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Dianions as Formal Oxidants: Synthesis and Characterization of Aromatic Dilithionickeloles from 1,4-Dilithio-1,3-butadienes and [Ni(cod)$_2$]**

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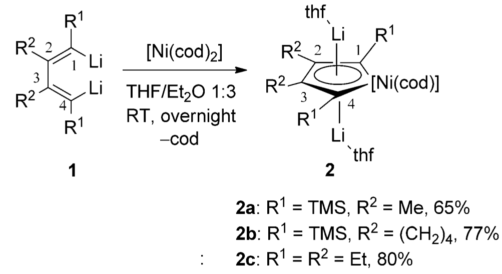
Abstract: *Organolithium compounds can behave as reductants but never as oxidants in redox reactions. Reported herein is that 1,4-dilithio-1,3-butadienes reacted with [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) to deliver dilithionickeloles. Single-crystal X-ray structural analysis revealed a coplanar structure of dilithionickeloles with an averaging of bond lengths. XPS data confirmed the oxidation state of Ni in dilithionickeloles was Ni^{2+}. ^{7}Li NMR spectra of dilithionickeloles and theoretical calculations revealed a considerable aromatic character. In this redox reaction, the dilithio dianionic compounds behaved as formal oxidants, thus oxidizing Ni^0 into Ni^{2+}. These results demonstrated that organolithium compounds with π-conjugation could be used as oxidants and could continue to accept extra electrons.*



Scheme 1. Preparation of the dilithionickeloles **2**. cod = 1,5-cyclooctadiene, THF = tetrahydrofuran, thf = tetrahydrofuran, TMS = trimethylsilyl.

Redox reactions are common in chemistry and biological processes. In redox reactions, oxidants gain electrons or decrease in oxidation state, while reductants lose electrons or increase in oxidation state. Therefore, the widely used organolithium reagents (RLi) can participate in redox reactions as reductants, because they have high electron densities on their carbanions and easily give up electrons. Because these carbanions in the organolithium reagents are rather electron-rich and it is difficult to accept electrons, they are conceptually not considered oxidants. In fact there is no report of utilizing such organometallic compounds as oxidants.[1]

We have been working on the reaction chemistry and synthetic applications of dianions with π-conjugation, especially 1,4-dilithio-1,3-butadienes (dilithio reagents for short).[2] It was reported that nickel(0) complexes could react with stoichiometric amounts of alkyllithium reagents to afford Ni^0 ate complexes.[3] We envisioned that a redox reaction might take place if we treated our conjugated dilithio reagents with low-valent transition-metal complexes such as nickel(0) complexes. Herein, we report that butadienyl dianions reacted as formal oxidants with [Ni(cod)$_2$], thus oxidizing the Ni^0 atom to Ni^{2+} and resulting in the formation of divalent aromatic dilithionickeloles.

As shown in Scheme 1, the reaction between [Ni(cod)$_2$] and the dilithio reagents **1** proceeded smoothly in the mixed solvent of THF and Et$_2$O (1:3) at room temperature, thus affording the dilithionickeloles **2a–c** as dark-red crystalline compounds in good to excellent yields upon isolation. Crystals of **2a–c** suitable for single-crystal X-ray structural analysis were obtained after recrystallization.

Figure 1 shows the single-crystal X-ray structure of **2a** (for the structures of **2b** and **2c**, see the Supporting Information).

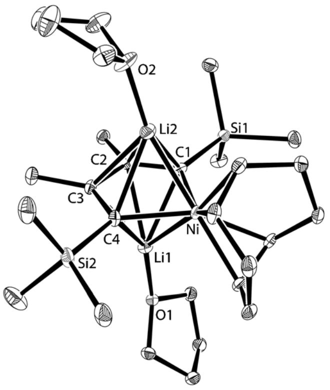


Figure 1. ORTEP drawing of **2a** with thermal ellipsoids plots drawn at 30% probability for non-H atoms. All H atoms were omitted for clarity.

Both lithium atoms lie above and below the nickelole core in an η^5 fashion. The skeleton ring (Ni-C1-C2-C3-C4) is planar with a 539.6° sum of internal angles. The C−C bond lengths [C1-C2: 1.401(3) Å, C2-C3: 1.477(3) Å, C3-C4: 1.407(4) Å] are average, compared to those in the starting material **1a**

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[C1-C2: 1.359(5) Å, C2-C3: 1.539(5) Å, C3-C4: 1.352(6) Å].[4] The other two products (**2b** and **2c**) demonstrated similar structural features.

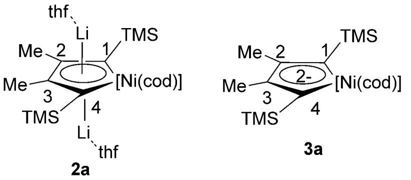
To confirm the valence of the nickel atom in the dilithionickeloles, X-ray photoelectron spectroscopy (XPS) measurements were carried out. The XPS of **2a** detected the Ni $2p_{3/2}$ binding energy at 855.5 eV (see Figure S5 in the Supporting Information), thus falling within the range for Ni^{2+}.[5] This result strongly suggested that a redox reaction took place, in which the Ni^0 atom was oxidized to Ni^{2+} by the dianion **1a**.

It should be noted that recently, several main-group dilithiometalloles including dilithiostannoles,[6] dilithioplumboles,[7] and dilithioalumoles[8b] have been elegantly synthesized by Saito, Tokitoh, and co-workers from the reaction between an excess amount of metal lithium and the corresponding metalloles. These main-group metallole dianions have been well characterized, thus showing similar structures and considerable aromatic character. However, in comparison with our present work, these main-group metallole dianions were all generated by a common redox reaction using the added metal lithium as the reductant. Our synthetic strategy and concept were totally different. We treated linear dianions directly with a zero-valent transition-metal complex. In this context, the electron-rich butadienyl dianions could react not only as reactants, but also as oxidants to accept electrons.

The chemistry of metal-containing aromatics is a fascinating topic and has attracted much attention recently.[9,10] To further confirm the aromaticity of dilithionickeloles, ^{7}Li NMR spectroscopy was carried out in [D$_8$]THF with 0.1M LiCl in [D$_8$]THF as the external standard. The signal attributable to **2a** was found at $\delta = -5.77$ ppm, which is out of the range for normal organolithium compounds ($\delta = -2.0$ to 1.5 ppm). This low-frequency resonance is evidently caused by the strong shielding effect of the diatropic ring current, again clearly indicating the aromatic nature of **2a**. In its ^{13}C NMR spectrum, the sp^2-carbon atoms of the 1,5-cyclooctadiene (cod) ligand displayed a singlet at $\delta = 70.0$ ppm, an upfield shift compared to that of free cod ($\delta = 129.3$ ppm) and [Ni(cod)$_2$] ($\delta = 90.4$ ppm). The two carbon atoms bonded with the nickel atom (C1 and C4) showed a singlet at $\delta = 199.8$ ppm, a downfield shift as compared with the resonance in **1a** ($\delta = 192.3$ ppm). The other two carbon atoms (C2 and C3) displayed a singlet at $\delta = 150.3$ ppm, a large upfield shift relative to **1a** ($\delta = 165.0$ ppm).

For a better understanding of the structures of the dilithionickeloles **2**, density functional theory (DFT) calculations were carried out using Gaussian 09.[11] Geometric structures of **2a** and the non-lithium-coordinated **3a** were optimized at the B3PW91 level.[12] The 6-31G(d) basis set[13] was used for Si, C, H, and Li atoms. The LanL2DZ basis set[14] was used for the Ni atom (see the Supporting Information). In the optimized structures, all the C−C and C−Ni bond lengths of **2a** were consistent with the X-ray structure (Figure 2). Moreover, the optimized structure of **3a** was coplanar and did not have significant difference compared to that of **2a**.

The ^{7}Li NMR chemical shift of **2a** was then calculated based on the optimized structure using gauge-independent atomic orbital (GIAO) computations.[15] The 6-311+G(d) basis set[16] was used for Si, C, H, and Li atoms. The LanL2DZ basis set was used for the nickel atom. The chemical shift of lithium atoms ($\delta = -4.7$ ppm) was in accordance with the experimental value. The nucleus-independent chemical shift (NICS; a simple and efficient tool to judge aromaticity) of **2a** was also calculated.[17] The considerable negative NICS(0) value (−8.55 ppm) and the NICS(1) value (−10.30 ppm) at the center of the NiC$_4$ ring of **2a** again strongly suggested that **2a** was aromatic.



2a **3a**

	Crystal structure of **2a**	Theoretical structure of **2a**	Theoretical structure of **3a**
Ni−C1, Ni−C4	2.027(2), 2.012(2)	2.057, 2.062	2.024, 2.024
C1−C2, C3−C4	1.401(3), 1.407(4)	1.403, 1.404	1.381, 1.382
C2−C3	1.477(3)	1.482	1.469

Figure 2. Comparison of the bond lengths [Å] between the crystal structure and the theoretical structure.

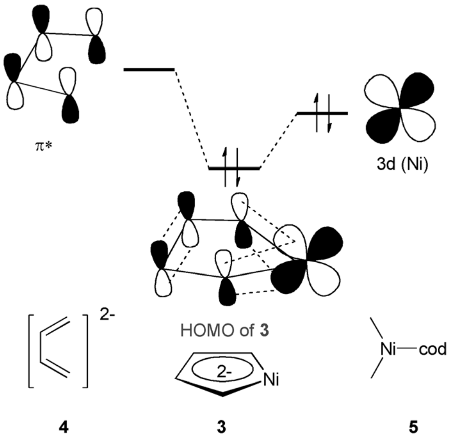
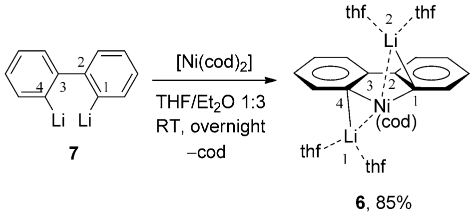


Figure 3. Frontier orbitals of the non-lithium-coordinated **3**.

As **3a** had a similar structure to that of **2a**, we proposed the frontier orbitals of **3** to elucidate the electronic structures of **2**. As shown in Figure 3, the π* orbital of **4** and the occupied 3d orbital of **5** could overlap. The origin of the aromaticity of **3** could be ascribed to the delocalization of electrons from the 3d orbital in the nickel atom into the vacant π* orbital of the butadiene moiety. The whole process might be understood in the following steps. First, the [Ni(cod)$_2$] in the solution released one cod to form the active species [Ni(cod)]. Then the butadienyl dianion moiety coordinated to the [Ni(cod)], thus forming two classic C−Ni σ bonds. Because of the difference in electronegativity between C and Ni, the negative charge was still concentrated in the butadiene moiety. Finally, the occupied 3d orbital of Ni shared its electrons with the vacant π^* orbital of the butadiene moiety, thus forming the delocalized 6π-electron system. Generation of aromaticity is considered as the main driving force for the success of this reaction. In this process, the butadienyl skeleton is formally reduced.

From the above results, we envisioned that the dilithio-dibenzonickelole **6** could also be synthesized by the same strategy (Scheme 2). When the dilithiobiphenyl **7** was treated



Scheme 2. Preparation of the dilithiodibenzonickelole **6**.

with [Ni(cod)$_2$] at room temperature, the white suspension changed into a dark solution gradually. After natural volatilization for 24 hours in a glove box, the crimson crystals of **6** were obtained in 85 % yield.

The single-crystal X-ray structural analysis of **6** was carried out (Figure 4). The C−C bond lengths of the nickelole [C1−C2: 1.438 (5) Å, C2−C3: 1.479(6) Å, C3−C4: 1.427(5) Å] were also average, compared to those in the starting material **7** [C1−C2: 1.416 Å, C2−C3: 1.513 Å, C3−C4: 1.409 Å].[18] The C–C double bonds in the nickelole [C1−C2: 1.438 (5) Å] were remarkably longer than those in the dibenzo ring [C10−C11: 1.355 (7) Å]. Moreover, the bond length of Li1−C3 [2.695 (8) Å] is much longer than that of Li1−C4 [2.235 (8) Å]. The Li−Ni bond length is nearly 2.50 Å, thus indicating a weak Li–Ni interaction.[3c]

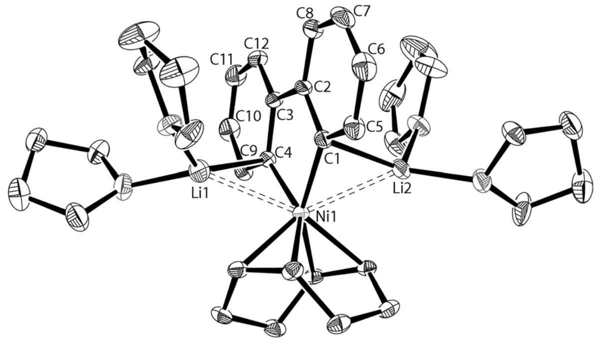


Figure 4. ORTEP drawing of **6** with thermal ellipsoids plots drawn at 30% probability for non-H atoms and selected bond lengths [Å] and angles [°]. All H atoms were omitted for clarity.

Although a similar planar skeleton was observed, the structure of **6** was different from that of **2**. Both lithium atoms have two coordinating thf ligands (only one thf coordinating to Li in **2**). The lithium atoms in **6** are not arranged in η^5 fashion as those in **2**, and means that the lithium atoms are not centered above/below the nickelole. In fact the Li1-Ni-C4 and Li2-Ni-C5 planes are almost perpendicular to the nickelole plane. As a result, the ^{7}Li NMR chemical shift of **6** is less negative ($\delta = -1.68$ ppm), which is also consistent well with the result of the theoretical calculation ($\delta = -1.62$ ppm). These results indicate that **6** has weaker aromatic character. The smaller negative NICS(0) value (−3.45 ppm) and the NICS(1) value (−4.97 ppm) at the center of the nickelole supported this conclusion.

XPS measurements were also carried out. XPS of **6** detected the Ni 2p$_{3/2}$ binding energy at 852.5 eV (see Figure S6), thus falling within the range for Ni^0.[5] From above results, we consider that **6** is more likely to be a Ni^0 ate complex.[3]

In summary, we have synthesized and structurally characterized the first series of the dilithionickeloles **2** and dilithio-dibenzonickelole **6**. In this redox reaction, the dilithio butadienyldianions behaved as formal oxidants, thus oxidizing the Ni^0 atom to Ni^{2+}. These results demonstrated that organolithium compounds with π-conjugation could be used as oxidants and could continue to accept extra electrons. We believe this novel finding will broaden the utilization of anionic compounds and inspire new possibilities in synthetic chemistry and organometallic chemistry.

Keywords: aromaticity · lithium · nickel · oxidation · redox chemistry

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