Three-membered unsaturated rings have been widely utilized in organic synthesis due to their inherent highly strained structures. Although much research has been applied to ring-expansion reactions of such strained ring systems, pathways other than [3+2] cycloadditions have rarely been observed in their reactions with alkynes, and to date, no [3+1] cycloaditions of isolated three-membered unsaturated rings with alkynes have been reported. Here we demonstrate an unprecedented [3+1] cycloaddition in which a fused metalla-azirine is used as a template to generate a series of planar CCCCX-type (X = N, O, S) pentadentate carbolong complexes 3–6. A series of substituted alkynes was tested for further exploration of the scope and mechanism for the [3+1] cycloaddition reactions. Complexes 3–6 represent rare examples of planar pentadentate complexes that assemble four π-conjugated fused rings by one bridgehead atom. These novel complexes are thermally stable in air and absorb ultraviolet, visible, and near-infrared light, and thus are potentially applicable in photoelectric devices and pharmaceuticals.

Keywords: [3+1] cycloaddition reaction, DFT calculations, metallacycles, strained rings, planar pentadentate chelates, carbolong complexes
**Introduction**

Ring-expansion reactions of compounds with small rings are one of the fundamental transformations in organic synthesis. Among the various strained rings, three-membered unsaturated rings are common and can serve as three-atom synthons in a variety of addition reactions taking advantage of their high reactivity, which is derived from ring strain. With the exception of certain synthetic equivalents or analogues, however, previously reported addition reactions of alkynes to these three-membered unsaturated rings were seen as ring-expansion transformations, typically following a [3+2] cycloaddition pathway. For example, highly strained cyclopropenes can be used in [3+2] cycloaddition reactions with alkynes to form five-membered rings (Figure 1a, left). Analogous reactions have also been reported in low-valent metal-mediated oxidative cyclometalation of alkynes, which can yield metalla-cyclopentadienes via the metalla-cyclopropenes, which can yield metallacyclopentadienes. As another paradigm of strained azacyclic rings, 2H-azirines have successfully undergone diverse ring-expansion reactions by different bond cleavage modes, providing expedient approaches to five-membered N-heterocyclic skeletons (Figure 1b, left). In sharp contrast, there appear to be no reports on the reactions of analogous azametallacycles—that is, metalla-azirines—with alkynes. In fact, reactivities of metalla-azirines have rarely been explored.

Polydentate complexes are among the most widely studied complexes because of their fascinating structures and various functions. Although an expanding variety of complexes with planar bidentate, tridentate, or tetradentate ligands has attracted tremendous research interest, the synthesis of planar high-coordination complexes, such as pentadentate complexes, has proven to be very difficult to achieve. The coordinating atoms in those reported polydentate complexes are primarily drawn from a range of donor heteroatoms including N, O, P, and S. To date, the synthesis of complexes with carbons as the sole principal sites of a pentadentate ligand is very rare, probably owing to their inaccessible and atypical geometries.

Recently, we have developed a series of unique carborelated complexes, which are metal bridgehead polycyclic frameworks featuring a long carbon chain (>7 C) coordinated to a metal atom via at least three metal–carbon bonds. Herein, we report the first [3+1] cycloadditions of metalla-azirines with alkynes; therefore, an azametallacyclobutene skeleton can be generated in congested metallacyclic systems, leading to the formation of remarkable CCCCX-type (X = N, O, S) pentadentate carbolong complexes, in which all of the five coordinated atoms of the pentadentate ligands lie in an equatorial plane.

**Results and Discussion**

Osmapentalyne was employed as a precursor in the synthesis of a desired metalla-azirine. Treatment of 1 with sodium azide (NaN₃) in dichloromethane (DCM) at room temperature led to the formation of complex 2, which was isolated as a green solid in 65% yield (Figure 2). Crystals of 2 suitable for X-ray crystallographic analysis were obtained from a saturated solution of 2 in DCM at room temperature.

The X-ray data (Figure 2b) show that the three-membered metalla-azirine moiety is fused to the bicyclic framework, with the osmium atom adopting a pentagonal bipyramidal coordination geometry. The Os–N distance of 2.424(7) Å in 2 is within the range of 1.636–2.544 Å for Os–N single bond distances. The three Os–C bond distances in 2 are comparable to those in reported osmapentalenes, and the osmapentalene ring in 2 has C–C bond lengths that are invariably intermediate between double and single bonds. The strained metalla-azirine ring is coplanar with the five-membered rings, and this is reflected by the very small mean deviation of 0.005 Å from the least-squares plane. Probably due to the stabilization of the aromatic osmapentalene framework, complex 2 is a highly stable solid that can persist for several months when exposed to air at room temperature or even when heated to 80 °C in air for 3 h. The carboazidation of alkynes by azides, for example trimethylsilyl azide, has been extensively explored and reported to afford 1-azidoalkenes, which can be subsequently converted to 2H-azirines. Such reactions have not yet been achieved in metal carbyne triple-bond systems. Very recently, we constrained transition-metal carbony units into a tricyclic ring system and realized the first [3+2] cycloadditions of a late...
transition-metal carbyne with organic azides. Here, the formation of the fused metalla-azirine (2) from metallapentalene (1) is the first synthesis of a metalla-azirine by [2+1] cycloaddition reaction of a metal carbyne with an azide.

With the strained metalla-azirine precursor 2 in hand, we proceeded to investigate its reactivity with alkynes. As shown in Figure 2a, the reaction of 2 with terminal alkynes containing carboxyl or ester groups in the presence of AgBF₄ at room temperature furnished the unexpected tetracyclic complex (3) in good yields. The unsymmetrical molecular structure of 3a was elucidated by single-crystal X-ray crystallographic analysis. It turns out that the metalla-azirine moiety of 2 has been added a carbon atom from an alkynyl to form the four-membered pentalene unit, but falls within the range of Os–C single and double bonds (1.894–2.162 Å), and could be attributed to the strain induced by the four-membered ring. Close inspection of the C–C–N–C–O bond distances in the tetracyclic framework of 3a suggests bond length equalization within the fused rings. The four fused metalloacycles are nearly coplanar, as indicated by the mean deviation of 0.0630 Å from the least-squares plane through Os1, O1, N1, and C10. The corresponding bond lengths, together with the planarity of the metallacycles, indicate extensive π-electron delocalization over the 13 atoms of the tetracyclic skeleton in 3a. These facts suggest that 3a–A is the dominant resonance structure of four possible resonance structures (Figure 3).

To shed light on the mechanism of the unusual [3+1] cycloadditions of the fused metalla-azirine 2 with alkynes, a number of substituted alkynes were tested under the same reaction conditions. In situ NMR experiments suggest that complex 2 is unreactive toward internal alkynes (such as dimethyl acetylenedicarboxylate and acetylenedicarboxylic acid), alkyl-substituted terminal alkynes (such as cyclopropylacetylene and 1-pentyne), and other substituted terminal alkynes (such

**Figure 2** | (a) Reactions of osmapentalyne 1 with sodium azide and metalla-azirine 2 with alkynes. (b) and (c) Solid-state structures of 2 (b) and 3a’ (the counterion is Cl) (c) by X-ray crystallography with 50% probability ellipsoids. Solvent molecules, the counterion, and phenyl groups in PPh₃ are omitted for clarity. Selected experimental bond distances (Å) and angles (deg) for 2: Os(1)–C(1) 2.092(8), Os(1)–C(4) 2.078(8), Os(1)–C(7) 2.011(8), Os(1)–N(1) 2.424(7), C(1)–C(2) 1.460(12), C(2)–C(3) 1.371(12), C(3)–C(4) 1.420(12), C(4)–C(5) 1.355(12), C(5)–C(6) 1.416(13), C(6)–C(7) 1.407(12), C(1)–N(1) 1.207(7), Os(1)–C(1)–C(2) 119.2(6), C(1)–Os(1)–N(1) 29.9(3), C(1)–N(1)–Os(1) 59.7(5), N(1)–C(1)–Os(1) 90.5(6). For 3a: Os(1)–C(1) 2.063(4), Os(1)–C(4) 2.078(5), Os(1)–C(7) 2.088(4), Os(1)–Os(1) 2.102(4), Os(1)–O(1) 2.129(3), C(1)–C(2) 1.455(6), C(2)–C(3) 1.378(6), C(3)–C(4) 1.425(6), C(4)–C(5) 1.374(7), C(5)–C(6) 1.424(6), C(6)–C(7) 1.385(6), C(1)–N(1) 1.324(6), C(8)–N(1) 1.404(6), C(8)–N(1) 1.333(6), C(9)–C(10) 1.458(6), C(10)–O(1) 1.309(6); Os(1)–C(1)–N(1) 110.1(3), C(1)–N(1)–C(8) 89.9(3), N(1)–C(8)–Os(1) 104.7(3), C(8)–Os(1)–C(1) 55.16(17).
as ethynyltrimethylsilane and 3-bromopropyne). The reaction of complex 2 with phenylacetylene derivatives (such as phenylacetylene and 4-nitrophenylacetylene) led to mixtures without the target products. Furthermore, when the reaction of complex 2 with methyl 3-deuteriopropiolate instead of methyl propiolate was performed, the deuterated product 3b was achieved (see Supporting Information Figure S13 for NMR details).

We inferred that [3+1] cycloadditions of metalla-azirine with terminal alkynes containing carboxyl or ester groups might be highly favored by the formation of a five-membered O-heterocycle, owing to an important stabilization contribution from the tethered ring structure. Accordingly, we investigated whether terminal alkynes with other heteroatom-containing substituents were reactive. As shown in Figure 2a, similar [3+1] cyclo-addition reactions took place with 2-ethylthiophene, 2-ethylpyridine, and 2-ethylaminiline. The desired tetracyclic complexes (4, 5, and 6, respectively) were isolated in high yields and identified by NMR and elemental analysis. It is noteworthy that complex 4 represents the first example of a pentadentate CCCCX complex.

On the basis of these experimental observations, we propose the following mechanism for the reaction of 2 with alkynes, using the formation of 5 as an example (Figure 4). The reaction of 2 with a terminal alkyne in the presence of a silver salt may initially generate the π-alkyne complex (A). Subsequent isomerization of mononuclear \( \eta^2 \)-complex A could generate the metal-vinylidene \( \eta^1 \)-complex (B), which is kinetically favorable with a small barrier of 8.8 kcal/mol. Nucleophilic addition of the nitrogen atom in the metalla-azirine ring to the \( \alpha \)-carbon atom of the metal-vinylidene would lead to the formation of a four-membered aza-metallacyclobutene. At this point, the coordination geometry at the metal allows the pyridyl to coordinate with the metal center, affording the tethered five-membered metallacycle that is an important contributor to the final tetracyclic complex (5). Our density functional theory (DFT) calculations support the mechanisms and reveal that the formal [3+1] cycloaddition process from B to 5 is indeed exergonic.

These CCCCX (X = N, O, S) complexes exhibit high thermal stability both in solution and in the solid state. For example, solid 3a can survive for several months when exposed to air at room temperature, or even when heated to 130 °C in air for more than 3 h. The stability of

![Figure 4](https://example.com/figure4.png)  
*Figure 4 | Gibbs free-energy profile for the DFT-calculated formation mechanism of complex 5 at 298 K. The computed free energies are in kcal/mol.*

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carbolong compounds probably originates not only from the pentadentate ligands with CCCX frameworks, but also chelating effects and steric protection (such as PPh3 groups). The large π-systems might possess some novel properties, therefore we examined the ultraviolet-visible (UV-Vis) absorption spectra of these unique polydentate chelates 3-6 (at a concentration of 1 × 10−4 M). As shown in Figure 5, the metal-bridgehead tetracyclic complexes 3-6 show remarkably broad absorption from the UV to the visible and up to 850 nm (the near-infrared region). For instance, the absorption maximum of the tetracyclic complex 6 (λmax = 703 nm) is more redshifted than 3-5, probably due to its better conjugation. Time-dependent DFT calculations at the B3LYP/6-31G(d) level were used to describe the absorption spectra of 3-6. The absorption maximum of tetracyclic complexes 3-6 can be assigned to the HOMO→LUMO electronic transitions (see Supporting Information Table S1 for details).

Conclusion

In summary, we report several formal [3+1] cycloadditions of metallo-azirine with terminal alkynes. Substituents containing heteroatoms are crucial for the success of these reactions, since they enable the formation of fused tetracyclic systems and stabilize the resulting four-membered ring. This method is operationally straightforward and provides a distinct advance toward the production of unusual CCCX-type (X = N, O, S) carbolong complexes, in which all of the five coordinating atoms lie in the equatorial plane. Collectively, our findings offer a valuable supplement to the construction of planar pentadentate chelates. Studies on the delivery of these strained carbolong complexes into other structurally sophisticated frameworks are the subject of ongoing work.

Supporting Information

Supporting Information is available.

Conflict of Interest

The authors declare no competing interests.

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