Aromaticity is one of the most fundamental and interesting topics in organic chemistry. Traditional π-aromaticity is characterized by π-electron delocalization in closed circuits of unsaturated compounds and σ-aromaticity is characterized by the delocalization contributed by σ-electrons, which was first proposed by Dewar to explain the abnormal magnetic behaviour of cyclopropane. Subsequently, other systems, such as hydrogen clusters, inorganic rings, metal clusters and metallacycloprenes, featuring delocalized σ-conjugation, were suggested to have σ-aromatic character. The terms π- and σ-aromaticity are used to describe the electron delocalization of many cyclic compounds. Both π- and σ-aromaticity endow molecules with aromatic stabilization, leading to products with lower energies. Therefore, aromaticity-driven reactions play a crucial role in synthetic chemistry. Currently, π-aromaticity-driven strategies are well known to guide the synthesis of aromatic compounds, but reactions induced by σ-aromaticity have seldom been reported.

The synthesis and transformation of small heterocycles are valuable in synthetic chemistry. The small metallacycles, metallacyclobutadienes and metallacycloprenes, are intriguing species because of their rich reactivity and catalytic applications. Metallacyclobutadienes are well known in alkyne metathesis and polymer synthesis, while metallacycloprenes play important roles in organometallic chemistry, such as ring-expansion polymerization for macracyclic polyenes, selective coupling and activation of C–H bonds. Thus, the synthesis, reactivity and structural properties of these metallacycles have attracted continuous attention. In general, small metallacycles tend to undergo ring expansion by insertion of unsaturated species into the M–C bond or to participate in rearrangement/addition processes, resulting in opening of the metallacycles. However, the ring-contraction reaction of small metallacycles is challenging due to ring-strain effects, especially in the smallest four-to-three ring-contraction reaction. Considerable effort has been devoted to studying such ring-contraction reactions, such as the migration process in metallacyclobutanes and the conversion of metallacyclobutanes to several metal–allene complexes. However, ring contraction of metallacyclobutadienes was proposed as a key step only for the formation of metallacycloprenes via reactions of metal carbynes with alkenes/phosphaalkynes.
Experimental evidence for the ring contraction of metallacyclobutadienes remains sparse.

Here we report an aromaticity relay strategy to realize the structurally defined ring contraction of metallacyclobutadiene to metallacyclopentene (Fig. 1). Combined experimental and computational studies indicate that the transformation occurs via two consecutive steps along a ring opening–reclosing pathway and involves versatile aromaticity switches in the metallacycles. Initially, the acid-promoted release of the π-antiaromaticity of the osmacyclobutadiene moiety afforded a vinlycarbene fragment. Subsequently, the unusual generation of a strained three-membered ring from vinlycarbene occurred and was found to be driven by the σ-aromaticity of the osmacyclopentene. This aromaticity relay provides driving forces that lead to transformations inaccessible by other methods.

**Results and discussion**

**Synthesis and characterization of 1, 2a–2c and 3a–3c**

We previously developed a series of aromatic metal bridgehead polycyclic frameworks with a triphenylphosphonium substituent attached to the metallacycle. The bulky triphenylphosphonium group stabilizes the metallacyclic skeletons but may reduce the reactivity due to its steric and electron-withdrawing properties. Accordingly, we designed and synthesized an osmapentalyne (1) with a chloride substituent instead of triphenylphosphonium at C2 through the treatment of OsCl2(PPh3)2 with a multithiyl (L1) in the presence of excess tetrabutylammonium chloride. A plausible mechanism for the formation of compound 1 is presented in Supplementary Scheme 1. The structure of 1 was identified by NMR spectroscopy and high-resolution mass spectrometry. When osmapentalyne 1 was treated with different terminal alkynes, including p-toluenesulfonylacetylene, methyl propiolate and propiolic acid, all bearing electron-deficient groups, the [2 + 2] cycloaddition reactions occurred within 5 min, affording osmacyclobutadienes 2a–2c in high yields (>90%) (Fig. 2a). The driving force for this reaction was attributed to the release of the large ring strain caused by extreme distortion of the M=C=C carbonyl carbon angle in the five-membered ring of osmapentalyne. Similar reactions have been investigated previously.

The structure of complex 2a was confirmed by single-crystal X-ray diffraction analysis. As shown in Fig. 2b, complex 2a has a planar metallocyclic structure, as reflected by the mean deviation from the least-squares plane (0.022 Å) through Os1 and C1–C9. In the four-membered ring (4MR) of 2a, the bond lengths of Os1–C7 (2.064 Å), C7–C8 (1.425 Å), C8–C9 (1.335 Å) and Os1–C9 (2.218 Å) show a notable bond alternation (Fig. 2c). The Wiberg bond index of Os1–C8 is calculated to be 0.02, indicating a negligible interaction (Supplementary Fig. 2). The structure of complex 2a was further supported by NMR spectroscopy. In the 1H NMR spectrum, the singlet signal attributed to C9H at δ = 13.29 ppm was assigned to OsCH. Notably, the signal attributed to C9H of metallacyclobutadiene 2a was observed at δ = 5.41 ppm, showing a remarkable upfield shift compared with those of aromatic metallacycles. In the 13C(1H) NMR spectrum, the characteristic signal of C7 in 2a was observed at δ = 173.3 ppm, shifting 136.7 ppm compared with the signal of C7 in complex 2 (310.0 ppm), revealing the conversion from metal carbonyl to metal carbene. The main NMR chemical shifts (δ) of 1 and 2a are shown in Fig. 2d. The [2 + 2] cycloaddition reaction of metal carbynes with alkynes has been used to synthesize metallacyclobutadienes containing, for example, tantalum, molybdenum, tungsten and rhenium. In contrast, this method has rarely been used for the synthesis of metallacyclobutadienes containing late transition metals, the reactivity of which has rarely been studied. With osmacyclobutadienes 2a–2c in hand, we investigated their chemical reactions.

Complexes 2a–2c were treated with 10 equiv. of CF3COOH in CH2Cl2 at r.t. for 3 h, resulting in reddish-brown complexes 3a–3c in isolated yields of 40–60% (Fig. 2a). The structure of 3a was confirmed by single-crystal X-ray diffraction. As shown in Fig. 2b, the metal was shared by the propene and pentalene rings in 3a. Similar to that in 2a, ring contraction involves the cleavage of Os1–C9 and the formation of Os1–C8. The ten atoms (Os1 and C1–C9) in 3a are almost coplanar, and the mean deviation from the least-squares plane is only 0.025 Å. The Os1–C7 distance (2.008 Å) of 3a is shorter than the Os1–C7 distance (2.064 Å) of 2a, indicating some Os=C double-bond character. The comparable distances of Os1–C7 (2.008 Å) and Os1–C1 (2.027 Å) suggest the contribution of resonance forms 3a versus 3a-1 (Supplementary Table 2). Compared with the Os1–C9 distance (2.218 Å) of 2a, the Os1–C8 distance (2.169 Å) of 3a is shorter and is characteristic of metallacyclopentenes (Fig. 2c). The C7–C8 bond length of 1.363 Å is within range of bond lengths of typical single and double C–C bonds. All the bond distances of Os1–C7, Os1–C8 and C7–C8 in 3a are comparable with those of reported aromatic metallacyclopentene. The C8–C9 bond length (1.325 Å) is typical of C=C double bonds. The 1H NMR spectrum of 3a displays a characteristic signal at δ = 12.81 ppm attributed to C9H. Both the C’H and C9 signals at δ = 6.45 and 113.6 ppm, respectively, suggest that C9 is a vinyl carbon atom. Similar structures of 3b and 3c were also determined by single-crystal X-ray diffraction (Supplementary Figs. 3 and 4).

Chemical reactions of metallacyclobutadienes have been investigated previously, including the [2 + 2] retrocycloaddition to afford carbonyl complexes and alkynes, alkene/CO insertion and the formation of metallabenzenes/other cyclic carbene complexes or reduction elimination products, such as π2-cyclopentadienyl and π2-cyclopentenyl complexes. Metallacyclobutadienes have also been proposed as intermediates in the formation of vinylcarbene complexes or metalcylopentene complexes from reactions of metal carbynes with alkynes/phosphoalkynes. In principle, metallacyclobutadienes tend to undergo ring expansion or ring opening. In fact the transformation of 2a to 3a may represent the first observation of a structurally well-defined ring contraction of metallacyclobutadiene to metallacyclopentene. Analogous complexes as π2-1-metalla(methylene)cyclopropenes (π2-n-allyl complexes) have been reported, which have usually been synthesized by transformations from π2-allyl complexes, or reactions of metal sources with unsaturated substrates, such as allenes and alkynes.

Theoretical and experimental investigation of the mechanism

Density functional theory (DFT) calculations were performed to investigate the mechanism of the formation of 3a. The computed Gibbs free energy profile of the key reaction steps is shown as a black line in Fig. 3. The initial attack of CF3COOH led to the cleavage of the Os–C9 single bond in 2a and the formation of C9–H, generating Int 4a (Int, intermediate) via a transition state (TS1). The protonation process has...
Ph 

A: 

1. OsCl(PPh3)3 

2. Bu4NCI, CH2Cl2, r.t. 

ClH2Cl2, r.t. 

1 1 

[Ph] OsCl(PPh3)3 

CH2Cl2, r.t. 

CF3COOH 

B: 

Complex 2a 

Complex 3a 

C: 

2a: R = Ts, yield = 90% 

2b: R = COOMe, yield = 92% 

2c: R = COOH, yield = 95% 

3a: R = Ts, yield = 40% 

3b: R = COOMe, yield = 52% 

3c: R = COOH, yield = 60% 

D: 

| Bond length | Os1–C7 | Os1–C8 | Os1–C9 | C7–C8 | C8–C9 |
|-------------|--------|--------|--------|-------|-------|
| 2a          | 2.064(3) | – | 2.128(3) | 1.425(4) | 1.338(5) |
| 3a          | 2.008(8) | 2.169(2) | – | 1.363(3) | 1.325(3) |

Fig. 2 | Synthesis and characterization of precursor 1, [2 + 2] cycloaddition products 2a–2c and ring-contraction products 3a–3c. a. Synthesis of osmapentalyne 1 and its reactions with alkynes via formal [2 + 2] cycloaddition to yield complexes 2a–2c and the synthesis of 3a–3c by reactions of 2a–2c with CF3COOH. Ts, p-toluenesulfonyl group. b. X-ray crystal structures for 2a and 3a drawn at the 50% probability level. c. Selected bond lengths (Å) for 2a and 3a. d. Selected NMR chemical shifts (ppm) for 1, 2a and 3a. 

an energy barrier of 14.2 kcal mol−1 and is exergonic by 9.9 kcal mol−1; therefore, this reaction is theoretically facile. Subsequently, elimination of C3H4 yields the final energetically favourable product 3a from Int 4a with an energy barrier of 10.7 kcal mol−1 and this process is exergonic by 16.9 kcal mol−1.

Control experiments were performed to further confirm the proposed mechanism. Different amounts of acids were tested in reactions monitored by 31P{1H} NMR spectroscopy. As shown in Fig. 4b, upon reaction of complex 2a with 10 equiv. of CF3COOH, product 3a was obtained exclusively. However, when the reaction was carried out in the presence of 20 equiv. of CF3COOH, a new singlet at 17.45 ppm in the 31P{1H} NMR spectrum, attributed to species 4a, was observed. A series of parallel experiments showed that the content of 4a increased gradually as the amount of acid increased. When the acid level exceeded 50 equiv., the relative ratio of 3a and 4a remained almost unchanged. It can be assumed that the excess acid stabilized intermediate 4a. When dilution experiments were conducted by the addition of CH2Cl2 to the reaction mixture of 3a and 4a, compound 4a was gradually converted into 3a with decreasing acid concentration. Based on these results, 4a was concluded to be an intermediate in the formation of 3a, and the transformation from intermediate 4a to final product 3a was inhibited by excess CF3COOH. Other acids were tested in the formation of 4a. Fortunately, upon treatment of 2a with excess HBF4·Et2O, a 4a analogue named 4A was isolated as the main product. This analogue was completely converted into 3a by heating the in situ mixture to 55 °C (Fig. 4a).

Single-crystal X-ray diffraction showed that 4A is an osmapentalene bearing a vinyl group attached at C7. As shown in Fig. 4c, the metal is coordinated with six atoms, namely, three carbon atoms (C1, C4 and C7), two phosphorus atoms and a chlorine atom, leading to a coordinated unsaturated 16-electron osmium centre. The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47 The bond lengths of Os1–C1 (1.962 Å) and Os1–C7 (2.021 Å) are comparable to previous observations in osmapentalenes (1.926–2.084 Å).47
The combined experiments and DFT calculations confirmed that ring contraction proceeds through a ring opening–reclosing pathway involving acid-mediated protonation and deprotonation via vinylecarbene species (4A'). Notably, the Gibbs free energy profile suggested that 3a with a strained metallocyclopentene is more stable than 4A. To address this issue, the aromaticity of each of these species was investigated.

Theoretical studies of aromaticity

Nucleus-independent chemical shift (NICS) calculations were performed based on simplified model compounds 2a, 3a' and 4A', in which PHI groups were used to replace the PPh₃ ligands and the phenyl ring attached to C3 was omitted. As shown in Fig. 5a, the positive NICS(1)zz value of the fused 4MR is 25.8 ppm. The NICS(1)zz values of the two fused five-membered rings (SMR) (−3.7 and 3.3 ppm) imply non-aromaticity. In sharp contrast, the two fused 5MRs of 3a' show NICS(1)zz to have significantly reduced negative values (−15.1 and −22.6 ppm), revealing the aromaticity of 3a'. The ring opening of the 4MR relieves the antiaromaticity of the metallocyclobutadiene in 2a and results in enhancement of the aromaticity of the two 5MRs in 4A'. The new generation of the aromatic 3MR in 3a' is supported by the negative NICS(1)zz value of −30.4 ppm. The other two fused SMRs of 3a' with large negative NICS(1)zz values of −17.0 and −17.6 ppm suggest that the aromaticity is maintained. Coincidentally, the NICS(1)zz grids demonstrate that the inner cavity area of metallocyclobutadiene in 2a is deshielded (red, positive values), while the inner cavity area of metallocyclopentene in 3a' is shielded (blue, negative values) (Fig. 5a).

Anisotropy of the induced current density (ACID) analysis also supported the aromaticity changes in these complexes (Fig. 5b and Supplementary Figs. 15–17). Distinct counterclockwise circulation of 2a' (Fig. 5b, left) was observed in the fused osmacyclobutadiene, suggesting antiaromaticity, whereas the clockwise circulation observed in two fused SMRs demonstrated the aromaticity of 4A' (Fig. 5b, middle), and the clockwise circulation along the periphery of the whole metallatricycle of 3a' (Fig. 5b, right) indicated expansion of the global aromaticity. To further examine our hypothesis of the (anti)aromaticity of complexes 2a' and 3a' and the σ and π contributions therein, diverse theoretical criterions were employed. The main occupied σ molecular orbitals for 2a' and 3a' have been defined (Supplementary Fig. 12). Canonical molecular orbital (MO) NICS calculations were performed to identify the σ- and π-orbital contributions separately. Sophisticated (CMO) NICS including components of the σ and π contributions to the a, b and c rings in complexes 2a' and 3a' at distances d (0.0–3.0 Å) were studied (Supplementary Fig. 13). The computed NICS(0)zz value is positive for 2a' (42.3 ppm) and the computed NICS(0)zz value is negative for 3a' (−59.6 ppm), suggesting a π-antiaromatic character of the 4MR in 2a' and a σ-aromatic character of the 3MR in 3a'. Notably, ring b has a more negative NICS(0)zz value (−3.7 ppm) than ring c (3.3 ppm) in 2a'. This could be attributed to an anticlockwise current in the 4MR, which could enhance the ring current of the central ring b because these two ring currents proceed in the same direction along the M–C7 bond (Supplementary Fig. 14a). Additionally, the bifurcation values 0.27 of the electron localization function basins contributed by π component (ELFₘ) basins for the C7–C8 bond in the metallocyclobutadiene framework of 2a' also suggest antiaromaticity (Supplementary Fig. 14b). The dissected NICS(0) and NICS(1)zz in complex 3a' were selected to evaluate the nature of the possible σ-aromaticity in the 3MR. The total diamagnetic contribution of the NICS(0) value for the 3MR from the six occupied π highest occupied molecular orbitals (HOMO, HOMO-1, HOMO-3, HOMO-19, HOMO-25 and HOMO-28) was −9.2 ppm, whereas the NICS(0) value from all the σ orbitals (−28.4 ppm) was much more negative, indicating that σ-aromaticity is dominant in the 3MR and is the major contribution to aromaticity in the 3MR in 3a' (Fig. 5c), which is consistent with the σ-aromatic character of reported metallocyclopentenes.
The σ-aromaticity in the unsaturated 3MR of 3a′ is further supported by ACID analysis contributed by different orbitals. As shown in Fig. 5d, the current density vectors plotted on the ACID isosurface indicate a diatropic ring current in the 3MR which appears only in the σ system, whereas the diatropic ring current in the π system is displayed only along the periphery of the fused 5MR in 3a′, confirming σ-aromaticity in the three-membered metallacyclopropene and π-aromaticity in fused 5MR of 3a′, respectively (Supplementary Fig. 18).

The stability of osmacyclopropene in 3a′ can be investigated by means of two isodesmic reactions (Fig. 5e). The endothermic (+36.8 and +37.7 kcal mol⁻¹) nature of the cleavage of the Os–C or C–C bonds means of two isodesmic reactions (Fig. 5e). The endothermic (+36.8 and +37.7 kcal mol⁻¹) nature of the cleavage of the Os–C or C–C bonds attributed to the two aldehyde groups.

The Mulliken charge and natural population analysis charge calculations showed that the electron charge of the C9 site is more negative than that of the C1 atom, which is explained well by the observation of electrophilic substitution preferentially occurring at the vinyl group (Supplementary Fig. 19). Electrophilic substitution and an oxidation reaction both occurred at the exocyclic positions of 3a, suggesting the high stability and resistance to oxidation of the metallatricyclic moiety, in accordance with its aromatic character.

The ultraviolet–visible absorption spectra of metallacycles 2a–2c display an absorption maximum at approximately 470 nm, slightly redshifted compared with that of osmapentalyne (1) (Fig. 6c). They also have weak and broad absorption band tails at 700–800 nm, which are typical bathochromic shifts of near-infrared bands attributed to the decrease in optical band gaps, in accordance with the antiaromatic character. The near-infrared absorption of 2a–2c exhibits photothermal properties; for example, the temperature of the solution containing 1.00 mg ml⁻¹ for 2c increased from 25.5 °C to 46.6 °C within 7 min under irradiation at 808 nm by a laser at a laser power density of 1.0 W cm⁻² (Fig. 6d). Metallacycles 3a–3c gave rise to two obvious absorption peaks at wavelengths of ~340 and ~510 nm. Compared with 3a, electrophilic substitution products 5a and 5b exhibited similar absorption properties, while the oxidation product 6a gave rise to two slightly redshifted broad absorption peaks.

**Conclusion**
We have described an unusual acid-induced ring contraction of metallacyclobutadiene to metallacyclopropene via a ring opening–reclosing process. The successful isolation of the key intermediate and the formation of 4a by ³¹P{¹H} NMR spectroscopy. Parallel reactions of 10, 20, 30 and 50 equiv. of CF₃COOH with 2a (left). The in situ reaction system (30 equiv. of CF₃COOH with 2a) was diluted to 5/7, 5/9 and 1/2 of its original concentration (right). c. X-ray crystal structure of cation of intermediate 4A drawn at the 50% probability level. The phenyl groups in PPh₃ have been omitted for clarity.
Fig. 5 | Aromaticity evaluation of model compounds 2a’, 4A’ and 3a’ by theoretical criteria. a, \(zz\) component of the NICS (NICS(1)\(_{zz}\)) values and NICS(1)\(_{zz}\) grids for model compounds 2a’, 4A’ and 3a’. NICS(1)\(_{zz}\) was calculated at 1.0 Å above the ring centres. Each grid is parallel to the fused ring with 0.01 Å resolution and 40,000 points. A fixed colour scale (−30.0 to +30.0 ppm) is used in all grids for a visual comparison. Projections of the framework are presented on the maps and connected by lines. b, The isosurface value of the ACID plots of 2a’ (left), 4A’ (middle) and 3a’ (right). The ACID plots are 0.030 a.u. The magnetic field vector is orthogonal with respect to the ring plane and is directed upward (the corresponding paratropic (red arrow) and diatropic (blue arrow) ring currents are shown). c, Partial key occupied \(\pi\) HOMOs and their energies (first row) together with their contributions to NICS(0) and NICS(1)\(_{zz}\) (second row, in ppm) for model complex 3a’. d, The ACID plot of 3a’ contributed by the \(\sigma\) system (left) or the \(\pi\) system (right) is displayed with an isosurface value of 0.030 a.u. e, Isodesmic reactions for 3a’. \(\Delta E\) indicates the energy gap between the products and reactants. All energies are given in kcal mol\(^{-1}\).
results of theoretical calculations confirm that the driving force of aromatization plays a vital role in the reaction. The \( \pi \)-aromaticity-driven ring opening of an antiaromatic metallacyclobutadiene followed by \( \sigma \)-aromaticity-driven ring reclosing resulted in the expansion of global aromaticity. Versatile aromaticity switches in these metallacycles have been observed, that is, from \( \pi \)-anti-/non-aromaticity to \( \pi \)-aromaticity and further to \( \pi \)-aromaticity-driven ring contraction in small metallacycles and provide new insight into aromaticity-driven relay strategies in synthetic transformations.

**Methods**

**General methods**

Compounds 5-1, 5-2 and L1 were synthesized according to the literature\(^\text{15}\).

**Synthesis of complex 1**

Under a nitrogen atmosphere, a mixture of L1 (256 mg, 1.14 mmol), OsCl\(_2\)(PPh\(_3\))\(_2\) (1.00 g, 0.95 mmol) and \( \text{n-Bu}_4\text{NCl} \) (1.00 g, 3.60 mmol) was stirred in CH\(_2\)Cl\(_2\) (25 ml) at r.t. for 15 min to give a brown solution. The solution was evaporated under vacuum to a volume of approximately 2 ml. Then, the solution was purified by column chromatography (alumina gel; eluent, CH\(_2\)Cl\(_2\)) to give I (425 mg, 45%) as a yellow solid.

**Synthesis of complex 2a**

Under a nitrogen atmosphere, a mixture of complex 1 (500 mg, 0.50 mmol) and \( p \)-toluenesulfonylacetylene (400 mg, 2.50 mmol) was stirred in CH\(_2\)Cl\(_2\) (25 ml) at r.t. for 5 min to give a brown solution. The solution was evaporated under vacuum to a volume of approximately 2 ml. Then a mixed solvent (Et\(_2\)O/petroleum ether = 1:4 v/v, 50 ml) was added to the solution. The brown precipitate was collected by filtration, washed with mixed solvent (Et\(_2\)O/petroleum ether = 1:4 v/v, 2 × 50 ml) and dried under vacuum to give 2a (527 mg, 90%) as a brown solid.

**Synthesis of complex 3a**

Under a nitrogen atmosphere, trifluoroacetic acid (500 \( \mu \)l, 6.73 mmol) was added to a solution of complex 2a (500 mg, 0.43 mmol) in CH\(_2\)Cl\(_2\) (25 ml). The reaction mixture was stirred at r.t. for 3 h to give a mandarin red solution. The solution was evaporated under vacuum to a volume of approximately 2 ml. Then the solution was purified by column chromatography (silica gel; eluent, CH\(_2\)Cl\(_2\) and CH\(_2\)Cl\(_2\)/Me\(_2\)CO = 100:1 v/v) to give 3a (200 mg, 40%) as a reddish-brown solid.

**Synthesis of complex 4A**

Under a nitrogen atmosphere, a solution of HBF\(_4\)·Et\(_2\)O (50–55 w/w) was added to a solution of complex 2a (50 mg, 42.5 \( \mu \)mol) in CH\(_2\)Cl\(_2\) (0.5 ml). The reaction mixture was stirred at r.t. for 30 min to give an orange solution of 4A (approximately 80% yield...
based on H and 31P{1H} NMR, which was characterized by in situ 1H NMR. 31P{1H} NMR and 13C{1H} NMR. Complex 4A is stable only under strong acidic conditions.

**Data availability**

All characterization data and experimental protocols are included in this Article and/or the Supplementary Information. Details of the synthesis and characterization of compounds S-1, S-2, L1, 2a–2c, 3a–3c, 4A, 5a, 5b and 6a can be found in the Supplementary Information. For general information, synthesis and characterization, see Supplementary Information, pages 2–13. For control experiments, see Supplementary Figs. 1–3. For crystallographic analysis, see Supplementary Figs. 4–10 and Supplementary Tables 1–10. For thermal stability tests, see Supplementary Table 11. For kinetic study, see Supplementary Fig. 11. For the mechanism for the formation of compound 1, see Supplementary Scheme 1. For computational methods, see Supplementary Figs. 12–23. For NMR spectra and ESI-MS spectra, see Supplementary Figs. 24–70. Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under accession numbers 2103042 (2a), 2103166 (2b), 2103168 (3c), 2103171 (4A), 2103169 (5b) and 2103170 (6a). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

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Author contributions
H.X. and Y.-M.L. conceived the project. K.Z. and Y.L. performed the experiments. K.Z., Y.L., H.X. and Y.-M.L. analysed and interpreted the experimental data. K.R. and Y.H. designed and performed the theoretical calculations. K.Z., Y.L. and Y.-M.L. prepared the manuscript. Y.L. and K.Z. prepared the Supplementary Information. All the authors discussed the results and contributed to the preparation of the final manuscript.

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The authors declare no competing interests.

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