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Square-Planar Alkylidyne–Osmium and Five-Coordinate Alkylidene–Osmium Complexes: Controlling the Transformation from Hydride-Alkylidyne to Alkylidene

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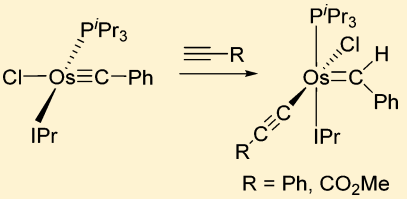
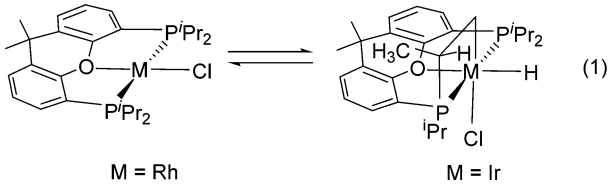
Supporting Information

ABSTRACT: Square-planar alkylidyne and five-coordinate alkylidene mixed $^{i}Pr_3P$–Os–IPr (IPr = 1,3-bis(diisopropylphenyl)imidazolylidene) complexes have been discovered and characterized, and their formation has been rationalized. The cationic five-coordinate hydride-alkylidyne compounds $[OsHX(\equiv CPh)(IPr)(P^iPr_3)]OTf$ (X = Cl (**1**), F (**4**); OTf = CF_3SO_3) undergo deprotonation with KO^tBu to afford the *trans*-halide-alkylidyne square-planar derivatives $OsX(\equiv CPh)(IPr)(P^iPr_3)$ (X = Cl (**2**), F (**5**)). Oxidative addition of the C(sp)–H bond of phenylacetylene and methyl propiolate along the Cl–Os–CPh axis of **2** with the hydrogen atom directed to the alkylidyne leads to alkynyl-*cis*-hydride-alkylidyne intermediates, which rapidly evolve into the five-coordinate alkylidene complexes $Os(C\equiv CR)Cl(=CHPh)(IPr)(P^iPr_3)$ (R = Ph (**6**), CO_2Me (**7**)) as a consequence of the migration of the hydride from the metal center to the C_α atom of the alkylidyne. Oxidative addition of the C(sp)–H bond of methyl propiolate along the X–Os–CPh axis of **2** and **5** with the hydrogen atom directed to the halide gives the alkynyl-*trans*-hydride-alkylidyne derivatives $OsH(C\equiv CCO_2Me)X(\equiv CPh)(IPr)(P^iPr_3)$ (X = Cl (**8**), F (**9**)). Complex **8** evolves into **7**. However, complex **9** containing the stronger π-donor fluoride is stable. The oxidative addition of HCl to **2** selectively yields the *cis*-hydride-alkylidyne compound $OsHCl_2(\equiv CPh)(IPr)(P^iPr_3)$ (**10**), which is also stable.



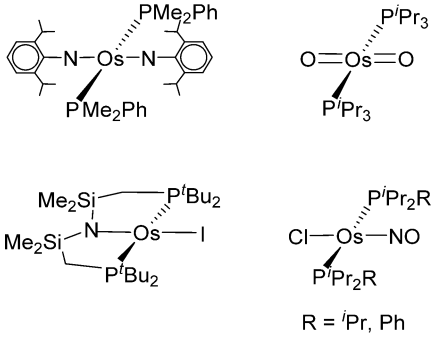
INTRODUCTION

Unsaturated transition metal complexes play a decisive role in homogeneous catalysis. Those of platinum group metals are particularly efficient for developing atom-economic processes and therefore are especially relevant from an environmental point of view.[1] The unsaturated character is favored by less basic metal centers. While an almost unlimited number of d^8 square-planar rhodium complexes[2] are known with 16-valence electrons, the number of iridium compounds of this type is much lower.[3] A nice example of this trend is shown by eq 1. In contrast to



$RhCl\{xant(P^iPr_2)_2\}$ ($xant(P^iPr_2)_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene), the iridium analogue activates a C–H bond of a methyl substituent of the phosphine to afford a saturated d^6 species.[4] In contrast to group 9, only a few families of square-planar ruthenium complexes have been described,[5] whereas the osmium compounds are limited to *trans*-$Os(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2(PMe_2Ph)_2$,[6] *trans*-$Os(O)_2(P^iPr_3)_2$,[7] $Os\{\kappa^3\text{-}P,N,P\text{-}[N(SiMe_2CH_2P^tBu_2)_2]\}I$,[8] and *trans*-$OsCl(NO)(P^iPr_2R)$ (R = ^{i}Pr, Ph),[9] the latter being the only truly d^8 square-planar compounds (Chart 1).

Chart 1. Previously Isolated Square-Planar Osmium Complexes



The unsaturated ruthenium complexes are dominated by five-coordinate species.[10] Within this type of compounds, the alkylidene catalysts for olefin metathesis, $RuCl_2(=CHR)(PR_3')_2$, occupy a prominent place.[11] In agreement with the trend denoted by eq 1, the osmium counterparts evolve into six-coordinate hydride-alkylidyne derivatives (eq 2).[12] As a consequence, the isolated neutral five-coordinate osmium-alkylidene complexes are carbon-disubstituted and as rare as the d^8 square-planar species of this element (Chart 2). Lin, Jia, and co-workers observed in 2011 that unstable osmabenzynes

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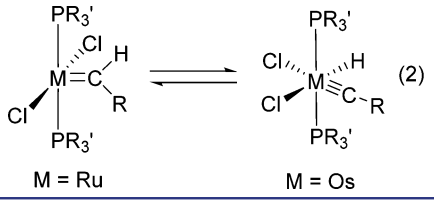
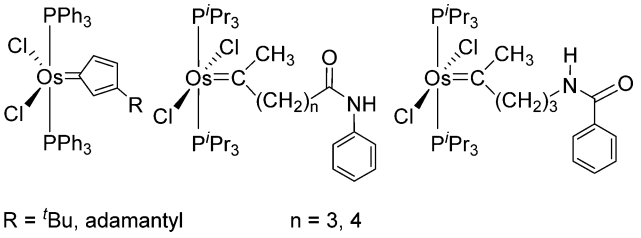
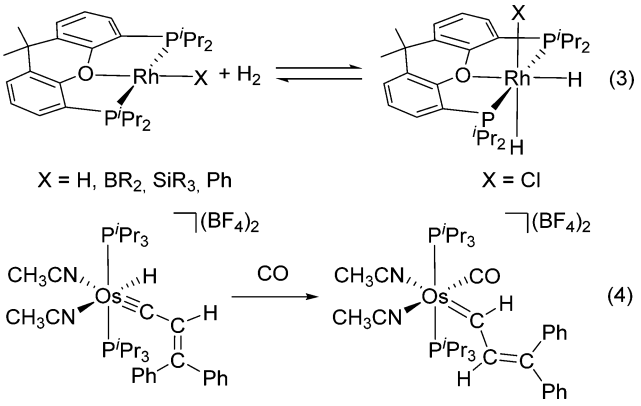


Chart 2. Previously Isolated Neutral Five-Coordinate Alkylidene−Osmium Complexes



rearrange into cyclopentadienylidene derivatives,[13] and we have recently reported the amide-directed synthesis of $OsCl_2\{=C(CH_3)(CH_2)_nC(O)NHPh\}(P^iPr_3)_2$ (n = 3, 4) and $OsCl_2\{=C(CH_3)(CH_2)_3NHC(O)Ph\}(P^iPr_3)_2$.[14] The alkylidene-amide derivatives are unstable in spite of being carbon-disubstituted and evolve into six-coordinate hydride-alkylidyne compounds.

The electron richness of the metal center, and therefore the saturated or unsaturated character of the complex, can be also governed with the ligands. As a proof of concept, eq 3 must be

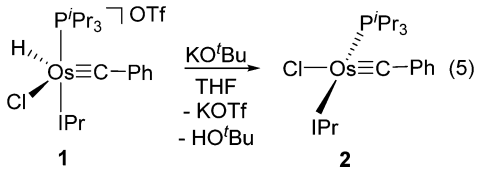


pointed out. For $RhX\{xant(P^iPr_2)_2\}$ complexes, it has been observed that strong π-donor groups, such as chloride, stabilize saturated d^6 species, whereas σ-donor ligands, such as hydride, silyl, boryl, or aryl, favor d^8 square-planar derivatives.[4,15] In the same sense, the electron density impoverishment of the osmium center increases the stability of the alkylidene form. Thus, the coordination of a π-acceptor group, such as CO, facilitates the transformation from hydride-alkylidyne to alkylidene (eq 4).[16]

A remarkable π-acceptor capacity of the p_z orbital at the metalated carbon atom of N-heterocyclic carbenes (NHCs), which has no counterpart in phosphines, has been recently demonstrated by means of DFT calculations using AIM and NBO methods.[17] The complementary properties of NHC and phosphine ligands provide to the mixed R_3P-M-NHC complexes special stability toward distribution reactions and allow a subtle governing of the electron density of the metal center.[18] In this Article, we demonstrate that d^8 square-planar alkylidyne and five-coordinate alkylidene−osmium complexes can be stabilized with the help of a mixed R_3P−Os−NHC skeleton and that the transformation from alkylidene to hydride-alkylidyne follows the same electronic pattern as the oxidative additions from d^8 to d^6.

RESULTS AND DISCUSSION

Square-Planar Alkylidyne Complexes. Transition metal hydride complexes are usually amphoteric. Thus, they act not only as hydride donors but also as Brønsted−Lowry acids.[19] In agreement with this, treatment of tetrahydrofuran solutions of the five-coordinate hydride-alkylidyne cation $[OsHCl(\equiv CPh)(IPr)(P^iPr_3)]OTf$ (**1**, IPr = 1,3-bis(diisopropylphenyl)-imidazolylidene, OTf = CF_3SO_3) with 1.1 equiv of potassium *tert*-butoxide (KO^tBu) leads to proton abstraction and the formation of the 16-valence-electron square-planar complex $OsCl(\equiv CPh)(IPr)(P^iPr_3)$ (**2**), which was isolated as a green solid in 70% yield (eq 5). In the search for **2**, we had previously



treated complex **1** with a water solution of NaOH. Unfortunately, in that case, replacement of the chloride ligand by a hydroxide group took place, to form $[OsH(OH)(\equiv CPh)(IPr)(P^iPr_3)]$-OTf (**3**), instead of hydride removal.[18b]

Complex **2** was characterized by X-ray diffraction analysis. Figure 1 shows a view of the molecule. The structure

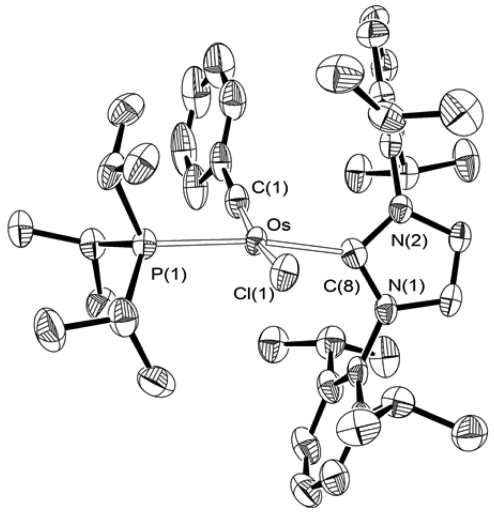


Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (deg): Os−Cl(1) = 2.4323(16), Os−P(1) = 2.3635(17), Os−C(8) = 2.095(6), Os−C(1) = 1.722(7); C(8)−Os−P(1) = 168.83(19), C(1)−Os−Cl(1) = 164.9(2). Displacement ellipsoids are given at the 50% probability level.

demonstrates the formation of this novel species. The coordination geometry around the osmium atom is certainly square-planar, with the chloride *trans* disposed to the alkylidyne (Cl(1)−Os−C(1) = 164.9(2)°) and the NHC ligand *trans* disposed to the phosphine (C(8)−Os−P(1) = 168.83(19)°). The greatest deviation from the best plane through Os, C(1), C(8), Cl(1), and P(1) atoms is 0.219(3) Å and involves C(1). The Os−C(1) bond length of 1.722(7) Å supports an Os−C triple bond and therefore the alkylidyne formulation,[20] whereas the Os−C(8) distance of 2.095(6) Å is consistent with a normal

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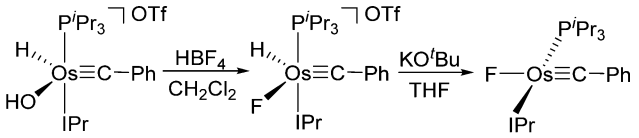
coordination for the NHC ligand.[21] In agreement with the stereochemistry shown in Figure 1, the $^{13}C\{^1H\}$ NMR spectrum of **2**, in benzene-d_6, at room temperature shows the alkylidyne and NHC OsC resonances at 229.0 and 196.5 ppm as doublets with C−P coupling constants of 13.6 and 83.4 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 43.6 ppm. In the visible region, the absorption spectrum of a 5.9×10^{-5} M pentane solution shows two main absorptions centered at 446 and 610 nm, which were assigned to HOMO−1 → LUMO+1 and HOMO−1 → LUMO transitions, respectively, on the basis of time-dependent DFT calculations.

The mixed ^{i}Pr$_3$P−Os−IPr skeleton also stabilizes a fluoride counterpart of **2**, which is more challenging than the latter because of the higher π-donor power of the halide. The compound has been prepared according to Scheme 1, starting

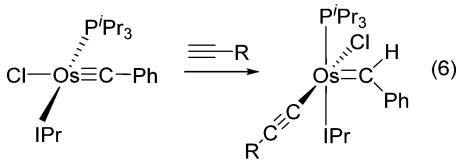
Scheme 1. Formation of the Fluorine-Alkylidyne Complex 5



3 **4** **5**

from **3**. In agreement with the marked trend of the BF_4^- anion to decompose in the presence of bases, releasing fluoride,[22] the addition of 1.1 equiv of $HBF_4 \cdot OEt_2$ to dichloromethane solutions of **3** leads to the fluoride derivative [OsHF(≡CPh)(IPr)-(P^{i}Pr$_3$)]OTf (**4**), as a result of replacement of the hydroxide ligand of the starting complex by the halide. This compound was isolated as a yellow solid in 90% yield. The presence of the fluoride at the metal coordination sphere is strongly supported by the ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectra, in dichloromethane-d_2, at room temperature. In the ^1H NMR spectrum, the hydride ligand appears at −15.52 ppm as a double doublet with H−F and H−P coupling constants of 27.0 and 14.2 Hz, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows the alkylidyne and NHC OsC resonances at 275.4 and 185.4 ppm, respectively. The first of them appears as a double doublet with C−F and C−P coupling constants of 69.9 and 8.2 Hz, whereas the second one is observed as a doublet with a C−P coupling constant of 91.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains at 50.6 ppm a doublet with a P−F coupling constant of 35.2 Hz. The ^{19}F spectrum shows a singlet at −78.9 ppm due to the OTf anion and a double doublet at −118.0 assigned to the fluoride ligand. In accordance with **1**, complex **4** undergoes proton abstraction. Thus, treatment of its tetrahydrofuran solutions with 1.1 equiv of KO^{t}Bu affords the square-planar derivative OsF(≡CPh)(IPr)(P^{i}Pr$_3$) (**5**), which was isolated as a red solid in 71% yield. The fluoride *trans*-alkylidyne disposition is strongly supported by the $^{13}C\{^1H\}$ NMR spectrum of the complex, in benzene-d_6, at room temperature. It shows at 236.8 ppm a double doublet with a large C−F coupling constant of 133.9 Hz, and a C−P coupling constant of 13.6 Hz, corresponding to the alkylidyne C_α carbon atom. The carbene OsC resonance is observed at 198.5 ppm, also as a double doublet but with C−F and C−P coupling constants of 11.2 and 92.4 Hz, respectively. The $^{31}P\{^1H\}$ and ^{19}F NMR spectra show doublets ($^2J_{P-F}$ = 47.8 Hz) at 51.4 and −178.7 ppm, respectively.

Five-Coordinate Alkylidene Complexes. The square-planar complex **2** reacts with terminal alkynes such as phenylacetylene and methyl propiolate to give the five-coordinate alkylidene derivatives Os(C≡CR)Cl(=CHPh)-(IPr)(P^{i}Pr$_3$) (R = Ph (**6**), CO_2Me (**7**)), as a result of the formal addition of the C(sp)−H bond of the alkyne to the Os−C triple bond of **2** (eq 6). These compounds were isolated as purple (**6**)



(6)

2 R = Ph (**6**), CO_2Me (**7**)

and red (**7**) solids in 74% and 82% yield, respectively. In contrast to the bis(phosphine) derivatives $OsCl_2\{=C(CH_3)(CH_2)_nC(O)NHPh\}(P^iPr_3)_2$ (n = 2, 3) and $OsCl_2\{=C(CH_3)(CH_2)_3NHC(O)Ph\}(P^iPr_3)_2$, complexes **6** and **7** are stable and do not evolve into the corresponding hydride-alkylidyne species in spite of the monosubstituted character of their alkylidene ligand.

The formation of this elusive type of compounds was confirmed by means of the X-ray diffraction structure of **6**. Figure 2 gives a view of the molecule. The geometry around the

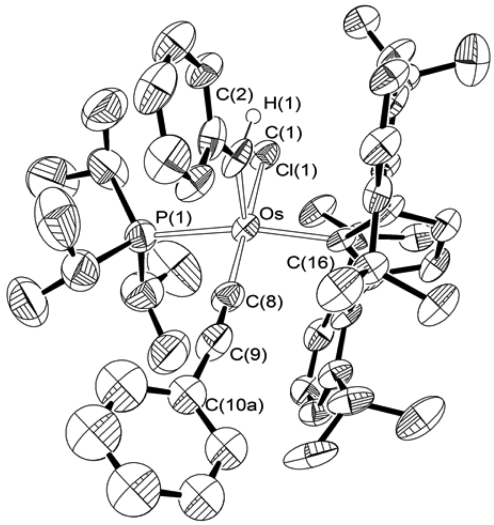


Figure 2. Molecular diagram of **6**. Selected bond lengths (Å) and angles (deg): Os−Cl(1) = 2.481(3), Os−P(1) = 2.405(4), Os−C(16) = 2.074(10), Os−C(8) = 1.975(12), Os−C(1) = 1.810(16), C(8)−C(9) = 1.211(18); Os−C(8)−C(9) = 177.1(13), Cl(1)−Os−C(8) = 173.9(4), C(8)−C(9)−C(10a) = 172.0(2), C(16)−Os−P(1) = 158.3(3), Os−C(1)−C(2) = 140.5(12), C(1)−Os−C(16) = 101.7(5), C(1)−Os−C(8) = 99.6(6), C(1)−Os−P(1) = 98.5(4), C(1)−Os−Cl(1) = 86.3(5). Displacement ellipsoids are given at the 50% probability level.

metal center can be rationalized as a square pyramid with the alkylidene in the apex. At the base, the chloride lies *trans* to the alkynyl group (Cl(1)−Os−C(8) = 173.9(4)°), and the NHC ligand is *trans* disposed to the phosphine (C(16)−Os−P(1) = 158.3(3)°). The four atoms forming the base are approximately in a plane, whereas the osmium atom is located 0.281(5) Å above this plane toward the apical position. The Os−C(1) bond length of 1.810(16) Å is consistent with a double bond and supports the alkylidene formulation.[14,16a,23] In agreement with the sp^2 hybridization at C(1), the angle Os−C(1)−C(2) is 140.5(12)°. The osmium−alkynyl distance of 1.975(12) Å (Os−C(8)) agrees with an Os−C(sp) single bond[24] and indicates a low degree of metal-to-ligand back-bonding.[25] The

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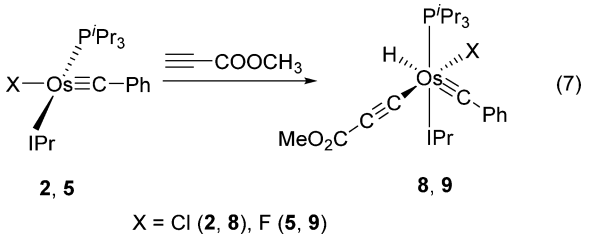
C(8)−C(9) bond length and the Os−C(8)−C(9) angle are 1.211(18) Å and 171.1(13)°, respectively. The Os−NHC distance of 2.074(10) Å (Os−C(16)) is statistically identical to that of **2**.

The purple color of **6** is consistent with its electronic spectrum. Thus, in the visible region, the absorption spectrum of a 7.7×10^{-5} M pentane solution exhibits a broad absorption centered at about 552 nm, which was assigned to a HOMO → LUMO+1 transition on the basis of time-dependent DFT calculations.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **6** and **7**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 2. The ^{1}H NMR spectra contain a singlet at about 24 ppm, characteristic for an Os=CH hydrogen. In the ^{13}C{^{1}H} NMR spectra, the resonances due to the metalated carbon atoms of the alkylidene, NHC, and alkynyl ligands are observed as doublets at 246.7 ($^{2}J_{C-P}$ = 5.7 Hz), 187.3 ($^{2}J_{C-P}$ = 71.5 Hz), and 102.0 ($^{2}J_{C-P}$ = 10.8 Hz) ppm for **6** and at 246.9 ($^{2}J_{C-P}$ = 4.2 Hz), 187.5 ($^{2}J_{C-P}$ = 68.8 Hz), and 116.45 ($^{2}J_{C-P}$ = 10.2 Hz) for **7**. The ^{31}P{^{1}H} NMR spectra show a singlet at 29.9 ppm for **6** and at 33.4 ppm for **7**.

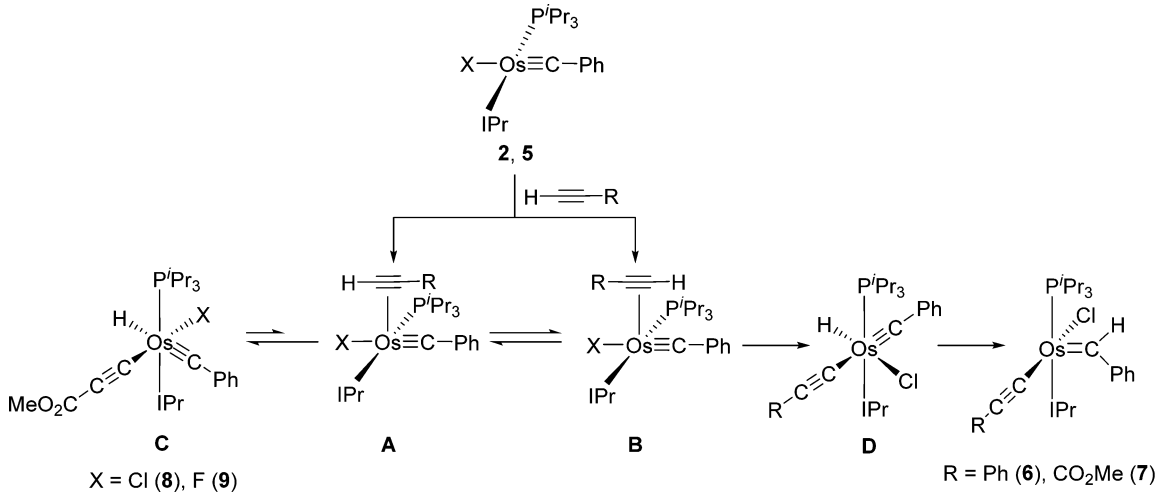
The course of the reactions summarized in eq 6 has a marked dependence upon the alkyne substituent. According to the ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixtures in toluene, at room temperature, the formation of **6** is quantitative after 3 h, whereas the quantitative formation of **7** needs about 52 h, or about 12 h at 60 °C. During the reaction of **2** with phenylacetylene to give **6**, no intermediate species were detected. However, during the reaction of **2** with methyl propiolate to afford **7**, the transitory formation of the hydride-alkynyl-alkylidyne species OsH(C≡CCO$_2$Me)Cl(≡CPh)(IPr)(P^{i}Pr$_3$) (**8**) is clearly observed; it can be isolated as a pure orange solid in 85% yield after 5 min of reaction. Its formation is strongly supported by the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the reaction mixture, and the isolated orange solid in benzene-d_6. In agreement with the presence of the hydride ligand, the ^{1}H NMR spectrum contains at −2.27 ppm a doublet with a H−P coupling constant of 28.2 Hz. In the ^{13}C{^{1}H} NMR spectrum, the metalated carbon atoms of the alkylidyne, NHC, and alkynyl ligands appear at 283.2, 173.1, and 92.9 ppm as doublets with C−P coupling constants of 4.0, 74.1, and 8.6 Hz, respectively. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 24.3 ppm, which is split into a doublet under off-resonance conditions.



Influence of the π-Donor Power of the Halide on the Formation of Five-Coordinate Alkylidene Complexes. The square-planar fluoride complex **5** also reacts with methyl propiolate. The reaction leads to the hydride-alkynyl-alkylidyne derivative OsH(C≡CCO$_2$Me)F(≡CPh)(IPr)(P^{i}Pr$_3$) (**9**), as a result of the oxidative addition of the C(sp)−H bond of the alkyne to **5**. At room temperature, in toluene, the transformation is quantitative after 15 min. Complex **9**, which was isolated as a red solid in 73% yield, is the fluoride counterpart of **8**. Although the migration of the hydride from the metal center to the alkylidyne C$_\alpha$ atom is not observed in this case, the chemical shifts in the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **9**, in benzene-d_6, at room temperature are very similar to those observed in the NMR spectra of **8**. This suggests that both compounds have the same stereochemistry, which is that shown in eq 7, according to the H−F, C−F, H−P, and C−P coupling constants. The resonance corresponding to the hydride, which lies *trans* to the alkylidyne ligand, appears at lower field in the higher field region of the ^{1}H NMR spectrum, −0.46 ppm, consistent with the high *trans* effect of the alkylidyne. The H−F and H−P coupling constants of 7.8 and 28.3 Hz, respectively, support the *cis* disposition of the hydride to both fluoride and phosphine. In the ^{13}C{^{1}H} NMR spectrum, the alkylidyne, NHC, and alkynyl OsC resonances are observed at 284.4, 176.8, and 95.8 ppm, respectively, as double doublets. The C−P and C−F coupling constants, in the NHC and alkynyl resonances, of 81.4 and 50.6 Hz prove the NHC *trans* phosphine and alkynyl *trans* fluoride dispositions. Doublets ($^{2}J_{P-F}$ = 29.6 Hz) at 31.0 and −153.4 ppm in the ^{31}P{^{1}H} and ^{19}F NMR spectra, respectively, are also characteristic features of **9**.

The oxidative addition of methyl propiolate to **2** and **5** to give **8** and **9** and the formation of the five-coordinate alkylidenes **6** and **7** can be rationalized according to Scheme 2. It is well

Scheme 2. Oxidative Addition of Phenylacetylene and Methyl Propiolate to 2 and 5: Hydride-Alkylidyne *versus* Alkylidene



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established that the formation of hydride-alkynyl transition metal complexes by addition of terminal alkynes to unsaturated compounds occurs via the initial coordination of the carbon−carbon triple bond of the alkyne to the metal center, to form π-alkyne intermediates.[26] Subsequently, the metal center slips to the C−H bond to form η^2-(C,H)-species.[27] Thus, the oxidative addition to square-planar complexes, such as **2** and **5**, is a diastereoselective process with specific C−H bond orientation.[4,28] At first glance, the oxidative addition of the alkyne to these compounds can take place along the $^{i}Pr_3P$−Os−IPr or X−Os−CPh axis, the latter being favored from a steric point of view. Addition along the X−Os−CPh axis can occur with the hydrogen directed toward the halide and the substituent of the alkyne on the alkylidyne (**A**) or vice versa (**B**). The first orientation leads to isomers **C**, with the hydride *trans* disposed to the alkylidyne and the halide (X) *trans* disposed to the alkynyl group, whereas the second one affords isomers **D** containing the alkylidyne *cis* disposed to the hydride and *trans* to the alkynyl group. Concerted migration of the hydride from the metal center to the alkylidyne C_α atom in **D** gives the five-coordinate alkylidene derivatives **6** and **7**. Complexes **8** and **9** are particular cases of **C** and therefore result from the oxidative addition of the C(sp)−H bond of methyl propiolate through **A**. This disposition avoids the close contact between the electron-rich halide and the CO_2Me group.

The *trans* disposition of hydride and alkylidyne ligands in **8** prevents the direct migration of the hydride to the alkylidyne, because the process is concerted.[16b] So, complex **8** is not an intermediate in the formation of **7** from **2** and methyl propiolate, but a side kinetic isomer. In this context, it should be noted that the formation of **6**, where repulsive interactions between the chloride and the alkyne substituent do not take place during the oxidative addition process, is much faster. The transformation of **8** into **7** should involve reductive elimination of the alkyne to regenerate **A**. Thus, the alkyne could change its orientation into **B**, by rotation around the coordination axis, in order to afford a **D**-type isomer. To gain insight into the process, the isomerization was followed by $^{31}P\{^1H\}$ NMR spectroscopy as a function of time between 293 and 333 K. As shown in Figure 3 for the transformation at 323 K, the increase of **7** with the corresponding decrease of **8** is an exponential function of time, in agreement with a first-order process. This, along with the fact that no intermediate species were detected during the isomerization, suggests that the reductive elimination of the alkyne to form **A** is the rate-determining step of the conversion of **8** into **7**. The activation parameters obtained from the Eyring analysis (Figure 4), $\Delta H^{\ddagger} = 20 \pm 1$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -4 \pm 4$ cal·mol^{-1}·K, are consistent with this.

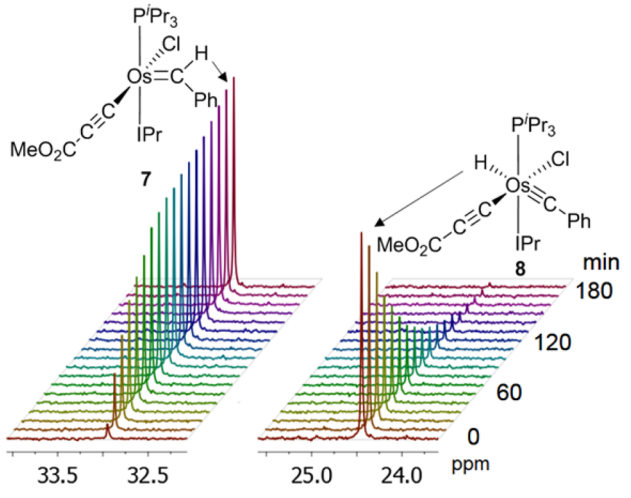


Figure 3. Stacked $^{31}P\{^1H\}$ NMR spectra illustrating the transformation from **8** into **7** in C_6D_6 at 323 K.

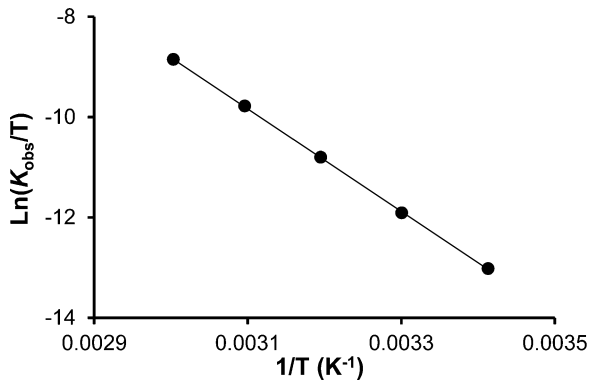
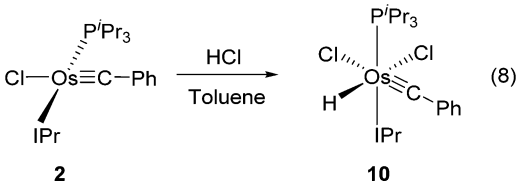


Figure 4. Eyring plot of k_{obs} for the transformation from **8** into **7**.

The higher π-donor power of fluoride with regard to chloride[29] stabilizes **9** with regard to **8**, toward the reductive elimination of the alkyne. This explains why complex **9** does not evolve into a fluoride counterpart of **7**. In addition, it should be mentioned that the π-donor capacity of the ligand *trans* disposed to the alkylidyne in **D**-type isomers controls the hydride migration. In fact, substitution of the alkynyl group by a strong π-donor chloride prevents the formation of the alkylidene. As a proof of concept, we have observed that complex **2** reacts with HCl in toluene to give the *cis*-hydride-alkylidyne $OsHCl_2(IPr)(P^iPr_3)$ (**10**), which does not evolve into the corresponding alkylidene (eq 8). Complex **10** was isolated as a pink solid in 62% yield. In



(8)

agreement with the presence of the hydride ligand in the complex, the ^1H NMR spectrum, in benzene-d_6, at room temperature shows at −5.95 ppm a doublet with a H−P coupling constant of 16.5 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the alkylidyne and NHC resonances appear at 256.5 and 168.2 ppm as doublets with C−P coupling constants of 12.9 and 96.5 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 11.4 ppm, which is split into a doublet under off-resonance conditions.

CONCLUDING REMARKS

This study reveals the existence of 16-valence-electron square-planar alkylidyne−osmium and stable five-coordinate monosubstituted alkylidene−osmium complexes and demonstrates that the transformation from alkylidene to hydride-alkylidyne follows the same electronic pattern as the oxidative additions from d^8 to d^6; i.e., π-donor halides destabilize the monosubstituted alkylidene and favor the hydride−alkylidyne form.

Square-planar alkylidyne complexes have been prepared by deprotonation of cationic five-coordinate hydride-alkylidyne

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precursors through a formal reduction of the metal center. The five-coordinate alkylidene compounds result from the addition of the C(sp)−H bond of terminal alkynes to the Os−C triple bond of the square-planar alkylidyne derivatives. The addition regenerates the initial oxidation state of the metal center.

The addition of the C(sp)−H bond of the alkyne to the Os−C triple bond occurs in stages. The square-planar alkylidyne complexes coordinate the C−C triple bond of the alkyne. Subsequent oxidative addition of the C(sp)−H bond leads to an alkynyl-*cis*-hydride-alkylidyne intermediate, which evolves into the alkylidene product by migration of the hydride from the metal center to the C_α atom of the alkylidyne. The lack of π-electrons at the donor C_α atom of the alkynyl ligand seems to be the driving force for the migration. In contrast to the alkynyl group, the π-donor chloride prevents the hydride migration and stabilizes the hydride-alkylidyne intermediate.

In conclusion, elusive 16-valence-electron square-planar alkylidyne and five-coordinate alkylidene complexes of a third-row transition metal have been prepared, isolated in the solid state, and characterized by X-ray diffraction analysis, and their formation has been rationalized.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Shlenck-tube techniques. Solvents (except THF and benzene, which were dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. Reagents were dried by standard procedures and distilled under argon prior to use. The starting materials [OsHCl(≡CPh)(IPr)(P^iPr_3)]OTf and [OsH(OH)(≡CPh)(IPr)(P^iPr_3)]OTf were prepared by the published methods.[18a,d] ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectra were recorded on Bruker Avance 300 MHz and Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$), external 85% H_3PO_4 ($^{31}P\{^1H\}$), or external $CFCl_3$ (^{19}F). Coupling constants J are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a PerkinElmer Spectrum 100 FT-IR spectrometer. UV−vis spectra were recorded on an Evolution 600 spectrophotometer. C, H, and O analyses were carried out with a PerkinElmer 2400 CHNS/O analyzer. Electrospray mass spectra were acquired using a time-of-flight hybrid quadrupole time-of-fly spectrometer (Bruker Daltonics, Bremen, Germany).

Preparation of OsCl(≡CPh)(IPr)(P^iPr_3) (2). An orange solution of [OsHCl(≡CPh)(IPr)(P^iPr_3)]OTf (**1**) (100 mg, 0.12 mmol) in THF (5 mL) was treated with potassium *tert*-butoxide (12.4 mg, 0.13 mmol). The resulting mixture was stirred for 5 min at room temperature. After this time, the resulting dark green solution was evaporated to dryness. The residue was filtered through Celite with pentane and evaporated to dryness, affording a green solid. Yield: 60 mg (70%). Anal. Calcd for $C_{43}H_{62}ClN_2OsP$: C, 59.80; H, 7.24 N, 3.24. Found: C, 59.74; H, 7.47; N, 3.06. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.30 (t, $^3J_{H-H}$ = 7.6, 3H, CPh, Ph), 7.15 (d, $^3J_{H-H}$ = 7.6, 4H, Ph), 7.09 (d, $^3J_{H-H}$ = 7.6, 2H, CPh), 6.89 (s, 2H, NCH), 6.70 (t, $^3J_{H-H}$ = 7.7, 2H, CPh), 3.78 (sept, $^3J_{H-H}$ = 7.0, 4H, C*H*CH$_3$), 2.35 (dsept, $^2J_{H-P}$ = 8.7, $^3J_{H-H}$ = 7.3, 3H, PCH), 1.35, 1.14 (both d, $^3J_{H-H}$ = 6.8, 24H, CHC*H*$_3$), 1.20 (dd, $^3J_{H-P}$ = 12.7, $^3J_{H-H}$ = 7.2, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 43.6 (s). $^{13}C\{^1H\}$-APT NMR, HSQC, and HMBC (75.4 MHz, C_6D_6, 298 K): δ 229.0 (d, $^2J_{C-P}$ = 13.6, Os≡C), 196.5 (d, $^2J_{C-P}$ = 83.4, OsC), 147.0 (s, C_{ipso}-CPh), 146.9 (s, Ph), 138.2 (s, C_{ipso}-Ph), 129.3 (s, Ph), 127.9, 125.3 (both s, C*Ph*), 124.1 (s, Ph), 124.0 (s, C*Ph*), 123.4 (s, NCH), 29.8 (s, *C*HCH$_3$), 27.7, 27.3 (both s, PCH), 26.1, 23.3 (both s, CH*C*H$_3$), 20.9 (s, PCH*C*H$_3$).

Preparation of [OsHF(≡CPh)(IPr)(P^iPr_3)]OTf (4). A yellow solution of [OsH(OH)(≡CPh)(IPr)(P^iPr_3)]OTf (**3**) (100 mg, 0.1 mmol) in dichloromethane (5 mL) was treated with $HBF_4{\cdot}OEt_2$ (16 μL, 0.11 mmol). The resulting mixture was stirred for 1 h at room temperature. After this time, the resulting yellow solution was evaporated to dryness. The addition of 3 mL of diethyl ether caused the formation of a yellow solid which was washed with diethyl ether (3 × 3 mL) and dried under vacuo. Yield: 90 mg (90%). Anal. Calcd for $C_{44}H_{63}F_4N_2O_3OsPS$: C, 52.99; H, 6.37; N, 2.81; S, 3.21. Found: C, 52.97; H, 6.53; N, 2.81; S, 3.58. MS (electrospray, m/z): $C_{43}H_{63}FN_2OsP$, 849.4; found, 849.4. IR (cm^{-1}): ν(OsH) 2180. ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.68 (t, $^3J_{H-H}$ = 7.7, 1H, CPh), 7.50−7.41 (4H, Ph), 7.30 (s, 2H, NCH), 7.21 (dd, $^3J_{H-H}$ = 7.7, 2H, CPh), 7.08 (dd, $^3J_{H-H}$ = 7.3, $^4J_{H-H}$ = 2.1, 2H, Ph), 6.76 (d, $^3J_{H-H}$ = 7.7, 2H, CPh), 3.06, 2.57 (both sept, $^3J_{H-H}$ = 7.2, 4H, C*H*CH$_3$), 2.26 (dsept, $^2J_{H-P}$ = 9.7, $^3J_{H-H}$ = 7.1, 3H, PCH), 1.53, 1.15, 1.13, 1.10 (all d, $^3J_{H-H}$ = 6.8, 24H, CHC*H*$_3$), 0.88, 0.85 (both dd, $^3J_{H-P}$ = 14.0, $^3J_{H-H}$ = 7.1, 18H, PCHC*H*$_3$), −15.52 (dd, $^2J_{H-P}$ = 14.2, $^2J_{H-F}$ = 27.0, 1H, OsH). ^{19}F NMR (287.2 MHz, CD_2Cl_2, 298 K): δ −78.9 (s, CF_3SO_3), −118.0 (dd, $^2J_{F-P}$ = 35.2, $^2J_{F-H}$ = 27.0, OsF). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 298 K): δ 50.6 (d, $^2J_{P-F}$ = 35.2). $^{13}C\{^1H\}$-APT NMR, HSQC, and HMBC (75.4 MHz, CD_2Cl_2, 298 K): δ 275.4 (dd, $^2J_{C-F}$ = 69.9, $^2J_{C-P}$ = 8.2, Os≡C), 185.4 (d, $^2J_{C-P}$ = 91.0, OsC), 147.4, 146.2 (both s, Ph), 144.5 (s, C_{ipso}-Ph), 134.5 (s, C_{ipso}-CPh), 133.9 (s, C*Ph*), 131.9 (s, Ph), 129.4 (s, C*Ph*), 129.3 (s, Ph), 126.0 (s, NCH), 125.6 (s, C*Ph*), 124.9 (s, Ph), 29.6, 29.4 (both s, *C*HCH$_3$), 26.1, 25.5, 23.5 (all s, CH*C*H$_3$), 25.7 (d, $^1J_{C-P}$ = 27.8, PCH), 19.6 (d, $^2J_{C-P}$ = 23.1, PCH*C*H$_3$).

Preparation of OsF(≡CPh)(IPr)(P^iPr_3) (5). A yellow solution of **4** (100 mg, 0.12 mmol) in THF (5 mL) was treated with potassium *tert*-butoxide (12.4 mg, 0.13 mmol). The resulting mixture was stirred for 5 min at room temperature. After this time, the resulting dark red solution was evaporated to dryness. The residue was filtered through Celite with pentane and evaporated to dryness, affording a red solid. Yield: 60 mg (71%). Anal. Calcd for $C_{43}H_{62}FN_2OsP$: C, 60.96; H, 7.38 N, 3.31. Found: C, 60.94; H, 7.62; N, 3.30. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.28, 7.15 (both d, $^3J_{H-H}$ = 8.2, 6H, Ph), 7.07 (dt, $^3J_{H-H}$ = 7.4, $^4J_{H-H}$ = 1.3, 1H, CPh), 7.00 (dd, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 1.3, 2H, CPh), 6.79 (s, 2H, NCH), 6.73 (dd, $^3J_{H-H}$ = 8.0, $^3J_{H-H}$ = 7.4, 2H, CPh), 3.61 (sept, $^3J_{H-H}$ = 6.8, 4H, C*H*CH$_3$), 2.15 (dsept, $^2J_{H-P}$ = 9.0, $^3J_{H-H}$ = 7.2, 3H, PC*H*), 1.43, 1.19 (both d, $^3J_{H-H}$ = 6.8, 24H, CHC*H*$_3$), 1.23 (dd, $^3J_{H-P}$ = 12.7, $^3J_{H-H}$ = 7.2, 18H, PCHC*H*$_3$). ^{19}F NMR (287.2 MHz, C_6D_6, 298 K): δ −178.7 (d, $^2J_{F-P}$ = 47.8, OsF). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 51.4 (d, $^2J_{P-F}$ = 47.8). $^{13}C\{^1H\}$-APT NMR, HSQC, and HMBC (75.4 MHz, C_6D_6, 298 K): δ 236.8 (dd, $^2J_{C-F}$ = 133.9, $^2J_{C-P}$ = 13.6, Os≡C), 198.5 (d, $^2J_{C-P}$ = 92.4, $^2J_{C-F}$ = 11.2, Os=C), 149.4 (d, $^2J_{C-F}$ = 11.5, C_{ipso}-CPh), 146.7 (s, Ph), 138.4 (s, C_{ipso}-Ph), 129.0 (s, CPh), 127.4 (s, Ph), 124.8 (s, CPh), 124.0 (s, Ph), 123.8 (s, CPh, Ph), 123.3 (s, NCH), 29.7 (s, *C*HCH$_3$), 25.9 (s, PCH), 25.6, 23.7 (both s, CH*C*H$_3$), 20.6 (s, PCH*C*H$_3$).

Preparation of Os(C≡CPh)Cl(=CHPh)(IPr)(P^iPr_3) (6). A green solution of **2** (100 mg, 0.12 mmol) in pentane (5 mL) was treated with phenylacetylene (32 μL, 0.3 mmol). The resulting mixture was stirred for 3 h at room temperature. After this time, the resulting dark purple solution was filtered through Celite and evaporated to dryness, affording a purple solid. Yield: 83 mg (74%). Anal. Calcd for $C_{51}H_{68}ClN_2OsP$: C, 63.43; H, 7.10 N, 2.90. Found: C, 63.10; H, 7.18; N, 2.96. MS (electrospray, m/z): $C_{51}H_{68}N_2OsP$ [M−Cl], 931.5; found, 931.5. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 24.16 (s, 1H, Os=C*H*Ph), 7.42−7.34 (5H, CPh), 7.32−7.17 (1H, Ph), 7.00−6.92 (5H, CPh), 6.73 (t, $^3J_{H-H}$ = 7.8, 2H, Ph), 6.92−6.83 (2H, Ph), 6.64, 6.63 (both s, 2H, NCH), 6.58−6.52 (1H, Ph), 4.33, 3.83, 3.75, 3.65 (all sept, $^3J_{H-H}$ = 6.6, 4H, C*H*CH$_3$), 2.77 (dsept, $^2J_{H-P}$ = 10.4, $^3J_{H-H}$ = 7.2, 3H, PCH), 1.75, 1.73, 1.49, 1.36, 1.08, 1.04 (all d, $^3J_{H-H}$ = 6.5, 24H, CHC*H*$_3$), 0.90, 0.73 (ambos dd, $^2J_{H-P}$ = 13.5, $^3J_{H-H}$ = 7.3, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 29.9 (s). $^{13}C\{^1H\}$-APT NMR, HSQC, and HMBC (75.4 MHz, C_6D_6, 298 K): δ 246.7 (d, $^2J_{C-P}$ = 5.7, Os=*C*HPh), 187.3 (d, $^2J_{C-P}$ = 71.5, OsC), 162.6 (s, C_{ipso}-Os=CH*Ph*), 148.9, 147.1, 146.0, 145.2 (all s, Ph), 137.6, 135.5 (both s, C_{ipso}-Ph), 134.0, 130.9, 130.4 (all s, CPh), 129.8 (s, Ph), 129.3 (s, Os−C≡*C*-Ph), 128.6, 127.6, 127.4 (all s, CPh), 125.5 (s, NCH), 125.0, 124.3, 123.9, 123.8 (all s, Ph), 123.6 (s, C-Os-C≡C-*Ph*), 102.0 (d, $^2J_{C-P}$ = 10.8, Os-*C*≡C-Ph), 29.5, 29.4, 28.5, 28.1 (all s, *C*HCH$_3$), 27.5, 26.5, 26.4, 22.9 (all s, CHCH$_3$), 24.2, 23.9, 23.6 (all s, PCH), 19.8, 19.2 (both s, PCHCH$_3$).

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Preparation of Os(C≡C-COOCH$_3$)Cl(=CHPh)(IPr)(P^{i}Pr$_3$) (7). A green solution of **2** (100 mg, 0.12 mmol) in toluene (5 mL) was treated with methyl propiolate (21 μL, 0.24 mmol). The resulting mixture was stirred overnight at 60 °C. After this time, the resulting dark red solution was filtered through Celite and evaporated to dryness, affording a red solid. Yield: 90 mg (82%). Anal. Calcd for $C_{47}H_{66}ClN_2O_2OsP$: C, 59.57; H, 7.02; N, 2.96. Found: C, 59.42; H, 7.00; N, 2.91. MS (electrospray, *m*/*z*): $C_{47}H_{66}N_2O_2OsP$ [M−Cl], 913.5; found, 913.5. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 22.59 (s, 1H, Os=C*H*Ph), 7.32−6.98 (5H, CH*Ph*), 6.87 (d, $^3J_{H-H}$ = 7.7, 1H, Ph), 6.71−6.56 (5H, Ph), 6.61 (s, 1H, NCH), 4.17, 3.86 (both sept, $^3J_{H-H}$ = 6.6, 2H, C*H*CH$_3$), 3.69 (s, 3H, CH$_3$), 3.66, 3.50 (both sept, $^3J_{H-H}$ = 6.6, 2H, C*H*CH$_3$), 2.81 (dsept, 3H, $^2J_{H-P}$ = 10.1, $^3J_{H-H}$ = 7.2, PCH), 1.84, 1.69, 1.66, 1.13, 1.10, 1.07, 1.05, 1.01 (all d, $^3J_{H-H}$ = 6.6, 24H, CHC*H*$_3$), 0.87, 0.64 (both dd, $^3J_{H-P}$ = 13.8, $^3J_{H-H}$ = 7.2, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 33.4 (s). ^{13}C{^{1}H}-APT NMR, HSQC, and HMBC (75.4 MHz, C_6D_6, 298 K): δ 246.9 (d, $^2J_{C-P}$ = 4.2, Os=*C*HPh), 187.5 (d, $^2J_{C-P}$ = 68.8, OsC), 161.0 (s, C$_{ipso}$-CPh), 151.9 (s, C≡C-COOCH$_3$), 148.8, 147.9, 145.9 (all s, Ph), 137.3, 135.2 (both s, C$_{ipso}$-Ph), 131.1, 130.1, 129.6, 128.8, 128.7 (all s, CPh), 125.1, 124.5, 124.1 (all s, Ph), 123.8 (s, NCH), 116.45 (d, $^2J_{C-P}$ = 10.2, C≡C−COOCH$_3$), 51.0 (s, C≡C−COOCH$_3$), 30.2 (s, C≡*C*-COOCH$_3$), 29.4, 29.1, 28.8, 28.0 (all s, *C*HCH$_3$), 27.5, 26.5, 22.8 (all s, CHCH$_3$), 23.9, 23.5 (both d, $^1J_{C-P}$ = 4.4, PCH), 19.9, 19.0 (s, PCH*C*H$_3$).

Preparation of OsH(C≡C−COOCH$_3$)Cl(≡CPh)(IPr)(P^{i}Pr$_3$) (8). A green solution of **2** (100 mg, 0.12 mmol) in pentane (5 mL) was treated with methyl propiolate (21 μL, 0.24 mmol). The resulting mixture was stirred for 5 min at room temperature. After this time, the resulting red solution was filtered through Celite and evaporated to dryness. The addition of 3 mL of cold pentane caused the formation of an orange solid which was washed with pentane (3 × 3 mL) and dried under vacuo. Yield: 93 mg (85%). Anal. Calcd for $C_{47}H_{66}ClN_2O_2OsP$: C, 59.57; H, 7.02 N, 2.96. Found: C, 59.22; H, 6.98; N, 2.96. MS (electrospray, *m*/*z*): $C_{47}H_{66}N_2O_2OsP$ [M−Cl], 913.5; found, 913.5. IR (cm^{-1}): ν(OsH) 2098. ^{1}H NMR (400 MHz, C_7D_8, 233 K): δ 7.49 (d, $^3J_{H-H}$ = 7.7, 1H, Ph), 7.41 (t, $^3J_{H-H}$ = 7.7, 1H, Ph), 7.32 (t, $^3J_{H-H}$ = 7.7, 1H, Ph), 7.25−7.13 (2H, CPh), 7.08 (s, 1H, CPh), 6.96 (t, $^3J_{H-H}$ = 7.7, 2H, CPh), 6.92 (s, 1H, NCH), 6.89 (d, $^3J_{H-H}$ = 7.8, 1H, Ph), 6.71 (s, 1H, NCH), 6.66, 6.56 (both d, $^3J_{H-H}$ = 7.8, 2H, Ph), 4.22, 3.55 (both sept, $^3J_{H-H}$ = 6.7, 3H, C*H*CH$_3$), 3.58 (s, 3H, CH$_3$), 3.45 (sept, $^3J_{H-H}$ = 6.7, 1H, C*H*CH$_3$), 2.72 (br, 3H, PCH), 1.97, 1.78, 1.76, 1.66, 1.28, 1.25 (all d, $^3J_{H-H}$ = 6.7, 24H, CHC*H*$_3$), 1.17, 0.86 (both dd, $^2J_{H-P}$ = 13.8, $^3J_{H-H}$ = 7.1, 18H, PCHC*H*$_3$), −2.27 (d, $^2J_{H-P}$ = 28.2, 1H, OsH). ^{31}P{^{1}H} NMR (162.0 MHz, C_7D_8, 233 K): δ 24.3 (s). ^{13}C{^{1}H}-APT NMR, HSQC, and HMBC (100.6 MHz, C_7D_8, 233 K): δ 283.2 (d, $^2J_{C-P}$ = 4.0, Os≡C), 173.1 (d, $^2J_{C-P}$ = 74.1, OsC), 154.3 (s, C≡C-COOCH$_3$), 150.6 (s, C$_{ipso}$-CPh), 147.2, 146.9, 146.6, 145.5 (all s, Ph), 140.2, 139.4 (both s, C$_{ipso}$-Ph), 130.0, 129.9 (both s, Ph), 129.7, 128.9, 127.3 (all s, CPh), 126.0 (s, NCH), 125.0, 124.9, 124.1 (all s, Ph), 123.6 (s, NCH), 104.8 (s, C≡C-COOCH$_3$), 92.9 (d, $^2J_{C-P}$ = 8.6, C≡C−COOCH$_3$), 51.4 (s, C≡C−COOCH$_3$), 30.1, 29.4, 28.7 (all s, CHCH$_3$), 27.4, 27.2, 26.5, 26.1, 24.8 (all s, CHCH$_3$), 24.5 (s, PCH), 19.9, 18.8 (both s, PCHCH$_3$).

Preparation of OsH(C≡C−COOCH$_3$)F(≡CPh)(IPr)(P^{i}Pr$_3$) (9). A red solution of **5** (100 mg, 0.12 mmol) in benzene (5 mL) was treated with methyl propiolate (11 μL, 0.12 mmol). The resulting mixture was stirred for 15 min at room temperature. After this time, the resulting red solution was filtered through Celite and evaporated to dryness, affording a red solid. Yield: 80 mg (73%). Anal. Calcd for $C_{47}H_{66}FN_2O_2OsP$: C, 60.62; H, 7.14 N, 3.01. Found: C, 60.28; H, 7.00; N, 2.98. MS (electrospray, *m*/*z*): $C_{48}H_{66}FN_2O_2OsP$ [M+H], 933.5; found, 933.5. IR (cm^{-1}): ν(OsH) 2097. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.93 (d, $^3J_{H-H}$ = 7.8, 2H, CPh), 7.21 (d, $^3J_{H-H}$ = 7.6, 2H, Ph), 7.12 (t, $^3J_{H-H}$ = 7.4, 1H, CPh), 7.07−6.67 (2H, CPh), 6.93 (t, $^3J_{H-H}$ = 7.6, 4H, Ph), 6.71 (s, 2H, NCH), 3.58, 3.20 (both m, 4H, C*H*CH$_3$), 3.45 (dsept, $^3J_{H-P}$ = 10.2, $^3J_{H-H}$ = 7.10, 3H, PCH), 1.81, 1.54, 1.20, 1.12 (all d, $^3J_{H-H}$ = 6.7, 24H, CHC*H*$_3$), 1.00, 0.95 (both dd, $^2J_{H-P}$ = 13.4, $^3J_{H-H}$ = 7.10, 18H, PCHC*H*$_3$), −0.46 (dd, $^2J_{H-P}$ = 28.3, $^2J_{H-F}$ = 7.8, 1H, OsH). ^{19}F NMR (287.2 MHz, C_6D_6, 298 K): δ −153.4 (dd, $^2J_{F-P}$ = 29.6, $^2J_{F-H}$ = 7.8). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 31.0 (d, $^2J_{P-F}$ = 29.6). ^{13}C{^{1}H}-APT NMR, HSQC, and HMBC (75.4 MHz, C_6D_6, 298 K): δ 284.4 (broad, Os≡C), 176.8 (dd, $^2J_{C-P}$ = 81.4, $^2J_{C-F}$ = 8.3, OsC), 153.9 (s, C≡C-COOCH$_3$), 150.2 (s, C$_{ipso}$-CPh), 147.0, 146.6 (both s, Ph), 139.3 (s, C$_{ipso}$-Ph), 129.9, 129.7, 129.6 (all s, CPh), 127.2, 123.9, 123.8 (all s, Ph), 123.6 (s, NCH), 106.1 (d, $^3J_{C-F}$ = 12.6, C≡*C*-COOCH$_3$), 95.8 (dd, $^2J_{C-F}$ = 50.6, $^2J_{C-P}$ = 6.8, *C*≡C−COOCH$_3$), 50.8 (s, C≡C−COOCH$_3$), 29.1, 29.0 (both s, CHCH$_3$), 26.7, 25.8 (both s, CHCH$_3$), 24.9 (d, $^1J_{C-P}$ = 26.3, PCH), 23.2, 22.8 (both s, CHCH$_3$), 19.3 (d, $^2J_{C-P}$ = 7.11, PCHCH$_3$).

Preparation of OsHCl$_2$(≡CPh)(IPr)(P^{i}Pr$_3$) (10). A green solution of **2** (100 mg, 0.12 mmol) in toluene (5 mL) was treated with HCl (1 mL, 0.12 M). The resulting mixture was stirred for 2 h at room temperature. After this time, the resulting pale red solution was evaporated to dryness. The addition of 3 mL of cold pentane caused the formation of a pink solid which was washed with pentane (3 × 3 mL) and dried under vacuo. Yield: 65 mg (62%). Anal. Calcd for $C_{43}H_{63}Cl_2N_2OsP$: C, 57.38; H, 7.06; N, 3.11. Found: C, 57.52; H, 6.74; N, 3.41. MS (electrospray, *m*/*z*): $C_{43}H_{63}ClN_2OsP$, 865.4; found, 865.4. IR (cm^{-1}): ν(OsH) 2151. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.38 (m, 2H, CPh), 7.30 (t, $^3J_{H-H}$ = 7.6, 2H, Ph), 7.24, 7.12 (both dd, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.8, 4H, Ph), 7.02 (t, $^3J_{H-H}$ = 7.5, 1H, CPh), 6.70 (t, $^3J_{H-H}$ = 8.2, $^3J_{H-H}$ = 7.5, 2H, CPh), 6.65 (s, 2H, NCH), 3.52, 3.29 (both sept, $^3J_{H-H}$ = 6.7, 4H, C*H*CH$_3$), 2.43 (dsept, $^2J_{H-P}$ = 9.4, $^3J_{H-H}$ = 7.1, 3H, PCH), 1.52, 1.28, 1.07, 1.06 (all d, $^3J_{H-H}$ = 6.7, 24H, CHC*H*$_3$), 1.22, 1.14 (both dd, $^3J_{H-P}$ = 13.1, $^3J_{H-H}$ = 7.1, 18H, PCHC*H*$_3$), −5.95 (d, $^2J_{H-P}$ = 16.5, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 11.4 (s). ^{13}C{^{1}H}-APT NMR, HSQC, and HMBC (75.4 MHz, C_6D_6, 298 K): δ 256.5 (d, $^2J_{C-P}$ = 12.9, Os≡C), 168.2 (d, $^2J_{C-P}$ = 96.5, OsC), 148.2 (s, C$_{ipso}$-CPh), 146.9, 146.3 (both s, Ph), 139.5 (s, C$_{ipso}$-Ph), 130.0, 128.8, 129.6 (all s, C*Ph*), 129.3, 128.6 (both s, Ph), 128.0 (s, C*Ph*), 125.8 (s, NCH), 124.2, 123.6 (both s, Ph), 29.1 (s, CHCH$_3$), 26.5, 26.4, 23.3, 23.2 (all s, CHCH$_3$), 26.2, 25.8 (both s, PCH), 20.2, 19.9 (both s, PCHCH$_3$).

Structural Analysis of Complexes 2 and 6. X-ray data were collected for the complexes on a Bruker Smart APEX Duo (**2**) or Smart APEX (**6**) diffractometers equipped with a normal or fine focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (**2**) or 30 mA (**6**). Data were collected over the complete sphere. Each frame exposure time was 60 s (**2**) or 30 s (**6**), covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[30] The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97,[31] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed in the least Fourier maps or calculated, and refined freely or using a restricted riding model. In both structures, pentane solvent molecules were observed in the asymmetric unit and were refined with restrained geometry and isotropic thermal parameters. In **6**, the phenyl group of the alkynyl ligand was observed disordered in two positions and refined with two moieties with complementary occupancy factors, restrained geometry, and isotropic thermal parameters.

Crystal Data for **2**. $C_{43}H_{62}ClN_2OsP{\cdot}0.5(C_5H_{12})$, M_W = 899.64, red, irregular block (0.22 × 0.19 × 0.15), tetragonal, space group $P4_2/n$, *a* = 24.642(3) Å, *b* = 24.642(3) Å, *c* = 16.016(2) Å, *V* = 9725(2) Å^3, *Z* = 8, *Z*′ = 1, D_{calc} = 1.229 g cm^{-3}, *F*(000) = 3704, *T* = 100(2) K, μ = 2.739 mm^{-1}; 103 123 measured reflections (2θ = 3−58°, ω scans = 0.3°), 12 728 unique (R_{int} = 0.0755); min./max. transmission factors = 0.697/0.862; final agreement factors R_1 = 0.0499 (7669 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.1621; data/restraints/parameters = 12 728/44/510; GoF = 1.096. Largest peak and hole: 3.033 (close to osmium atom) and −0.157 e/Å^3.

Crystal Data for **6**. $C_{51}H_{68}ClN_2OsP{\cdot}C_5H_{12}$, M_W = 1037.84, purple, irregular block (0.11 × 0.07 × 0.06), monoclinic, space group $P2_1/c$, *a* = 12.5093(11) Å, *b* = 13.2893(12) Å, *c* = 31.967(3) Å, β = 93.9270(10)°, *V* = 5301.7(8) Å^3, *Z* = 4, *Z*′ = 1, D_{calc} = 1.300 g cm^{-3}, *F*(000) = 2152, *T* = 100(2) K, μ = 2.522 mm^{-1}; 40 780 measured reflections (2θ = 3−51°, ω scans = 0.3°), 9860 unique (R_{int} = 0.0914); min./max. transmission factors = 0.701/0.862; final agreement factors R_1 = 0.0968 (7296 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1962; data/restraints/

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parameters 9860/16/520; GoF = 1.219. Largest peak and hole: 2.453 (close to osmium atom) and −3.843 e/Å^3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05825.

$^{31}P\{^1H\}$ NMR spectra for the transformation from **8** into **7** in C_6D_6, experimental and calculated absorption spectra of complexes **2** and **6**, and computational details (PDF)

Cartesian coordinates of calculated complexes **2** and **6** (XYZ)

X-ray crystallography data for **2** (CIF)

X-ray crystallography data for **6** (CIF)

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Notes

The authors declare no competing financial interest.

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