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Reactions of Osmium Hydrido Alkenylcarbyne with Allenoates: Insertion and [3 + 2] Annulation

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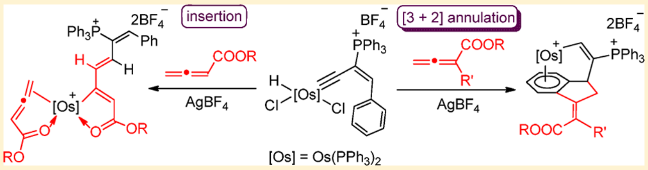
Supporting Information

ABSTRACT: Treatment of the osmium hydrido alkenylcarbyne complex $[OsH\{\equiv CC(PPh_3){=}CHPh\}(PPh_3)_2Cl_2]BF_4$ (**1**) with allenoates ($CH_2{=}C{=}CHCOOR$, R = Me, Et) in the presence of excess $AgBF_4$ leads to the insertion products **2**/**3**. The reactions of complex **1** with substituted allenoates, i.e., diethyl 2-vinylidenesuccinate ($CH_2{=}C{=}C(CH_2COOEt)(COOEt)$) and ethyl penta-2,3-dienoate ($CH(CH_3){=}C{=}CH(COOEt)$), result in the formation of [3 + 2] annulation products **4** and **6**, respectively. Mechanisms of the reactions have been proposed with the isolation of the key intermediates. The results reveal that the divergent pathways for these reactions are mainly of steric origin.



INTRODUCTION

Metal carbenes and metal carbynes, i.e., transition metal complexes with a multiple metal−carbon bond, have been widely exploited because of their unique properties[1,2] and important applications in organic synthesis.[3,4] To date, the distinguished performances in metathesis reactions with an unsaturated compound are immensely attractive, such as olefin[5]/enyne[6] metathesis of metal carbenes and alkyne metathesis[7] of metal carbynes.

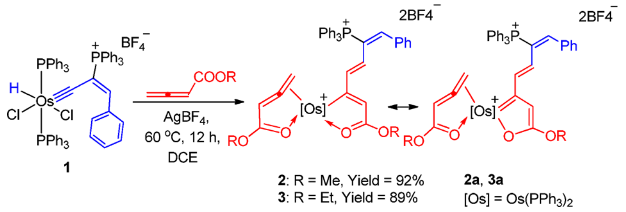
Allenes contain two cumulative double bonds, a motif that is of significant importance to synthetic practitioners, especially through reactions mediated by transition metal catalysts.[8] However, there are only a few examples in the literature concerning the reactions of metal carbenes with allenes.[9−11] To the best of our knowledge, reactions of metal carbynes with allenes have never been reported to date.

In 2009, we reported the synthesis of osmium hydrido alkenylcarbyne complex $[OsH\{\equiv CC(PPh_3){=}CHPh\}(PPh_3)_2Cl_2]BF_4$ (**1**), which can undergo a formal [4 + 2] cycloaddition reaction with acetonitrile to produce the osmapyridine complex and the osmapyridinium complex.[12] In addition, the intramolecular C−H activation of **1** led to the formation of osmanaphthalene and osmanaphthalyne.[13] Herein, we study the reactivity of complex **1** with allenoates, which can selectively undergo insertion or [3 + 2] annulation reactions. Moreover, the detailed mechanisms of the reactions are also addressed, including the influence of the substituents of the allenoates on the reactions.

RESULTS AND DISCUSSION

Insertion Reactions of Osmium Hydrido Alkenylcarbyne Complex 1 with Allenoates. As shown in Scheme 1, the mixture of **1**, methyl buta-2,3-dienoate ($CH_2{=}C{=}CHCOOMe$), and excess $AgBF_4$ was heated at 60 °C for 12 h in 1,2-dichloroethane (DCE), which led to the formation of **2**. Complex **2** was isolated as an orange solid in 92% yield. Similarly, complex **3** was obtained in 89% yield when ethyl buta-2,3-dienoate ($CH_2{=}C{=}CHCOOEt$) was subjected to the reaction. Both the solid and solution forms of complexes **2** and **3** were stable toward air and moisture. Complexes **2** and **3** were characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. The structures were further confirmed by single-crystal X-ray diffraction.

Scheme 1. Insertion Reactions of Osmium Hydrido Alkenylcarbyne Complex 1 with Allenoates



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As shown in Figure 1, complex **2** contains an osmafuran structure, derived from the insertion of allenoate's terminal C=C bond into the Os≡C bond of complex **1**. Another allenoate is coordinated to the metal center as a ligand. The coordination geometry around the osmium atom can be regarded as a distorted octahedron with the allenoate ligand and the osmafuran ring lying in the equatorial plane. The remaining axial coordination sites are occupied by the two PPh_3 ligands. The five atoms of the osmafuran ring (Os1−C11−C12−C13−O1) are nearly coplanar, with a mean deviation from the least-squares plane of 0.0308 Å. The bond lengths within the osmafuran ring are comparable to those of the reported examples.[14] The structural parameters indicated that the metallacycle of **2** could be represented by two resonance structures, **2** and **2a** (Scheme 1), with **2** as the more dominant structure.

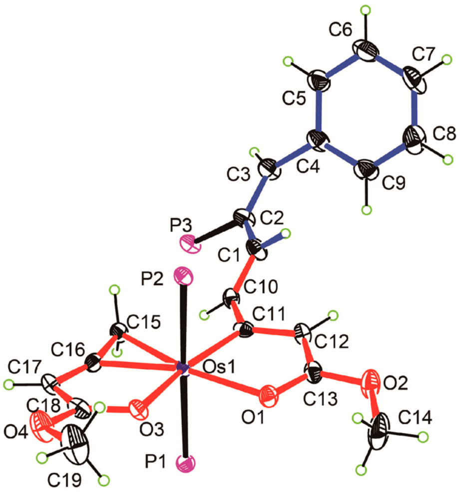
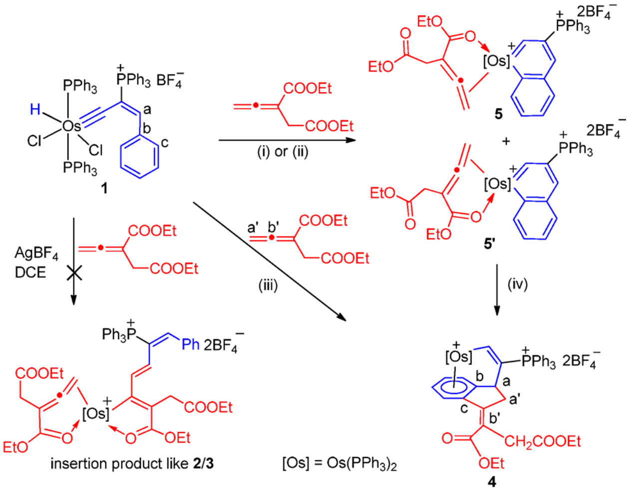


Figure 1. Molecular structure of complex **2** (ellipsoids at the 50% probability level). The phenyl rings in the PPh_3 groups and the counteranion are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Os1−C11 2.045(4), C11−C12 1.372(7), C12−C13 1.412(7), C13−O1 1.265(6), Os1−O1 2.122(3), Os1−C15 2.161(4), Os1−C16 2.006(4), Os1−O3 2.185(3), C15−C16 1.390(6), C16−C17 1.335(7), C17−C18 1.429(7), O3−C18 1.258(6), C11−C10 1.465(6), C1−C10 1.343(7), C1−C2 1.466(6), C2−C3 1.362(7), C3−C4 1.464(7); C12−C11−Os1 114.4(3), C11−C12−C13 114.2(4), O1−C13−C12 120.4(4), C11−Os1−O1 77.88(15), C16−C15−Os1 64.6(2), C16−Os1−C15 38.75(18), C15−C16−Os1 76.6(3), C17−C16−C15 160.2(4), C16−C17−C18 110.0(4), O3−C18−C17 119.3(4), C18−O3−Os1 114.3(3), C16−Os1−O3 73.34(15), C12−C11−C10 117.6(4), C1−C10−C11 124.5(4), C10−C1−C2 126.6(4), C1−C2−C3 124.1(4), C2−C3−C4 127.6(4). The ORTEP representation of complex **3** is shown in the Supporting Information.

The NMR spectroscopic analysis of complex **2** is consistent with the X-ray structure. In particular, in the ^1H NMR spectrum, the H12 signal was observed at 6.0 ppm. With the aid of $^1H-^{13}C$ HSQC and $^1H-^{13}C$ HMBC, the protons H10 and H3 can be assigned at 6.3 and 7.1 ppm, respectively. However, it is difficult to attribute the signals of H1 and the corresponding C1, as they are both located in the aromatic region. In the ^{13}C NMR spectrum of **2**, the carbon signals of the osmafuran ring were observed at 199.6 (C11), 117.5 (C12), and 180.1 (C13) ppm. The signals of the carbons C2, C3, and C10 can be attributed at 116.7, 156.5, and 146.1 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum showed two singlets at 23.7 ($CPPh_3$) and −0.5 ppm ($OsPPh_3$). The molecular formula of **2** was observed at 644.1777 in the HRMS spectrum, which is in agreement with the calculated value for $[M]^{2+}$ (644.1776).

[3 + 2] Annulation Reactions of Osmium Hydrido Alkenylcarbyne Complex 1 with Allenoates. To expand the reaction scope, complex **1** was treated with diethyl 2-vinylidenesuccinate ($CH_2{=}C{=}C(CH_2COOEt)(COOEt)$) and excess $AgBF_4$ in DCE at 60 °C. Unexpectedly, a [3 + 2] annulation complex **4** was afforded in 48% yield and the insertion-product-like complexes **2**/**3** were not detected (Scheme 2).

Scheme 2. [3 + 2] Annulation Reaction of Osmium Hydrido Alkenylcarbyne Complex 1 with Diethyl 2-Vinylidenesuccinate



(i) $AgBF_4$, DCE, RT, 5 h, 95%, **5**:**5'** = 1:1
(ii) $AgBF_4$, DCE, 60 °C, 1h, 95%, **5**:**5'** = 2:3
(iii) $AgBF_4$, DCE, 60 °C, 2 d, 48%
(iv) DCE, 60 °C, 2 d, 51%

Due to its poor solubility in common organic solvents, the attempt to obtain the full NMR spectroscopy characterization of complex **4** failed. Fortunately, complex **4** was quite stable toward air and moisture; after recrystallization of the crude product, a single crystal of **4** was obtained, making it possible to determine its solid-state structure.

As shown in Figure 2, **4** adopts a typical three-legged piano-stool structure with the η^6-benzene, two PPh_3, and the alkenyl carbon atom connected to the metal center. Interestingly, the X-ray crystallographic analysis demonstrated that the exocyclic double bond of the newly formed five-membered ring solely adopted a *Z* configuration, with the ester group and the coordinated phenyl *cis* to each other.

To obtain mechanistic information, the reaction time was shortened and the reaction temperature was decreased. Fortunately, two inseparable isomers, osmanaphthalene intermediates **5** and **5′**, were isolated as a red solid in 95% yield. The complexes **5** and **5′** were relatively stable toward air and moisture. Since **5** and **5′** were diastereomers, they can be distinguished by NMR spectroscopy. In the ^1H NMR spectrum, the characteristic resonances of OsC*H* were observed at 16.4 and 17.1 ppm for **5** and **5′**, respectively. The $^{31}P\{^1H\}$ NMR spectrum showed two $OsPPh_3$ signals at 3.8 and 7.2 ppm, and two $CPPh_3$ signals were observed at 22.8 and 23.8 ppm. The molecular structure of one of the isomers has been confirmed by an X-ray diffraction study. As shown in Figure 3, the

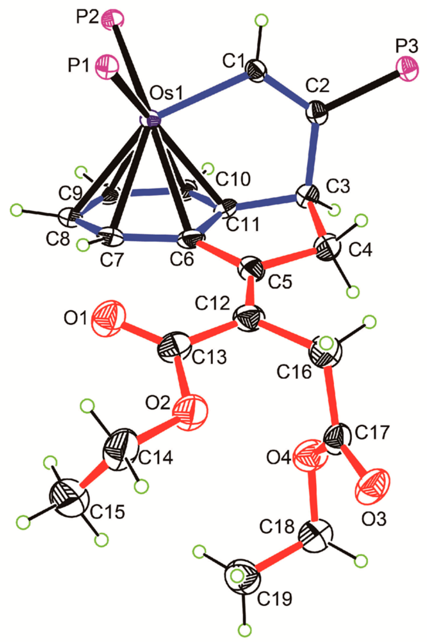


Figure 2. Molecular structure of complex **4** (only the *S* enantiomer is shown; ellipsoids are at the 50% probability level). The phenyl rings in PPh_3 groups and the counteranion are omitted for clarity.

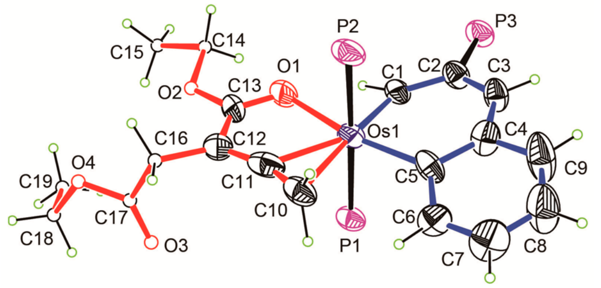


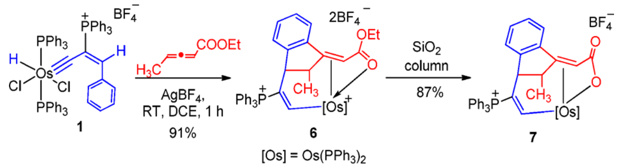
Figure 3. Molecular structure of complex **5** (ellipsoids at the 50% probability level). The phenyl rings in PPh_3 groups and the counteranion are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Os1−C1 1.944(8), C1−C2 1.422(10), C2−C3 1.380(10), C3−C4 1.406(11), C4−C5 1.425(11), Os1−C5 2.067(8), Os1−C10 2.341(8), Os1−C11 2.135(9), Os1−O1 2.224(5); Os1−C1−C2 134.3(6), C1−C2−C3 119.2(7), C2−C3−C4 125.9(7), C3−C4−C5 126.9(7), C4−C5−Os1 122.8(6).

coordinated allenoate and the carbon ring of osmanaphthalene occupy the equatorial plane, and the phosphine ligands are mutually *trans* in the axial direction.

When heated at 60 °C for 2 days, the mixture of **5** and **5′** could be converted to the expected annulation product **4**. This indicates that osmanaphthalenes were the key intermediate for the [3 + 2] annulation reaction. Transition-metal-catalyzed [3 + 2] annulation reactions are one of the most efficient and convenient methods for the synthesis of carbo- and heterocycles in organic synthesis.[15] Among these reactions, the five-membered metallacycles via the aromatic C−H bond activation approach were widely accepted as key intermediates,[15c] which can further react with various unsaturated molecules such as alkynes, alkenes, allenes, and benzynes to give final cyclic products. In contrast, the six-membered metallacycles have been rarely proposed as the intermediates of these [3 + 2] annulation reactions.[16] The aromatic nature of the osmanaphthalene intermediates **5** and **5′** may be crucial for their stability.

For a further understanding of the reaction, the case of a nonterminal allenoate was also investigated. As shown in Scheme 3, the reaction of **1**, $AgBF_4$, and ethyl penta-2,3-dienoate ($CH(CH_3){=}C{=}CH(COOEt)$) produced the net [3 + 2] annulation product **6**. Similarly, the insertion product was not detected. After silica gel treatment, the hydrolysis product **7** could be obtained (Scheme 3). Complex **7** was stable toward both air and moisture. The structure of complex **7** has been confirmed by an X-ray diffraction study (Figure 4), NMR spectroscopy, HRMS, and elemental analysis. The complexes **6** and **7** have similar overall structural features to complex **4**, despite that they have a different metal coordination mode. The difference may be attributed to the steric effect of the terminal methyl group. In agreement with complex **4**, the exocyclic double bond of **7** also exhibited the *Z* configuration with the phenyl and the ester group *cis* to each other.

Scheme 3. [3 + 2] Annulation Reaction of Osmium Hydrido Alkenylcarbyne Complex 1 with Allenoate $CH(CH_3){=}C{=}CH(COOEt)$



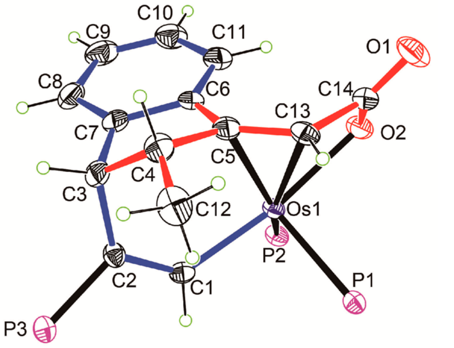
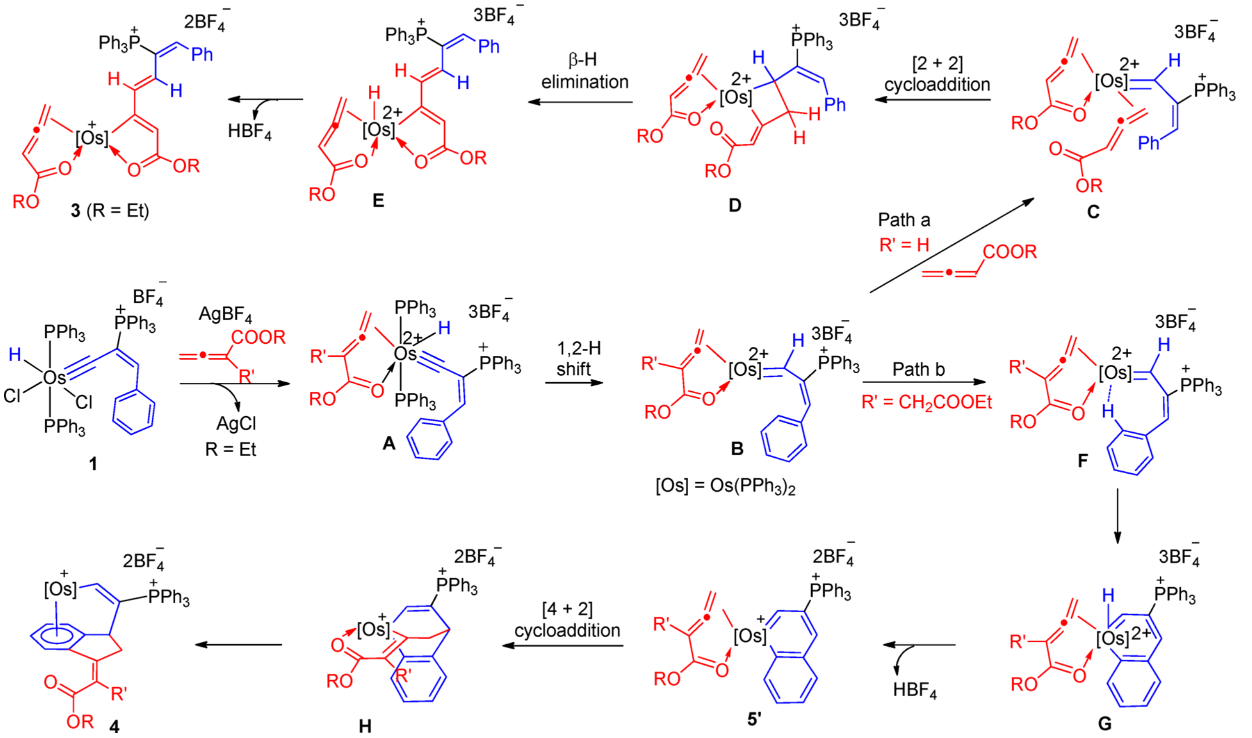


Figure 4. Molecular structure of complex **7** (only the *S* enantiomer is shown; ellipsoids are at the 50% probability level). The phenyl rings in PPh_3 groups and the counteranion are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Os1−C1 2.047(2), C1−C2 1.371(3), C2−C3 1.533(3), C3−C4 1.550(4), C4−C5 1.519(3), C5−C6 1.478(4), C6−C7 1.417(4), C3−C7 1.509(4), C5−C13 1.382(4), C4−C12 1.507(4), Os1−C5 2.234(2), Os1−C13 2.283(2), Os1−O2 2.1824(17); Os1−C1−C2 129.30(18), C1−C2−C3 121.6(2), C2−C3−C4 109.7(2), C2−C3−C7 108.7(2), C3−C4−C5 101.4(2), C4−C5−C6 106.2(2), C5−C6−C7 107.6(2), C3−C7−C6 109.5(2), C4−C3−C7 101.5(2), C4−C5−C13 125.0(2), C5−C4−C12 118.1(2).

Mechanistic Consideration for the Reactions of 1 with Allenoates. Inspired by the fact that only one equivalent of allenoates participates in the [3 + 2] annulation reactions, we conjectured that using one equivalent of methyl/ethyl buta-2,3-dienoate ($CH_2{=}C{=}CHCOOR$ (R = Me/Et)) with complex **1** may lead to the annulation products. However, we still just get the insertion products **2**/**3** in lower yield, and the [3 + 2] annulation products were not detected. Thus, the amount of allenoates was not related to the divergent pathway.

Scheme 4. Proposed Mechanisms for the Formation of Complexes 3 and 4[a]



[a] For clarity, only one of the two orientations of the bidentate-coordinated allenoate is presented. A rationale of the other coordination mode is shown in the Supporting Information.

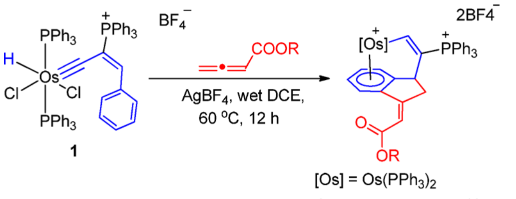
On the basis of the characterized structures and the experimental conditions, we speculated that the substituents of the allenoates may play the key role and the selectivity of the reactions is mainly of steric origin. A possible rationale that accounts for the formation of the insertion product **3** and the [3 + 2] annulation product **4** is shown in Scheme 4 as an example. Reaction of complex **1** with excess $AgBF_4$ and an equivalent of allenoate may initially generate the allenoate-coordinated intermediate **A**. 1,2-Hydrogen shift from the metal center to the carbyne carbon atom of **A** affords alkenylcarbene intermediate **B**. A number of transformations involving hydride carbyne and carbene species have been investigated experimentally and computationally in the literature.[12a,17] From **B**, for different allenoates, there are two possible paths, i.e., paths **a** and **b**, leading to the formation of the complex **3** and **4**, respectively.

In path **a**, another ethyl buta-2,3-dienoate ($CH_2{=}C{=}CHCOOEt$) may coordinate to the metal center with its terminal double bond to produce the intermediate **C**. Subsequent [2 + 2] cycloaddition and β-H elimination,[18] accompanied by the release of HBF_4, would give the osmafuran product **3**.

In path **b**, coordination of another bulky diethyl 2-vinylidenesuccinate ($CH_2{=}C{=}C(CH_2COOEt)(COOEt)$) to the metal center of **B** is unfavorable due to steric effects. Alternatively, the *ortho* C−H bond of the phenyl ring of **F** could be activated to give the intermediate **G**. Upon release of HBF_4, the above-mentioned osmanaphthalene intermediate **5′** was formed. We have reported the similar intramolecular C−H activation of **1**, which gave rise to the formation of osmanaphthalene and osmanaphthalyne,[13] previously. The following metalla-[4 + 2] cycloaddition[9b] (to form the osmafuran intermediates **H**) and reductive elimination could yield the racemic [3 + 2] annulation complex **4**. Thus, the selective *Z* configuration of the exocyclic double bond of final product **4**, in which the phenyl and the ester group are *cis* to each other, could be rationalized by the formation of the osmafuran intermediates **H**.

Unexpectedly, the [3 + 2] annulation product **8** derived from complex **1** and methylbuta-2,3-dienoate ($CH_2{=}C{=}CHCOOMe$) was obtained in 64% yield when the reaction was performed in wet DCE (Scheme 5). The structure of **8** was unambiguously characterized by X-ray crystallographic analysis. As shown in Figure 5 and Table 1, the structural parameters of complex **8** are similar to those of **4**. In the exocyclic double bond of the five-membered ring, the ester and coordinated phenyl group are confirmed to be *cis* to each other. The NMR data associated with **8** are also similar to those of **4** (see Table 2), as expected. Similarly, product **9** was obtained in 61% yield from the reaction of **1** with ethyl buta-2,3-dienoate ($CH_2{=}C{=}CHCOOEt$) under the same conditions. Both complexes **8** and **9** were stable in air or moisture. As analogous reactions, the intermediates closely related to the osmanaphthalene

Scheme 5. [3 + 2] Annulation Reactions of Osmium Hydrido Alkenylcarbyne Complex 1 with Methyl/Ethyl Buta-2,3-dienoates



[Os] = Os(PPh3)2
8: R = Me, Yield = 64%
9: R = Et, Yield = 61%

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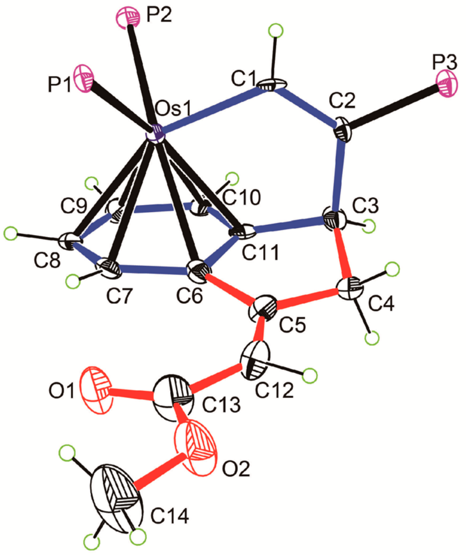


Figure 5. Molecular structure of complex **8** (only the *S* enantiomer is shown; ellipsoids are at the 50% probability level). The phenyl rings in the PPh_3 groups and the counteranion are omitted for clarity.

Table 1. Selected Bond Lengths and Angles for 4, 8, and 9[a]

	4	**8**	**9**
	Bond Lengths [Å]		
Os1−C1	2.082(3)	2.072(6)	2.076(5)
C1−C2	1.356(4)	1.344(7)	1.344(7)
C2−C3	1.532(4)	1.530(8)	1.514(7)
C3−C4	1.549(4)	1.528(8)	1.543(7)
C4−C5	1.541(4)	1.521(8)	1.525(7)
C5−C6	1.473(4)	1.473(8)	1.479(7)
C5−C12	1.348(5)	1.316(9)	1.331(7)
C6−C11	1.432(4)	1.449(8)	1.448(7)
C3−C11	1.506(4)	1.526(8)	1.510(7)
	Bond Angles [deg]		
Os1−C1−C2	119.0(2)	120.0(4)	119.0(4)
C1−C2−C3	119.5(3)	119.9(5)	120.6(4)
C2−C3−C11	106.4(2)	106.2(4)	106.1(4)
C2−C3−C4	112.0(3)	111.9(5)	111.3(4)
C3−C4−C5	107.2(3)	107.8(5)	107.4(4)
C3−C11−C6	111.5(3)	109.8(5)	110.6(4)
C4−C5−C6	106.7(3)	106.2(5)	107.0(4)
C5−C6−C11	108.6(3)	108.5(5)	108.1(4)

[a] ORTEP representation of complex **9** is shown in the Supporting Information.

Table 2. Selected NMR Spectroscopic Data for Complexes 4, 8, and 9

	δ (^1H) [ppm]				δ (^{31}P) [ppm]	
	H1	H3	H4	H12	$OsPPh_3$	$CPPh_3$
4	9.0	4.6	2.1/2.5		−10.5/−10.9	13.7
8	9.0	4.7	2.2/2.7	5.4	−10.9/−12.2	14.0
9	9.0	4.7	2.2/2.6	5.4	−10.9/−12.0	14.0

intermediates **5**/**5′** can also be identified by *in situ* NMR in these reactions.[19]

It is interesting that trace amounts of water in the solvent make a difference. According to the mechanism shown in Scheme 4, we conjectured that the water in the solvent may coordinate to the metal center of **B** and hinder another coordination of allenoate, thus only leading to the formation of annulation complexes **8**/**9**. It is also possible that water may promote a concerted metalation deprotonation[20] of **B** to generate related osmanaphthalene intermediates.

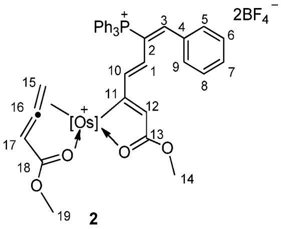
■ CONCLUSIONS

We demonstrated the reactivity of an osmium hydrido alkenylcarbyne complex with several allenoates. For the unsubstitued allenoates, the insertion products or the [3 + 2] annulation products can be obtained in anhydrous solvent or wet solvent, respectively. For substituted terminal or internal allenoates, rather than observing the insertion reaction, the net [3 + 2] annulation products were isolated instead. The results reveal that the divergent pathways for these reactions are mainly of steric effect. Notably, the isolated osmanaphthalene intermediates and the *Z* configuration exocyclic double bond of the [3 + 2] annulation products are all consistent with the proposed mechanism.

■ EXPERIMENTAL SECTION

General Comments. All syntheses were carried out under an inert atmosphere (N_2) by means of standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane, chloroform) under N_2 prior to use. Reagents were used as received from commercial sources without further purification. The starting material $[OsH(\equiv CC(PPh_3){=}CHPh)(PPh_3)_2Cl_2]BF_4$ (**1**) was synthesized according to the previously published procedure.[12a] Allenoates are prepared according to the literature.[21,22] NMR spectroscopic experiments were performed on a Bruker AV-400 spectrometer (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz), a Bruker AV-500 spectrometer (^1H, 500.2 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz), or a Bruker Ascend 600 spectrometer (^1H, 600.1 MHz; ^{13}C, 150.9 MHz; ^{31}P, 242.9 MHz) at room temperature. ^1H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), quartet (q), and broad (br). The HRMS experiments were recorded on a Bruker En Apex Ultra 7.0T FT-MS. Elemental analysis data were obtained on an Elementar Analysen system GmbH Vario EL III instrument.

Preparation and Characterization of Complex 2. The compound $CH_2{=}C{=}CHCOOMe$ (0.72 mmol, 71 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and $AgBF_4$ (0.72 mmol, 140 mg) in dichloroethane (15 mL). The mixture was sealed in a Schlenk tube and stirred at 60 °C for 12 h to give an orange suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. The residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give complex **2** as an orange solid. Yield: 323 mg, 92%. ^1H NMR (500.2 MHz, CD_2Cl_2): δ = 2.5 (br, 2H, $C^{15}H$), 3.4 (s, 3H, $C^{19}H$), 3.6 (s, 3H, $C^{14}H$), 6.0 (s, 1H, $C^{12}H$), 6.3 (d, ^3J(H, H) = 16.6 Hz, 1H, $C^{10}H$), 6.9 (s, 1H, $C^{17}H$), 7.1 (br, 1H, C^3H), 6.8−7.8 (53H, Phs, C^1H, and the above-mentioned $C^{17}H$, C^3H). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ = 23.7 (s, $CPPh_3$), −0.5 (s, $OsPPh_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, plus



2

$[Os] = Os(PPh_3)_2$

DOI: 10.1021/acs.organomet.5b00242
Organometallics 2015, 34, 1742−1750

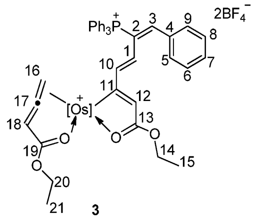
Table 3. Crystal Data and Structure Refinement for **2**, **4**, **5**, **7**, and **8**

	2·3CH_2Cl_2	**4**·CH_2Cl_2	**5**·CH_2Cl_2	**7**	**8**·$C_2H_4Cl_2$
formula	$C_{76}H_{69}O_4Cl_6OsP_3B_2F_8$	$C_{74}H_{67}O_4Cl_2OsP_3B_2F_8$	$C_{74}H_{67}B_2Cl_2F_8O_4OsP_3$	C_{68} $H_{56}O_2OsP_3BF_4$	$C_{70}H_{61}O_2Cl_2OsP_3B_2F_8$
M_r	1715.74	1547.91	1547.93	1275.05	1461.82
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	10.51660(10)	20.2277(2)	13.0016(4)	10.8669(2)	19.8637(7)
b [Å]	27.7404(2)	22.4748(2)	13.3826(9)	13.1380(3)	23.1808(5)
c [Å]	25.6209(2)	15.2161(2)	22.8476(6)	20.8981(4)	14.2062(4)
α [deg]	90.00	90.00	78.5660(10)	91.8740(10)	90.00
β [deg]	99.8730(10)	111.5490(10)	80.8660(10)	102.4020(10)	109.839(4)
γ [deg]	90.00	90.00	61.9190(10)	109.7640(10)	90.00
V [Å^3]	7363.81(11)	6433.94(12)	3427.9(3)	2724.27(10)	6153.1(3)
Z	4	4	2	2	4
ρ_{calcd} [g cm^{-3}]	1.548	1.598	1.500	1.554	1.578
μ [mm^{-1}]	6.477	5.850	2.079	2.491	2.309
$F(000)$	3448.0	3120.0	1560.0	1284.0	2936.0
θ range [deg]	3.19 to 62.10	3.69 to 76.38	6.008 to 49.998	3.00 to 27.48	3.36 to 25.00
reflns collected	22 830	61 996	44 509	44 507	27 590
indep reflns	11 478	13 422	12 045	12 478	10 814
obsd reflns [$I \geq 2\sigma(I)$]	11 063	12 626	9125	11 581	8323
data/restraints/params	11 478/0/901	13 422/0/847	12 045/204/1113	12 478/0/712	10 814/0/793
GOF on F^2	1.055	1.027	1.104	1.037	0.905
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0425/0.1079	0.0323/0.0876	0.0698/0.1576	0.0277/0.0627	0.0434/0.1209
R_1/wR_2 (all data)	0.0437/0.1088	0.0344/0.0894	0.0958/0.1848	0.0342/0.0652	0.0654/0.1358
largest peak/hole [e Å^{-3}]	1.928/−1.482	1.797/−1.332	1.81/−2.66	1.914/−1.768	2.234/−1.310
CCDC no.[a]	1039697	1039704	1039715	1039705	1039699

[a] These files contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMBC, and ^{13}C–dept 135, CD_2Cl_2): δ = 219.3 (s, C^{16}), 199.6 (br, C^{11}), 184.5 (s, C^{18}), 180.1 (s, C^{13}), 156.5 (d, $^2J(P, C)$ = 11.0 Hz, C^3), 146.1 (d, $^3J(P, C)$ = 6.1 Hz, C^{10}), 117.5 (s, C^{12}), 116.7 (d, $^1J(P, C)$ = 80.7 Hz, C^2), 102.7 (s, C^{17}), 54.2 (s, C^{14}), 54.2 (s, C^{19}), 13.2 (s, C^{15}), 116.2−135.1 (Phs, C^1, and the above-mentioned C^2, C^{12}). HRMS (ESI): m/z calcd for $[C_{73}H_{63}O_4OsP_3]^{2+}$ 644.1776; found 644.1777. Anal. Calcd (%) for $C_{73}H_{63}B_2F_8O_4OsP_3$: C 60.01, H 4.35. Found: C 59.99, H 4.51.

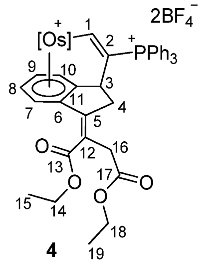
Preparation and Characterization of Complex 3. The compound $CH_2{=}C{=}CHCOOEt$ (0.72 mmol, 81 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and $AgBF_4$ (0.72 mmol, 140 mg) in dichloroethane (15 mL). The mixture was sealed in a Schlenk tube and stirred at 60 °C for 12 h to give an orange suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. The residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give complex **3** as an orange solid. Yield: 318 mg, 89%. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.9 (t, $^3J(H, H)$ = 5.8 Hz, 3H, $C^{21}H$), 1.0 (t, $^3J(H, H)$ = 5.8 Hz, 3H, $C^{15}H$), 2.3 (br, 2H, $C^{16}H$), 3.8 (q, $^3J(H, H)$ = 5.8 Hz, 2H, $C^{20}H$), 4.0 (q, $^3J(H, H)$ = 5.8 Hz, $C^{14}H$), 6.0 (s, 1H, $C^{12}H$), 6.3 (d, $^3J(H, H)$ = 16.3 Hz, 1H, $C^{10}H$), 6.9 (s, 1H, $C^{18}H$), 7.1 (br, 1H, C^3H), 6.8–7.8 (53H, Phs, C^1H and the above-mentioned $C^{18}H$, C^3H). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 23.6 (s, $CPPh_3$), −0.4 (s, $OsPPh_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, plus $^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMBC, and ^{13}C–dept 135, $CDCl_3$): δ = 219.0 (s, C^{17}), 199.0 (br, C^{11}), 183.7 (s, C^{19}), 179.4 (s, C^{13}), 156.5 (d, $^2J(P, C)$ = 11.6 Hz, C^3), 145.6 (d, $^3J(P, C)$ = 5.7 Hz, C^{10}), 117.5 (s, C^{12}), 116.5 (d, $^1J(P, C)$ = 80.9 Hz, C^2), 102.5 (s, C^{18}), 63.9 (s, C^{14}), 63.5 (s, C^{20}), 13.1 (s, C^{16}), 13.0 and 12.8 (s, C^{15} and C^{21}), 116.0−134.6 (Phs, C^1 and the above-mentioned C^{12}, C^2). HRMS (ESI): m/z calcd for $[C_{75}H_{67}O_4OsP_3]^{2+}$ 658.1932; found 658.1945. Anal. Calcd (%) for $C_{75}H_{67}B_2F_8O_4OsP_3$: C 60.49, H 4.54. Found: C 60.57, H 4.82.



3

[Os] = Os(PPh$_3$)$_2$

Preparation and Characterization of Complex 4. The compound $CH_2{=}C{=}C(COOEt)(CH_2COOEt)$ (0.72 mmol, 143 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and $AgBF_4$ (0.72 mmol, 140 mg) in dichloroethane (15 mL). The mixture was sealed in a Schlenk tube and stirred at 60 °C for 2 d to give a brown suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. Addition of diethyl ether (20 mL) to the residual gave a brown precipitate, the precipitate was collected by filtration and washed with DCM (3 × 2 mL), and complex **4** could be separated out as a light yellow solid. Yield: 169 mg, 48%. Due to its poor solubility in common organic solvents, complex **4** was characterized only by ^1H NMR and ^{31}P NMR. ^1H NMR (500.2 MHz, d_6-DMSO): δ = 1.0 (t, $^3J(H, H)$ = 7.0 Hz, 3H, $C^{15}H$ or $C^{19}H$), 1.1 (t, $^3J(H, H)$ = 7.0 Hz, 3H, $C^{15}H$ or



4

[Os] = Os(PPh$_3$)$_2$

DOI: 10.1021/acs.organomet.5b00242
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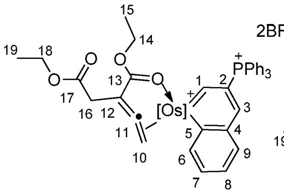
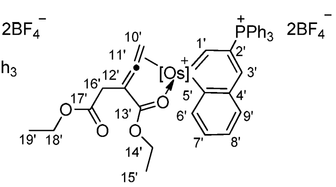
C^{19}*H*), 2.1 (d, ^2J(H, H) = 19.1 Hz, 1H, C^4*H*), 2.5 (overlapped with the signal of residual DMSO, 1H, C^4*H*), 2.8 (d, ^2J(H, H) = 17.5 Hz, 1H, C^{16}*H*), 3.0 (d, ^2J(H, H) = 17.5 Hz, 1H, C^{16}*H*), 3.8 (q, ^3J(H, H) = 7.0 Hz, 2H, C^{14}*H* or C^{18}*H*), 4.0 (q, ^3J(H, H) = 7.0 Hz, 2H, C^{14}*H* or C^{18}*H*), 4.6 (d, ^3J(H, H) = 7.4 Hz, 1H, C^3*H*), 5.4–8.0 (49H, Phs), 9.0 (d, ^3J(P, H) = 20.9 Hz, 1H, C^1*H*). ^{31}P{^{1}H} NMR (202.5 MHz, d_6-DMSO): δ = 13.7 (s, C*P*Ph$_3$), −10.5 (d, ^2J(P, P) = 31.6 Hz, Os*P*Ph$_3$), −10.9 (d, ^2J(P, P) = 31.6 Hz, Os*P*Ph$_3$). HRMS (ESI): *m*/*z* calcd for [$C_{73}H_{65}O_4OsP_3$+BF$_4$]$^+$ 1377.3752; found 1377.3780. Anal. Calcd (%) for $C_{73}H_{65}B_2F_8O_4OsP_3$: C 59.93, H 4.48. Found: C 59.84, H 4.33.

Preparation and Characterization of Complexes 5 and 5′. The compound CH$_2$═C═C(COOEt)(CH$_2$COOEt) (0.72 mmol, 143 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and AgBF$_4$ (0.72 mmol, 140 mg) in dichloroethane (15 mL). The mixture was stirred at room temperature for 5 h or stirred at 60 °C for 1 h to give a red suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. Addition of diethyl ether (20 mL) to the residual gave the mixture of **5** and **5′** as a red solid. Yield: 334 mg, 95%. ^{1}H NMR (600.1 MHz, CD$_2$Cl$_2$): δ = 1.1−1.2 (m, 12H, C^{15}*H*, C^{19}*H*, C$^{15′}$*H*, C$^{19′}$*H*), 2.9 (br, 2H, C^{16}*H*), 3.0 (br, 2H, C$^{16′}$*H*), 3.8 (q, ^3J(H, H) = 7.1 Hz, 2H, C$^{14′}$*H*), 3.9 (br, 2H, C^{10}*H*), 4.0 (q, ^3J(H, H) = 7.1 Hz, 2H, C^{18}*H*), 4.1 (q, ^3J(H, H) = 7.1 Hz, 2H, C$^{18′}$*H*), 4.3 (q, ^3J(H, H) = 7.1 Hz, 2H, C^{14}*H*), 4.4 (br, 2H, C$^{10′}$*H*), 8.5 (d, ^3J(P, H) = 8.1 Hz, 1H, C$^{3′}$*H*), 16.4 (d, ^3J(P, H) = 21.6 Hz, 1H, C^1*H*), 17.1 (d, ^3J(P, H) = 20.3 Hz, 1H, C$^{1′}$*H*), 6.5−7.9 (99H, C^3*H* and Phs). ^{31}P{^{1}H} NMR (242.9 MHz, CD$_2$Cl$_2$): δ = 23.8 (s, C*P*Ph$_3$ of **5′**), 7.2 (s, Os*P*Ph$_3$ of **5′**), 22.8 (s, C*P*Ph$_3$ of **5**), 3.8 (s, Os*P*Ph$_3$ of **5**). ^{13}C{^{1}H} NMR (150.9 MHz, plus ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC, and ^{13}C−dept 135, CD$_2$Cl$_2$): δ = 274.9 (br, C^1), 260.9 (br, C$^{1′}$), 215.2 (t, ^2J(P, C) = 4.2 Hz, C^{11}), 213.8 (t, ^2J(P, C) = 4.1 Hz, C$^{11′}$), 206.2 (t, ^2J(P, C) = 7.6 Hz, C$^{5′}$), 185.7 (s, C$^{13′}$), 182.1 (s, C^{13}), 174.9 (d, ^2J(P, C) = 17.3 Hz, C^3), 174.3 (t, ^2J(P, C) = 7.5 Hz, C^5), 169.0 (d, ^2J(P, C) = 16.3 Hz, C$^{3′}$), 168.9 (s, C$^{17′}$), 168.5 (s, C^{17}), 115.7 (d, ^1J(P, C) = 77.9 Hz, C$^{2′}$), 114.0 (d, ^1J(P, C) = 78.8 Hz, C^2), 113.9 (s, C$^{12′}$), 113.1 (s, C^{12}), 66.9 (s, C$^{14′}$), 66.8 (s, C^{14}), 61.6 (s, C$^{18′}$), 61.5 (s, C^{18}), 47.8 (s, C$^{10′}$), 44.5 (s, C^{10}), 38.2 (s, C$^{16′}$), 37.7 (s, C^{16}), 13.04−14.03 (C^{15}, C^{19}, C$^{15′}$, C$^{19′}$), 116.7−149.8 (Phs). HRMS (ESI): *m*/*z* calcd for [$C_{73}H_{65}O_4OsP_3$+BF$_4$]$^+$ 1377.3752; found 1377.3711. Anal. Calcd (%) for $C_{73}H_{65}B_2F_8O_4OsP_3$: C 59.93, H 4.48. Found: C 59.59, H 4.25.



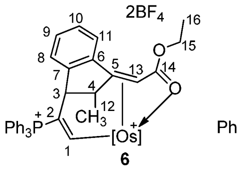
5



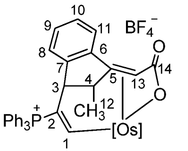
[Os] = Os(PPh$_3$)$_2$

5′

Preparation and Characterization of Complexes 6 and 7. The compound CH(CH$_3$)═C═CHCOOEt (0.72 mmol, 91 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and AgBF$_4$ (0.72 mmol, 140 mg) in dichloroethane (15 mL). The mixture was stirred at RT for 1 h to give a green suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. Addition of diethyl ether (20 mL) to the residual gave complex **6** as a green solid. Yield: 304 mg, 91%. Complex **7** was obtained as a green solid when **6** was further purified by column chromatography (silica gel, eluent: dichloromethane/methanol = 20:1). Yield: 242 mg, 87%.



6



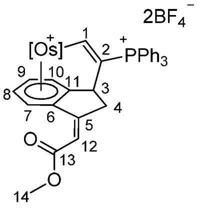
7

[Os] = Os(PPh$_3$)$_2$

Complex **6**. ^{1}H NMR (600.1 MHz, CD$_2$Cl$_2$): δ = 0.39 (d, ^3J(H, H) = 5.5 Hz, 3H, C^{12}*H*), 1.3 (dd, apparent t, ^3J(H, H) = 7.3 Hz, 3H, C^{16}*H*), 3.7 (s, 1H, C^{13}*H*), 3.8 (br, 1H, C^4*H*), 4.2 (dq, ^3J(H, H) = 7.3 Hz, ^2J(H, H) = 17.5 Hz, 1H, C^{15}*H*), 4.6 (dd, ^3J(P, H) = 9.9 Hz, ^3J(H, H) = 4.5 Hz, 1H, C^3*H*), 4.7 (dq, ^3J(H, H) = 7.3 Hz, ^2J(H, H) = 17.5 Hz, 1H, C^{15}*H*), 12.2 (d, ^3J(P, H) = 24.1 Hz, 1H, C^1*H*), 6.6−7.8 (49H, Phs). ^{31}P{^{1}H} NMR (242.9 MHz, CD$_2$Cl$_2$): δ = 15.2 (s, C*P*Ph$_3$), −11.7 (d, ^2J(P, P) = 13.4 Hz, Os*P*Ph$_3$), −15.2 (d, ^2J(P, P) = 13.4 Hz, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (150.9 MHz, plus ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC, and ^{13}C−dept 135, CD$_2$Cl$_2$): δ = 175.0 (s, C^{14}), 171.5 (br, C^1), 166.8 (d, ^3J(P, C) = 4.9 Hz, C^7), 117.4 (d, ^1J(P, C) = 71.9 Hz, C^2), 116.8 (s, C^5), 98.9 (s, C^6), 66.0 (s, C^{15}), 63.9 (d, ^2J(P, C) = 11.4 Hz, C^{13}), 51.9 (d, ^2J(P, C) = 20.1 Hz, C^3), 44.6 (s, C^4), 12.6 (s, C^{16}), 11.9 (s, C^{12}), 119.4−138.5 (Phs). HRMS (ESI): *m*/*z* calcd for [$C_{70}H_{61}O_2OsP_3$]$^{2+}$ 609.1748; found 609.1743. Anal. Calcd (%) for $C_{70}H_{61}B_2F_8O_2OsP_3$: C 60.44, H 4.42. Found: C 60.25, H 4.73.

Complex **7**. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 0.37 (d, ^3J(H, H) = 6.6 Hz, 3H, C^{12}*H*), 3.5 (br, 1H, C^4*H*), 3.7 (d, ^3J(P, H) = 3.1 Hz, 1H, C^{13}*H*), 4.3 (dd, ^3J(P, H) = 10.9 Hz, ^3J(H, H) = 5.4 Hz, 1H, C^3*H*), 12.2 (d, ^3J(P, H) = 26.5 Hz, 1H, C^1*H*), 6.3−7.7 (49H, Phs). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ = 15.4 (s, C*P*Ph$_3$), −10.3 (d, ^2J(P, P) = 16.8 Hz, Os*P*Ph$_3$), −15.4 (d, ^2J(P, P) = 16.8 Hz, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, plus ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC, and ^{13}C−dept 135, CDCl$_3$): δ = 185.1 (br, C^1), 170.5 (s, C^{14}), 164.5 (d, ^3J(P, C) = 5.1 Hz, C^7), 114.7 (d, ^1J(P, C) = 70.8 Hz, C^2), 113.8 (s, C^5), 105.1 (s, C^6), 78.5 (d, ^2J(P, C) = 11.7 Hz, C^{13}), 52.4 (d, ^2J(P, C) = 21.9 Hz, C^3), 44.5 (s, C^4), 13.1 (s, C^{12}), 120.9−137.9 (Phs). HRMS (ESI): *m*/*z* calcd for [$C_{68}H_{56}O_2OsP_3$]$^+$ 1189.3109; found 1189.3105. Anal. Calcd (%) for $C_{68}H_{56}BF_4O_2OsP_3$: C 64.05, H 4.43. Found: C 64.39, H 4.77.

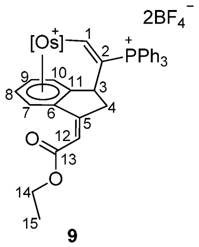
Preparation and Characterization of Complex 8. The compound CH$_2$═C═CHCOOMe (0.72 mmol, 71 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and AgBF$_4$ (0.72 mmol, 140 mg) in wet dichloroethane (15 mL). The mixture was sealed in a Schlenk tube and stirred at 60 °C for 12 h to give a brown suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. Addition of diethyl ether (20 mL) to the residual gave a brown precipitate, the precipitate was collected by filtration and washed with DCM (3 × 2 mL), and complex **8** could be separated out as a light yellow solid. Yield: 209 mg, 64%. Due to its poor solubility in common organic solvents, complex **8** was characterized only by ^{1}H NMR and ^{31}P NMR. ^{1}H NMR (500.2 MHz, d_6-DMSO): δ = 2.2 (d, ^2J(H, H) = 19.2 Hz, 1H, C^4*H*), 2.7 (dd, ^2J(H, H) = 19.2 Hz, ^3J(H, H) = 8.5 Hz, 1H, C^4*H*), 3.4 (s, 3H, C^{14}*H*), 4.7 (d, ^3J(H, H) = 8.5 Hz, 1H, C^3*H*), 5.3 (br, 1H, proton on Phs), 5.4 (s, 1H, C^{12}*H*), 6.1 (br, 1H, proton on Phs), 6.7−8.0 (47H, Phs), 9.0 (d, ^3J(P, H) = 21.3 Hz, 1H, C^1*H*). ^{31}P{^{1}H} NMR (202.5 MHz, d_6-DMSO): δ =14.0 (s, C*P*Ph$_3$), −10.9 (d, ^2J(P, P) = 33.4 Hz, Os*P*Ph$_3$), −12.2 (d, ^2J(P, P) = 33.4 Hz, Os*P*Ph$_3$). HRMS (ESI): *m*/*z* calcd for [$C_{68}H_{57}O_2OsP_3$]$^{2+}$ 595.1591; found 595.1599. Anal. Calcd (%) for $C_{68}H_{57}B_2F_8O_2OsP_3$: C 59.92, H 4.22. Found: C 59.51, H 4.61.[23]



8

[Os] = Os(PPh$_3$)$_2$

Preparation and Characterization of Complex 9. The compound CH$_2$═C═CHCOOEt (0.72 mmol, 81 mg) was added to a suspension of compound **1** (300 mg, 0.24 mmol) and AgBF$_4$ (0.72 mmol, 140 mg) in wet dichloroethane (15 mL). The mixture was sealed in a Schlenk tube and stirred at 60 °C for 12 h to give a brown suspension. The AgCl precipitate was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL.



9

[Os] = Os(PPh$_3$)$_2$

Addition of diethyl ether (20 mL) to the residual gave a brown precipitate, the precipitate was collected by filtration and washed with DCM (3 × 2 mL), and complex **9** could be separated out as a light yellow solid. Yield: 202 mg, 61%. Due to its poor solubility in common organic solvents, complex **9** was only characterized by ^{1}H NMR and ^{31}P NMR. ^{1}H NMR (400.1 MHz, d_6-DMSO): δ = 1.1 (t, ^3J(H, H) = 6.3 Hz, 3H, C^{15}*H*), 2.2 (d, ^2J(H, H) = 19.1 Hz, 1H, C^4*H*), 2.6 (dd, ^2J(H, H) = 19.1 Hz, ^3J(H, H) = 8.3 Hz, 1H, C^4*H*), 3.8 (q, ^3J(H, H) = 6.3 Hz, 2H, C^{14}*H*), 4.7 (d, ^3J(H, H) = 8.3 Hz, 1H, C^3*H*), 5.3 (br, 1H, proton on Phs), 5.4 (s, 1H, C^{12}*H*), 6.1 (d, ^3J(H, H) = 6.1 Hz, 1H, proton on Phs), 6.7–8.0 (47H, Phs), 9.0 (d, ^3J(P, H) = 21.9 Hz, 1H, C^1*H*). ^{31}P{^{1}H} NMR (162.0 MHz, d_6-DMSO): δ = 14.0 (dd, apparent t, ^4J(P, P) = 3.4 Hz, ^4J(P, P) = 3.4 Hz, C*P*Ph$_3$), −10.9 (dd, ^2J(P, P) = 31.4 Hz, ^4J(P, P) = 3.4 Hz, Os*P*Ph$_3$), −12.0 (dd, ^2J(P, P) = 31.4 Hz, ^4J(P, P) = 3.4 Hz, Os*P*Ph$_3$). HRMS (ESI): *m/z* calcd for [$C_{69}H_{59}O_2OsP_3$]$^{2+}$ 602.1670; found 602.1689. Anal. Calcd (%) for $C_{69}H_{59}B_2F_8O_2OsP_3$: C 60.19, H 4.32. Found: C 60.16, H 4.35.

Crystallographic Analysis. Single crystals suitable for X-ray diffraction of **2**, **5**, and **7** were grown from a dichloromethane solution layered with hexane. A crystal suitable for X-ray diffraction of **8** was grown from a dichloroethane/methanol solution layered with hexane, whereas a crystal suitable for X-ray diffraction of **4** was grown from a dichloromethane/methanol solution layered with hexane. Single-crystal X-ray diffraction data were collected on an Agilent SuperNova diffractometer or a Rigaku R-AXIS SPIDER IP CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) or Cu Kα radiation (λ = 1.541 78 Å). All of the data were corrected for absorption effects by using the multiscan technique. All of the structures were solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F^2 using the SHELXTL program package. All of the non-hydrogen atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were placed at their idealized positions and assumed the riding model unless otherwise stated. The solvent molecules CH_2Cl_2, phenyl groups on PPh$_3$, and the BF$_4^-$ groups in **5** are disordered and were refined with suitable restraints. For further details on the crystal data, data collection, and refinements, see Table 3. Crystal data and structure refinement for **3** and **9** are shown in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for complexes **3** and **9**, a rationale of the other coordination mode of allenoates, and copies of ^{1}H, ^{31}P, and ^{13}C NMR spectra of all new products are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews of metal carbene, see: (a) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271–288. (b) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964–4002. (c) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145–180. (d) Dzik, W. I.; Zhang, X. P.; de Bruin, B. *Inorg. Chem.* **2011**, *50*, 9896–9903. (e) Fernández, I.; Cossío, F. P.; Sierra, M. A. *Acc. Chem. Res.* **2011**, *44*, 479–490. (f) Xue, Z.-L.; Morton, L. A. *J. Organomet. Chem.* **2011**, *696*, 3924–3934. (g) Herndon, J. W. *Coord. Chem. Rev.* **2013**, *257*, 2899–3003. (h) Cao, X.-Y.; Zhao, Q.; Lin, Z.; Xia, H. *Acc. Chem. Res.* **2014**, *47*, 341–354.

(2) For reviews of metal carbyne, see: (a) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281–2309. (b) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167–2187. (c) Chen, J.; Jia, G. *Coord. Chem. Rev.* **2013**, *257*, 2491–2521. (d) Jia, G. *Organometallics* **2013**, *32*, 6852–6866. (e) Shi, C.; Jia, G. *Coord. Chem. Rev.* **2013**, *257*, 666–701. For some recent reports of metal carbynes: (f) Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T.; Xie, Z.; Schleyer, P. v. R.; Xia, H. *Nat. Chem.* **2013**, *5*, 698–703. (g) Chen, J.; Zhang, C.; Xie, T.; Wen, T. B.; Zhang, H.; Xia, H. *Organometallics* **2013**, *32*, 3993–4001. (h) Zhu, C.; Luo, M.; Zhu, Q.; Zhu, J.; Schleyer, P. v. R.; Wu, J. I. C.; Lu, X.; Xia, H. *Nat. Commun.* **2014**, *5*, 3265. (i) Zhu, C.; Zhu, Q.; Fan, J.; Zhu, J.; He, X.; Cao, X.-Y.; Xia, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 6232–6236.

(3) (a) Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40*, 1857–1869. (b) Kress, S.; Blechert, S. *Chem. Soc. Rev.* **2012**, *41*, 4389–4408. (c) Zhu, S.-F.; Zhou, Q.-L. *Acc. Chem. Res.* **2012**, *45*, 1365–1377. (d) Obradors, C.; Echavarren, A. M. *Acc. Chem. Res.* **2013**, *47*, 902–912. (e) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236–247. (f) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151–5162.

(4) (a) Jyothish, K.; Zhang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 8478–8480. (b) Füerstner, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 2794–2819.

(5) (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29. (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592–4633. (c) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117–7140. (d) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243–251. (e) Nolan, S. P.; Clavier, H. *Chem. Soc. Rev.* **2010**, *39*, 3305–3316.

(6) (a) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317–1382. (b) Hansen, E. C.; Lee, D. *Acc. Chem. Res.* **2006**, *39*, 509–519. (c) Villar, H.; Frings, M.; Bolm, C. *Chem. Soc. Rev.* **2007**, *36*, 55–66.

(7) (a) Zhang, W.; Moore, J. S. *Adv. Synth. Catal.* **2007**, *349*, 93–120. (b) Schrock, R. R. *Chem. Commun.* **2013**, *49*, 5529–5531. (c) Yang, H.; Jin, Y.; Du, Y.; Zhang, W. *J. Mater. Chem. A* **2014**, *2*, 5986–5993.

(8) (a) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701–712. (b) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133–1150. (c) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783–816. (d) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994–2009. (e) Adams, C. S.; Weatherly, C. D.; Burke, E. G.; Schomaker, J. M. *Chem. Soc. Rev.* **2014**, *43*, 3136–3163. (f) Alcaide, B.; Almendros, P. *Acc. Chem. Res.* **2014**, *47*, 939–952. (g) Kitagaki, S.; Inagaki, F.; Mukai, C. *Chem. Soc. Rev.* **2014**, *43*, 2956–2978. (h) Ye, J.; Ma, S. *Acc. Chem. Res.* **2014**, *47*, 989–1000.

(9) For metathesis and cycloaddition reactions of metal carbenes with allenes, see: (a) Ahmed, M.; Arnauld, T.; Barrett, A. G. M.; Braddock, D. C.; Flack, K.; Procopiou, P. A. *Org. Lett.* **2000**, *2*, 551–553. (b) Barluenga, J.; Vicente, R.; Barrio, P.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2004**, *126*, 5974–5975. (c) Barluenga, J.; Vicente, R.; Barrio, P.; López, L. A.; Tomás, M.; Borge, J. *J. Am. Chem. Soc.* **2004**, *126*, 14354–14355. (d) Barluenga, J.; Vicente, R.; López, L. A.; Tomás, M. *Tetrahedron* **2005**, *61*, 11327–11332. (e) Murakami, M.;

Kadowaki, S.; Matsuda, T. *Org. Lett.* **2005**, *7*, 3953−3956. (f) Barluenga, J.; Vicente, R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2006**, *128*, 7050−7054. (g) Barluenga, J.; Vicente, R.; López, L. A.; Tomás, M. *Tetrahedron* **2010**, *66*, 6335−6339.

(10) For "ene-like" reaction of Fischer chromium carbene complexes with vinylidenecyclopropenes, see: Chong-Cheng, H.; Fu-Chun, W.; Ming-Chang, P. Y.; Jyh-Horng, S. *J. Organomet. Chem.* **1994**, *474*, 123−128.

(11) For the formation of metal trimethylenemethane complexes by the reaction of metal carbenes with allenes, see: (a) Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed.* **1987**, *26*, 357−359. (b) Aumann, R.; Melchers, H. D. *J. Organomet. Chem.* **1988**, *355*, 351−358. (c) Aumann, R.; Trentmann, B. *Chem. Ber.* **1989**, *122*, 1977−1982. (d) Aumann, R.; Trentmann, B. *Chem. Ber.* **1991**, *124*, 2335−2342. (e) Fryzuk, M. D.; Joshi, K.; Rettig, S. J. *Organometallics* **1991**, *10*, 1642−1644. (f) Bai, T.; Ma, S.; Jia, G. *Coord. Chem. Rev.* **2009**, *253*, 423−448.

(12) (a) Liu, B.; Wang, H.; Xie, H.; Zeng, B.; Chen, J.; Tao, J.; Bin Wen, T.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5430−5434. (b) Liu, B.; Zhao, Q.; Wang, H.; Chen, J.; Cao, X.; Cao, Z.; Xia, H. *Chin. J. Chem.* **2012**, *30*, 2158−2168.

(13) Liu, B.; Xie, H.; Wang, H.; Wu, L.; Zhao, Q.; Chen, J.; Bin Wen, T.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5461−5464.

(14) (a) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662−1668. (b) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428−1438. (c) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680−4690. (d) Gong, L.; Lin, Y.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1101−1111. (e) Lin, Y.; Gong, L.; Xu, H.; He, X.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1524−1533. (f) Liu, B.; Zhao, Q.; Wang, H.; Zeng, B.; Cao, X.-Y.; Xia, H. *Sci. China Chem.* **2013**, *56*, 1105−1111. (g) Tsui, W.-K.; Chung, L.-H.; Tsang, W.-H.; Yeung, C.-F.; Chiu, C.-H.; Lo, H.-S.; Wong, C.-Y. *Organometallics* **2015**, *34*, 1005−1012.

(15) (a) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 8181−8184. (b) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 10630−10634. (c) Mannathan, S.; Cheng, C.-H. *J. Chin. Chem. Soc.* **2014**, *61*, 59−66.

(16) Nan, J.; Zuo, Z.; Luo, L.; Bai, L.; Zheng, H.; Yuan, Y.; Liu, J.; Luan, X.; Wang, Y. *J. Am. Chem. Soc.* **2013**, *135*, 17306−17309.

(17) (a) Bannwart, E.; Jacobsen, H.; Furno, F.; Berke, H. *Organometallics* **2000**, *19*, 3605−3619. (b) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184−11195. (c) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2037−2041.

(18) (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252−3254. (b) Thorn, D. L. *Organometallics* **1982**, *1*, 879−881. (c) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **1999**, 1141−1149. (d) Leduc, A.-M.; Salameh, A.; Soulivong, D.; Chabanas, M.; Basset, J.-M.; Coperet, C.; Solans-Monfort, X.; Clot, E.; Eisenstein, O.; Boehm, V. P. W.; Roeper, M. *J. Am. Chem. Soc.* **2008**, *130*, 6288−6297.

(19) More detailed results are given in the Supporting Information.

(20) (a) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 10848−10849. (b) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826−1834. (c) Fagnou, K. *Top. Curr. Chem.* **2010**, *292*, 35−56. (d) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Org. Chem.* **2011**, *77*, 658−668. (e) Pahls, D. R.; Allen, K. E.; Goldberg, K. I.; Cundari, T. R. *Organometallics* **2014**, *33*, 6413−6419.

(21) Rout, L.; Harned, A. M. *Chem.—Eur. J.* **2009**, *15*, 12926−12928.

(22) Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544−547.

(23) Although the elemental analysis result of complex **8** was slightly outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date.