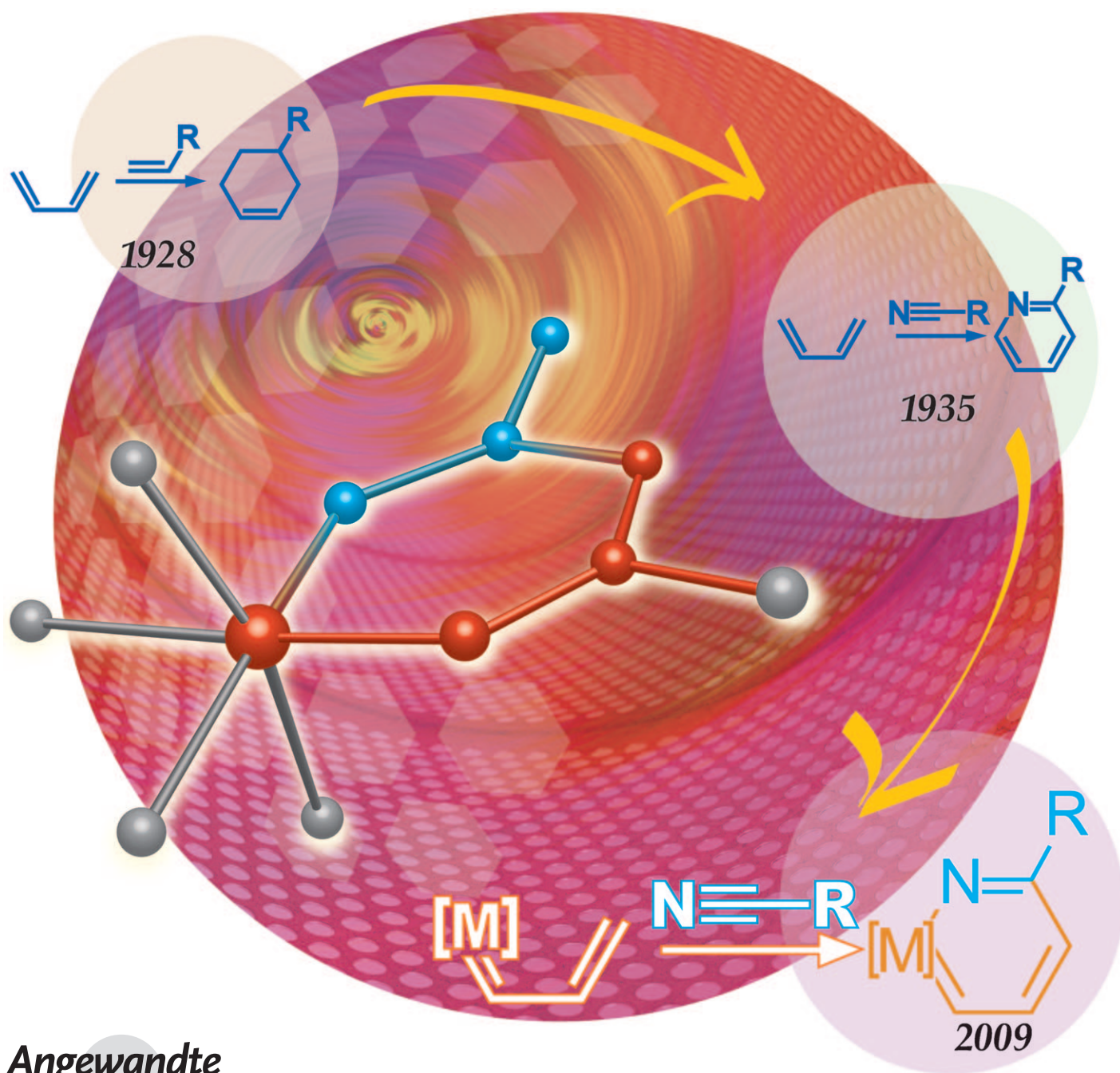


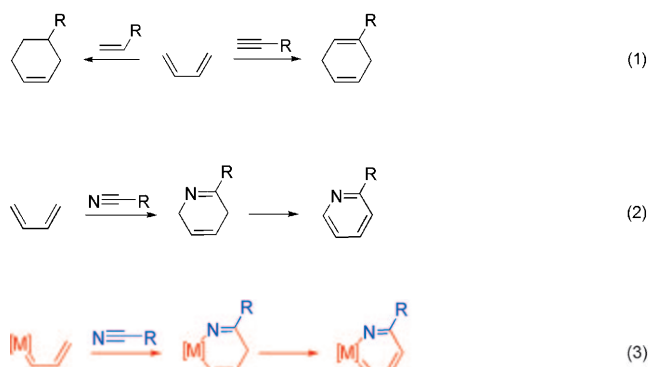
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction**

Bin Liu, Huijuan Wang, Hujun Xie, Birong Zeng, Jinxiang Chen, Jun Tao, Ting Bin Wen, Zexing Cao, and Haiping Xia*



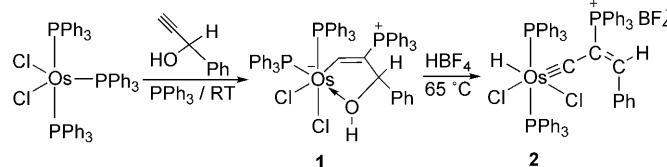
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As one of the most important cycloaddition reactions, the Diels–Alder reaction^[1] is widely used in modern organic synthesis [Eq. (1)]. In contrast, hetero-Diels–Alder reactions^[2] using nitriles as the dienophile [Eq. (2)] remain relatively rare.^[3] Recently, the activation of 1,3-dienes by organolithium reagents was reported, and their formal [4+2] reaction with nitriles becomes feasible.^[3a–d] To the best of our knowledge, however, the [4+2] cycloaddition reaction between 1-metalla-1,3-dienes and nitriles has not been reported [Eq. (3)].



The chemistry of transition-metal-containing aromatic metallacycles is currently attracting significant attention.^[4] While considerable progress has been made in the synthesis of metallabenzene,^[4a,c–f] the heteroatom-containing analogues such as metallapyrylium,^[5] metallathiabenzene,^[6] metallapyridine,^[7] metallapyrrole,^[8] and metallathio-pene^[9] are relatively less developed. In a search of new routes to heteroatom-containing aromatic metallacycles, we studied the reaction between 1-metalla-1,3-dienes and nitriles [Eq. (3)]. Herein, we would like to report an unprecedented formal [4+2] cycloaddition between the hydrido alkenylcarbyne complex [OsHCl₂(=C–C(PPh₃)=CHPh)(PPh₃)₂]BF₄ (**2**) and acetonitrile, which affords the first metallapyridinium complex. The deprotonation of the osmapyridinium complex by *n*BuLi to give an osmapyridine is also described.

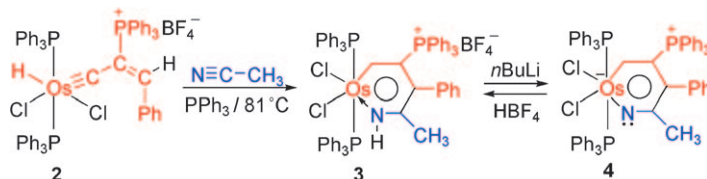
Treatment of [OsCl₂(PPh₃)₃] with HC≡CCH(OH)Ph in tetrahydrofuran produced the osmacyclic complex **1**, which was isolated as a yellow solid in 85% yield (Scheme 1). Compound **1** may be formed by the nucleophilic attack of PPh₃ on the coordinated alkyne^[10] followed by the coordina-



Scheme 1. Preparation of osmium hydrido alkenylcarbyne **2**.

tion of hydroxy group through lone pair of electrons on the oxygen atom. It is well known that the hydroxy group can be easily removed from organic ligands by treatment with acid. When a suspension of **1** in methanol was treated with HBF₄ and the mixture was heated at reflux, a green precipitate was obtained in 50% yield, which was identified as the osmium hydrido alkenylcarbyne complex **2**. Apparently, α -hydride elimination occurred after dehydration (see Scheme 1 in the Supporting Information).^[11] Both **1** and **2** were characterized by NMR spectroscopy and elemental analysis, and their structures were further confirmed by single-crystal X-ray diffraction (see Figures S1 and S2 in the Supporting Information).^[11]

When compound **2** reacted with acetonitrile at reflux, the unexpected product **3** formed in a formal [4+2] cycloaddition and was isolated in 53% yield. The yield improved to 84% in the presence of PPh₃ (Scheme 2). Interestingly, deprotonation of **3** by *n*BuLi in tetrahydrofuran at 0 °C produced osmapyridine **4**, which was isolated in 52% yield. Treatment of **4** with HBF₄ regenerated **3** quantitatively. In this regard, **3** can be viewed as an osmapyridinium compound.



Scheme 2. Preparation of **3** and **4**.

Complexes **3** and **4** have been structurally characterized by single-crystal X-ray diffraction analysis. The metallacycle of **3** is almost planar (Figure 1). The deviations (in Å) from the best plane are 0.0216 (Os1), 0.0102 (C1), 0.0098 (C2), 0.0178 (C3), 0.0060 (C4), and 0.0254 (N1). The Os1–C1 bond length (1.943(9) Å) is similar to that found in the reported osmabenzene.^[12] The Os–N distance (1.952(7) Å) is between the reported values of Os–N single bonds (2.072(7) and 2.067(5) Å)^[13a] and an Os–N double bond (1.873(5) Å).^[13b] The C–C distances of the metallacycle are also intermediate between the typical lengths of carbon–carbon single and double bonds, without significant bond-length alternation. The C4–N1 distance (1.294(12) Å) is similar to the reported value (1.290(10) Å).^[13a] The sum of angles in the ring constructed by Os1, C1, C2, C3, C4, and N1 is 719.9°, which is almost identical to the ideal value of 720°. The Os–C, Os–N, and C–C bond lengths within the six-membered ring, together with its planar nature, indicate that the metallacycle has a

[*] B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, Prof. Dr. J. Tao, Prof. Dr. T. B. Wen, Prof. Dr. Z. Cao, Prof. Dr. H. Xia
State Key Laboratory of Physical Chemistry of Solid Surfaces
College of Chemistry and Chemical Engineering, Xiamen University
Xiamen 361005 (P.R. China)
Fax: (+86) 592-218-6628
E-mail: hpxia@xmu.edu.cn

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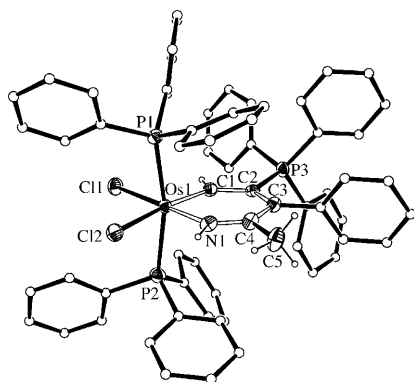
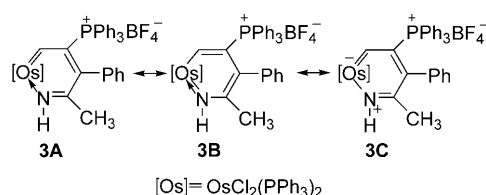


Figure 1. X-ray crystal structure of **3** (ellipsoids at the 50% probability level). Some of the hydrogen atoms and the counteranion are omitted for clarity.

delocalized nature with contributions from the resonance structures **3A–C** (Scheme 3). Thus the structure of **3** can be described as a delocalized osmacycle containing a coordinated imine group (**3A** and **3B**). When the pyridinium nature is considered, the iminium form **3C** is operative.



Scheme 3. Resonance structures of **3**.

As shown in Figure 2, the main structure of **4** is similar to **3**. However, the osmium atom is out of the plane of the metallacyclic carbon atoms by 0.218 Å, and the dihedral angle between the C1–C2–C3–C4–N1 plane and the C1–Os1–N1 plane is 8.9°. This nonplanarity is not uncommon in metalbenzenes and has been investigated theoretically.^[14] The Os1–C1 bond (1.969(8) Å) is a little longer than the analogous bond in **3** but still within the range of Os–C bonds found in osmabenzene.^[12] The Os1–N1 bond

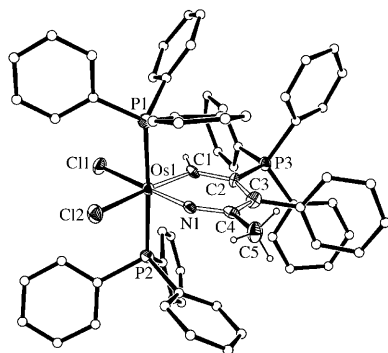
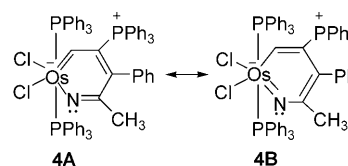


Figure 2. X-ray crystal structure of **4** (ellipsoids at the 50% probability level). Some of the hydrogen atoms are omitted for clarity.

(1.974(6) Å) is also slightly longer than that of **3** (1.952(7) Å), which may suggest that the resonance structure **4A** (containing an Os–N single bond) shown in Scheme 4 has



Scheme 4. Resonance structures of **4**.

more contribution than **4B** (containing Os=N bond). That is different from the previously reported tantalapyridine which prefers the Ta=N bond form.^[7] The C4–N1 bond (1.326(10) Å) is longer than that of **3** (1.294(12) Å) and comparable to that of tantalapyridine (1.34 Å).^[7] All the other C–C bonds in the metallacycle are intermediate between single and double carbon–carbon bonds. All of the bond lengths around the metallacycle would indicate a delocalized structure.

Complex **3** has also been characterized by NMR spectroscopy. The most notable feature is the unusually low-field chemical shifts for the ¹H NMR signals of OsCH and NH observed at δ = 48.01 (d, J (PH) = 20.3 Hz) and δ = 25.38 (s) ppm, respectively, which would be attributed to partial paramagnetism (vide infra). The ³¹P{¹H} NMR spectrum shows two signals at δ = 13.75 and 11.22 ppm assignable to CPh₃P and OsPPh₃, respectively. The ¹³C{¹H} NMR spectrum displays the signals of C1, C2, C3, C4, and C5 at 201.2, 123.2, 147.7, 234.4, and 25.6 ppm, respectively.

The ³¹P{¹H} NMR signals of **4** cannot be observed at room temperature or even at lower temperatures (200–293 K), while the ¹H NMR spectrum displays several irregular broad signals at these temperatures. This phenomenon together with the above-mentioned unusually low-field ¹H NMR signals of OsCH and NH in **3** suggest that both complexes are paramagnetic; this was also confirmed by the magnetic measurement experiments (see Figure S3 in the Supporting Information).^[11] The results show that the magnetic susceptibility of **4** is higher than **3**. The Os^{IV} (5d⁴) centers in **3** and **4** would greatly influence the NMR behavior of the hydrogen atoms attached to the neighboring C and N atoms. Our calculational results also indicate the paramagnetic properties of **3** and **4** (see Table S1 in the Supporting Information).^[11] Specifically, the triplet state of **4** is more stable than the singlet state by 2.2 kcal mol^{−1} at the B3LYP level. Similarly, the energy difference between the singlet and triplet states of **3** is very small, and the triplet state is slightly lower in energy than the singlet state by 0.5 kcal mol^{−1} by B3LYP. Although predicted relative stabilities may depend on the methods used for various spin states of **3** and **4**, their coexistence can be expected. In the paramagnetic states, the net spin populations basically reside on the metal center Os^{IV}; the Os-bonded C and N atoms also exhibit some paramagnetism, and these paramagnetic centers could strikingly modify the NMR behavior of the neighboring hydrogen atoms as observed in our experiments.

Furthermore, the predicted nucleus-independent chemical shifts (NICS values) of complexes **3** and **4** are -7.7 and -4.6 , respectively. These values are comparable to that of organic pyridine (-8.0) and suggest the aromaticity of **3** and **4**. The NICS value, the planarity, and high stability indicate that **3** exhibits higher aromaticity than **4**. Consistent with this result, compound **3** is highly stable toward air and moisture. A solution of **3** in dichloromethane was nearly unchanged in air after one week. The solid sample can be heated in air at 120°C for 5 h without notable decomposition. In contrast, a solution of **4** in dichloromethane decomposes quickly to unidentified species at room temperature in air.

A plausible mechanism for the formation of **3** and **4** is shown in Scheme 5. The migration of the hydride ligand to the carbyne carbon atom should afford the pentacoordinate alkenylcarbene intermediate **B**. Coordination of an acetonitrile molecule to **B** could give **C**. Coupling of the electrophilic C(sp) atom of the activated acetonitrile molecule^[15] in **C** with the γ -carbon atom of the alkenylcarbene ligand should lead to **D**. Dissociation of H^+ from the γ -carbon center together with the counterion BF_4^- affords osmapyridine **4**. Under the reaction conditions, the nitrogen atom can be easily protonated by the initially dissociated H^+ , leading to the formation of the final product **3**. When the reaction was performed in the presence of D_2O , the formation of **3** was accompanied by the deuteration of the nitrogen atom, which supports the proposed mechanism. It is important to note that although osmium prefers high oxidation states^[16] and **2** should be more favorable in energy than **B**, the transformation of **2** to **B** is feasible when more stable compounds such as **3** and **4** are formed. In other words, the energy released by formation of the aromatic compounds **3** and **4** would considerably compensate for the conversion of **2** to **B**. Furthermore, the transformation of an osmium hydrido carbyne complex to an osmium carbene has already been reported.^[17] In addition, when **1** was treated with HBF_4 and the reaction mixture in acetonitrile was heated at reflux, formation of **3** was observed together with other unidentified compounds by ^1H NMR spectroscopy. However, the yield was relatively low. According to Scheme 5, it seems that neutralization of the free HBF_4 generated in the reaction system may suppress the formation of **3**, and then **4** can be isolated directly from the reaction. Unfortunately, carbyne **2** is unstable and decomposed to unidentified species in the presence of common bases such as

NEt_3 , K_2CO_3 , and Na_2CO_3 , and thus **4** cannot be isolated by this method.

It is known that the formal $[4+2]$ cycloaddition reactions of vinylimido complexes of titanocene with nitriles, ketones, and imines can afford compounds containing the elements of the imido ligand.^[18] Very recently, the reaction between cobaltacyclobutene and alkene was first reported to give the 1,4-diene complexes.^[19] This reaction involved the conversion of the cobaltacyclobutene to a cobalt vinylcarbene intermediate, which underwent a $[4+2]$ cycloaddition reaction with the alkene. The route to **3** and **4** involves a formal $[4+2]$ cycloaddition reaction between acetonitrile and the osmium hydrido alkenylcarbyne complex, which is used as the precursor of the 1-metalla-1,3-diene. Our method represents a new reaction pattern and makes the synthesis of some interesting nitrogen-containing osmacycles practicable.

Azametallabenzenes are very rare. To the best of our knowledge, the only reported example is the tantalapyridine.^[7] This early-transition-metal-containing metallapyridine has discrete single and double bonds around the metal-lacycle.^[4a,7] In contrast, **4** is the first late-transition-metal-containing metallapyridine with a relatively delocalized structure, and **3** is the first metallapyridinium. Moreover, the paramagnetism of **3** and **4** is unique among the aromatic metallacycles. Consequently, both **3** and **4** would expand the scope of the chemistry of the transition-metal-containing aromatic metallacycles.

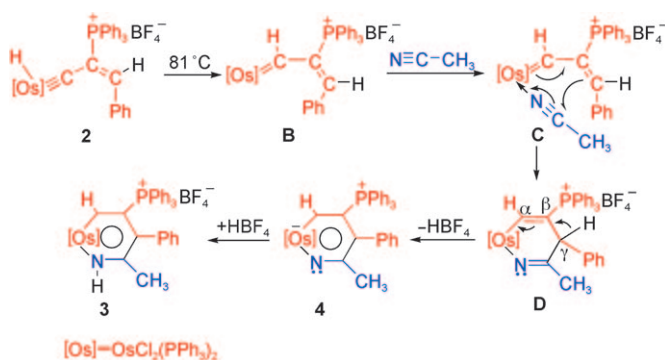
In summary, we have found an unprecedented formal $[4+2]$ cycloaddition reaction between osmium hydrido alkenylcarbyne **2** and acetonitrile, which affords the first metallapyridinium **3**. This new reaction pattern may be potentially useful to prepare other interesting heteroatom-containing metallacycles. Deprotonation of **3** gives the first osmapyridine **4**. The paramagnetism found in these two azaosmabenzenes **3** and **4** causes the unexpected NMR properties and deserves further investigation. The expansion of this novel $[4+2]$ synthetic strategy is ongoing.

Experimental Section

3: A solution of **2** (500 mg, 0.40 mmol) in 20 mL acetonitrile was heated at reflux for about 4 h in the presence of PPh_3 (1.05 g, 4.0 mmol). The solution was concentrated to a volume of about 1 mL. Subsequent addition of diethyl ether (10 mL) gave a brown precipitate, which was washed with diethyl ether and dried in vacuo. Yield: 455 mg, 84%. ^1H NMR (300.1 MHz, CD_2Cl_2): δ = 48.01 (d, $J(\text{PH})$ = 20.3 Hz, OsCH), 25.38 (s, NH), 1.98 ppm (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 14.51 (s, CPh_3), 10.82 ppm (s, OsPPh_3); $^{13}\text{C}\{^1\text{H}\}$ NMR plus HMQC (100.6 MHz, CD_2Cl_2): δ = 234.4 (d, $J(\text{PC})$ = 13.8 Hz, $\text{OsNHC}(\text{CH}_3)$), 201.2 (t, $J(\text{PC})$ = 9.1 Hz, OsCH), 147.7 (d, $J(\text{PC})$ = 11.8 Hz, $\text{OsCHC}(\text{PPh}_3)\text{CPh}$), 123.2 (d, $J(\text{PC})$ = 69.8 Hz, $\text{OsCHC}(\text{PPh}_3)$), 139.8–117.2 (m, other aromatic carbon atoms), 25.6 ppm (s, CH_3); Anal. calcd for $\text{C}_{65}\text{H}_{54}\text{Cl}_2\text{P}_3\text{BF}_4\text{NO}$: C 60.47, H 4.29, N 1.09; found: C 60.49, H 4.67, N 0.90.

4: A suspension of **3** (200 mg, 0.15 mmol) in 10 mL tetrahydrofuran was treated with $n\text{BuLi}$ (72 μL , 0.18 mmol) at 0°C . The reactant dissolved quickly and the color of the solution changed to dark red. The reaction mixture was retained at 0°C for about 2 d, giving some red crystals. Yield: 94 mg, 52%. Anal. calcd for $\text{C}_{65}\text{H}_{54}\text{Cl}_2\text{P}_3\text{NO}$: C 64.89; H 4.52; N 1.16. Found: C 64.62, H 4.50, N 1.13.

1 and **2:** See the Supporting Information for details.



Scheme 5. Proposed mechanism for the formation of **3**.

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Keywords: aromaticity · cycloaddition · metallacycles · osmium · paramagnetism

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