

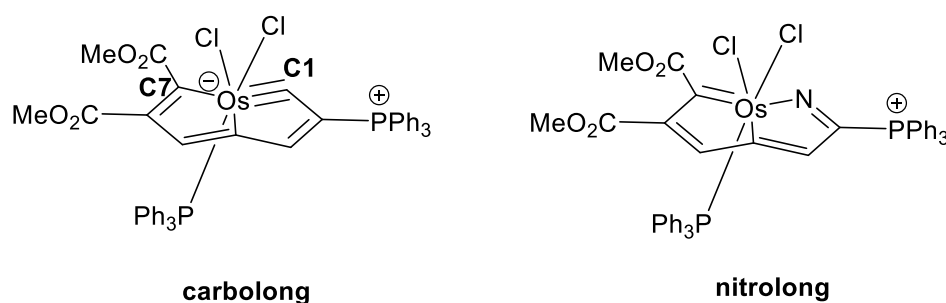
Properties of nitrolong: Geometric and Electronic Structures, Redox Behavior, and Aromaticity

Yumiao Ma^a

a. BSJ Institute, Beijing, People's Republic of China, 100084. ymma@bsj-institute.top

In recent years, Nailong (an anime character) has garnered significant attention. Within the realm of chemistry, a class of N-substituted analogs of carbolong compounds, termed nitrolong, can be envisioned. The first N-substituted carbolong compound was reported by Xia Haiping in 2023, synthesized using azo compounds (Chem. Commun., 2023, 59, 4173 – 4176). In this structure, two carbon atoms in the backbone were replaced with nitrogen atoms.

However, this substitution pattern is insufficient to define the compound as nitrolong. In this work, nitrolong is defined as a compound in which the characteristic C–Os triple bond of carbolong is replaced by an N–Os bond. Compared to the neutral carbolong, nitrolong carries a positive charge.



Scheme 1. Structures of carbolong and nitrolong

This study addresses the following key questions:

1. What is the bond order of the Os–N bond in nitrolong molecules?
2. What are the redox behaviors of carbolong and nitrolong molecules?
3. How does the aromaticity of carbolong and nitrolong molecules change upon single- and double-electron reduction?

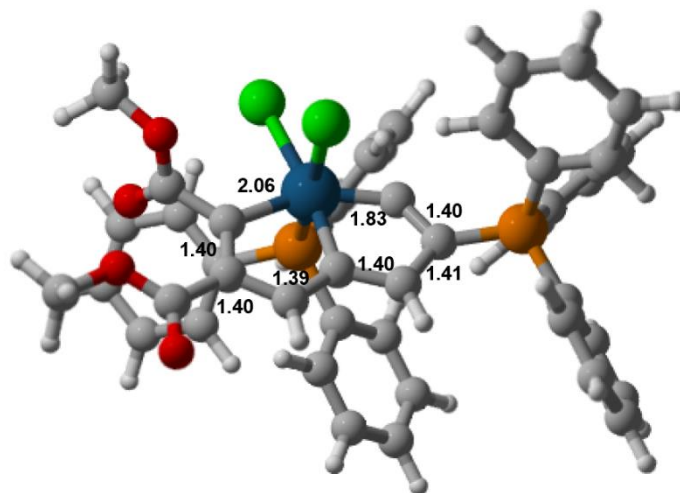
Geometric Structure and Bonding

Both carbolong and nitrolong exhibit singlet ground states. At the PBE0-D3BJ/def2-TZVP/SMD(MeCN)//PBE0-D3BJ/def2-SVP/SMD(MeCN) level of theory, their triplet states are higher in free energy than the ground states by 31.1 and 20.6 kcal/mol, respectively.

The ground-state geometry of carbolong demonstrates significant bond-length equalization, with all C–C bonds in the ring being approximately 1.40 Å. The C1–Os bond is notably short

(1.83 Å), while the C7–Os bond is longer (2.06 Å), indicating substantial differences in bond order. Indeed, the Fuzzy bond orders of the C–Os bonds are 1.13 and 1.87, respectively.

(a)



(b)

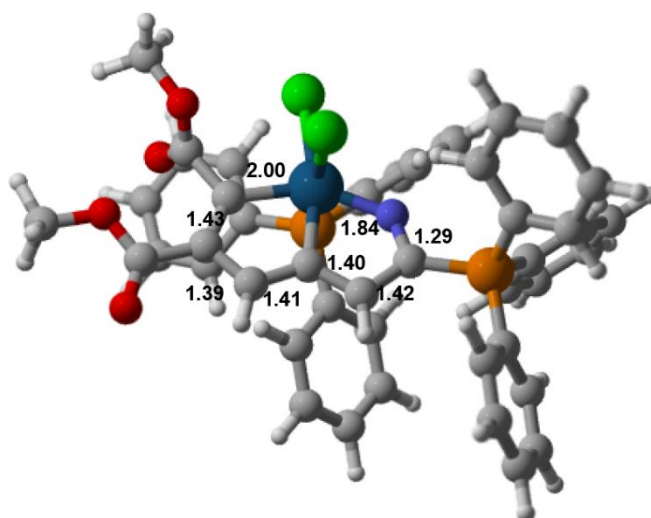


Figure 1. Molecular structures of (a) carbolong and (b) nitrolong

Upon introducing the nitrogen atom, conjugation is partially disrupted, as evidenced by slightly reduced bond-length equalization within the ring. The N–Os bond length is 1.84 Å, which, given nitrogen's smaller atomic radius, suggests a lower bond order compared to the C–Os triple bond in carbolong. Indeed, the Fuzzy bond order of N–Os decreases to 1.69. Conversely, the remaining C–Os bond shortens to 2.00 Å, with its bond order increasing to 1.26. Localized molecular orbitals indicate that in carbolong, the C1–Os bond consists of one σ -bond and two orthogonal π -bonds, forming a triple bond. In nitrolong, however, the

localized molecular orbitals reveal only a three-center C–Os–N interaction. Considering the changes in bond length, it is evident that the N–Os bond in nitrolong cannot be described as a triple bond. Instead, the bonding is better represented by two equivalent resonance structures.

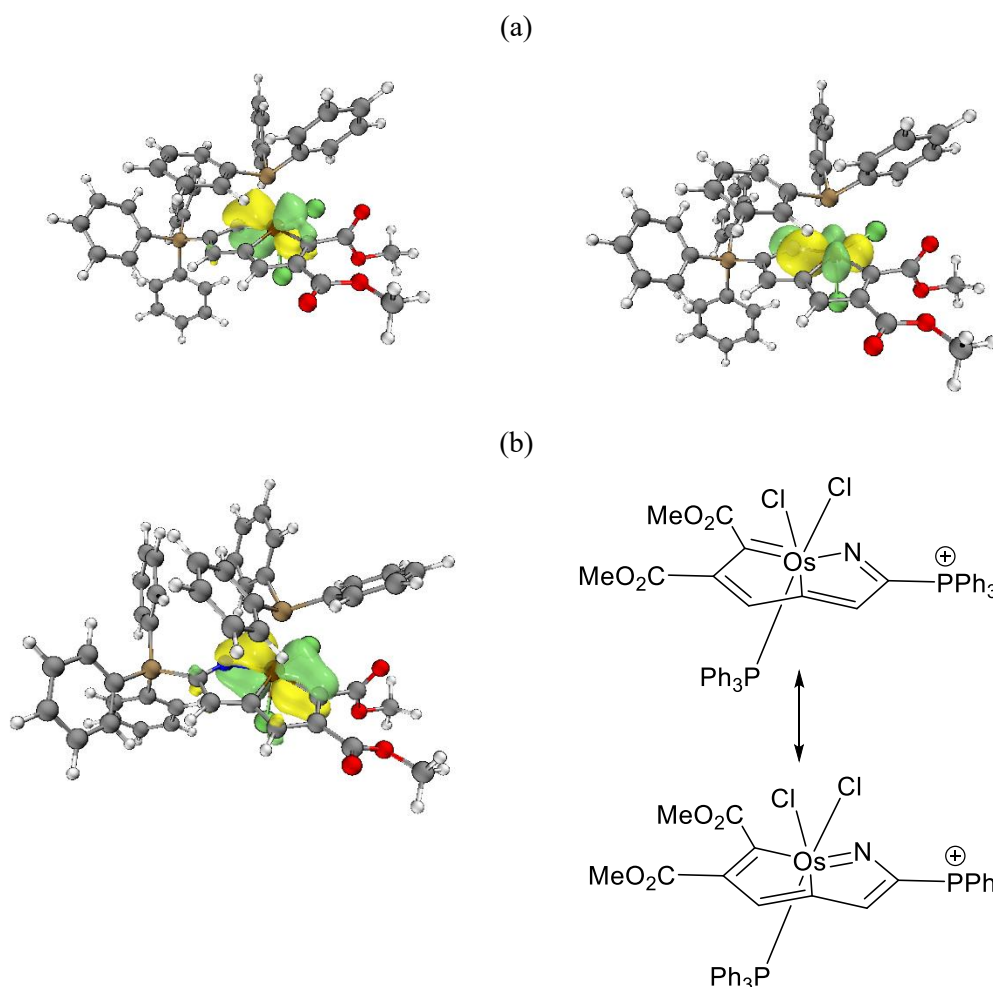


Figure 2. Localized orbitals related to the N–Os or C–Os π -bonds for carbolong (a) and nitrolong (b)

Redox Behavior

carbolong and its analogs constitute a $4n$ electron Craig aromatic system. This raises an intriguing question: if they are doubly reduced, would they become $4n+2$ Hückel aromatic or Craig antiaromatic? This requires an understanding of their redox behavior. carbolong is challenging to reduce in acetonitrile. Its calculated single- and double-electron reduction potentials are -1.18 V and -1.54 V, respectively. In contrast, nitrolong, carrying a positive charge, is far easier to reduce, with single- and double-electron reduction potentials of -0.06 V and 0.01 V (relative to NHE). This indicates that nitrolong is readily reduced, with the

addition of two electrons being particularly favorable. Thus, nitrolong serves as an ideal platform for investigating the aromaticity of reduced carbolong analogs. The ground-state spin multiplicities of the doubly reduced states differ between carbolong and nitrolong. The doubly reduced ground state of carbolong is a closed-shell singlet, with its free energy 8.5 kcal/mol lower than the triplet state. In contrast, the doubly reduced ground state of nitrolong is a triplet, nearly degenerate with the open-shell singlet (1.8 kcal/mol). Figure 3 illustrates the spin density distributions of carbolong and nitrolong in their reduced states.

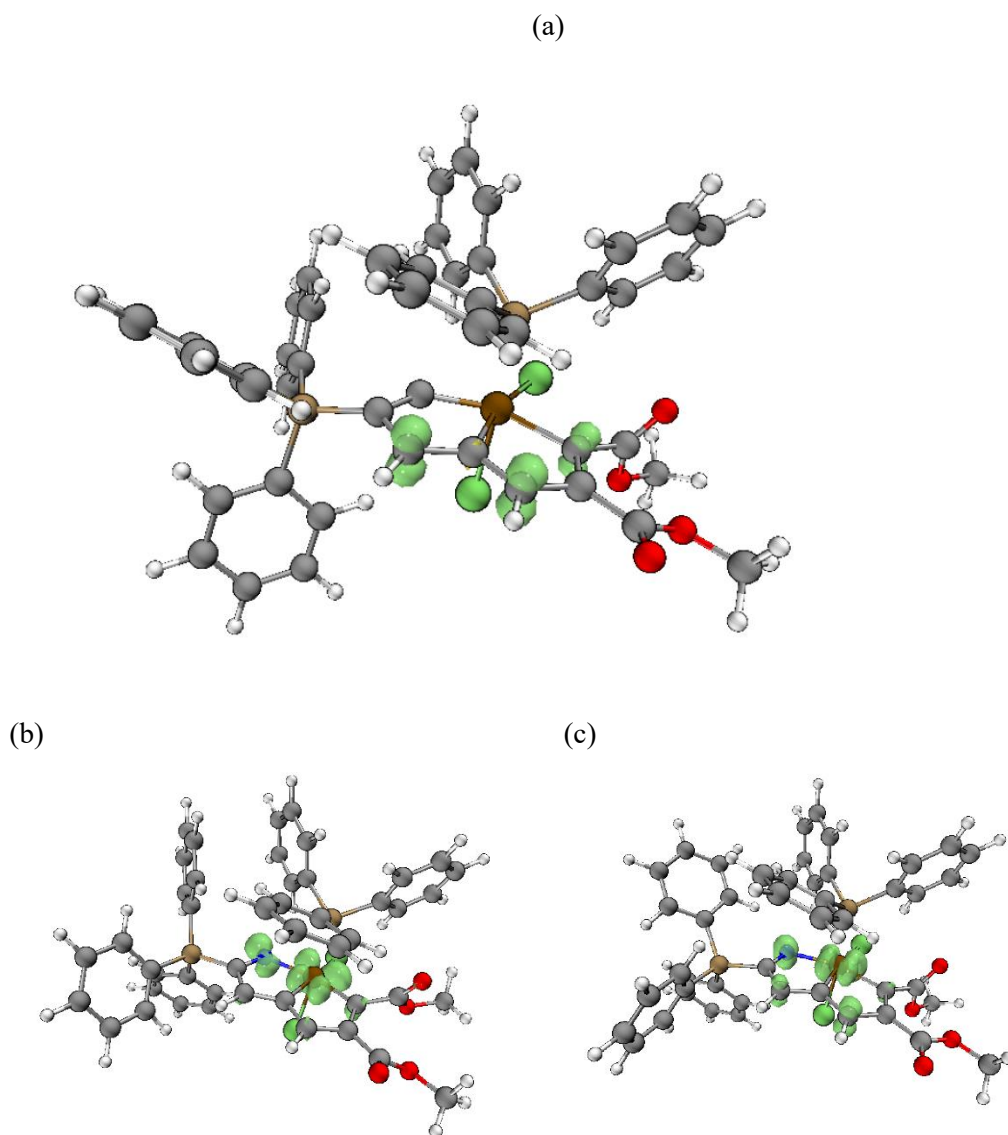


Figure 3. Spin densities of carbolong and nitrolong reduced states (a) carbolong (single-electron reduced) (b) nitrolong (single-electron reduced) (c) nitrolong (double-electron reduced)

In both the single- and double-electron reduced states, the C1–Os bond length in carbolong remains nearly unchanged (1.84 Å). However, the C7–Os bond elongates to 2.12 Å (single-electron reduced) and 2.19 Å (double-electron reduced), with both rings exhibiting substantial

bond-length alternation. Spin density analysis reveals that the electrons occupy the π^* orbitals of the planar conjugated system. The geometry of the ester group plays a critical role: due to steric repulsion from adjacent ester groups, the ester on C7 adopts a perpendicular conformation, stabilizing C7 as an enolate anion in the doubly reduced state. This results in the elongated C7–Os bond and stabilizes the singlet ground state. In contrast, nitrolong undergoes concurrent elongation of the C–Os and N–Os bonds upon reduction, with bond lengths reaching 1.96 Å and 2.05 Å in the single- and double-electron reduced states, respectively. This is consistent with the spin density distribution, which shows that the additional electrons in nitrolong are localized on the N–Os bond and the Os d-orbitals, likely due to nitrogen's higher electronegativity.

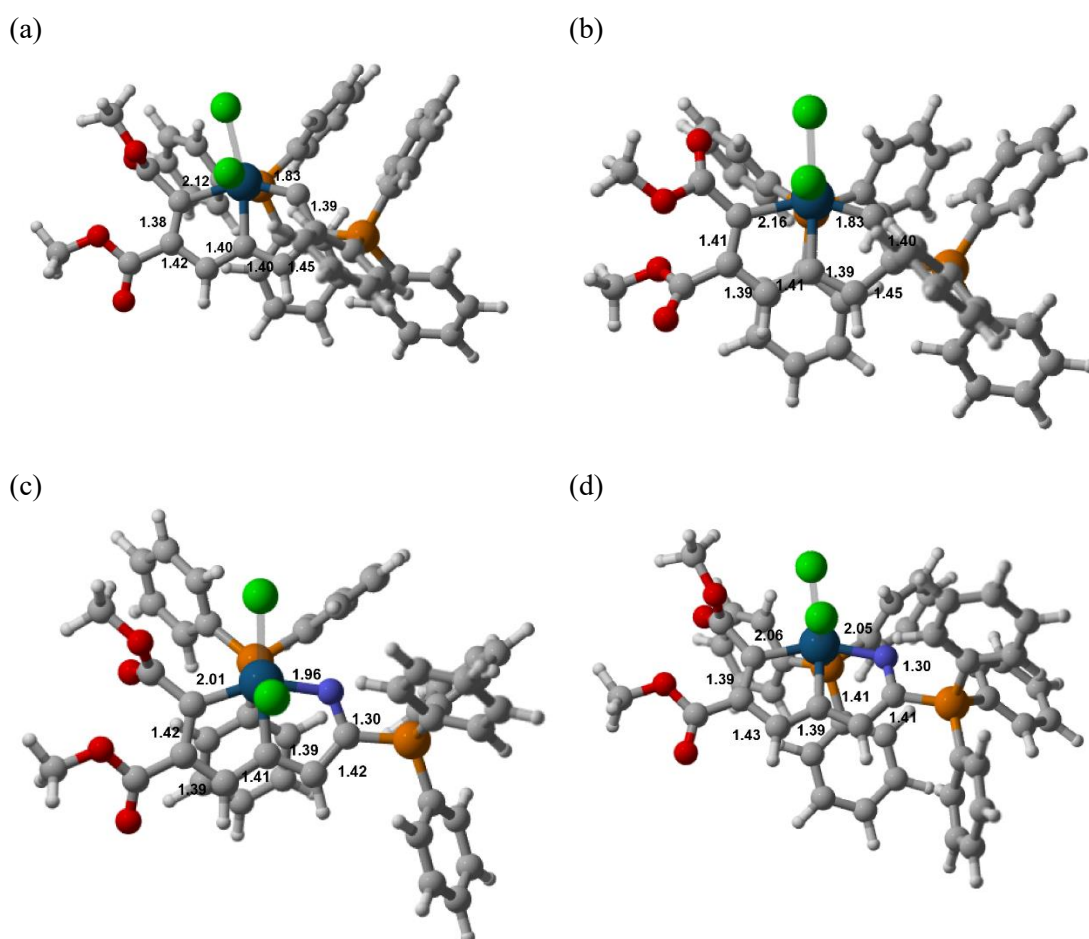


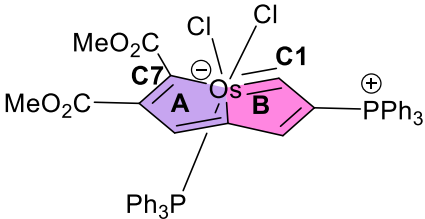
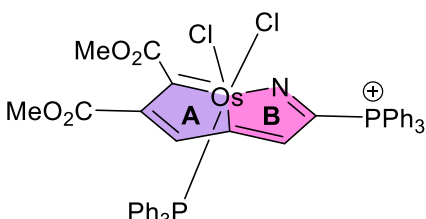
Figure 4. Geometries of reduced states (a) carbolong (single-electron reduced) (b) carbolong (double-electron reduced, singlet) (c) nitrolong (single-electron reduced) (d) nitrolong (double-electron reduced, triplet)

Aromaticity

For simplicity, aromaticity is assessed using the Nucleus-Independent Chemical Shift (NICS). The ground state of carbolong exhibits Craig aromaticity, while its triplet state is either non-

aromatic or weakly antiaromatic, consistent with the pronounced bond-length alternation observed in its geometry. As electrons occupy the π^* orbitals upon reduction, carbolong becomes non-aromatic in both the single- and double-electron reduced states. nitrolong, however, behaves differently. In its triplet state, the electronic excitation is localized on the orthogonal $\pi(\text{Os}-\text{N})$ bond (as evident from the spin density in Figure 4), allowing it to retain aromaticity. Because the added electrons also occupy the $\pi^*(\text{Os}-\text{N})$ orbital, both the single-electron reduced state and the singlet double-electron reduced state of nitrolong remain aromatic. The doubly reduced triplet state of nitrolong is the sole member of this series to lose aromaticity. In this state, the $\pi^*(\text{Os}-\text{N})$ orbital is fully occupied, and subsequent excitation to the triplet state forces electrons into the extended conjugated system, thereby disrupting aromaticity.

Table 1. NICS(0) values of carbolong and nitrolong in various states

	carbolong		nitrolong	
	Ring A	Ring B	Ring A	Ring B
Neutral (S0)	-5.7	-10.0	-10.1	-11.2
Neutral (T1)	+1.7	+5.9	-5.6	-4.2
1e-reduced	+1.8	-2.1	-4.7	-9.2
2e-reduced (S)	+3.5	+3.4	-4.3	-3.6
2e-reduced (T)	+1.4	-2.3	+0.3	+2.8

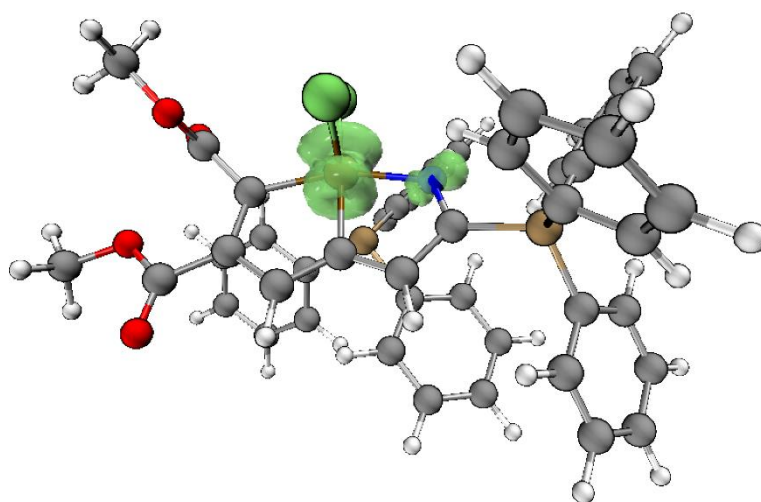


Figure 5. Spin density of nitrolong in the triplet state