Nickel Complexes with Two Types of Noninnocent Ligands: α-Diimine and Phenazine

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Ⓢ *Supporting Information*

ABSTRACT: The α-diimine nickel dibromo complex LNiBr$_2$ (L = [(2,6-iPr$_2$C$_6$H$_3$)NC(Me)]$_2$) reacts with various amounts of potassium metal and phenazine (Phz) to afford the complexes [LNi(η^4-C$_4$-Phz)] (**1**) and [K(DME)]$_2$[(LNi)$_2$(μ-η^1:η^1-N,N-Phz)] (**2**), in which the Phz molecule adopts significantly different coordination modes with different oxidation states of Phz, Ni, and L.
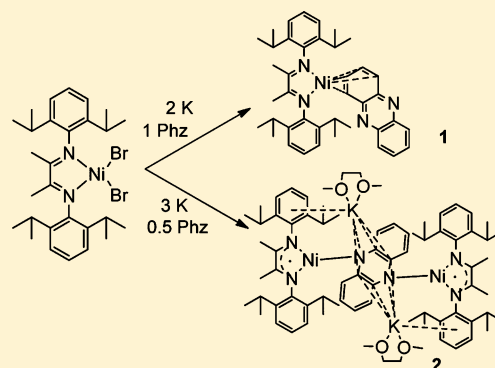
Phenazine (Phz) is involved in many electron transfer processes due to its easily reducible (−0.364 V vs SCE) nature.[1,2] It has been recognized as a noninnocent ligand, and the reduced Phz (radical anion or dianion) ligands can form complexes with main group metals,[3,4] transition metals,[5] and lanthanides and actinides.[6] In these complexes, the redox transformations are modulated by the Phz ligand serving as an "electron reservoir" that can reversibly accept and donate electrons.[4] On the other hand, as a weak bridging ligand, phenazine can act as the "organic linker" in the construction of 1D and 2D metal coordination networks as well as layered complexes by the noncovalent interactions (hydrogen bonding or π−π stacking).[7] However, nickel complexes with reduced Phz ligands have not been reported.

Since Brookhart reported that nickel(II) α-diimine complexes are highly active catalysts for olefin polymerization,[8] this class of complexes stirred up great interest.[9] Moreover, the α-diimines are also well-known noninnocent ligands that can form a wide range of complexes in the neutral and singly or doubly reduced states. Our recent research has focused on metal complexes containing low-valent, low-coordinate metal ions stabilized by α-diimines.[10] These complexes show interesting reactivity toward organic molecules through various electron transfer processes involving the metal centers and ligands.[10e,f] In the current work, an investigation of the noninnocence of both the α-diimine and Phz ligands was carried out, which display interesting redox properties and result in two nickel complexes with a variety of oxidation states of Phz, Ni, and α-diimine and significantly different coordination modes of Phz.
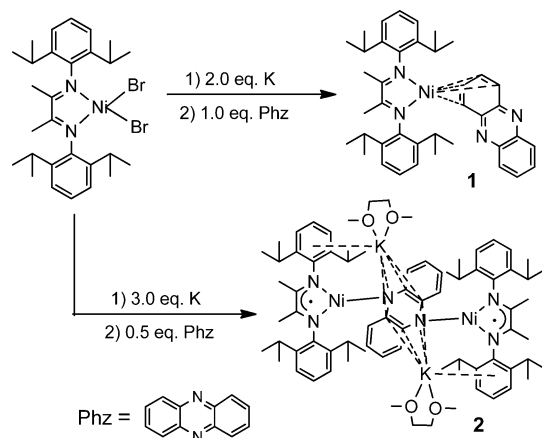
■ RESULTS AND DISCUSSION

The dibromo nickel(II) precursor LNiBr$_2$ (L = [(2,6-iPr$_2$C$_6$H$_3$)NC(Me)]$_2$) is inert to Phz in the absence of reducing agents. However, as illustrated in Scheme 1, when LNiBr$_2$ was first reduced by 2.0 equiv of potassium metal and then reacted with 1.0 equiv of Phz, the mononuclear complex [LNi(η^4-C$_4$-Phz)] (**1**) was isolated in 60% yield as black-purple crystals. In addition, treatment of LNiBr$_2$ with 3.0 equiv of K metal followed by reaction with 0.5 equiv of Phz afforded the dinuclear, three-coordinate nickel compound, [K(DME)]$_2$[(LNi)$_2$(μ-η^1:η^1-N,N-Phz)] (**2**), as dark-green crystals. The complexes are thermally stable under argon but are sensitive to air and moisture. Very interestingly, the molecular structures of **1** and **2** reveal two coordination modes for Phz. Complex **1** contains a Phz ligand that is η^4-coordinating to the Ni atom by using only one carbocyclic ring, while complex **2** is a centrosymmetric dimer wherein the Phz ligand bridges two

Scheme 1. Synthesis of Complexes 1 and 2


the coordinating ring. The Ni−C distances of the outer carbon atoms (av. 2.039 Å of C31 and C32) are shorter than those to the central carbons (av. 2.242 Å of C30 and C33). This is similar to the reported Mo complex $(\eta^4\text{-}C_4\text{-Phz})_2\text{Mo(PMe}_3)_2$ that has two folded $\eta^4\text{-}C_4$-Phz molecules.[5] The average C−N bond length of the Phz molecule retains 1.35 Å which can be found in free Phz.[12] The C−C distances of the coordinated carbocyclic ring (from 1.400(3) to 1.453(3) Å) are obviously longer than those (from 1.371(3) to 1.419(3) Å) of the other (uncoordinated) carbocyclic ring in complex **1**.

Complex **1** contains two redox active ligands, the α-diimine L and Phz, as well as the transition metal nickel, and thus an investigation of the electron transfer during the reduction by the alkali metal is necessary. It is known that the oxidation state of α-diimine ligands can be conveniently judged by the C−N and C−C bond lengths of the central C_2N_2 core.[10,13] These values (C−N: 1.316(2) and 1.314(2) Å and C−C: 1.456(2) Å) in complex **1** correspond to a neutral ligand L^0. Considering the analogy of the η^4-coordination mode of Phz to butadiene, the complex appears to have the formal oxidation state Ni(0) and neutral Phz. Moreover, the NMR spectrum of **1** shows sharp signals, and it is EPR silent in frozen Et$_2$O solution at 77 K, demonstrating the diamagnetism of complex **1**. The electronic structure of **1** was further proven by DFT computations at the B3LYP/6-31G level with the broken symmetry (BS) formalism in the singlet state. The optimized structure agrees well with the X-ray data (Table S1, Supporting Information). A Mulliken spin density analysis reveals zero spin density on the Ni centers, which supports the assignment of a Ni(0) center coordinated by the neutral α-diimine and Phz ligands. The HOMO−2 demonstrates the metal-to-ligand backbonding (Figure S4).

The dinuclear complex **2** (Figure 2) shows a centrosymmetric structure with a Phz molecule bridging two [K-(DME)]·[LNi] moieties. The Ni centers are 3-fold coordinated by a ligand L and one N atom of the bridging Phz in a trigonal-planar geometry; thus it can be considered as a nickel amido complex. The Ni−N bond length to the Phz ligand is 1.934(2) Å, while those to the α-diimine ligand L are 1.955(2) and

nickel centers via the nitrogen atoms. In fact, since in complex **1** the other carbocyclic ring of Phz is free from interaction with metals, the parallel reaction with 0.5 equiv of Phz was also carried out in an attempt to synthesize the 2:1 (nickel to Phz) complex. A color change of the reaction solution from deep green to dark blue was observed; unfortunately, the product could not be isolated.

In the mononuclear complex [LNi(η^4-C$_4$-Phz)] (**1**) (Figure 1), the Ni atom is chelated by an α-diimine ligand L (Ni−N
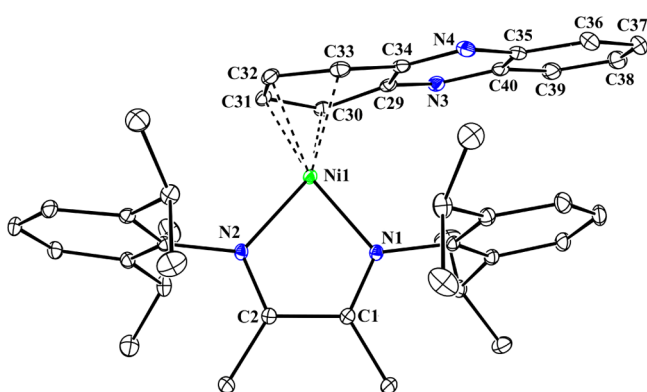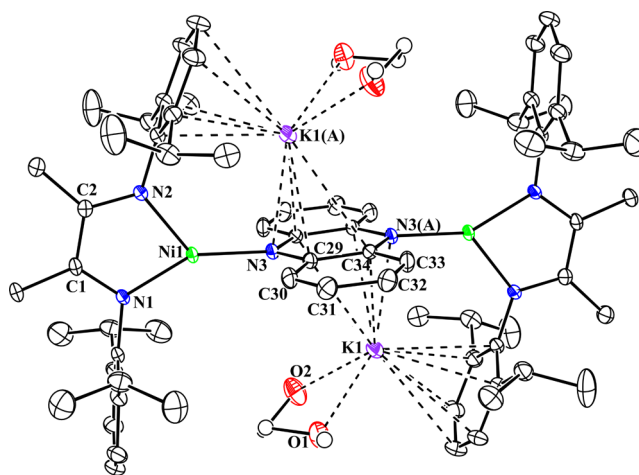

Figure 1. Molecular structure of **1** (thermal ellipsoids are set at the 20% probability level; hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Ni1−N1 1.9153(14), Ni1−N2 1.9379(14), Ni1−C31 2.0299(18), Ni1−C33 2.2432(19), N1−C1 1.316(2), C1−C2 1.456(2), C2−N2 1.314(2), C30−C31 1.405(3), C31−C32 1.413(3), C32−C33 1.400(3), C29−C34 1.453(2), C29−N3 1.327(2), C34−N4 1.320(2), C40−N3 1.377(2), C35−N4 1.372(3), N1−Ni1−N2 81.92(6).

distances: 1.9379(14) and 1.9153(14) Å and interacts with one of the carbocyclic rings of the Phz molecule in an η^4 manner, which is similar to the interaction of α-diimine-nickel complexes with butadiene.[11] This coordination mode for Phz is very rare; the only examples were reported very recently in two molybdenum complexes.[5] The η^4-coordination mode is reflected by the ^{1}H NMR spectrum, in which the signals of the protons on the coordinating carbocyclic ring (at δ = 5.61 ppm for H31 and H32, and δ = 5.16 ppm for H30 and H33) are shifted to higher field by $\Delta\delta$ = 2.04 and 2.08 ppm, respectively, compared to the uncoordinated carbocyclic ring. The Phz ligand in **1** is significantly distorted from planar, being folded by 14.8° at the central (C30 and C33) carbon atoms of

Figure 2. Molecular structure of **2** (thermal ellipsoids are set at the 20% probability level; hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Ni1−N1 1.928(2), Ni1−N2 1.955(2), Ni1−N3 1.934(2), N1−C1 1.351(4), C1−C2 1.401(4), C2−N2 1.353(4), N3−C29 1.401(4), N3−C34 1.411(4), C29−C34 1.435(4), K1−N3 2.861(2), K1−O1 2.653(3), K1−O2 2.725(3), N1−Ni1−N2 81.33(9). Symmetry code A): 1−x, 1−y, 1−z.

1.928(2) Å, the longer one possibly resulting from the interaction of the $[K(DME)]^+$ unit with the aryl ring. Two DME-solvated K^+ ions sit above and below the bridging Phz ligand and being bonded by one aryl ring of the α-diimine ligand and the Phz molecule in an η^6/η^4 fashion. The crystallographic symmetry constrains the two C_2N_2Ni planes to be parallel to each other, which are nearly perpendicular (dihedral angle 86.7°) to the Phz moiety.

The Phz molecule in **2** is close to planar with longer N–C distances (1.401(4) Å/1.411(4) Å) than those (1.35 Å) in the neutral Phz,[4,12] corresponding to its dianionic form.[3,6] Different from the η^4-coordination of one carbocyclic ring in complex **1**, the Phz moiety coordinates to the nickel centers by the N atoms (μ-η^1:η^1-bonding mode). The structure of **2** compares with the complexes $[Mg_2Br_2(\eta^1:\eta^1\text{-Phz})(thf)_6]\cdot[MgBr_2(thf)_4]$,[3] $[(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)U]_2[\eta^1:\eta^1\text{-Phz}]$,[6f] and $[(\eta^5\text{-}C_5Me_5)_2M]_2[\eta^3:\eta^3\text{-Phz}]$ (M = Yb, Sm, La, or Lu)[6a–d] with the dianion Phz^{2-}. However, in the later four lanthanide complexes, the Phz bridges the metal ions using three adjacent atoms in an aza-allyl mode on each side rather than using only the N atom. On the other hand, the C–N (1.351(4)/1.353(4) Å) and C–C (1.401(4) Å) bond distances of the C_2N_2 moiety of the α-diimine L in **2** indicate the monoanionic π radical character. The total negative charges of the Phz and α-diimine ligands (−4) are counterbalanced by two K^+ ions and two Ni centers. Thus, the nickel centers display the formal oxidation state of +1.

DFT and EPR studies were carried out to elucidate the electronic structure of **2**. DFT geometry optimizations were performed on a model compound $[K(H_2O)_2]_2[\{(C_6H_3\text{–}NCH)_2Ni\}_2(\mu\text{-}\eta^1:\eta^1\text{-N,N-Phz})]$ (**2′**) in the singlet ($S = 0$), triplet ($S = 1$), and quintet ($S = 2$) spin states, respectively, at the B3LYP/6-31G level. The results demonstrate that the quintet spin state is energetically more favored by 30.09 and 25.50 kcal mol^{-1}, respectively, than the singlet and triplet states, implying the existence of the paramagnetic Ni(I) centers and ligand radicals. This is also consistent with the EPR studies. The EPR spectrum of **2** in the solid state at 77 K shows four components (Figure S1, Supporting Information). The g_1 component appears at 2.412, g_2 at 2.339, and g_3 at 2.136, which clearly establish the presence of Ni(I) cores.[14] The experimental signal is in good agreement with the simulated one (Figure S2) and is also similar to literature reports on related systems.[14] The fourth peak at $g = 2.012$ is attributable to the organic radical (L$^{\bullet-}$). In addition, the room-temperature EPR spectrum of **2** shows the hyperfine structure and a broad signal (Figure S3, Supporting Information). The 10-lined signal of the hyperfine structure is well resolved and agrees with the simulated one (Figure 3), which can be explained as originating from the superimposition of overlapping quintets (due to two equivalent ^{14}N nuclei, $I = 1$) and septets (due to six equivalent ^{1}H nuclei of two methyl groups, $I = 1/2$) of the ligand L. The g value of 2.017 compares well with the reported compounds containing radical diimine ligands.[10d,15]

In conclusion, two nickel complexes with the noninnocent α-diimine (L) and phenazine (Phz) ligands have been synthesized from the reduction of the dibromo nickel(II) compound LNiBr$_2$ and Phz. The mononuclear complex **1** contains a Ni(0) center coordinated by a neutral α-diimine and a Phz ligand, while in the dinuclear complex **2** the α-diimine ligands are radical monoanions, the Phz displays the dianion form, and the nickel shows the formal oxidation state of +1. Accordingly, the Phz coordinates to nickel in an η^4-fashion through one of the
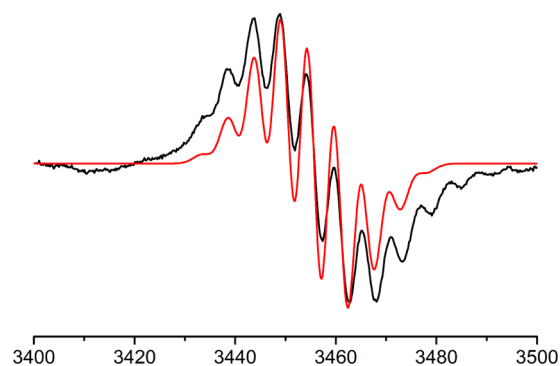
Figure 3. X-band EPR spectrum of complex **2** in DME at room temperature (black: experimental; red: simulated).

carbocyclic rings in **1**, whereas it bridges two nickel atoms via the nitrogen atoms in complex **2**.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations with air- and moisture-sensitive compounds were carried out under argon with standard Schlenk or drybox techniques. The solvents (DME and Et$_2$O) were dried using appropriate methods and distilled under argon prior to use. Benzene-d_6 was dried over Na/K alloy. NMR spectra were recorded on a Mercury Plus-400 spectrometer in benzene-d_6. EPR spectra were recorded on a Bruker EMX-10/12 spectrometer. IR spectrum was recorded (thin film on KBr plate) using a Nicolet AVATAR 360 FT-IR spectrometer. Elemental analyses were performed with an Elementar VarioEL III instrument. Phz (99%) was purchased from Alfa Aesar. LNiBr$_2$ was prepared according to a published procedure.[8]

Synthesis of [LNi(η^4-C$_4$-Phz)] (1). Potassium (0.080 g, 2.0 mmol) was added to a suspension of LNiBr$_2$ (0.31 g, 1.0 mmol) in Et$_2$O (30 mL), and the mixture was stirred for 2 days at room temperature, upon which a color change from brown-red to dark green was observed. Then Phz (0.180 g, 1.0 mmol) was added, and the mixture was stirred further for 1 day to generate a dark purple color. After filtration of the mixture and concentration of the filtrate to ca. 8 mL, the solution was stored at room temperature for several days to afford dark purple crystals of **1** (0.39 g, 60%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 0.89$ (d, 24H, $J = 6.8$ Hz, CH(CH_3)$_2$), 2.10 (s, 6H, N-CCH_3), 2.87 (m, 4H, CH(CH$_3$)$_2$), 5.16 (m, 2H, Phz-H), 5.61 (m, 2H, Phz-H), 7.00−7.15 ppm (m, 6H, C$_6H_3$), 7.24 (m, 2H, Phz-H), 7.65 (m, 2H, Phz-H). ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): $\delta = 14.2$ (N–CCH_3), 23.5 (CH(CH$_3$)$_2$), 26.7 (CH(CH$_3$)$_2$), 147.8 (N-CCH$_3$), 122.3−140.8 (aryl-C). IR (KBr, ν/cm^{-1}): 1638, 1565, 1451, 1383, 1317, 1292, 1188, 1110, 1090, 978, 943, 868, 786, 747, 681. Anal. Calcd for C$_{40}$H$_{48}$N$_4$Ni (643.51): C 74.65, H 7.52, N 8.71. Found: C 74.12, H 7.21, N 8.82.

Synthesis of [K(DME)]$_2$[(LNi)$_2$(μ-η^1:η^1-N,N-Phz)] (2). LNiBr$_2$ (0.31 g, 1.0 mmol) and potassium (0.12 g, 3.0 mmol) were suspended in a mixed solvent (20 mL, Et$_2$O: DME = 3:1 v/v) and stirred for 2 days at room temperature to generate a dark brown color. Then Phz (0.09 g, 0.50 mmol) was added, and the stirring continued for another 1 day with the color changed to dark green. The solution was filtered, and the filtrate was concentrated to ca. 8 mL and stored at room temperature for several days to yield **2** as dark-green crystals (0.12 g, 16%). EPR (DME, room temperature), $g = 2.017$ and $g = 2.100$ (broad signal); EPR (solid state, 77 K): $g_1 = 2.412$, $g_2 = 2.339$, $g_3 = 2.136$, and $g = 2.012$. IR (KBr, ν/cm^{-1}): 1642, 1580, 1458, 1437, 1385, 1315, 1253, 1188, 1102, 1060, 985, 932, 861, 787, 7739, 690. Anal. Calcd for C$_{84}$H$_{128}$N$_6$O$_6$K$_2$Ni$_2$ (1513.54): C 66.66, H 8.52, N 5.55. Found: C 66.03, H 8.63, N 5.42.

Crystal Data for 1 (C$_{40}$H$_{48}$N$_4$Ni). $M = 643.51$, monoclinic, space group $P2_1/c$, $a = 10.4103(13)$ Å, $b = 18.630(2)$ Å, $c = 17.843(2)$ Å, $\beta = 98.3530(10)°$, $V = 3423.9(7)$ Å^3, $D_{calc} = 1.248$ g cm^{-3}, $Z = 4$, $\mu = 0.600$

mm^{-1}; 22 231 reflections collected, R_{int} = 0.0278, $R1$ = 0.0293, $wR2$ = 0.0847 ($I > 2\sigma(I)$).

Crystal Data for 2 (C$_{84}$H$_{128}$N$_6$K$_2$Ni$_2$O$_6$). M = 1513.54, triclinic, space group P-1, a = 10.7791(17) Å, b = 13.479(2) Å, c = 15.832(2) Å, α = 94.520(2)°, β = 107.634(2)°, γ = 102.176(2)°, V = 2117.5(6) Å^3, D_{calc} = 1.187 gcm^{-3}, Z = 1, μ = 0.595 mm^{-1}; 15 195 reflections collected, R_{int} = 0.0292, $R1$ = 0.0509, $wR2$ = 0.1483 ($I > 2\sigma(I)$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details and crystallographic information files (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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