Amide-Directed Formation of Five-Coordinate Osmium Alkylidenes from Alkynes

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Supporting Information

ABSTRACT: The amide-directed synthesis of five-coordinate osmium alkylidene derivatives from alkynes is reported. These types of complexes, which have been elusive until now because of the tendency of osmium to give hydride alkylidyne species, are prepared by reaction of the dihydride OsH2Cl2(PiPr3)2 (1) with terminal alkynes containing a distal amide group. Complex 1 reacts with N-phenylhex-5-ynamide and N-phenylhepta-6-ynamide to give OsCl2{═C(CH3)(CH2)nNH(CO)Ph}(PiPr3)2 (n = 3 (2), 4 (3)). The relative position of carbonyl and NH groups in the organic substrates has no influence on the reaction. Thus, treatment of 1 with N-(pent-4-yn-1-yl)benzamide leads to OsCl2{═C(CH3)(CH2)3NHC(O)Ph}(PiPr3)2 (4). The new compounds are intermediate species in the cleavage of the C−C triple bond of the alkynes. Under mild conditions, they undergo the rupture of the Cα−CH3 bond of the alkylidene, which comes from the alkyne triple bond, to afford six-coordinate hydride−alkylidyne derivatives. In dichloromethane, complex 2 gives a 10:7 mixture of OsHCl2{≡C(CH2)2C(O)NHPh}(PiPr3)2 (5) and OsHCl2{≡CHCH(CH2)2C(O)NHPh}(PiPr3)2 (6). The first complex contains a linear separation between the alkylidyne Cα atom and the amide group, whereas the spacer is branched in the second complex. In contrast to the case for 2, complex 4 selectively affords OsHCl2{≡C(CH2)2NH(CO)Ph}(PiPr3)2 (7). In spite of their instability, these compounds give the alkylidene−allene metathesis, being a useful entry to five-coordinate vinylidene complexes, including the dicarbon-disubstituted OsCl2{═C═CMe2}(PiPr3)2 (8) and the monosubstituted OsCl2{═C═CHCy}(PiPr3)2 (9).

INTRODUCTION

One of the milestones in the chemistry of the last few decades is without doubt the discovery of well-defined ruthenium alkylidene catalysts for olefin metathesis.1 Inspired by methodologies previously used to prepare tungsten alkylidenes, in 1992 and 1993, Grubbs and co-workers carried out the addition of diphenylcyclopropene to RuCl2(PPh3)3, followed by phosphine exchange, which gave rise to the five-coordinate alkenyl−alkylidyne derivatives RuCl2(═CHCH═CPh2)(PR3)2 (Scheme 1).2 In 1995, they extended the procedure to alkyl- and arylalkylidenes by using alkyl- and arylidiazalkanes instead of diphenylcyclopropene.3

We worked on the osmium counterparts, in parallel. Thus, in 1993, we reported that the reactions of the complex OsH2Cl2(PiPr3)2 with terminal alkynes, alkynols, and enynes yield the hydride alkylidyne oxidized forms (Scheme 2).4 In 1998, Caulton and co-workers observed that the reactions with olefins led to equimolecular amounts of hydrogenated olefin and

Scheme 1

Scheme 2

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the corresponding hydride alkylidyne derivatives.\textsuperscript{5} Most recently, we have shown that these types of compounds can be also prepared from gem-disubstituted allenes and internal enynes.\textsuperscript{6} The behavior of OsH\textsubscript{2}Cl\textsubscript{2}((PPh\textsubscript{3})\textsubscript{2}) is common for unsaturated osmium dihydride complexes, affording dihydrogen tautomers by coordination of electron-poor Lewis bases.\textsuperscript{7}

The ruthenium alkylidene complexes shown in Scheme 1 and the osmium hydride–alkylidyne derivatives of Scheme 2 are both parts of the same redox equilibrium (eq 1). Ruthenium, more oxidizing than osmium, favors the reduced form. However, osmium is more reducing than ruthenium and, preferring saturated species, stabilizes the saturated oxidized form. The transformation from alkylidene to alkylidyne migration has been reported for a variety of metals of groups 6–8.\textsuperscript{8} The reverse reaction, in which a 1,2-hydrogen shift from the alkylidene C\textsubscript{α} atom to the metal occurs, has been mainly observed for osmium\textsuperscript{9} and rhenium.\textsuperscript{10} Because the reactions summarized by eq 1 are redox processes, the position of the equilibria and the activation energy of the transformation are governed not only by the metal center but also by the coligands of the complexes. For instance, the sequential replacement of the chloride ligands of OsHCl\textsubscript{2}(≡CCH≡CPh\textsubscript{2})(PP\textsubscript{3})\textsubscript{2} by acetonitrile molecules produces a sequential decrease of the activation energy of the hydride migration from the metal center to the alkylidyne carbon atom, as a consequence of the gradual decrease of the electron richness of the metal center.\textsuperscript{11} A carbonyl group increases further the stability of the alkylidene form.\textsuperscript{12}

Five-coordinate osmium alkylidene complexes related to those shown in Scheme 1 are largely unknown, with the notable exception of two cyclopentadienyldiene derivatives described by Lin, Jia, and co-workers, resulting from a ligand rearrangement of unstable osmabenzyne species (eq 2).\textsuperscript{13} Grubbs has also reported that the precursor OsCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} undergoes a reaction similar to that of RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} with diphenylcyclopropene, to afford the osmium analogues of RuCl\textsubscript{2}(≡CHCCH≡CPh\textsubscript{2})-(PPh\textsubscript{3})\textsubscript{2}.\textsuperscript{2\textsuperscript{a,14}} Although no experimental evidence has been given.

DFT calculations suggest that five-coordinate osmium alkylidene and six-coordinate osmium hydride alkylidene have similar energies.\textsuperscript{11} Therefore, at first glance, the alkylidene form might be accessible, provided there is a viable synthetic approach and relatively high activation energy for the interconversion. Herein we demonstrate that introducing an amide group in the alkylic chain of the substituent of a terminal alkyne allows control and relatively high activation energy for the interconversion. We also show that they are intermediate species for the cleavage of the carbon–carbon triple bond of the alkyne and present an entry to interesting vinylidene complexes by metathesis with allenes.

\section*{RESULTS AND DISCUSSION}

\subsection*{Five-Coordinated Alkylidene Complexes}

In recent years there have been many reports on the use of internal directing groups to control reaction rates and selectivity in metal-promoted processes.\textsuperscript{15} In some cases these groups are located in relatively distant positions of the reaction functionality.\textsuperscript{16} On these bases we wanted to explore the effect of a weakly coordinating distal amide group in the reaction of terminal alkynes with the dihydride complex OsH\textsubscript{2}Cl\textsubscript{2}((PPh\textsubscript{3})\textsubscript{2}) (1). In contrast to reactions shown in Scheme 2, stirring of this compound with 2.0 equiv of N-phenylhex-5-ynamide and N-phenylept-6-ynamide, in fluorobenzene, at room temperature leads to the alkylidene derivatives OsCl\textsubscript{2}(≡C(CH\textsubscript{2})\textsubscript{3}C(O)NPh)(PPh\textsubscript{3})\textsubscript{2} (n = 3 (2), 4 (3)). These products result from the coordination of the alkyne moiety to the osmium atom of 1 and the subsequent migration of the hydride ligands to the terminal carbon atom (eq 3). The reactions took place in about 70\% yield, and therefore complexes 2 and 3 were isolated as pure purple solids in a moderate yield of over 40\%.

The formation of these unusual compounds was confirmed by means of the X-ray structure of 2. Figure 1 gives a view of the molecular geometry around the metal center can be rationalized as a square pyramid with the alkylidyne in the apex, trans phosphines (P(1)–Os–P(2) = 159.42(5)\textdegree), and trans chlorides (Cl(1)–Os–Cl(2) = 168.30(5)\textdegree). The four atoms P(1), P(2), Cl(1), and Cl(2) forming the base are approximately in one plane, whereas the osmium atom is located 0.3373(8) Å above this plane toward the apical position. The Os–C(1) bond length of 1.862(5) Å supports the Os–C
double-bond formulation. In agreement with the sp² hybridization at C(1), the angles around this atom are between 112.1(5) and 124.2(4). An extended view of the structure (Figure 2) reveals that the molecules of this complex form infinite chains by means of intermolecular N–H···O hydrogen bonds between the NH of the amide of a molecule and the amicd oxygen atom of the adjacent one. Thus, the intermolecular H(1)–O(1) separation of 2.05(7) Å is shorter than the sum of the van der Waals radii of hydrogen and oxygen (r_{vdW}(H) = 1.20 Å; r_{vdW}(O) = 1.52 Å), whereas the N(1)–H(1)–O(1) angle is almost linear (167(7)°).

The ^13C(^1H) and ^31P(^1H) NMR spectra of OsCl2{(CH2)2C(O)NHPh}(PiPr3)2 (1) and ^31P(^1H) NMR spectrum shows a singlet at 23.7 ppm. An extended view of the structure (Figure 4) reveals that, like those proposed that the coordination of the triple bond to the osmium atom of 1 produces the reduction of the metal center to afford π-alkyne dihydrogen species. These intermediates undergo HCl elimination and the tautomerization of the π-alkyne to vinylidene. Thus, the addition of the proton of the electrophilic C−Cl atom of the vinylidene and the coordination of the anion to the metal center yield the hydride alkylidyne derivatives (Scheme 3). In agreement with this, it has been observed that, in the presence of a base, the six-coordinate hydride alkylidyne complexes afford five-coordinate hydride vinylidene species. In the current case, the distal amide group prevents the tautomerization of the triple bond as a consequence of the weak coordination of its oxygen atom, which also exerts a directing effect for the hydride migration (path b in Scheme 3). Thus, there is an insertion of the triple bond into the Os–H bond of the generated monohydrides, followed by the addition of the proton of the eliminated HCl to the Cα atom of the resulting α-substituted alkenyl group, along with the displacement of the coordinated carbonyl group by chloride to give the alkylidene derivatives.

Alkylidene to Hydride Alkylidyne Evolution: The Alkylidene as Intermediate in the Cleavage of the Alkyne Triple Bond. Complexes 2 and 4 both evolve from alkylidene to hydride alkylidyne in spite of the substituted character of the alkylidene Cα atom.

Complex 2 experiences two different transformations, which are competitive in dichloromethane at 60 °C (Scheme 4). The migration of the methyl group from the Cα atom of the alkylidene ligand to the metal center and a subsequent methylidene extrusion yield the hydride alkylidyne derivative OsHCl2{(CH2)2C(O)NHPh}(PiPr3)2 (5), containing a linear spacer between the alkylidyne Cα atom and the amide (pathway a in Scheme 4). On the other hand, the activation of one of the C−H bonds of the CαH2 group and a concerted 1,2-methyl shift in the resulting osmacyclopentene22 give OsHCl{(CH2)2C(O)NHPh}(PiPr3)2 (6), with a branched spacer between the alkylidyne Cα atom and the amide (pathway b in Scheme 4). As a consequence of both processes, a 10:7 mixture of 5 and 6 was formed after 48 h.

White crystals of 5 suitable for X-ray diffraction analysis were obtained from the mixture. Figure 3 gives a view of the structure. The coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphines occupying trans positions (P(1)−Os−P(2) = 166.17(4)°). The perpendiculare plane is formed by the cis-disposed chloride ligands, the alkylidyne trans to Cl(1) (C(1)−Os−Cl(1) = 177.14(16)°), and the hydride disposed trans to Cl(2) (H(01)−Os−Cl(2) = 167.91(15)°). The Os−C(1) bond length of 1.706(5) Å is fully consistent with an Os−C(1) triple bond formulation.24,25 The ^1H, ^13C(^1H), and ^31P(^1H) NMR spectra, in dichloromethane-d2, at room temperature are consistent with the structure shown in Figure 2. In accordance with the presence of the hydride ligand, the ^1H NMR spectrum contains at 7.57 ppm a triplet with a coupling constant of 16.2 Hz. In the ^13C(^1H) NMR spectrum the alkylidyne C(1) atom displays a triplet (J_C−H = 4.3 Hz) at 272.7 ppm, corresponding to the Cα atom of the alkylidyne, whereas the ^31P(^1H) NMR spectrum shows a singlet at 8.7 ppm due to the equivalent phosphines.

The difference of behavior of the substrates shown in Scheme 2 and in eqs 3 and 4 merits some additional comments. It has been
van der Waals radii of hydrogen and chlorine ($r_{vdW}$(Cl) = 1.75 Å$^{18}$ and the N(1)−H(1)−Cl(2) angle is almost linear (169(4)$°$).

Complex 6 was characterized by NMR spectroscopy, in dichloromethane-$d_2$ at room temperature, including bidimensional $^{1}$H−$^{13}$C HSQC and $^{1}$H−$^{13}$C HMBC spectra (see the Supporting Information). In agreement with the presence of the hydride ligand, the $^{1}$H NMR spectrum shows the characteristic high-field resonance at $-7.07$ ppm, which appears as a triplet with a H−P coupling constant of 16.2 Hz. The most noticeable signal in the low-field region is a singlet at 1.74 ppm, corresponding to the methyl group of the branching separator. In the $^{13}$C($^{1}$H) NMR spectrum, the alkylidyne C$_α$ resonance is observed at 271.8 ppm, as a triplet with a C−P coupling constant of 11.4 Hz, whereas the signal due to the methyl group of the branched spacer appears at 22.5 ppm as a singlet. A singlet at 23.9 ppm in the $^{31}$P($^{1}$H) NMR spectrum supports the presence of equivalent phosphines in the complex.

The relative position of the carbonyl and the NH groups in the amide influences the behavior of the alkylidene and the structural properties of the resulting hydride alkylidyne product. In contrast to 2, complex 4 selectively evolves into OsHCl$_2$:C−(CH$_2$)$_3$NHC(O)Ph}(PiPr$_3$)$_2$ ($7$, the benzamide counterpart of 5, containing a linear spacer (eq 5). The transformation is quantitative after 7 h, although complex 7 was isolated as a white solid in low yield (35%) due to its high solubility in the usual organic solvents.

Complex 7 was also characterized by X-ray diffraction analysis. Figure 5 shows a view of the molecule. The coordination polyhedron around the osmium atom resembles that of 5 with P(1)−Os−P(2), C(1)−Os−Cl(1) = 167.15(3), C(1)−Os−Cl(2) = 177.14(16), H(01)−Os−Cl(2) = 167.9(15).
with the osmium alkylidyne separation in 5. The $^1$H, $^{13}$C($^1$H), and $^{31}$P($^1$H) NMR spectra, in dichloromethane- $d_2$ at room temperature are consistent with the structure shown in Figure 5 and agree well with those of 5. Thus, a triplet ($^3J_{H-P} = 16.8$ Hz) at $-7.17$ ppm in the $^1$H NMR spectrum, a triplet ($^1J_{C-H} = 10.8$ Hz) at 270.5 ppm in the $^{13}$C($^1$H) NMR spectrum, and a singlet at 21.4 ppm in the $^{31}$P($^1$H) NMR spectrum are the characteristic spectroscopic features of this compound. An extended view of the structure reveals that the separation between the NH hydrogen atom and the chloride ligand $trans$ disposed to hydride is also, in this case, short ($H(1)\cdots Cl(1) = 2.51(4)$ Å). However, in contrast to the case for 5, the association gives rise to dimers (Figure 6) instead of infinite chains.

The selective carbon–carbon bond cleavage by transition-metal complexes is of great interest due to its fundamental scientific relevance and potential utility in organic synthesis. The carbon–carbon triple bond is known to be one of the strongest bonds in organic molecules. In this context, the reactions summarized in Scheme 4 and eq 5 are certainly notable because they prove that the five-coordinate osmium alkylidenic complexes 2 and 4 are intermediate species in the osmium-mediated rupture of the carbon–carbon triple bond of N-phenylhex-5-ynamide and N-(phenyl-4-yn-1-yl)benzamide, respectively, under mild conditions. Previously achieved homogeneous metal-mediated cleavages of the alkyne triple bond have been performed under drastic conditions by means of metathesis reactions, which imply $M=M$, $C=C$, and $M=C$ triple bonds. A number of metal-mediated cleavages that involved water and propargyl rearrangement have been also reported, in addition to strategies involving the transformation of the alkyne into other functionalities.

Metathesis of Allenes. It is remarkable that despite the enormous progress in metathesis chemistry along the last decades we are only aware of one example of a metathesis of metal alkylidenes with allenenes, consisting of the reaction of RuCl$_2$(CHPh)(PCy$_3$)$_2$ with a large excess of propan-1,2-diene. Complex 2 reacts with allenenes such as 3-methyl-1,2-butadiene and cyclohexylallene to afford five-coordinate vinylidene derivatives (Scheme 5).

![Figure 5](image-url) Molecular diagram of complex 7 (50% probability ellipsoids). Hydrogen atoms (except hydride and NH) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 1.715(4), Os–Cl(1) = 2.5169(10), Os–Cl(2) = 2.4845(10); P(1)–Os–P(2) = 167.15(3), C(1)–Os–Cl(1) = 101.74(12), H(01)–Os–Cl(1) = 167.6(12), C(1)–Os–Cl(2) = 172.28(11).

![Figure 6](image-url) View of the interaction via hydrogen bonding in the structure of 7 (symmetry code $-x + 1, -y + 1, z$).

![Scheme 5](image-url) Scheme 5

Treatment of fluorobenzene solutions of 2 with 1.5 equiv of 3-methyl-1,2-butadiene, at room temperature, leads to 5-methyl-N-phenylhex-5-ename (isolated and characterized; see the Experimental Section) and OsCl$_2$(C=CMe)$_2$(PCy$_3$)$_2$ (8), which is notable because it is a rare example of dicarbon-disubstituted vinylidene in osmium chemistry. Transition-metal vinylidene complexes are most often synthesized by tautomerization of alkynes, and therefore the majority of them are monosubstituted. Heteroatom-substituted internal alkynes can yield disubstituted vinylidenes with a heteroatom at C$_β$. We have described the preparation of osmium borylvinylidene derivatives through a 1,3-boryl shift in alkynyl boryl intermediates. Dicarbon-disubstituted vinylidenes are generally salts, which have been prepared by electrophilic addition to the C$_β$ atom of an alkynyl ligand. Under appropriate conditions, it is also possible to form dicarbon-disubstituted vinylidenes starting from unfunctionalized internal alkynes. Vinylidenes with C$_β$ incorporated into five- or six-membered rings have been formed by dehydrative cyclization of terminal alkynals or by means of Diels–Alder reactions between the C$_β$–C$_γ$ double bond of an allenylidene ligand and a cyclic dienophile. Complex 8 was isolated as green crystals, in 57% yield, and characterized by X-ray diffraction analysis. The structure (Figure 7) proves the metathesis reactions between the alkylidene of 2 and the allene. The geometry around the osmium atom can be described as a distorted square pyramid with the vinylidene in the apex, trans phosphines (P(1)–Os–P(1A) = 173.08(3)°), and trans chlorides (Cl(1)–Os–Cl(1A) = 153.22(4)°). The donor...
These alkylidene compounds are intermediate species in the metal-mediated rupture of the carbon—carbon triple bond of the initial alkylene. Thus, they are unstable in spite of being disubstituted, something in agreement with the strongly reducing character of osmium and its marked preference to form saturated species. Indeed, the new compounds evolve upon slight heating or long standing toward six-coordinated hydride alkylidyne species, by means of interesting rearrangement processes, including the C—C=H bond of the alkylidene which comes from the alkylene triple bond. These rearrangements consist of either a 1,2-methyl shift from the alkylidene C atom to the metal center and subsequent methylidyne extrusion or a metal-promoted C—H bond activation of the C3H2 group of the alkyllic chain along with a 1,2-methyl shift. The alkylidene ligands of these compounds undergo metathesis with allenes to afford five-coordinated vinylidene species, being in this way a useful entry to interesting dicarbon-disubstituted vinylidene complexes.

In conclusion, the presence of a distal amide at the alkyllic chain of the substituent of a terminal alkylene allows the preparation of five-coordinate osmium alkylidene complexes by means of the direct reaction of these substrates with unsaturated dihydride compounds, which afford dihydrogen tautomers by coordination of weak Lewis bases. The new complexes are intermediate species in the osmium-mediated rupture of the carbon—carbon triple bond of these alkynes and useful starting materials for the preparation of dicarbon-disubstituted vinylidenes.

**EXPERIMENTAL SECTION**

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. 1H, 13C{1H}, and 31P{1H} NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, and Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (1H, 13C{1H}), or external 85% H3PO4 (31P{1H}). Coupling constants J and N are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a PerkinElmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a PerkinElmer 2400 CHNS/O analyzer. OsH2Cl2(PiPr3)2,36a,36b Hydride alkylidyne isomers. We now demonstrate that this new osmium-containing group at an appropriate position of the alkyllic chain of a terminal alkylene.

**Preparation of Complex 2.** A brown solution of OsH2Cl2(PPr3)2 (100 mg, 0.171 mmol) in fluorobenzene (6 mL) was treated with N-phenylethyl-5-ynamide (60 mg, 0.342 mmol) at room temperature. The mixture was stirred for 2.5 h. After this time, the resulting solution was evaporated to dryness. The residue was dissolved in ether and filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of methanol to the residue afforded a purple solid that was washed with methanol (3 x 2 mL) and dried in vacuo. Yield: 50 mg (38%). Anal. Calc. for C30H26N2O: C, 74.65; H, 5.92; N, 6.12. Found: C, 74.81; H, 5.87; N, 6.15.

**Preparation of Complex 3.** A brown solution of OsH2Cl2(PPr3)2 (100 mg, 0.171 mmol) in fluorobenzene (6 mL) was treated with N-phenylethyl-6-ynamide (70 mg, 0.432 mmol) at room temperature.
The mixture was stirred for 2.5 h. After this time, the resulting solution was evaporated to dryness. The residue was dissolved in ether and filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of methanol to the residue afforded a purple solid that was washed with methanol (3 × 2 mL) and dried in vacuo. Yield: 53 mg (39%). Analy. Calcld. for C28H56Cl2OsP2: C, 41.57; H, 7.32; N, 1.85. Found: C, 41.57; H, 7.32; N, 1.85. IR (cm−1): ν(C≡O) 1658 (s), ν(NH) 3319 (s). 1H NMR (300 MHz, CDCl3, 298 K): δ 7.80 (d, JH, H = 7.5, 2H, CH3), 4.74 (br, 1H, NH), 3.40 (q, JH, H = 7.0, 2H, CH2), 2.67 (m, 6H, PCH(CH3)2), 0.98 (m, 18H, PCH(CH3)2), 27.1 (m, 2H, CH2), 20.0 (s, CH3), 19.6 (s, PCH(CH3)2).

Preparation of Complex 6. A brown solution of OsH2Cl2(PiPr3)2 (100 mg, 0.171 mmol) in fluorenone (6 mL) was treated with 5-methyl-1,2-butyadiene (21 μL, 0.195 mmol) at room temperature. The mixture was stirred for 30 min. After this time, the resulting solution was evaporated to dryness. The residue was dissolved in diethyl ether and the solution filtered through alumina. The solvent was removed in vacuo to give a pale yellow oil. The 1H and 13C{1H} NMR spectrum of this oil show the presence of 5-methyl-N-phenylhex-5-eneamidine.

Spectroscopic data for 5-methyl-N-phenylhex-5-eneamidine are as follows. 1H NMR (300 MHz, CDCl3, 298 K): δ 8.21 (br, 1H, NH), 7.52 (d, JH, H = 7.3, 2H, CH2), 7.30 (m, 2H, CH2), 7.20 (t, JH, H = 7.3, 1H, CH3), 4.76 (br, 1H, NH), 4.71 (br, 1H, CH3), 2.34 (t, JH, H = 7.2, 2H, CH2), 2.11 (t, JH, H = 7.2, 2H, CH2), 1.90 (q, JH, H = 7.2, 2H, CH2), 1.73 (s, 3H, CH3), 1.94 (1H)−APT NMR, HMBCC, and HSQC (75.5 MHz, CDCl3, 298 K): δ 1713 (s, Os=C≡C), 1451 (s, H=C=C), 1381 (s, C=Ph), 1291 (s, CH3), 1243 (s, CH3), 1191 (s, CH3), 1109 (s, H=C≡C), 37.1 (s, CH3), 37.0 (s, CH3), 23.3 (s, CH3), 22.9 (s, CH3).

Preparation of Complex 9. A purple solution of 2 (100 mg, 0.130 mmol) in fluorenone (6 mL) was treated with cyclohexyllamine (20 μL, 0.130 mmol) at room temperature. The mixture was stirred for 30 min. After this time, the resulting solution was evaporated to dryness. The residue was dissolved in diethyl ether and the solution filtered through alumina. The solvent was removed in vacuo to give a pale yellow oil. The 1H and 13C{1H} NMR spectra of this oil show the presence of 5-methyl-N-phenylhex-5-eneamidine.
Organometallics

Structural Analysis of Complexes 2, 5, 7, and 8. X-ray data were collected for the complexes on a Bruker Smart APEX CCD (2) or APEX CCD DUO (5, 7 and 8) diffractometer equipped with a normal-focus, 2.1 kW sealed-tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (5) or 30 mA (2, 7, and 8). Data were collected over the complete sphere. Each frame exposure time was 10 s (5, 7 and 8) or 30 s (2) covering 0.3° in o. Data were corrected for absorption by using a multiscan method applied with the SADABS program.17 The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F2 with SHELXL97,18 including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the least-squares Fourier maps or calculated and refined freely or using a restricted riding model. Hydrogens bonded to metal atoms were observed in the last cycles of refinements but refined too close to metals; therefore, a restricted refinement model was used for all of them (δ(Os−H = 1.59(1) Å)). 5 and 7 crystallizes with two molecules of CH2Cl2.

Crystal data for 5: C29H55Cl2NOOsP2, M0 796.63, colorless, irregular block (0.11 × 0.06 × 0.02), triclinic, space group P1, a = 8.849(4) Å, b = 12.110(3) Å, c = 19.188(5) Å, α = 93.888(4), β = 92.002(4), γ = 105.872(4), V = 170.81(4) Å3, Z = 2, D = 1.562 g cm−3, F(000) = 936, T = 153(2) K, μ = 3.749 mm−1; 18798 measured reflections (2θ = 3–58°, σ scans 0.3°), 7795 unique reflections (Rui = 0.0685); minimum/maximum transmission factors 0.347/0.492; final agreement factors R1 = 0.0375 (6964 observed reflections, I > 2σ(I)) and wR2 = 0.0750; refined Flack parameter 0.252(7); 7785/1/351 data/restraints/parameters; GOF = 1.050; largest peak and hole 2.866 (close to osmium atom) and −1.363 e Å−3.

Crystal data for 7: C29H55Cl2NOOsP2, M0 796.63, colorless, irregular block (0.09 × 0.08 × 0.05), monoclinic, space group P21/n, a = 15.747(4) Å, b = 13.012(3) Å, c = 20.173(5) Å, β = 105.651(4), V = 3987.0(17) Å3, Z = 4, D = 1, Dcalc = 1.544 g cm−3, F(000) = 1872, T = 100(2) K, μ = 3.705 mm−1; 36954 measured reflections (2θ = 3–57°, σ scans 0.3°), 10352 unique reflections (Rui = 0.0607); minimum/maximum transmission factors 0.736/0.862; final agreement factors R1 = 0.0356 (7741 observed reflections, I > 2σ(I)) and wR2 = 0.0719; 10352/1/397 data/restraints/parameters; GOF = 0.997; largest peak and hole 1.060 (close to osmium atoms) and −1.109 e Å−3.

Crystal data for 8: C31H56Cl2OsP2, M0 635.64, green, irregular block (0.16 × 0.11 × 0.08), monoclinic, space group C2/a, a = 21.184(3) Å, b = 9.6719(13) Å, c = 16.227(2) Å, β = 125.50(4)°, V = 2706.6(6) Å3, Z = 4, D = 0.5, Dcalc = 1.560 g cm−3, F(000) = 1280, T = 100(2) K, μ = 3.034 mm−1; 13794 measured reflections (2θ = 3–58°, σ scans 0.3°), 3544 unique reflections (Rui = 0.040); minimum/maximum transmission factors 0.711/0.862; final agreement factors R1 = 0.0215 (3345 observed reflections, I > 2σ(I)) and wR2 = 0.0484; 3544/0/131 data/restraints/parameters; GOF = 1.039; largest peak and hole 1.788 and −1.465 e Å−3.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge from the ACS Publications website at DOI: 10.1021/acs.organomet.6b00777.

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