \times 10^{-2} \text{ M})$ to $[\text{Ni}^{II}(\text{L}^{-})]^+$ (5.0 × 10⁻⁵ M) in CH₂Cl₂ at 30 °C. Inset: first-order plot based on the time-dependent absorption change at 640 nm. (b) Plot of k_{obs} vs. [1,4-cyclohexadiene]

a base such as triethylamine to the final reaction mixture generated $[Cu^{II}(L^{\bullet 2-})].$

In this study, reactivity of the cationic complexes, $[Ni^{II}(L^{-})]^+$ and $[Pd^{III}(L^{-2-})]^+$, was also examined under the same experimental conditions. Addition of an excess amount of 1,4-cyclohexadiene (CHD) to a CH₂Cl₂ solution of $[Ni^{II}(L^{-})]^+$ (5.0 × 10⁻⁵ M) readily resulted in the spectral changes as shown in Fig. 8(a). The products given by the oxidation reaction were determined to be benzene with GC-MS. The final spectrum of the reaction did not match the spectrum of $[Ni^{II}(L^{\bullet 2-})]$ itself, but addition of 1 equiv of triethylamine (base) to the final solution resulted in the appearance of absorption bands due to $[Ni^{II}(L^{\cdot 2})]$ as shown in Fig. S3(a). $[Pd^{III}(L^{\cdot 2-})]^+$ was also confirmed to show similar reactivity to that of $[Ni^{II}(L^{-})]^+$ (Fig. S3(b)). Thus, the reaction consequences of the both nickel and palladium complex are the same with those of the copper complex (Scheme 4) [33]. The reaction of nickel complex obeyed first-order kinetics in the presence of excess amount of CHD as shown in the inset of Fig. 8(a), and the pseudo-first-order rate constant (k_{obs}) increased with increasing the concentration of CHD. Plot of k_{obs} against the substrate concentration gave a straight line with a small intercept (Fig. 8(b)), from which the second-order rate constant k_2 and self-decomposition rate constant k_{dec} were determined as 0.15 M⁻¹.s⁻¹ and 5.7 × 10⁻⁴ s⁻¹ as the slope and the intercept, respectively. The reactivity of $[Pd^{III}(L^{2\bullet-})]^+$ toward CHD was also examined in the same way, and the second-order rate constant k_2 and the self-decomposition rate constant k_{dec} were determined as $0.52 \text{ M}^{-1}.\text{s}^{-1}$ and $2.8 \times 10^{-3} \text{ s}^{-1}$, respectively (Fig. S4). The self-decomposition rate constants k_{dec} determined were nearly equal to those directly determined by following the decrease of the absorption bands due to the cationic complex in the absence of the substrate $(6.2 \times 10^{-4} \text{ s}^{-1} \text{ for})$ $[Ni^{II}(L^{-})]^{+}$ and $2.4 \times 10^{-3} \text{ s}^{-1}$ for $[Pd^{III}(L^{2\bullet-})]^{+}$).

The rate constant k_2 (0.76 M⁻¹.s⁻¹) of the copper complex [Cu^{II}(L⁻)]⁺ is larger than those of the nickel and palladium complexes (0.15 M⁻¹.s⁻¹ and 0.52 M⁻¹.s⁻¹), which is not consistent with its negative value of $E_{1/2}^2$ as



Fig. 9. (a) Spectral change observed upon addition of 1,4-cyclohexadiene (0.20 M) to $[Pd^{II}(L^{*2-})]$ (5.0 × 10⁻⁵ M) in CH₂Cl₂ at 30 °C. Inset: first-order plot based on the time-dependent absorption change at 540 nm. (b) Plot of k_{obs} vs. [1,4-cyclohexadiene]

compared to those of the nickel and palladium complexes (Table 1). Reactivity of $[Pd^{III}(L^{2\bullet})]^+$ is somewhat larger than that of $[Ni^{II}(L^{-})]^+$, even though the $E^2_{1/2}$ values of these complexes are identical (Table 1). These differences in reactivity may be due to the different electronic configuration between the cationic complexes as discussed above.

Reactivity of one-electron oxidized complexes

 $[Cu^{II}(L^{-2-})]$ itself showed essentially no reactivity toward CHD, but it disproportionated into (1/2) $[Cu^{II}(L^{3-})]^-$ and (1/2) $[Cu^{II}(L^-)]^+$ in the treatment with CHD [33]. Thus, CHD was also converted to benzene by the reaction with generated $[Cu^{II}(L^-)]^+$ [33]. In this case, reaction followed second-order kinetics with respect to the concentration of the copper complex, indicating that the disproportionation process is the rete-determining step.

The neutral complex of nickel(II), $[Ni^{II}(L^{*2-})]$, did not show reactivity toward CHD under ambient conditions. In this case, photo irradiation induced the oxidation of CHD to give benzene and the starting nickel(II) complex $[Ni^{II}(L^{3-})]^-$ (after base treatment of the final reaction mixture). Details of this photochemical reaction will be reported elsewhere.

In the case of $[Pd^{II}(L^{\bullet^2-})]$, addition of CHD into the CH_2Cl_2 solution of the neutral complex $(5.0 \times 10^{-5} \text{ M})$ at 30 °C resulted in a spectral change shown in Fig. 9(a). The characteristic absorption bands due to $[Pd^{II}(L^{\bullet^2-})]$ decrease with a concomitant increase in the new absorption bands represented by the peak at 417 nm ($\varepsilon = 23,300 \text{ M}^{-1}.\text{cm}^{-1}$). The reaction obeyed first-order kinetics in the presence of a large excess of CHD as shown in the inset of Fig. 9(a). Plot of the first-order rate constant k_{obs} against the substrate concentration gave a linear line passing through the origin, from which the second-order rate constant k_2 was determined as $4.4 \times 10^{-3} \text{ M}^{-1}.\text{s}^{-1}$ (Fig. 9(b)). Addition

of 1 equiv of triethylamine to the final reaction mixture resulted in quantitative generation of the spectrum of $[Pd^{II}(L^{3-})]^-$ (starting material) (Fig. S5(a)). Contrary, addition of 1 equiv of 10-camphorsulfonic acid to $[Pd^{II}(L^{3-})]^-$ generated spectrum identical to that of the final reaction mixture of CHD and $[Pd^{II}(L^{\bullet 2-})]$ (Fig. S5(b)). The reactivity of one-electron oxidized complexes $[Pd^{II}(L^{\bullet 2-})]$ in the C–H bond activation reaction of CHD was two orders of magnitude lower, when compared to that of two-electron oxidized complex $[Pd^{III}(L^{2\bullet-})]^+$.

It is also interesting to note that $E_{1/2}^1$ values of all complexes are fairly similar as $E_{1/2}^1 = -0.06 \sim +0.07$ V, nevertheless, each one-electron oxidized complex [Cu^{II}(L^{•2-})], [Ni^{II}(L^{•2-})], and [Pd^{II}(L^{•2-})] exhibited different reactivity. It is likely to be due to the energy difference of O–H bonds of protonated aminophenol moiety [41].

EXPERIMENTAL

Materials and methods

The reagents and solvents used in this study except for the ligand and the complexes were commercial products of the highest available purity and were further purified by the standard methods, if necessary [34]. The ligand LH₂ was prepared according to the reported methods [33]. FT-IR spectra were recorded with a Shimadzu FTIR-8200PC. Electronic absorption spectra were measured using a Hewlett-Packard HP8453 diode array spectrophotometer or a Jasco V-570 UV/VIS/NIR spectrophotometer equipped with a Unisoku thermostated cell holder USP-203 designed for low temperature measurements. Mass spectra were recorded with a JEOL JMS-700T Tandem MS station or a JEOL JMS-700. NMR spectra were recorded on a JEOL ECP400, a JEOL ECS400, or a Varian UNITY INOVA 600 MHz. A concentric double tube was utilized to perform Evans

method. EPR spectra were taken on a JEOL X-band spectrometer (JES-RE1XE) under non-saturating microwave power conditions (1.0 mW) operating at 9.2 GHz. The magnitude of the modulation was chosen to optimize the resolution and the signal to noise ratio (S/N) of the observed spectrum. The *g* values were calibrated using an Mn^{2+} marker. Elemental analyses were recorded with a PerkinElmer or a Fisons Instruments EA1108 Elemental Analyzer.

X-ray structure determination

Each single crystal was mounted on a loop. Data from X-ray diffraction were collected at -170 °C by a VariMax with RAPID imaging plate two-dimensional area detector, using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) to $2\theta_{max}$ of 55°. All of the crystallographic calculations were performed using the Crystal Structure software package of the Molecular Structure Corporation (Crystal Structure: Crystal Structure Analysis Package version 3.8.1. Molecular Structure Corp. and Rigaku Corp. (2005)). The structures were solved with SIR2008 or SHELX97 and refined with CRYSTALS. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively.

Synthesis

 $(NEt_{4})[Ni^{II}(L^{3})]$. To an ethanol solution (1.0 mL) containing LH₃ (10.5 mg, 20 μ mol) and Ni^{II}(CH₃COO)₂· 4H₂O (5.0 mg, 20 µmol) was added 1.5 M tetraethylammonium hydroxide in methanol (40 µl, 60 µmol), and the mixture was stirred for 1 h at room temperature. Then, the solvent was removed by evaporation, and the product was recrystallized from the resulting residue using EtOH/n-hexane to give single crystals suitable for X-ray crystallographic analysis (6.1 mg, 43%). IR (KBr): v, cm⁻¹ 2951 (C–H), 1531, 1361 (NO₂). ¹H NMR (CDCl₃, 400 MHz): δ , ppm 1.06 (t, 12H, J = 7.2 Hz, (*CH*₃CH₂)₄N⁺), 1.29 (s, 18H, *CH*₃), 1.44 (s, 18H, *CH*₃), 3.23 (q, 8H, J = 7.2 Hz, (CH₃CH₂)₄N⁺), 6.97 (d, 2H, J =2.0 Hz, aromatic protons), 7.36 (d, 2H, J = 2.0 Hz, aromatic protons), 9.00 (s, 2H, H). MS (ESI): m/z 578.30, calcd. for $C_{30}H_{25}N_6NiO_4$ 578.25. Anal. calcd. for C₃₉H₆₂N₄O₄Ni·EtOH: C, 65.16; H, 9.07; N, 7.41. Found C, 65.11; H, 9.31; N, 7.49.

[Ni^{II}(L^{•2-})]. (Et₃NH)[Ni^{II}L] (27.3 mg, 40 μ mol) in CH₂Cl₂ (1.0 mL) was added to a CH₂Cl₂ solution (1.0 mL) containing AgSbF₆ (98%, 13.5 mg, 40 μ mol) with stirring at room temperature. The mixture was added dropwise to hexane (100 mL) with vigorous stirring. After reducing the volume of the resulting solution to 3 mL, the precipitates were filtered off. Evaporation of the filtrate gave dark red material, from which [Ni^{II}(L^{•2-})] was obtained as black crystals by recrystallization from hexane (15.1 mg, 65%). IR (KBr): *v*, cm⁻¹ 2953 (C–H), 1561, 1360 (NO₂). Anal. calcd. for C₃₁H₄₂N₃O₄Ni: C, 64.26; H, 7.31; N, 7.25. Found C, 64.12; H, 7.25; N, 7.14.

 $(NBu_4)[Pd^{II}(L^{3-})]$. To a CH₂Cl₂ solution (3.0 mL) containing LH₃ (52.4 mg, 100 μ mol) and Pd^{II}(CH₃COO)₂ (22.5 mg, 100 µmol) was added triethylamine (42 mL, 300 µmol) and the mixture was stirred for an hour at room temperature. The reaction mixture was added dropwise to *n*-hexane (60 mL) to give orange powder. The collected powder and (Bu)₄NBr (322 mg, 1.0 mmol) was dissolved in MeOH-CH₂Cl₂ (v:v = 1:1), and slow evaporation of the solvent gave orange crystals suitable for X-ray crystallographic analysis (44.0 mg, 51%). IR (KBr): v, cm⁻¹ 2957 (C–H), 1540, 1361 (NO₂). ¹H NMR (CDCl₃, 400 MHz): δ , ppm 0.76 $(t, 12H, J = 7.2 \text{ Hz} (CH_2CH_2CH_2CH_2)_4\text{N}^+), 1.01$ (m, 8H, $(CH_3CH_2CH_2CH_2)_4N^+$), 1.34 (m, 27H, CH_3 and $(CH_3CH_2CH_2CH_2)_4N^+$, 2.99 (t, 8H, J = 8.4 Hz, $(CH_3CH_2CH_2CH_2)_4N^+$, 7.08 (s, 2H, aromatic protons), 7.54 (s, 2H, aromatic protons), 9.30 (s, 2H, H). MS (ESI): m/z 626.15, calcd. for C₃₀H₂₅N₆NiO₄ 626.22. Anal. calcd. for C₄₇H₇₈N₄O₄Pd·0.5H₂O: C, 64.25; H, 9.06; N, 6.38. Found C, 64.17; H, 9.29; N, 6.43.

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[Pd^{II}(L^{•2})]. (Et₃NH)[Pd^{II}L] (6.0 mg, 8.2 μmol) in CH₂Cl₂ (0.50 μL) was added to a CH₂Cl₂ solution (0.50 mL) containing AgSbF₆ (98%, 2.8 mg, 8.2 μmol) with stirring at room temperature. The mixture was added dropwise to hexane (30 mL) with vigorous stirring. After reducing the volume of the resulting solution to 3 mL, the precipitates were filtered off. Evaporation of the filtrate gave dark red material, from which [Pd^{II}(L^{•2})] was obtained as black crystals by recrystallization from hexane (mg, 49%). IR (KBr): *v*, cm⁻¹ 2952 (C–H), 1547, 1362 (NO₂). Anal. calcd. for C₃₁H₄₂N₃O₄Pd: C, 59.37; H, 6.75; N, 6.70. Found C, 59.60; H, 6.84; N, 6.59.

CONCLUSION

In this study, a new type of Ni and Pd complexes supported by the non-innocent β -diketiminate ligand containing two phenol groups has been developed and the structures, physical properties, and redox behaviors of the nickel(II) and the palladium(II) complexes, $[M^{II}(L^{3-})]^{-}$, have been examined in detail. The oneelectron oxidation of $[Ni^{II}(L^{3-})]^{-}$ gave $[Ni^{II}(L^{\bullet 2-})]$, where the supporting ligand is oxidized to provide nickel(II)phenoxyl radical complexes exhibiting the characteristic absorption spectra in the visible-to-NIR region. Further one-electron oxidation of $[Ni^{II}(L^{\bullet 2-})]$ gave the two-electron oxidation product $[Ni^{II}(L^{-})]^{+}$, where the oxidation also takes place at the ligand moiety. The oneand two-electron oxidation of $[Pd^{II}(L^{3-})]^{-}$ gave $[Pd^{II}(L^{\bullet 2-})]$ and $[Pd^{III}(L^{\bullet 2-})]^+$, respectively, where the supporting ligand is oxidized in the former, whereas the metal center is mainly oxidized in the later.

The two-electron-oxidation complexes $[Ni^{II}(L^{-})]^+$ and $[Pd^{II}(L^{2\bullet})]^+$ exhibited hydrogen atom abstraction ability from CHD as in the case of the copper complex with same ligand. However, the reactivity was slightly lower than

that of the Cu-complex. The reaction of one-electronoxidation complex [Ni^{II}($L^{\bullet 2-}$)] with CHD included photo-induced oxidation of CHD, whereas one-electronoxidation complex [Pd^{II}($L^{\bullet 2-}$)] showed thermal hydrogen atom abstraction ability from CHD. The reactivity of twoelectron oxidized complexes [Ni^{II}(L^{-})]⁺ and [Pd^{III}($L^{2\bullet-}$)]⁺ in the C–H bond activation reaction of CHD is much higher than that of the one-electron oxidized complex [Ni^{II}($L^{\bullet 2-}$)] and [Pd^{II}($L^{\bullet 2-}$)]. These results will provide further insights into the redox functions of transitionmetal organic radical species.

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Supporting information

Crystallographic data (Tables S1 and S2) and additional spectroscopic and kinetic data (Figs S1–S5) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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