VIP **Aromatic Rhodacycles** *Very Important Paper*

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1,3-Butadienyl Dianions as Non-Innocent Ligands: Synthesis and Characterization of Aromatic Dilithio Rhodacycles**

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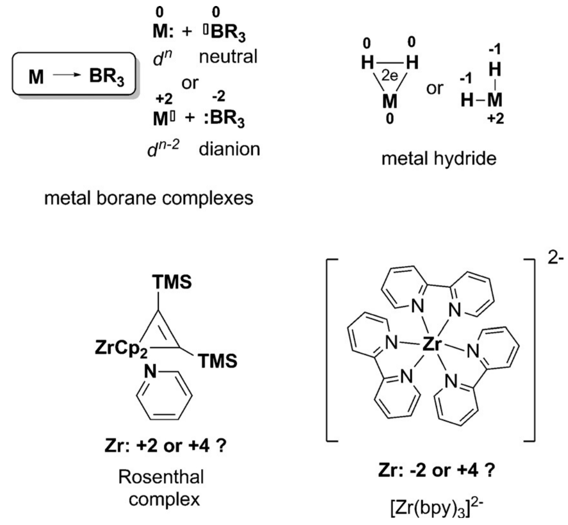
Abstract: *Herein we report that 1,4-dilithio-1,3-butadienes, a type of 1,3-butadienyl dianion, can act as non-innocent ligands, taking electrons from low-valent transition metals. Dilithio reagents reacted with [{RhCl(cod)}$_2$] to give dilithio rhodacycle* ***3a***. *Single-crystal X-ray structural analysis revealed the structure of* ***3a*** *with averaged bond lengths. XPS data suggested that the oxidation state of Rh in* ***3a*** *was more likely to be Rh^{3+}. CDA/ECDA confirmed the electron-transfer process. ^{7}Li NMR spectra of* ***3a*** *and theoretical calculations revealed a considerable aromatic character. In this process, the dilithio compounds behaved as non-innocent ligands and formal oxidants. These results demonstrated that organolithium compounds with suitable π-conjugation could be used as electron acceptor.*

Recently we reported the first example in which organolithium reagents might behaved as formal oxidants.[1] In that reaction, 1,4-dilithio-1,3-butadienes **1** (dilithio reagents for short) reacted with [Ni(cod)$_2$], offering aromatic dilithionickeloles as the final products. Ni^0 was assumed to be oxidized to Ni^{II} by the dilithio reagents based on X-ray photoelectron spectroscopy (XPS) data. However, as our conclusion seems to be in conflict with classic theory of formal oxidation states,[1,2] further examples and evidence is required to discuss this topic more deeply.

The oxidation state is a convenient tool to count electrons in redox reactions and electrochemistry. However, as this concept is based on the ionic approximation and electronegativity, this would cause some problems in certain cases.[3] For example, if a metal center is bonded by the more electronegative atoms as a Lewis acid (e.g. transition metal borane complexes), the oxidation state of the center metal would be confusing (Scheme 1). Some chemists consider the BX$_3$ ligand as a neutral ligand[4] whilst some others consider it as an oxidant, accepting two electrons from the metal, [BX$_3$]$^{2-}$.[5]



Scheme 1. Selected examples in which the counting of oxidation states causes ambiguity.

More examples are related to complexes with non-innocent ligands,[6] such as [Cp$_2$Zr(Pyridine)(Me$_3$SiC≡CSiMe$_3$)],[7] the oxidation state of the metal can be considered as either Zr^{II} or Zr^{IV}. The oxidation state of the metal center in transition metal–H$_2$ complexes could also be ambiguous. In some cases the H−H bond becomes longer but still remains, whilst in other cases the H−H bond is broken and the H−M−H bond is formed (Scheme 1).[8] Another interesting non-innocent ligand is 2,2′-bipyridine. It can undergo facile reduction to give a diamagnetic dianion, thus causing ambiguity in the valence of the metal center. In fact the actual oxidation state of the Zr in [Zr(bpy)$_3$]$^{2-}$ was considered to be more likely Zr^{IV}, not Zr^{-II} (Scheme 1).[9]

The ambiguity is caused by the concept of oxidation state which only assigns integer values of electrons to an isolated atom, even in covalent bonds. The ambiguity could be avoided by the Covalent Bond Classification (CBC) system suggested by Green and Parkin.[10] In CBC method, there are three types of ligands in organometallic compounds: L-ligand (Lewis base, for example, PR$_3$), X-ligand (interacting with the metal center by a covalent bond, for example, Cl), and Z-ligand (Lewis acid, for example, BX$_3$). As the CBC method considers the nature of metal–ligand covalent bonds within the molecule, the inappropriate points caused by oxidation state might be surmounted.

Based on the concept of non-innocent ligand,[6] the CBC method,[10] and our previous work on dilithionickeloles,[1] dilithio reagents can be used as special non-innocent ligands and regarded as Z-type ligands. Because using formal oxidation state to measure the valence of metal center

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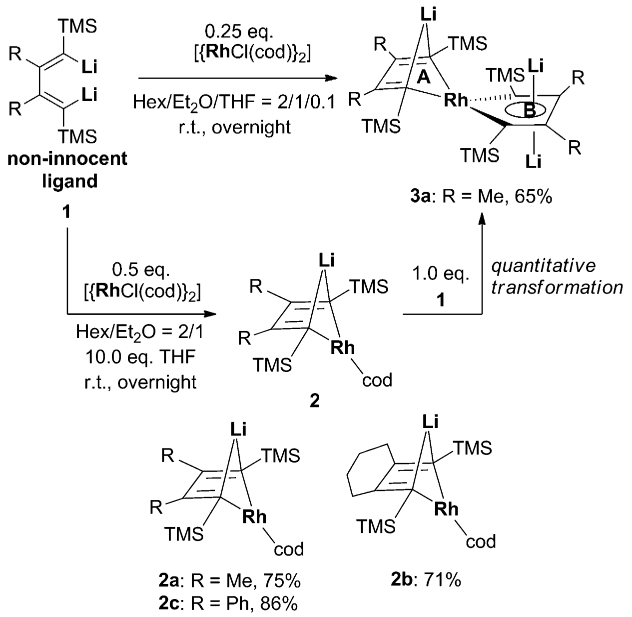
would be ambiguous as mentioned above, the spectra and theoretical calculation should be carried out to judge the extent of electron transfer. Herein, we report that the dilithio reagents **1** react with rhodium ate complex **2**, resulting in the formation of aromatic dilithio rhodacycles **3** (Scheme 2).



Scheme 2. Preparation of rhodium ate complexes **2** and **3a**.

Rhodium catalysts are widely used in organic chemistry.[11] These reactions usually involve Rh^{I}/Rh^{III} processes and five-membered metallacyclic rhodium intermediates. Inspired by these facts, we envisioned that specific Rh^{I} complexes might be oxidized by dilithio reagents.

Dilithio reagents **1** can be easily prepared based on our previous work.[12] Dilithio reagent **1a** (R = Me) was then used as the example to test our proposal. The reaction of 0.25 equivalent of $[\{RhCl(cod)\}_2]$ (cod = cyclooctadiene) with **1a** in the mixed solvent of hexane, diethyl ether, and tetrahydrofuran was complete at room temperature overnight. After recrystallization from hexane and tetrahydrofuran slowly at room temperature in a glove box, the dilithio rhodacycle **3a**, suitable for single-crystal X-ray structural analysis and NMR spectroscopy, could be obtained as a dark red crystalline compound isolated in 65% yield (Scheme 2).

Rhodium ate complexes **2**, the crucial intermediates, were also isolated and characterized. Treatment of **1** with 0.5 equivalent of $[\{RhCl(cod)\}_2]$ in the mixture of hexane, diethyl ether, and tetrahydrofuran at room temperature overnight could provide Rh^{I} ate complexes **2** as dark red solids isolated in good yields (Scheme 2). Single crystals of **2a–c** suitable for single-crystal X-ray structural analysis could be obtained. The intermediate compound **2a** could react further with 1.0 equivalent of **1a**, offering **3a** almost quantitatively as detected by in situ NMR spectroscopy.

Figure 1 shows the single-crystal X-ray structure of **2a** (for the structures of **2b** and **2c**, see Supporting Information). As these rhodium ate complexes **2** have similar structures, herein we only discuss **2a** as an example. There is a Rh/Li double bridge in **2a**, with the two Rh-C(sp^2) bond lengths being 2.069(8) Å and 2.095(7) Å, respectively. The lithium bridge leads to a small C-Rh-C angle 82.9(3)°.

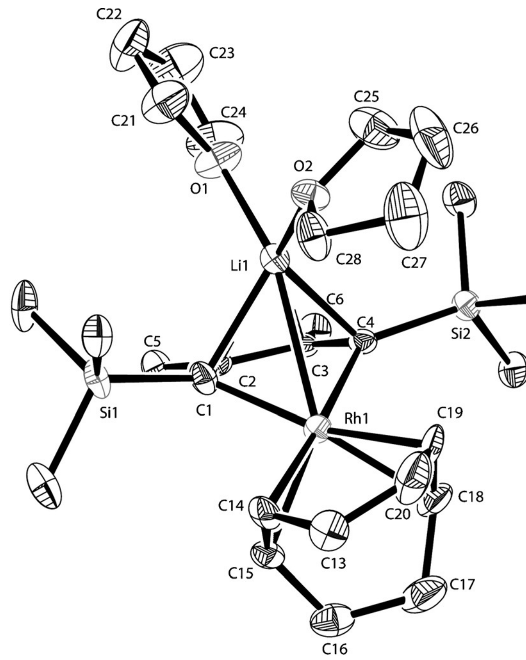


Figure 1. ORTEP drawing of **2a**, thermal ellipsoids set at 30% probability. All H atoms are omitted for clarity.

The molecular structure of **3a** determined by X-ray diffraction analysis is shown in Figure 2.[13] The Rh center is still tetracoordinate, with the cod ligand being replaced by one dilithio **1a**. The Rh/Li double bridge on the butadienyl skeleton remains (Ring A for short) in **3a**. The Rh−C(sp^2) bond lengths in Ring A are 2.057(7) Å and 2.071(6) Å, respectively, similar to those of **2a**. Ring A is almost perpendicular to the five-membered dilithio rhodium ring (Ring B for short). Ring B is planar with a 540.3° (theoretical

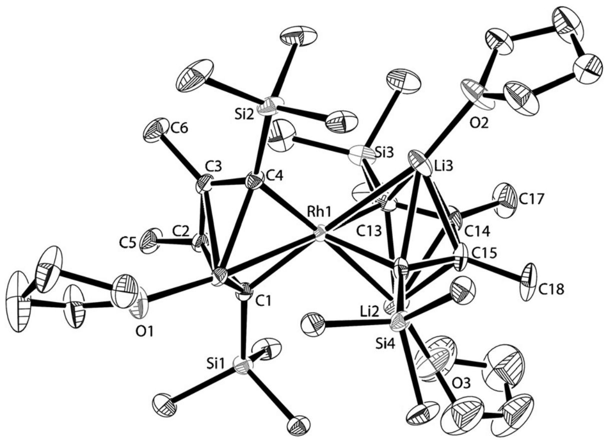


Figure 2. ORTEP drawing of **3a**, thermal ellipsoids set at 30% probability. All H atoms are omitted for clarity.

value, 540°) sum of internal angles (Figure 2). Ring B has two lithium atoms lying above and below it both in an η^5 fashion and each Li atom is coordinated with one THF molecule. The Rh–C bond lengths in Ring B are 2.016(7) Å and 2.017(7) Å, respectively, suggesting classic Rh^{III}–C(sp^2) bonds, not η^2-alkene Rh^{I}–C(sp^2) bonds (usually 2.105–2.195 Å).[14]

The C–C bond lengths in Ring A still show 1,3-diene character with bond alternation (Figure 3). However, in Ring B, the C–C bond lengths are averaged (1.439(10) Å, 1.411(10) Å, 1.424(10) Å, respectively), implying considerable delocalization of π electrons over this rhodacyclic ring. Although the chemistry of metal-containing aromatics has caught much attention and developed rapidly recently,[15–19] such a Rh-containing aromatic metallacycle is unprecedented.

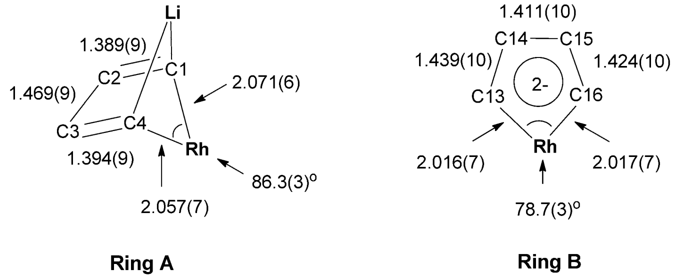


Figure 3. Structural formula and selected bond lengths [Å] of **3a**.

It should be noted that several main-group dilithiometalloles have been synthesized and well characterized recently by a common redox reaction between metal lithium and corresponding metalloles.[15–17] Although our synthetic concept and method are different, in terms of the valence of metal centers in final products, these other results have important reference value. Saito and co-workers reported that, based on the ^{119}Sn Mössbauer spectroscopy, the Sn centers in their dilithiostannoles were Sn^{II}, not Sn^{0} (Figure 4).[15b] These results correspond well with our explanation, in which the dilthio reagents can be regarded as Z-type and non-innocent ligands, thus acting as an electron acceptor (Figure 4).

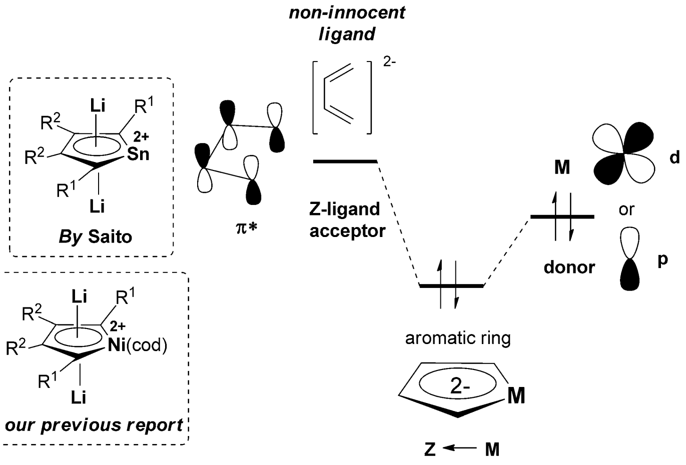
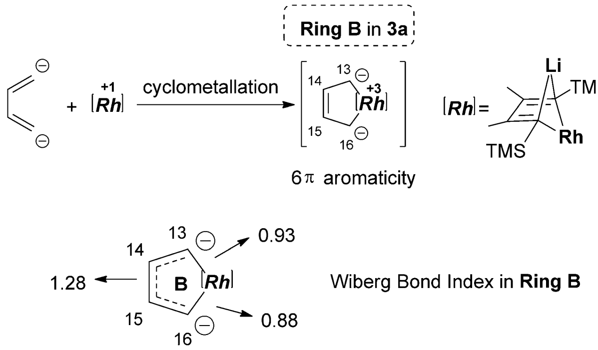


Figure 4. Dianions as Z-type ligands based on the CBC model.



Scheme 3. An explanation of the formation of Ring B.

As shown in Figure 3, the bond lengths of C13–C14 and C15–C16 in **3a** are longer than that of C14–C15. Thus, it is also reasonable to consider that the formation of Ring B was through a cyclometalation process (Scheme 3). In this explanation, Rh^{I} is oxidized to Rh^{III} via cyclometalation by dianions, forming two Rh–C σ bonds. C13 and C16 still remain carbanionic and each offer a p orbital with two electrons. The Rh center offers a vacant d orbital, while C14 and C15 each offer one electron and a p orbital, forming the 6π system together.

The bond index of **3a** has been calculated (Scheme 3). The Wiberg bond indexes of Rh-C13 and Rh-C16 in Ring B are 0.93 and 0.88, respectively, indicating classic Rh–C covalent bonds. As a comparison, the Wiberg bond indexes of Rh-C1 and Rh-C4 in Ring A are 0.66 and 0.65, respectively. The Wiberg bond indexes of C13-C14 and C14-C15 are similar (1.36 and 1.28 respectively). These results correspond well with our cyclometalation hypothesis.

The geometry of Rh in **3a** is tetrahedral, not square-planar expected for Rh^{I}. The tetrahedral structure is the preferred geometry of d^{10} configuration. Thus, **3a** might be also regarded as formal d^{10}-$[Rh^{-I}]^{-}$ species. To avoid this ambiguity, the CBC method is strongly recommended. The dilithio part should be regarded as a Z-type and non-innocent ligand. The extent of electron transfer should be determined by experimental spectroscopy and calculation.

To clarify the valence of the Rh atom in **3a**, an XPS measurement was carried out. The XPS detected the Rh $3d_{5/2}$ binding energy at 308.7 eV, which does not fall in the range for normal Rh^{I} species (307.8–308.5 eV).[20] Even Rh^{I} complexes with strong π-back-bonding ligands (π acid ligands, such as CO and alkenes) are still found in this $3d_{5/2}$ binding-energy range, thus **3a** should not be a Rh^{I} species. The $3d_{5/2}$ binding energy of most typical Rh^{III} species ranges from 308.8–310.5 eV. Based on these results, the Rh atom in **3a** is closer to a Rh^{III} species than Rh^{I} species.

To investigate the electron-transfer process, the charge-decomposition analysis (CDA) and extended charge-decomposition analysis (ECDA) of **3a** were then applied[21] based on its single-crystal structural data (See

Supporting Information for details). Complex **3a** was divided into two fragments, the acceptor with vacant π* orbital (dilthio part, Part A) and the donor (Rh-ate complex part, Part B). From the CDA results, Part A received considerable electron density from Part B ($d{-}b=0.445$). The electron transfer mainly occurred on HOMO−1 to HOMO−5. From the ECDA results, the net transfer of electrons from Part B to Part A is 0.112.

For the ^{13}C NMR spectra of **2a**, its two β carbon atoms (C2 and C3) in the butadienyl skeleton show a doublet at $\delta = 152.9$ ppm (d, $J = 2.1$ Hz), which is an upfield shift relative to those in the starting dilithio reagent **1a** ($\delta = 165.0$ ppm). The chemical shifts of the methyl group show a doublet at $\delta = 25.1$ ppm (d, $J = 2.1$ Hz) arising from to the Rh–C coupling. The other two products (**2b** and **2c**) have similar ^{13}C NMR features.

The ^{13}C NMR spectra of **3a** demonstrated large differences between Ring A and Ring B. The two β carbon atoms of butadienyl skeleton in Ring A show a doublet at $\delta = 127.2$ ppm (d, $J = 2.4$ Hz), a large upfield shift relative to those in **2a** ($\delta = 152.9$ ppm). The β carbon atoms of butadienyl skeleton in Ring B give rise to a singlet at $\delta = 134.6$ ppm without Rh–C coupling. The methyl group in Ring A also show doublets at $\delta = 20.3$ ppm (d, $J = 5.9$ Hz) and $\delta = 20.7$ ppm (d, $J = 4.1$ Hz), whereas those in Ring B give rise to a singlet at $\delta = 24.8$ ppm. In addition, there are three different chemical shifts for the TMS group ($\delta = 3.6$ ppm, 4.4 ppm and 4.9 ppm), indicating that **3a** is not perfectly symmetrical in solution.

To further investigate the products, ^{7}Li NMR spectroscopy was carried out (Table 1). ^{7}Li NMR was performed in [D$_8$]THF solvent with 0.1 M LiCl in [D$_8$]THF as the external standard. The ^{7}Li NMR chemical shifts attributable to rhodium ate complexes **2** are all small negative values, however still in the range of normal organolithium compounds. The ^{7}Li signals of **3a** are more negative. This low-frequency resonance of Ring A and Ring B should be evidently caused by the strong shielding effect of the diatropic ring current. The chemical shift of Li in Ring A is less negative ($\delta = -4.13$ ppm) than that in Ring B ($\delta = -6.27$ ppm), indicating the more aromatic nature of Ring B.

Table 1: ^{7} Li NMR chemical shifts of rhodium ate complexes.[a]

	2a	**2b**	**2c**	**3a**	
				Ring A	Ring B
δ ^{7}Li NMR	−2.14	−2.03	−2.35	−4.13	−6.27

[a] These NMR data were recorded in [D$_8$]THF with 0.1 M LiCl in [D$_8$]THF as the external standard.

For a better understanding of the structural features of dilithio rhodacycle **3a**, density functional theory (DFT) calculations were carried out by Gaussian 09.[22] Geometric structure of **3a** was optimized at the B3PW91 level.[23] The 6-31G(d) basis set[24] was used for Si, C, H, and Li atoms. The LanL2DZ basis set[25] was used for the Rh atom (see Supporting Information). In the optimized structure, all the C−C and C−Rh bond lengths were consistent with the X-ray structure. The ^{7}Li NMR chemical shift of **3a** was then calculated based on the optimized structure using Gauge-Independent Atomic Orbital (GIAO) computations.[26] The calculated chemical shift of Li atoms in Ring A and Ring B ($\delta = -4.6$ ppm and $\delta = -7.8$ ppm respectively) agree well with the experimental values ($\delta = -4.1$ ppm and $\delta = -6.3$ ppm). The nucleus-independent chemical shift (NICS) of **3a** was also calculated.[27] The considerably negative NICS(1) value (−13.8 ppm) of Ring B strongly suggested that it was aromatic, while the relatively small negative NICS(1) value (−5.7 ppm) in Ring A indicated non-negligible aromaticity.

In summary, two novel types of rhodium ate complexes **2** and **3a** have been successfully synthesized and characterized by X-ray diffraction analysis and NMR spectroscopy. The XPS data and the CDA/ECDA results suggested the increasing valence of the Rh center. The notable differences in the ^{13}C NMR spectra between rhodium bridge Ring A and rhodium cycle Ring B in **3a** indicated different electronic structures of the two rings. ^{7}Li NMR spectra of **3a** and theoretical calculations revealed a considerable aromatic character. All these results showed that dianions with suitable π-conjugation could also be used as non-innocent ligands, in which the dianions gain extra electrons. Other examples and new possibilities using this strategy in synthetic chemistry are currently under investigation.

Keywords: dianions · lithium · metallacycles · redox reaction · rhodium

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