

Facile C(sp²)/OR Bond Cleavage by Ru or OsGerman Ferrando,[†] H el ene G erard,[‡] Gregory J. Spivak,[†] Joseph N. Coalter, III,[†] John C. Huffman,[†] Odile Eisenstein,^{*,‡} and Kenneth G. Caulton^{*,†}

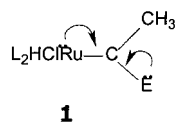
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Os(H)₃ClL₂ (L = PⁱPr₃ or P^tBu₂Me) are shown to be useful “precursors” to “OsHClL₂”, which react with vinyl ethers to form first an η²-olefin adduct and then isomerize to the carbenes, OsHCl[CMe(OR)]L₂. Subsequent R- and L-dependent reactions involve C(sp²)-OR bond cleavage, to make either carbyne or vinylidene complexes. The mechanisms of these reactions are explored, and the thermodynamic disparity of Ru versus Os and the influence of the OR group and the spectator phosphine ligands are discussed based on DFT (B3PW91) calculations.

Introduction

We have shown that the products of the unsaturated dimeric [RuHClL₂]₂ (L = PⁱPr₃) and a variety of olefins with donor substituents H₂C=CHE (E = OR, RNC(O)R') are the carbene complexes L₂HClRu=C(E)CH₃. We have analyzed the thermodynamics of this reaction in terms of the carbene carbon being stabilized by two π-donor substituents, E and RuHClL₂ (**1**).^{1,2}



We are interested in studying the analogous chemistry for osmium, particularly since there is considerable accumulated evidence^{2–5} that, in the same ligand environment, Os is considerably more π basic (i.e., reducing) than Ru. Since the necessary “OsHClL₂” reagent is unavailable for such a study, we report here our pursuit of this reagent, and its reactivity and DFT calculations that bear on the thermodynamics of its reactions.

Results

The synthesis of [RuHClL₂]₂ employs dehydrohalogenation of Ru(H)₂Cl₂L₂. Attempts to dehydrohalogenate Os(H)₂Cl₂L₂ analogously in C₆D₆ at 25 °C with LiMe, LiCH₂CMe₃ (also in Et₂O-*d*₁₀), or Li 2,2,6,6-tetramethyl piperidine (LiTMP) were generally unsatisfactory, even under mild conditions; only mixtures of products were obtained.

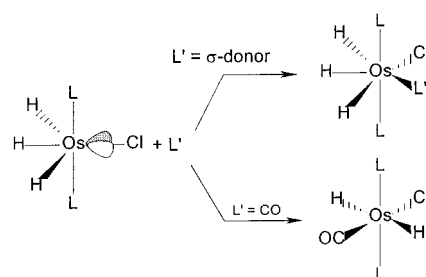
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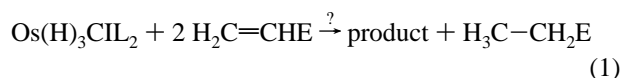
[‡] Universit e de Montpellier 2.

- (1) Coalter, J. N.; Spivak, G. J.; G erard, H.; Clot, E.; Davidson, E. R.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 9388.
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Scheme 1



Synthetic Alternatives. We therefore turned to Os(H)₃ClL₂ as a possible “functional equivalent” of OsHClL₂, provided the equimolar H₂ could somehow be removed. In a general sense, we hoped to render the H₂ innocuous by carrying out reactions with two moles of olefin, thereby scavenging the H₂ into alkane (eq 1).

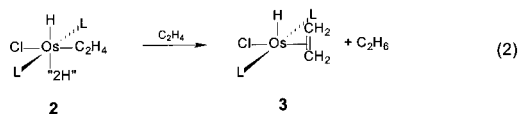


The low-temperature ligand addition chemistry of Os(H)₃ClL₂ has already been reported⁶ and is summarized in Scheme 1, where the LUMO of Os(H)₃ClL₂ is sketched. The σ donors L' are THF, MeCN, MeOH, NH₃, and PEt₃. To further investigate the reactivity of this starting material with a mild σ donor and poor π acidic reagent, 4-dimethylamino pyridine was chosen. The reaction proceeds immediately judging by the color change of the solution from brown to pale yellow. After 5 min, the reaction is complete, and the product obtained is the one expected for a σ donor, with the pyridine nitrogen bound to the metal center. In contrast, the product for L = CO is not that which would result from attack on the LUMO, and it is suggested to not be a kinetic product, but rather the thermodynamic product: it benefits from a trans push-pull Cl/CO interaction and the placement of the weakest ligand, H₂, trans to the potent trans effect hydride. Prior to studies with vinyl ethers, we studied the case of L' = C₂H₄.

- (6) Kuhlman, R.; Clot, E.; Leforestier, C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 10153.

Reaction of Os(H)₃ClL₂ with Ethylene (L = P^tBu₂Me).

These reagents react within 10 min in toluene to give an adduct. Especially remarkable is that this molecule shows *two* Os/H signals at 25 °C: -4.1 (triplet $J_{HP} = 21$ Hz, intensity 1) and -14.6 (t, $J_{HP} = 13$ Hz, intensity 2). The signals of coordinated C₂H₄ are broad, but that of free dissolved C₂H₄ is sharp at 25 °C. The lack of facile exchange between the metal bound H's is attributed to their mutually trans stereochemistry, **2**. Even at -70 °C and 400 MHz, the intensity 2 peak is not decoalesced, so we cannot be certain whether the "2H" are in fact two hydrides or η²-H₂. At this temperature, in toluene, their T_1 value is 77 ms,⁷ which indicates an H/H separation less than ~1.7 Å, but the T_1 value is somewhat long for H₂. As the temperature is raised (eq 2), ethane is produced (¹H NMR evidence) and excess ethylene binds to give **3**.

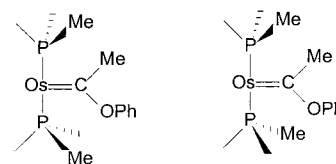


Key spectroscopic features of **3** are two ^tBu methyl chemical shifts (i.e., they are diastereotopic), virtual coupling for ^tBu protons, showing transoid phosphines, a very high field hydride chemical shift (-35.4 ppm) (showing no strong ligand trans to itself), and, at -40 °C, two ¹³C chemical shifts for coordinated ethylene, showing that the C=C vector eclipses the Os-H bond. At this low temperature, two olefin proton chemical shifts are observed. At 25 °C, both ethylenic ¹³C and ¹H inequivalences coalesce, which is consistent with rapid olefin rotation about its bond to Os. It is noteworthy that this deduced structure for **3** is wholly consistent with that of OsHCl(CO)L₂, where the double-faced π acid CO occupies the site of the single-faced olefin. It is also the structure observed for RuHCl(olefin)L₂. The olefin orientation minimizes steric repulsion with the bulky phosphines.

OsHCl(C₂H₄)(P^tBu₂Me)₂ adds H₂ at or below 25 °C to give the same 1:1 adduct **2** observed above; over a longer period of time (2 h), the reaction proceeds further to give OsH₅Cl(P^tBu₂Me)₂ and C₂H₆. If OsHCl(C₂H₄)(P^tBu₂Me)₂ is reacted with D₂ at -80 °C, D is detected in both negative chemical shift resonances of the six-coordinate adduct. Deuterium is already observed in the coordinated ethylene by -20 °C, and at 0 °C deuterated ethane is observed, along with Os(D)₃Cl(P^tBu₂Me)₂.

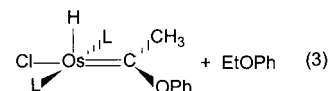
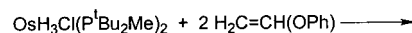
Reaction of Os(H)₃Cl(P^tBu₂Me)₂ with H₂C=CH(OPh). (A)

First Step. This reaction proceeds already at -80 °C in toluene-d₈ to give a 1:1 adduct, OsH₃Cl[H₂C=CH(OPh)]L₂. Three (broad) signals are seen for the coordinated vinyl protons. Because the vinyl ether is a prochiral olefin, binding it to the complex leaves the phosphines inequivalent, regardless of the conformation and the rate of rotation of coordinated olefin. In fact, the ³¹P{¹H} NMR spectrum shows an AB pattern with $J_{AB} = 167$ Hz. This value is smaller than the 250–350 Hz found when $\angle\text{P-M-P} \approx 180^\circ$ and indicates that this angle is significantly bent in this adduct. Analogous to OsH₃Cl(C₂H₄)L₂, the hydride region of OsH₃Cl[H₂C=CH(OPh)]L₂ shows a 1:2 ¹H NMR pattern at approximately -4 and -14.0 ppm. Below -60 °C, the intensity 1 peak is a doublet of doublets ($J_{P-H} = 28$ and 18 Hz), and as with the ethylene adduct, we are unable to conclusively determine whether the T_1 value of the -14 ppm resonance (57 ms at -70 °C) indicates merely

Scheme 2

two hydrides with an H-Os-H angle ~72° (i.e., planar pentagon) or a molecular H₂ ligand with a long H/H distance. However, this adduct structural type resembles that for the CO adduct in Scheme 1. The vinyl signals due to free and coordinated olefin broaden and reach coalescence at 0 °C, showing the reversibility of olefin binding to Os(H)₃Cl(P^tBu₂Me)₂.

(B) Second Step. In the presence of additional vinyl ether and at higher temperatures (e.g., evident already at -10 °C), the adduct evolves (eq 3) to eliminate equimolar ethyl phenyl ether and to form a carbene complex (complete within 2.5 h at 25 °C).



This carbene, OsHCl[C(OPh)Me]L₂, is the anticipated result of the OsHClL₂ fragment isomerizing the vinyl ether, as does the Ru analog.

The carbene complex is distinguished at RT by existing in benzene solution as two NMR-inequivalent rotamers (2:1 ratio) which differ by their conformation about their Os-P bonds. Their hydride peaks at 20 °C are broad (thus, no resolved structure) at -29.9 and -33.1 ppm. These each sharpen to apparent triplets on cooling to -30 °C. The ³¹P{¹H} NMR spectrum shows two broad peaks at 25 °C, but these decoalesce into two AB patterns (relative intensity 2:1) by -50 °C; each AB pattern (accidentally) has the same $J_{PP'}$ value of 307 Hz, which is consistent with a P-Os-P angle > 170°. This hindered rotation about Os-P single bonds (which begins to coalesce by ³¹P NMR at 25 °C) is consistent with the carbene plane eclipsing the P-Os-P vector (Scheme 2). At -50 °C, two resonances for the MeC (carbene) group appear at 2.35 and 2.87 ppm (intensity 2:1); this definitively confirms that the two species detected arise from Os-P conformational differences.

The observation of inequivalent phosphines in OsHCl[C(OPh)Me](P^tBu₂Me)₂ is unusual, first because it is not true of RuHCl[C(OR)Me](P^tPr₃)₂ (R = alkyl), which has a conformation where the carbene plane lies in or near the RuHCl plane. It is also unusual because it proves that the Os carbene complex shows no facile rotation around the Os/C bond at 25 °C, while rotation around the Ru/C bond is coalesced (by ¹H and by ³¹P NMR spectroscopies) at 25 °C; only at low temperatures are the two conformational isomers, **4a** and **4b**, decoalesced (eq 4, R = Et).

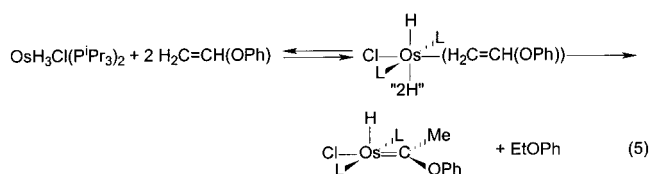


When OsHCl[C(Me)OPh](P^tBu₂Me)₂ was heated for 1 h at 80 °C in benzene, the carbene complex was totally consumed during this period, but the ¹H and ³¹P NMR spectra show an

unappealing mixture of products, none of which is a carbyne complex (see below). The growth of free $\text{P}^i\text{Bu}_2\text{Me}$ is symptomatic of unselective decomposition.

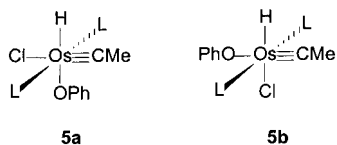
The Effect of Changing the Phosphine: P^iPr_3 . (A) **First Step.** $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ reacts with phenyl vinyl ether (1:2 mole ratio) in toluene- d_8 at -78°C to form the adduct $\text{OsH}_3\text{Cl}[\text{H}_2\text{C}=\text{CH}(\text{OPh})](\text{P}^i\text{Pr}_3)_2$. This shows three NMR peaks for coordinated vinyl hydrogen shifted upfield from free olefin values, and these integrate against ^iPr hydrogens to show that one olefin is coordinated. The ^iPr methyl signals are at least four doublets of virtual triplets, indicating that the phosphines are mutually trans, but are *inequivalent*. This is clearly inconsistent with the observation of a $^{31}\text{P}\{^1\text{H}\}$ NMR singlet from -78 to -40°C , and must be due to an AB spin system where $J_{\text{AB}} > \nu_{\text{A}} - \nu_{\text{B}}$. The adduct shows two hydride signals at -78°C , -4.2 ppm (triplet), and -14.1 ppm (broad) in a 1:2 ratio. The T_{1min} value for the -14.1 ppm signal is 45 ms at -60°C . At -40°C , this signal is resolved into a triplet with $J_{\text{HP}} = 11$ Hz. At 0°C , ^1H NMR signals of both free and coordinated phenyl vinyl ether broaden, as do the hydride peaks.

(B) **Second Step.** At 0°C , ethyl phenyl ether and a new $^{31}\text{P}\{^1\text{H}\}$ NMR AB pattern are observed; the J_{AB} value, 291 Hz, indicates a trans stereochemistry. A new hydride resonance grows simultaneously (-26 ppm, broad), as does a methyl (on a carbene C) signal at 2.9 ppm (eq 5). Peaks due to $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ also appear at 0°C , showing an entropically controlled equilibrium shift.



(C) **Third Step. C/O Cleavage Reaction.** $\text{OsHCl}[\text{C}(\text{OPh})\text{Me}](\text{P}^i\text{Pr}_3)_2$ is a metastable species, in contrast to its (persistent) Ru analogue. Within 5 h of initiating the reaction of $\text{Os}(\text{H})_3\text{ClL}_2$ and $\text{H}_2\text{C}=\text{CH}(\text{OPh})$ at 25°C , the carbene product has isomerized to form $\text{OsHCl}(\text{OPh})(\text{CMe})\text{L}_2$. The spectroscopic features most persuasive of this product structure are the carbyne ^{13}C chemical shift (269 ppm) and the ^1H NMR chemical shifts (-7.2 ppm, Os-H; and 0.63 ppm t, OsCMe ; both in C_6D_6), which are very similar to the values found for $\text{OsHCl}_2(\text{CMe})\text{L}_2$.⁸

While diastereotopic ^iPr methyl protons (and carbons) are consistent with structure **5a**, the data to this point are equally consistent with isomer **5b**.



To resolve this matter, ^1H NMR NOE experiments were undertaken. Irradiation of the ortho phenyl hydrogens enhanced the intensity of the hydride (11%) and ^iPr protons, but not of the carbyne methyl protons. As a control experiment, irradiation of the meta phenyl hydrogens enhanced only the para and ortho hydrogens. These results are only consistent with the isomer where PhO is cis to hydride.

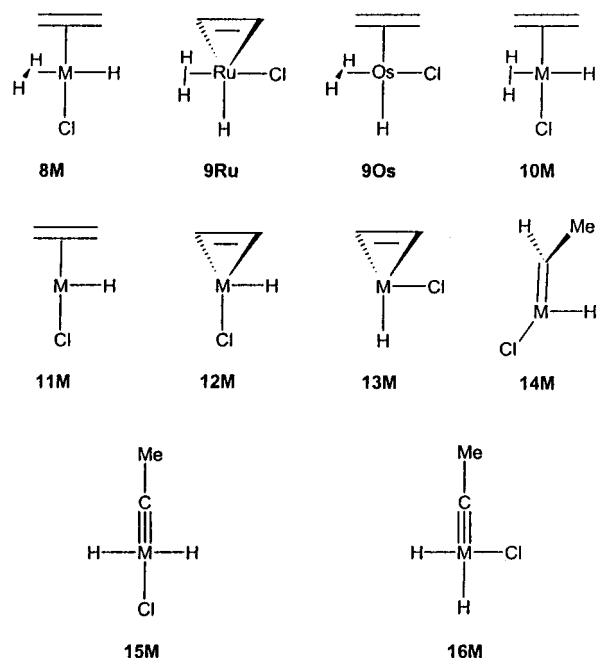
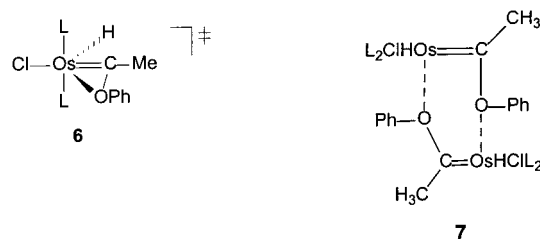


Figure 1. Schematic representation of the DFT (B3PW91) optimized structures for **8M–16M** ($\text{M} = \text{Os}, \text{Ru}$). For clarity, phosphines (PH_3) are not shown and are pointing toward and away from the plane displayed. All structures are minima except for **10Os**, which is a transition state for H_2 rotation.

The isomer **5b** with OPh trans to the carbyne is the thermodynamic product. It was heated at 60°C for 48 h in benzene, and isomer **5b** was recovered unchanged after this treatment. The site preference of the alkoxy group will be discussed in the computational studies section.

Isomerization Mechanism. (A) Bimolecular Pathway. The structure of isomer **b** clearly adds an element of complexity to any mechanistic speculation on the C/O bond scission event. A cis disposition of OPh and carbyne could be explained by a “least motion” mechanism through transition state **6**, but we have detected no such cis intermediate during the disappearance of $\text{OsHCl}[\text{C}(\text{OPh})\text{Me}](\text{P}^i\text{Pr}_3)_2$. We therefore considered several alternative mechanisms.

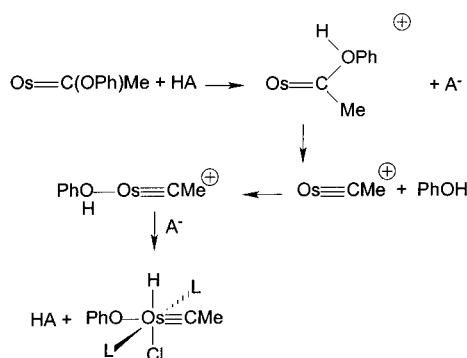


The rate of isomerization of $\text{OsHCl}[\text{C}(\text{OPh})(\text{Me})](\text{P}^i\text{Pr}_3)_2$ to the carbyne was monitored by ^1H NMR in C_6D_6 at 25°C . The decay of the carbene hydride signal was first-order in osmium (and the data failed in second-order plots). A mechanism second-order in Os (**7**) is thus excluded.

(B) **Acid Catalyst.** We established independently that stoichiometric addition of even the weak acid salt $[\text{Et}_3\text{NH}]\text{Cl}$ is sufficient to convert $\text{OsHCl}[\text{C}(\text{OPh})\text{Me}]\text{L}_2$ to $\text{OsHCl}_2(\text{CMe})\text{L}_2$, with liberation of phenol (25°C , 2 h, benzene). The dichloride/carbyne product was characterized by spectra and X-ray diffraction (see Experimental and Figure 5). This rapid C/O bond scission suggests that any acid HA could, even catalytically, effect the carbene-to-carbyne transformation (Scheme 3). This was tested by attempting to slow the OPh

(8) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. J. *Am. Chem. Soc.* **1993**, *115*, 4683. Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951.

Scheme 3

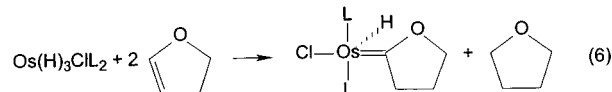


migration reaction by adding a scavenger for an acid catalyst. To test for an acid-catalyzed mechanism, the reaction rate was studied in the presence of added proton sponge (1,8-bisNMe₂-naphthalene), which was shown independently to not complex directly to reactant or product. Rates were again first-order in reactant concentration. In the presence of a 5:1 ratio of proton sponge:Os, the rate was suppressed by 14%, while a 10:1 ratio further suppressed the rate to 28% of the value found in the absence of proton sponge. This establishes that the migration reaction is indeed acid catalyzed, but the lack of saturation of such acid catalysis and the high base:Os ratio employed establish that the adventitious acid is a weak acid and/or that its concentration is low.

(C) Phosphine Dependence. To test the influence of the phosphine during the isomerization process, the reaction was run in the presence of 1 equiv of triisopropyl phosphine. The presence of phosphine slowed the reaction by 18%. The decrease in the reaction rate can be due to the phosphine a) acting as a weak base, scavenging traces of acid, or b) acting as inhibitor for the release of a phosphine during the isomerization.

Inhibition was tested by looking for phosphine exchange during the carbene-to-carbyne isomerization. The reaction between OsH₃Cl(PⁱPr₃)₂ and vinyl phenoxide was, therefore, carried out in the presence of 2 equiv of the isomeric phosphine, P^tBu₂Me. The free phosphine was added 20 min after the reagents were mixed, once the carbene is the main product; at that time, a small amount of OsH₃Cl(η²-H₂C=CH(OPh))(PⁱPr₃)₂ is still present. During the course of the reaction, a very small concentration of a new product, due to phosphine exchange at some stage of the reaction, was observed in the hydride region at -6.9 ppm. When the reaction had finished, the solution consisted of a main product, OsHCl(OPh)(C(CH₃))(PⁱPr₃)₂, along with minor quantities of the mixed phosphine species mentioned above. This solution was heated at 75 °C for 3 days and showed no change in the population of the species, indicating that the phosphine exchange does not occur in the hydrido-carbyne product. Thus, we conclude the identity of this mixed phosphine species is the carbyne derived from isomerization of the carbene OsHCl(=C(OPh)(Me))(P^tBu₂Me)(PⁱPr₃); phosphine exchange thus occurs before or during the isomerization, but only to an extent too small to be on the mechanistic path. Therefore, we attribute isomerization rate suppression to the Brønsted base action of the added PⁱPr₃.

Os(H)₃Cl(PⁱPr₃)₂ + 2,3-Dihydrofuran. When the vinyl ether is cyclic, there is a ring constraint against intramolecular migration to make a carbyne. In fact (eq 6), Os(H)₃ClL₂ (L = PⁱPr₃) reacts with two moles of this dihydrofuran at 25 °C in 22 h to produce THF (identified by ¹H NMR after vacuum transfer of the volatiles).

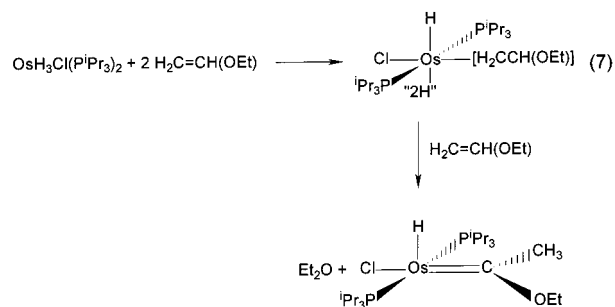


The major product remaining after vacuum transfer is the cyclic carbene complex. The product shows a hydride (triplet) chemical shift of -21.9 ppm and two diastereotopic P/CH₃ virtual triplets, indicating transoid phosphines. The ³¹P{¹H} NMR spectrum is an AB pattern, indicating that the carbene plane eclipses in the P-Os-P direction. The ring CH₂ protons show three chemical shifts, and these were assigned by spin decoupling experiments. The fact that three, not six, chemical shifts are observed for these hydrogens is explained by rotation around the Os=C bond, which is slow on the ³¹P NMR time scale, where an AB pattern is observed, but fast on the ¹H NMR time scale.

An Electron-Rich Ether Substituent: Reaction of OsH₃Cl-(P^tBu₂Me)₂ with Ethyl Vinyl Ether. Ethyl vinyl ether reacts to completion in benzene over 48 h at 25 °C with Os(H)₃Cl-(P^tBu₂Me)₂ (2:1 mole ratio) to give OsHCl[CMe(OEt)](P^tBu₂Me)₂. This reaction is thus distinctly slower than the analogous reaction with [RuHCl(PⁱPr₃)₂]₂.² The far upfield hydride chemical shift (-28 ppm) is consistent with a square-pyramidal structure with hydride trans to the empty site. The ^tBu groups show diastereotopic inequivalences by ¹H NMR. The ³¹P{¹H} NMR spectrum of the carbene complex is a singlet. Steady growth of Et₂O is observed (¹H NMR) during the reaction, thus establishing this as the fate of two of the three reagent hydride ligands. No intermediates are detected by ¹H or ³¹P NMR spectroscopy at 25 °C during the reaction, although the hydride signal of OsH₃Cl(P^tBu₂Me)₂ shows broadening due to exchange with a minor amount of olefin adduct. The carbene complex does not react further (e.g., no C/O cleavage with conversion to any carbyne complex) over 65 h at 25 °C in benzene.

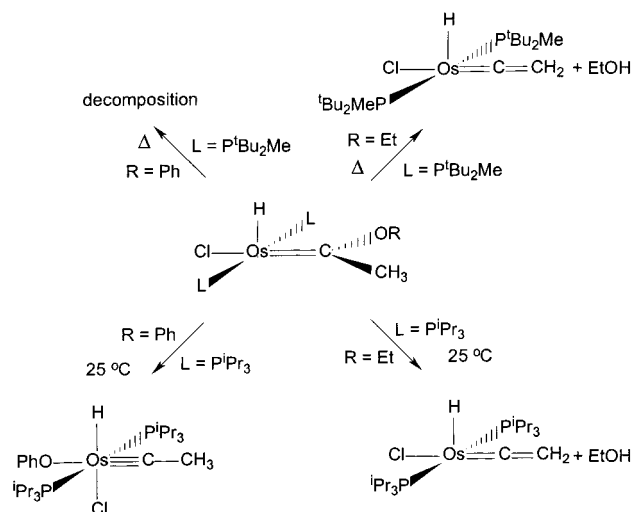
When OsHCl[CMe(OEt)](P^tBu₂Me)₂ is heated at 80 °C for 1.5 h in benzene, the carbene intensity declines, with formation of approximately equimolar amounts of the two known compounds, OsHCl(CCH₂)(P^tBu₂Me)₂ and OsHCl(CO)(P^tBu₂Me)₂. Further heating of this benzene solution causes further progress of this same conversion.

Reaction of OsH₃Cl(PⁱPr₃)₂ with Ethyl Vinyl Ether. (A) Initial Stages. This reaction proceeds through the intermediate η²-olefin adduct analogous to the phenyl analogue, although at a slower rate of conversion of adduct to carbene, as shown in eq 7.



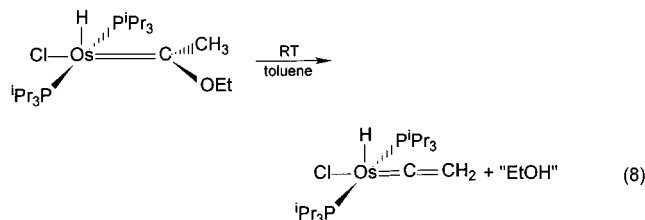
After 3 h at 25 °C, the η²-olefin adduct and the carbene (and Et₂O) are present. All observed resonances are consistent with analogues reported earlier here. In particular, the ³¹P{¹H} NMR spectrum is an AB pattern at 25 °C, which is consistent with the carbene plane alignment illustrated and with the OPh analogue. The expected diastereotopic inequivalence of the OCH₂ proton is not observed at 25 °C, indicating either

Scheme 4



accidental degeneracy or Os=C rotation at a rate sufficient to coalesce the ^1H inequivalence, but not yet the ^{31}P inequivalence.

(B) Subsequent Reaction. This carbene is metastable, and the following reaction is C(sp²)/O cleavage, but it proceeds differently from those for phenoxide. Over a period of 48 h, EtOH is eliminated by “loss” of a carbene methyl proton to give (60% yield) the vinylidene in eq 8; the P^tBu₂Me analogue is known.⁹



No hydride carbyne OsHCl(OEt)(CCH₃)(PⁱPr₃)₂ is observed by ^1H or $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. Such elimination contrasts to the more typical addition¹⁰ of the RO–H bond across a vinylidene C=C bond. Vacuum transfer of the reaction volatiles shows unreacted olefin and Et₂O (from the initial reaction of OsH₃–ClL₂ with EtOCHCH₂), but no EtOH. Since a secondary product in this reaction (40% yield) is OsHCl(CO)L₂, we presume that decarbonylation of liberated ethanol to CO, CH₄, and H₂ occurs, and CO is trapped to give OsHCl(CO)L₂, a thermodynamic “sink” in this area of chemistry.

A summary of the reactions of the carbene complex reported to this point appears in Scheme 4. Both carbenes containing P^tBu₂Me do react, but more slowly than the PⁱPr₃ analogues. For P^tBu₂Me, the ethoxy example reacts more slowly than the phenoxy, but the phenoxy fails to convert selectively to any single product. The ethoxy, when it reacts, does so like the PⁱPr₃ analogue. Although the NMR evidence of hindered phosphine rotation indicates that the P^tBu₂Me analogues are more crowded than those of PⁱPr₃, kinetic studies show that phosphine loss is not involved in OR migration. A more crowded environment should react faster if simply direct RO[–] dissociation were involved. However, a slower rate for the more crowded P^tBu₂Me examples is consistent with the associative step involved

in acid catalysis. These rate differences do not alter the general conclusion that OsHCl[CMe(OR)]L₂ species are only metastable toward further reaction.

Computational Studies. Scheme 5 (energies in kcal mol^{–1} for the most stable isomer of each species, without ZPE correction) provides a convenient summary of a variety of calculated energy differences for both Ru and Os. The calculations show that RuH₃ClL₂ and OsH₃ClL₂ have, respectively, a dihydrogen Ru(H)(H₂)ClL₂ and an osmium trihydride structure; these results are in agreement with previous experimental and theoretical studies.^{11,12} Removing H₂ from the osmium complex requires 47.1 kcal mol^{–1} (cf. 28.2 for Ru, Scheme 5a), illustrating the lesser tendency for Os to lose dihydrogen compared to Ru.

The Ethylene Reaction Products. (A) The Ethylene Adducts. All structures are schematically represented in Figure 1. Only selected structures will be shown accurately in Figure 2. For clarity, both such drawings have identical labels. Coordination of C₂H₄ to the unsaturated 16-electron complex MH₃(Cl)–L₂ (M=Ru, Os, L=PH₃) yields, in both cases, a dihydrogen complex. Structures with C₂H₄ trans to Cl (**8M**) or to H (**9M**) are close in energy. In the case of Os, **9Os** is 4.5 kcal mol^{–1} above **8Os**, which is the experimental structure observed. **9Ru** is 0.5 kcal mol^{–1} more stable than **8Ru**, which indicates no structural preference. H₂ bonded trans to the hydride (**8M**) is only slightly elongated (<0.85 Å), and the H/H and C/C distances are slightly (~0.02 Å) longer for Os than for Ru. C₂H₄ is found to be coplanar with the M–H bonds in **8M**. In **9M**, the orientation preference for H₂ and ethylene are different for the two metals (**9Ru** and **9Os**), but no significant rotational barrier is to be expected since **10M** (which is a transition state (TS) for M = Os and a minimum for M = Ru) is also close in energy to **9M**. The H/H distance is lengthened up to 1.23 Å (M=Os) when H₂ is trans to chloride (**9Os**), with a much shorter M–H bond length (1.69 (**9Ru**); 1.63 (**9Os**)). Whatever the binding and H₂ orientation, the P–M–P angle is significantly bent: 168.2–155.0°. This increases back-donation to the H₂ and ethylene ligands. In all isomers but one, the ethylene is found to prefer a conformation where the CC bond is in the bisector plane of the P–M–P angle. The well-known difficulty of calculating with accuracy an H–H distance in transition metal complexes¹³ and the proximity in energy of several structures with different H–H distances does not allow for the use of these calculations for a better estimate of the H–H distance.

The ethylene adducts without H₂ ligand were also optimized (**11M**–**13M**). For the two metals, a square pyramidal structure, **11M** (Cl–Ru–H = 96°, Cl–Os–H = 100.3°), is found, with an apical hydride and basal trans ethylene and Cl ligands. The CC bond length is unchanged from the H₂ adduct complexes (H₂ trans to H), a noteworthy result which underlines the small degree to which the bound H₂ perturbs the MHCl(C₂H₄)(PH₃)₂ moiety. The CC vector lies preferentially in the H–M–Cl plane, **11M** over **12M**, as observed experimentally. The phosphine ligands are coordinated in a more linear fashion (P–Os–P = 169.5° for Ru and 173.8° for Os). As expected, the ethylene is less strongly bonded to RuH(Cl)L₂ (bond dissociation energy, BDE = 39.2 kcal mol^{–1}) than to the Os analogue (54.9 kcal mol^{–1}). The isomers with apical Cl, **13M**, are minima that are

(9) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091.
 (10) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585, and references therein.

(11) (a) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314. (b) Burrow, T.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1995**, *34*, 2470.
 (12) Gusev, D.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.
 (13) Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601.

Scheme 5

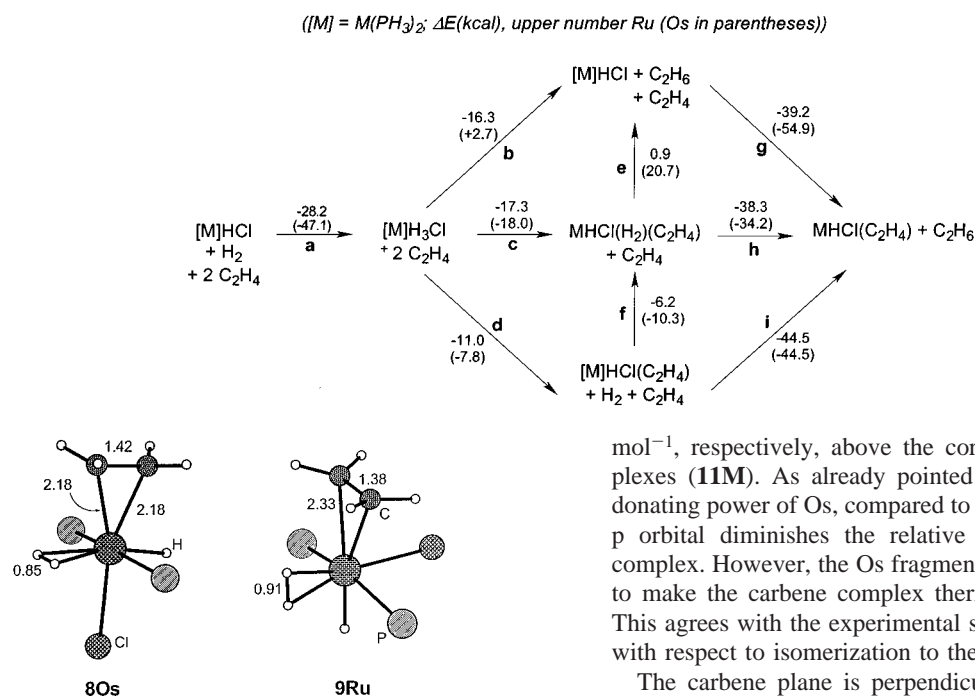


Figure 2. Selected structural parameters for the most stable DFT (B3PW91) optimized structure for MHCl(H₂)(C₂H₄)(PH₃)₂. M = Os (left), Ru (right). Distances are in Å. For clarity, H of PH₃ have been omitted.

considerably higher (18.9 kcal mol⁻¹ above **11M** for Ru and 26.0 kcal mol⁻¹ above **11M** for Os) in energy.

In the olefin/H₂ complexes, loss of either H₂ or of ethylene is energetically facile. In the case of Ru, the BDE of H₂ (Scheme 5, eq **f**) is 6.2 kcal mol⁻¹ and that of C₂H₄ (eq **e**) is 17.2 kcal mol⁻¹. For Os, the corresponding values are 10.3 (H₂) and 18.0 (C₂H₄). As expected, dihydrogen is the less strongly bonded ligand (e.g., Scheme 5, eq **d**). The BDE of H₂ to Ru is small enough to suggest that an H₂/ethylene complex should not be thermally stable. In the case of Os, reversible binding could be observed for H₂, although the two acceptor ligands are more equally bonded. To determine the role of Δ*S*, calculations of Δ*G* at 298 °C were carried out. They show that H₂ is calculated to be almost nonbonded for Os (Δ*G* = -1.2 kcal mol⁻¹), whereas the corresponding value for ethylene is 2.6 kcal mol⁻¹. This accounts for the thermal loss of H₂ from OsH(H₂)(Cl)-(C₂H₄)L₂.

(B) Ethylene Hydrogenation. Scheme 5 permits dissection of the metal-promoted hydrogenation reaction into component steps. Every step of Scheme 5, eq **a** + **c** + **h**, is exothermic for both metals. Even without compensatory binding of a second olefin to M, the Δ*E* of hydrogenation of ethylene itself (Scheme 5, eq **i**), -44.5 kcal mol⁻¹, makes the dehydrogenation of MH₃-Cl(PH₃)₂ by ethylene (Scheme 5, eq **b**) favorable (Ru) or nearly thermoneutral (Os); binding that second olefin (Scheme 5, eq **g**) makes both very favorable. Scheme 5, eq **e** shows that the uncompensated hydrogenation of coordinated olefin with coordinated H₂ in six-coordinated MHCl(H₂)(C₂H₄)(PH₃)₂, to give 14 electron MHCl(PH₃)₂, is quite unfavorable for Os. Thus, without that second olefin (i.e., for the 1:1:1 reaction of MHCl(PH₃)₂/H₂/C₂H₄), the global minimum is MHCl(H₂)(C₂H₄)-(PH₃)₂.

(C) The Isomeric MHCl(CHMe)(PH₃)₂ and MH₂Cl(CMe)-(PH₃)₂ Complexes. The 16 electron carbene MHCl(CHMe)-(PH₃)₂ (M = Ru, Os), **14M**, complexes are 15.9 and 8.0 kcal

mol⁻¹, respectively, above the corresponding ethylene complexes (**11M**). As already pointed out,^{1,2} the larger electron donating power of Os, compared to Ru, into the empty carbene p orbital diminishes the relative preference for the olefin complex. However, the Os fragment, by itself, is not sufficient to make the carbene complex thermodynamically accessible. This agrees with the experimental stability of OsHCl(C₂H₄)L₂ with respect to isomerization to the carbene complex.

The carbene plane is perpendicular to the molecular Cl-M-H plane (**14M**) for Ru and Os. The coordination at the metal has the Y shape (Cl-M-H ~ 140° and H-M-C less than 90°) that is typical of d⁶ ML₅ with one π donor ligand.^{2,14} The reasons for this coordination mode have been discussed previously.² In opposition to what is observed for the ethylene isomer, the perpendicular conformation is a TS (for rotation around M=C) (5.1 (M=Ru) and 11.1 (M=Os)) and not a minimum.

In the case of Os, the preferred carbyne complex, **15M**, (with two trans hydride ligands) is calculated to be 21.0 kcal mol⁻¹ above the ethylene complex. Its isomer, **16M**, with cis hydrides is 26.3 kcal mol⁻¹ above the ethylene complex. In the case of Ru, the two carbyne complexes are at very high energy above the ethylene complex (48.8 for trans hydrides and 47.3 for cis hydrides). While these results show that the computed 18 electron carbyne complexes are disfavored for both metal centers, it also appears that proper use of ligands and substituents could make the carbyne, with a higher metal oxidation state than the carbene, accessible for Os and not for Ru. Although these complexes are 18 electron hexacoordinated species, they are heavily distorted away from ideal octahedral geometry. This is illustrated (trans isomer) by the P-Os-P equal to 157.6° and H-Os-H equal to 158°. These two small angles increase the back donation of Os into the carbyne. The lack of symmetry in the cis isomer results in a geometry that has even greater distortions away from an octahedron. The factors that are responsible for this geometrical distortion are similar to that which are responsible for the nonoctahedral geometry of OsH₃-XL₂ and TaX(OH)₂(H)₂L.¹³

Methyl Vinyl Ether Reaction Products. (A) Methyl Vinyl Ether Adducts. Figure 3 shows schematic structures, and Figure 4 contains accurate representations of selected species, labeled identically. The vinyl ether complexes were only optimized for MHCl(PH₃)₂ (**17M** and **18M**). The case where H₂ also coordinated was not studied.

Optimization of the MHCl(PH₃)₂ (CH₂=CH(OMe)) gives results similar, for geometry and BDE, to that for C₂H₄. The BDE for vinyl ether are calculated to be 2–4 kcal mol⁻¹ less

(14) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

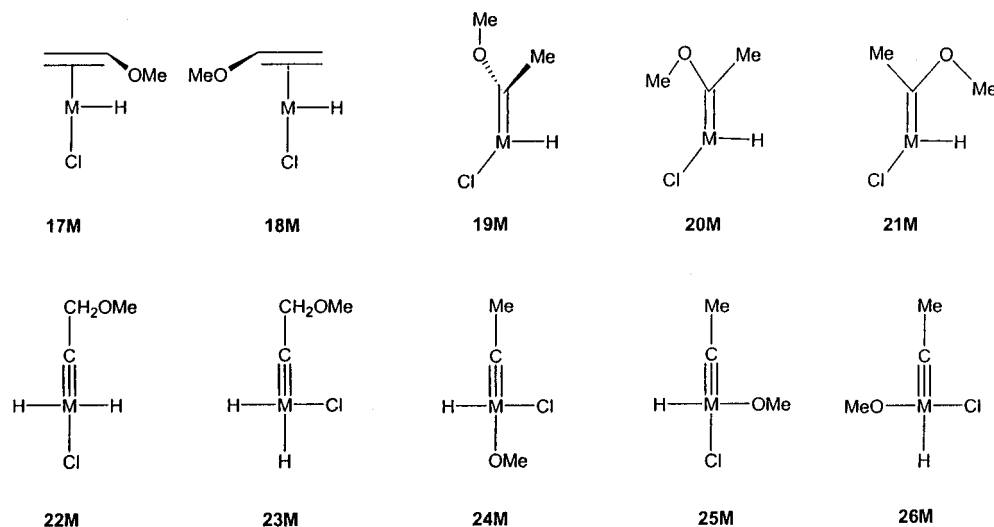


Figure 3. Schematic representation of the DFT (B3PW91) optimized structures for **17M–26M** ($M = \text{Os, Ru}$). For clarity, phosphines (PH_3) are not shown and are pointing toward and away from the plane shown. All structures are minima.

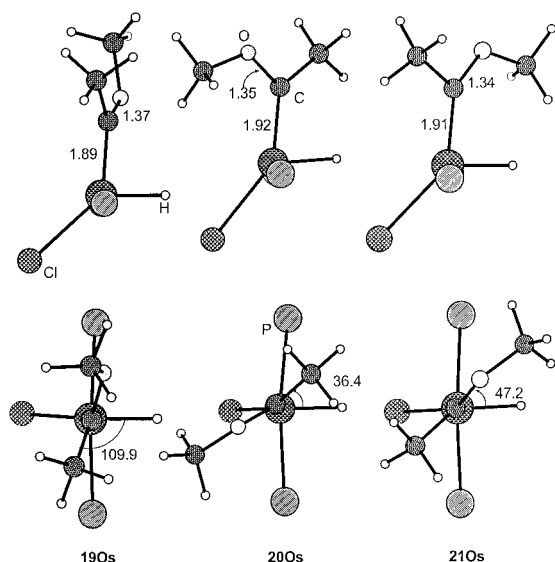


Figure 4. Selected structural parameters for all DFT (B3PW91) optimized conformers for $\text{OsHCl(CMe(OMe))(PH}_3)_2$, **19Os–21Os**. Structures are given viewed along the P–P direction (top) and along the C=Os bond (bottom). Distances are in Å and angles in degrees. For clarity, H of PH_3 have been omitted.

than those for C_2H_4 . The results for Ru were already presented and discussed.² No dramatic changes are observed for Os except for the expected larger BDE (by ~ 15 kcal/mol) of the vinyl ether ligand for Os than for Ru. The two conformations of coordination (OMe syn, **17M**, or anti to hydride, **18M**) are very close in energy. Even in the case where OMe is syn to the empty coordination site, the OMe group remains far from the metal center (≥ 3 Å).

(B) Carbene Isomers. $M=[\text{C(Me)(OMe)}]$ structures, which differ by the rotational conformation around the $M=C$ and $C-O$ bonds, were optimized (**19M–21M**). All conformers are essentially isoenergetic and, in contrast to the case of $\text{CH}(\text{CH}_3)$, are isoenergetic with the methyl vinyl ether adduct. As was already discussed for the case of Ru,² the combined presence of a π donor substituent (OMe) and the π donor metallic fragment (through an occupied d orbital) stabilizes the carbene complex with respect to the olefin adduct. There is almost no difference in behavior between Ru and Os, the latter being marginally more stabilizing to the carbene fragment. While

$\text{OsHCl(PH}_3)_2$ was more efficient than its Ru equivalent in diminishing the difference in energy between the C_2H_4 and $\text{CH}(\text{Me})$ isomers, this is not the case for $\text{CH}_2=\text{CH(OMe)}$. This is in part due to the fact that OMe and the metal fragment compete to give electrons to the empty carbene p orbital. The same interpretation was used to account for the lack of ligand influence (π donor versus π acceptor) for the thermodynamics of carbene complex formation in the case of Ru.¹⁵

The almost identical energies for three different conformations (less than 1.5 kcal mol⁻¹ energy difference between **19Os**, **20Os**, and **21Os**) around the $\text{Os}=\text{C}$ bond of the carbene group in $\text{OsHCl(CMe(OMe))(PH}_3)_2$ suggest the absence of any electronic preference. In none of the located minima is the carbene coplanar with the H-Os-Cl plane. Thus, any of these conformations could account for the observed orientation of the carbene since, in each case, the phosphines ligands are inequivalent. At the same time, rapid “rocking” of the carbene plane to opposite sides of the OsH(Cl)C plane in **20Os** and **21Os** would make the two P equivalent. The energetic barrier for this motion in **20M** was calculated to be less than 1.5 kcal mol⁻¹. A similar value is expected for **21Os**. Thus, the inequivalence of the phosphines is uniquely explained by structure **19Os**.

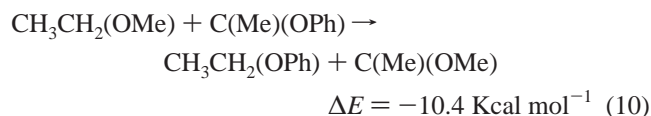
(C) Carbyne Isomers. Several isomeric carbyne complexes were calculated (**22M–26M**). Selected calculations presented for the case of C_2H_4 as a reagent have shown that the carbyne isomer was much more unfavorable with Ru than with Os. As a consequence, the discussion is focused on Os. Both $\text{Os}\equiv\text{CCH}_2\text{-OMe}$ carbyne complexes, **22Os** and **23Os**, are at very high energy with respect to the η^2 -olefin isomer **18Os** (>30 kcal mol⁻¹). In contrast, the CCH_3 carbyne complexes, **24Os** and **25Os**, in which the OMe group is bonded to the metal, are at much lower energy (<20 kcal mol⁻¹, cf Figure 3) except when the carbyne is trans to H, **26Os**, ($+39.5$ kcal mol⁻¹ above **17M** or **18Os**). The discussion will thus be focused on the two isomers with OMe trans to either the carbene or H. Comparison with experimental data shows some disagreement. Assuming that OMe is a model for OPh, it does show only a slight preference for OMe trans, not cis, to the carbene (1.9 kcal mol⁻¹ more stable than trans to H), which prevents drawing any conclusions from calculations on the coordination site preference of the alkoxy group. In addition, it does not account for the

(15) Gérard, H.; Clot, E.; Giessner-Prettre, C.; Caulton, K. G.; Davidson, E. R.; Eisenstein, O. *Organometallics* **2000**, *19*, 2291.

experimental thermodynamic drive for OMe migration to metal, since the carbene complex was calculated to be 17.1 kcal mol⁻¹ below the more stable carbyne isomer. Calculations of **24Os** were carried out with OPh in place of OMe. The endothermicity of the transformation is notably diminished, and the preferred carbyne (OPh trans to carbene) is only 9.6 kcal mol⁻¹ above the carbene complex (i.e., OPh versus OMe stabilizes the carbyne versus carbene by 17.1–9.6 = 7.5 kcal mol⁻¹). Using OMe for the sake of computation time, PH₃ was next replaced by PMe₃. The endothermicity is also notably diminished, and the preferred carbyne is only 7.3 kcal mol⁻¹ above the carbene complex (i.e., PMe₃ alone on the OMe species stabilizes the carbyne by 17.1–7.3 = 9.8 kcal mol⁻¹ versus PH₃). Combining the energy increments caused individually by the two substituents PMe₃ (9.8) and OPh (7.5) should lead to a reaction that is thermodynamically accessible. This result highlights the necessity for proper substituent representation to account for experimental observation.¹⁶

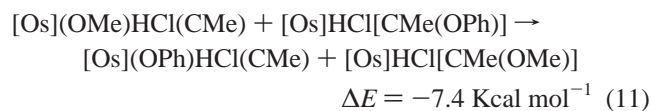
Bond lengths in the carbene complexes also reflect conventional substituent electronic effects. For OMe, Os–C = 1.89 Å and C–O(Me) = 1.36 Å in the carbene complex. In the OPh carbene complex, Os–C = 1.87 Å and C–O(Ph) = 1.39 Å. These changes (i.e., OMe is a better donor) are especially significant since there is no influence of R on the geometry of the carbyne complex, as shown by Os–C(carbyne) (1.74 Å) and Os–O(R) (2.09 Å) regardless of R, and thus, R also probably has little influence on the stability of the carbyne. The difference in energy between the two carbene and carbyne isomers is thus greater for the OR group that stabilizes the carbene more efficiently (i.e., OMe). To further confirm this interpretation, several isodesmic reactions and thermodynamic cycles were constructed.

The transformations shown in eqs 9 and 10 establish the preference for OMe (versus OPh) to stabilize an unsaturated fragment (carbene).



Both equations are exothermic, which shows that OMe stabilizes the free carbene group significantly more than does OPh. The preference of OPh to migrate to the metal was thus to be expected.

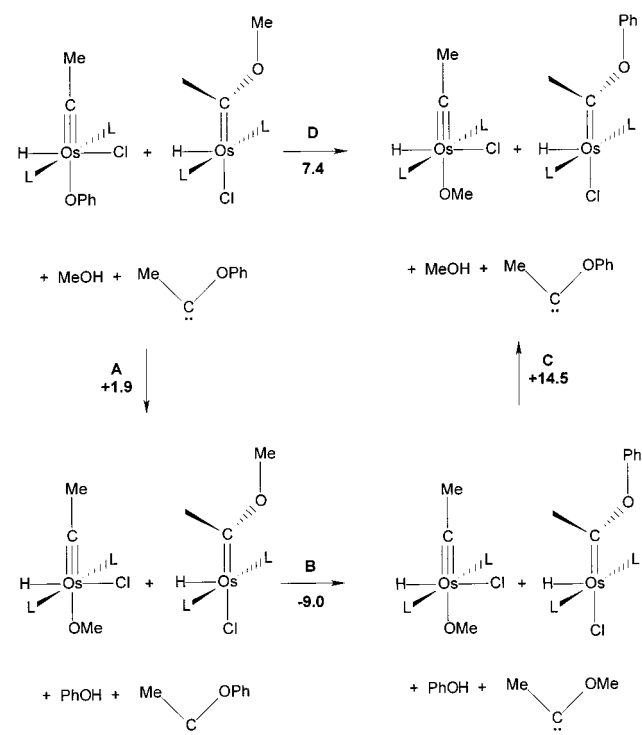
The differential effect of the metal fragment ([Os] = Os-(PH₃)₂) on the relative stability of the two carbenes (cf. eqs 9 or 10) is to diminish the exothermicity of the transformation of eq 11,



but the dominant effect of R is still apparent.

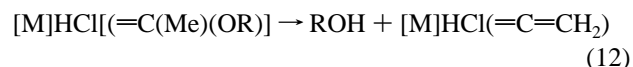
The thermodynamic cycle shown in Scheme 6 summarizes all the effects and permits identification of the controlling factors. Step A (nearly thermoneutral) illustrates that OPh and

Scheme 6



OMe have similar energetic preferences for H and for the metal of the carbene complex. Step B shows the importance of putting the more stabilizing OR group (OMe) on free carbene, not on coordinated carbene. Step C has already been discussed (it is the reverse of eq 9). The endothermicity of step D is thus not dominated by changes within the carbyne complexes (step A) but mostly by steps B and C, i.e., by change of the substituent on the carbene function.

(D) Formation of Vinylidene. The loss of ROH from the carbene complex to form a vinylidene complex has been calculated for MeOH (as a model for EtOH) and was found to be endothermic for both Ru and Os. The geometries of OsHCl(=C=CH₂)(PH₃)₂ and RuHCl(=C=CH₂)(PH₃)₂ are essentially identical and have been previously discussed.^{9,17} The energy difference for the transformation shown in eq 12



(where [M] = M(PH₃)₂) is less endothermic for Os (31.4 kcal mol⁻¹) than for Ru (23.6 kcal mol⁻¹). To evaluate the role of entropy on this reaction, the ΔG of reaction was calculated for the case of Os and was found to be only 7.6 kcal mol⁻¹. This value is small enough to show that the reaction is thermodynamically feasible and that the entropy plays an important role. The energy variation associated with eq 12 was found to decrease significantly when replacing PH₃ (23.6 kcal mol⁻¹) by PMe₃ (15.7 kcal mol⁻¹). Assuming similar entropy effects for the two phosphine ligands indicate that eq 12 is thermodynamically feasible.

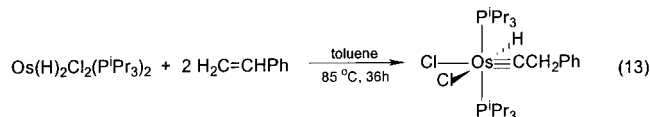
Experimental Evidence for HCl as a Participant in Related Reactions. We reported earlier¹⁸ the following reactivity (eq 13), which differs from the present work in using (1) a

(16) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; Garcia-Yebra, C.; Gutierrez-Puebla, E.; Oliván, M.; Onate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 4949.

(17) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 897.

(18) Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999.

M^{IV} dichloride and (2) no heteroatom substituent on the vinyl carbon.



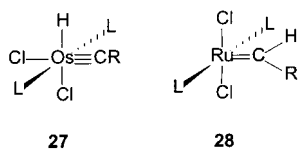
The analogous reaction occurs for the Ru analogue in CD_2Cl_2 , giving $\text{RuCl}_2(\text{carbene})\text{L}_2$, but in poor yield (50%) for styrene and only 15% yield for ethylene. While both $\text{MH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ reagents suffer from very low solubility in all available solvents, the reactions in eq 13 are significantly slower than those of MH_3CIL_2 with vinyl ethers. When $\text{OsH}_2\text{Cl}_2\text{L}_2$ and 3 equiv of $\text{CH}_2=\text{CH}(\text{O}^i\text{Bu})$ in C_7D_8 were heated at 115°C for 24 h, $\text{OsHCl}_2(\text{CCH}_3)\text{L}_2$ was the only osmium–phosphine complex formed (as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). The ^1H NMR spectrum of the same solution confirmed signals of $\text{OsHCl}_2(\text{CCH}_3)\text{L}_2$, unreacted $\text{CH}_2=\text{CH}(\text{O}^i\text{Bu})$, and also showed $\text{CH}_3\text{CH}_2\text{O}^i\text{Bu}$. Monitoring the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this reaction in an NMR probe between 75°C and 105°C over 6 h generally showed a decrease in concentration of $\text{OsH}_2\text{Cl}_2\text{L}_2$ and a concomitant increase in concentration of the carbyne $\text{OsHCl}_2(\text{CCH}_3)\text{L}_2$ ($\text{OsH}_2\text{Cl}_2\text{L}_2$ is sufficiently soluble to detect in aromatic solvents at temperatures above ca. 60°C). The elevated temperature ^1H NMR spectrum under the same conditions showed $\text{OsHCl}_2(\text{CCH}_3)\text{L}_2$. Scaling up the reaction between $\text{OsH}_2\text{Cl}_2\text{L}_2$ and $\text{CH}_2=\text{CH}(\text{O}^i\text{Bu})$ led to the isolation of pale yellow $\text{OsHCl}_2(\text{CCH}_3)\text{L}_2$.

When $\text{OsH}_2\text{Cl}_2\text{L}_2$ was heated for 10 h at 110°C in the presence of 3 equiv of $\text{CH}_2=\text{CH}(\text{OEt})$ in C_7D_8 , the carbyne $\text{OsHCl}_2(\text{CCH}_3)\text{L}_2$ was produced, along with free phosphine and $(\text{CH}_3\text{CH}_2)_2\text{O}$, as determined by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy ($\text{OsH}_2\text{Cl}_2\text{L}_2$ and $\text{CH}_2=\text{CH}(\text{OEt})$ were still present in solution after this time). The carbyne could be isolated in 39% yield once this reaction was scaled up.

Since we have now determined that the reaction of $\text{OsH}_2\text{Cl}_2\text{L}_2$ with $\text{H}_2\text{C}=\text{CH}(\text{OR})$ is slow, as it is for $\text{H}_2\text{C}=\text{CHR}$, the high activation energy must be characteristic of the $\text{M}(\text{H})_2\text{Cl}_2\text{L}_2$ unit. Since the (unusual, nonoctahedral) structure of $\text{M}(\text{H})_2\text{Cl}_2\text{L}_2$ is attributed to steric crowding,^{19,20} it may be that this accounts for the low rates in eq 13. The low rates may also be associated with the need to eliminate HCl; this is a reaction which is characteristic of $\text{Ru}(\text{H})_2\text{Cl}_2\text{L}_2$ reacting with nucleophiles, due to the +4 oxidation being uncharacteristically high for Ru. Coupled with the determination that free HX converts $\text{OsHCl}[\text{C}(\text{OR})\text{Me}]\text{L}_2$ to $\text{OsHClX}(\text{CMe})\text{L}_2$, this further supports the idea that even trace elimination of HCl is the cause of C/O cleavage in reactions employing $\text{M}(\text{H})_2\text{Cl}_2\text{L}_2$.

Discussion

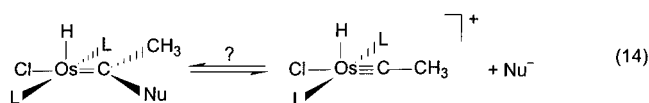
This report reinforces the idea that osmium in this ligand environment (i.e., one where no strong π acid carbonyl coligand depletes metal electron density) prefers the hydride carbyne redox isomer over the carbene. Thus, saturated high-valent osmium (27) contrasts to unsaturated lower valent ruthenium (28).



The present report extends this principle to cases where the

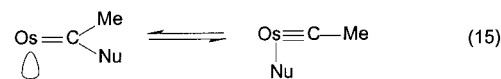
conversion for Os requires heteroatom migration, not merely hydrogen migration,¹⁸ by detecting an intermediate heteroatom-bearing carbene complex, which ultimately transforms to a carbyne.

Several aspects of our observations can be related to the level of nucleophilicity and/or Brønsted basicity of the heteroatom substituent on the vinyl group (eq 14).



This is certainly true of the kinetics of anionic dissociation of the nucleophile, a reaction that is promoted/assisted by Os π electron density donated to the emerging carbyne carbon and the stability of the emerging free nucleophile (i.e., better PhO^- than EtO^-). For the case of ethoxide, this anion is sufficiently Brønsted basic that it can deprotonate the Brønsted acidic carbyne methyl group to give the (initially unexpected) vinylidene ligand.

The identity of the nucleophile will also influence the thermodynamics of the carbene–to–carbyne rearrangement. In general, we have established that Os (versus Ru) “prefers” the saturated (carbyne) redox isomer. This has been described as having the benefit of the larger number of metal/ligand bonds (versus intraligand bonds), eq 15.



Equilibrium 15 (no stereochemistry implied) should be viewed as two (quasi) unsaturated centers, Os and carbon, in competition for a single nucleophile. Alternatively, this is a question of whether the Nu^- in eq 14 will attack Os or carbyne C. For less nucleophilic Nu, the more electrophilic (metal) center is the preferred site for Nu since only that electrophile can adequately elicit donation from Nu. Phenoxide, originally chosen in this study as a leaving group from carbon, thus migrates efficiently to Os.

Carbene Rotational Conformation. It might have been expected that the preferred rotational conformation around the $\text{M}=\text{C}(\text{OR})\text{R}'$ bond would be the same for $\text{M} = \text{Ru}$ and $\text{M} = \text{Os}$. In fact, it is not. Various conformers around the $\text{M}=\text{C}$ (and $\text{C}-\text{OMe}$) bonds were found computationally, but no strong conformational preference exists. In fact, these complexes exhibit a strong coupling between the $\text{Ru}=\text{C}$ and the $\text{C}-\text{OMe}$ conformation (19M–21M). The difference between the various conformers is less than 5 kcal/mol for both Os and Ru, using the PH_3 model. Because no strong electronic preference is found, no electronic difference can be deduced for Os versus Ru (back-donating ability, for example). The significant coupling between the $\text{Ru}=\text{C}$ and the $\text{C}-\text{OMe}$ conformation also implies subtle steric and electronic effects. This behavior is noticeably different from that of the $\text{C}(\text{H})(\text{Me})$ carbene, which exhibits only one rotational conformer. The difference is due to the strong π donation of the OMe ligand to the carbene carbon, which allows less back-donation from the metal center. In addition, the conformers are calculated to be so similar in energy in part because the $\text{M}(\text{H})(\text{Cl})$ (carbene carbon) plane adopts a shape (either Y-shaped or T-shaped) that allows for best back-donation

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for a given conformation; in this way, a major loss of back-donation is avoided in the less-preferred conformer.

Experimental Section

General Procedure. All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox. Solvents were dried, degassed, or distilled under argon from Na, Na/benzophenone, P₂O₅, CaH₂, and/or 4 Å molecular sieves and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in a glovebox. Complexes OsH₃ClL₂ (L = P^tBu₂Me, P^rPr₃) were synthesized according to published procedures.^{12,17} Traces of [Et₃NH]Cl which are retained as an impurity in OsH₃ClL₂ will rapidly transform OsHCl(OPh)(CMe)₂ to OsHCl₂(CMe)₂, so careful purification of the trihydride reagents is important. Commercially available vinyl ethers were used as received after drying and degassing, when applicable. Chemical shifts are referenced to residual protio solvent peaks (¹H), external H₃PO₄ (³¹P), external CFC₃ (¹⁹F), or natural abundance ¹³C peaks of the solvent (¹³C). NMR spectra were obtained on a Varian Gemini 2000 (300 MHz ¹H, 121.4 MHz ³¹P, 75 MHz ¹³C, 282 MHz ¹⁹F), a Varian Unity Inova instrument (400 MHz ¹H, 162 MHz ³¹P), or a Bruker AM spectrometer (500 MHz ¹H, 125.6 MHz ¹³C). All T₁ measurements were made at 300 MHz. The NOE experiment was performed at 400 MHz.

Reaction of OsH₃Cl(P^rPr₃)₂ with 4-(Dimethylamino)pyridine. In an NMR tube, OsH₃Cl(P^rPr₃)₂ (0.0100 g, 0.018 mmol) was dissolved in 0.8 mL of benzene-*d*₆, and 4-(dimethylamino)pyridine (0.0022 g, 0.018 mmol) was added to the solution. The color change is immediate from brown to pale yellow, and the reaction is complete within 5 min. The volatiles were removed under vacuo, and the residue was redissolved in benzene-*d*₆. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -12.8 (t, J_(HP) = 12.5 Hz, Os-H), 1.18 (dvt, N = 12.3 Hz, Os-P(CH(CH₃)₂)₃), 1.36 (dvt, N = 12.9 Hz, Os-P(CH(CH₃)₂)₃), 2.05 (s, Os-(NC₅H₄-(N(CH₃)₂))), 2.22 (m, Os-P(CH(CH₃)₂)₃), 5.83, 9.45 (m, Os-(NC₅H₄-(N(CH₃)₂))). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 20 °C): 25.7.

Synthesis of OsHCl(C₂H₄)(P^tBu₂Me)₂. The complex OsH₃Cl(P^tBu₂Me)₂ (0.15 g, 0.23 mmol) was dissolved in 20 mL of toluene, giving a brown solution. The solution was frozen, and the upper space was evacuated for 15 min and replaced by ethylene (1 atm). The system was allowed to react for 17 h at room temperature (20 °C), and the volatiles were removed under reduced pressure to dryness. A maroon-brownish colored solid is obtained. ¹H NMR (300 MHz, C₇D₈, 20 °C): δ -35.4 (t, J_(HP) = 11 Hz), 0.6 (s, P^tBu₂Me), 1.2 (vt, N = 12.9 Hz, P^tBu₂Me), 1.3 (vt, N = 12.9 Hz, P^tBu₂Me), 2.7 (br, Os(C₂H₄)). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, 20 °C): 12.3. ¹³C{¹H} NMR (75.4 MHz, C₇D₈, 20 °C): -5.0 (vt, J_(CP) = 10.5 Hz, P^tBu₂CH₃), 29.0 (s, P(C(CH₃)₃)₂Me), 30.6 (vt, J_(CP) = 2.4 Hz, P(C(CH₃)₃)₂Me), 35.8 (vt, J_(CP) = 11 Hz, P(C(CH₃)₃)₂Me), 40.1 (vt, J_(CP) = 10 Hz, P(C(CH₃)₃)₂Me), 23.9 (br, Os(C₂H₄)). ¹H NMR (300 MHz, C₇D₈, -80 °C): δ 2.5, 3.15 (br, Os(C₂H₄)). ¹³C{¹H} NMR (75.4 MHz, C₇D₈, -80 °C): 23.0, 25.5 (br, Os(C₂H₄)).

Reaction of OsH₃Cl(P^tBu₂Me)₂ and Ethylene. In an NMR tube, OsH₃Cl(P^tBu₂Me)₂ (0.010 g, 0.018 mmol) was dissolved in 0.5 mL of toluene-*d*₈. The solution was frozen, and the upper space was evacuated and replaced with ethylene (750 mm Hg, 0.09 mmol). The reaction was followed by ¹H and ³¹P{¹H} NMR. After 10 min, the main product is the "adduct" OsH₃Cl(η²-C₂H₄)(P^tBu₂Me)₂. Only diagnostic data are provided. ¹H NMR (300 MHz, C₇D₈, 20 °C): δ -14.63 (t, J_(HP) = 13 Hz, Os-H, 2H), -4.10 (t, J_(HP) = 21 Hz, Os-H, 1H), 2.78, 3.26 (s br, Os-(C₂H₄), 4H). ¹H NMR (300 MHz, C₇D₈, -70 °C): δ -14.6 (t, J_(HP) = 12 Hz, Os-H, 2H, T₁ 77 ms).

OsHCl(C₂H₄)(P^tBu₂Me)₂ with D₂. In an NMR tube, OsHCl(C₂H₄)(P^tBu₂Me)₂ (0.0130 g, 0.026 mmol) was dissolved in 0.8 mL of toluene. The solution was frozen to -78 °C, and the upper space was evacuated and replaced with excess D₂ (700 mm Hg). The solution was allowed to melt, and the NMR tube was shaken for 10 s to ensure proper contact between reagents. The NMR tube was placed in a precooled probe at -60 °C. The solution was monitored by ²D NMR every 20 °C while warming up to +20 °C.

OsHCl(C₂H₄)(P^tBu₂Me)₂ with H₂. In an NMR tube, OsHCl(C₂H₄)(P^tBu₂Me)₂ (0.0100 g, 0.0174 mmol) was dissolved in 0.5 mL

toluene-*d*₈. The solution was frozen, and the upper space was evacuated and replaced with excess H₂ (700 mm Hg). After 2 h, the main product is OsH₃Cl(P^tBu₂Me)₂.²¹ Upon vacuum removal of the volatiles, OsH₃Cl(P^tBu₂Me)₂¹² is recovered.

CH₂=CH(OC₆H₅)-Phenyl Vinyl Ether. Phenyl vinyl ether was prepared as detailed from the original procedure.²¹ 50.0 g (320 mmol) of β-chlorophenetole was placed in a 300 mL flask over 50.0 g (890 mmol) of powdered KOH. The slurry was refluxed overnight and then filtered. The filtrate showed approximately 50% conversion to the title compound by ¹H NMR and was obtained in 95% purity (≈10 g, 26%) by vacuum distillation, collecting the fraction boiling 55–58 °C (20 Torr). Stirring over Na and vacuum transfer (heat assisted) removed any halogen or hydroxyl impurities. ¹H NMR (25 °C, 500 MHz, C₆D₆): δ 4.18 (d, ³J_{H-H} = 6 Hz, 1H, CH₂=CH(OPh)), 4.74 (d, ³J_{H-H} = 14 Hz, 1H, CH₂=CH(Ph)), 6.37 (dd, ³J_{H-H} = 14 Hz, ³J_{H-H} = 6 Hz, 1H, CH₂=CH(OPh)), 6.82 (t, ³J_{H-H} = 8 Hz, 1H, *o*-C₆H₅), 6.85 (d, ³J_{H-H} = 8 Hz, 2H, *o*-C₆H₅), 7.00 (apparent t, ³J_{H-H} = 8 Hz, 2H, *o*-C₆H₅).

Synthesis of OsHCl(=C(OPh)(CH₃))(P^tBu₂Me)₂. In an NMR tube, OsH₃Cl(P^tBu₂Me)₂ (0.0100 g, 0.018 mmol) was dissolved in 0.5 mL of benzene-*d*₆, and vinyl phenoxide (4.37 μL, 0.036 mmol) was added to the solution. After 2 h at room temperature, the volatiles were removed under vacuum. The solid residue consists of two carbene rotational isomers in a 1:2 intensity ratio. The major isomer will be noted as isomer A, and the minor isomer will be noted as B. Only diagnostic data are provided. ¹H NMR (300 MHz, C₇D₈, -80 °C): δ -30.3 (t, J_(H-P) = 13 Hz, Os-H, A), -33.2 (t, J_(H-P) = 12 Hz, Os-H, B), 2.35 (s, Os=C(OPh)(CH₃), A), 2.87 (s, Os=C(OPh)(CH₃), B). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, -80 °C): 11.8, 19.2 (AB pattern, J_(A-B) = 307.6 Hz, A), 9.1, 11.1 (AB pattern, J_(A-B) = 307.2 Hz, B). ¹H NMR (300 MHz, C₇D₈, 25 °C): δ -29.9 (br, Os-H, A), -33.1 (br, Os-H, B), 2.35 (s, Os=C(OPh)(CH₃), A), 2.87 (s, Os=C(OPh)(CH₃), B). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, 25 °C): 10.7, 13.2, 18.3, 20.9 (br, center lines of the two AB pattern, A + B overlapped). ¹³C{¹H} NMR (125.6 MHz, C₆D₆, 25 °C): 4.3 (vt, N = 28 Hz, Os-P(CH₃)(C(CH₃)₃)₂), A + B), 29.4 (s, Os-P(CH₃)(C(CH₃)₃)₂), B), 29.8 (s, Os-P(CH₃)(C(CH₃)₃)₂), A + B), 30.2 (s, Os-P(CH₃)(C(CH₃)₃)₂), A), 36.8 (vt, N = 23 Hz, Os-P(CH₃)(C(CH₃)₃)₂), A), 37.3 (vt, N = 22 Hz, Os-P(CH₃)(C(CH₃)₃)₂), B), 63.0 (s, Os=C(OPh)(CH₃), A + B), 94.9, 108.9, 121.2, 122.7, 157.3, 159.9 (s, Os=C(OPh)(CH₃), B), 114.7, 117.4, 120.7, 123.2, 142.3, 148.5 (s, Os=C(OPh)(CH₃), A), 254.3 (t, J_(C-P) = 5.1 Hz, Os=C, A + B).

Reaction of OsH₃Cl(P^tBu₂Me)₂ and Vinyl Phenoxide at Low Temperatures. A solution of vinyl phenoxide (4.37 μL, 0.036 mmol) in toluene-*d*₈ was vacuum transferred into an NMR tube containing OsH₃Cl(P^tBu₂Me)₂ (0.0100 g, 0.018 mmol) and stored in liquid N₂. The solution was allowed to melt and shaken for 5 s prior to being immediately placed in a precooled probe at -80 °C. The peaks due to phosphine protons were broad and unresolved. Only diagnostic data for the olefin adduct are provided. ¹H NMR (300 MHz, C₇D₈, -80 °C): δ -14.02 (br, Os-H, 2H, T₁ 57 ms at -70 °C), -3.69 (dd, J_(H-P) = 18 Hz, J_(H-P) = 28 Hz, Os-H, 1H), 5.84 (br, Os-(H₂C=CH(OPh))), 3.0, 2.7 (br, Os-(H₂C=CH(OPh))). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, -80 °C): 20.6, 15.3 (AB pattern, J_(A-B) = 167 Hz).

Reaction of OsH₃Cl(P^rPr₃)₂ and Vinyl Phenoxide. In an NMR tube, the complex OsH₃Cl(P^rPr₃)₂ (0.010 g, 0.018 mmol) was dissolved in 0.8 mL of benzene-*d*₆, and vinyl phenoxide (4.37 μL, 0.036 mmol) was added to the solution. The reaction was followed by ¹H and ³¹P{¹H} NMR. After 10 min, carbene is the main product, along with some adduct. Only diagnostic data for the carbene are provided. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -26.0 (br, Os-H), 2.9 (m, Os=C(CH₃)(OPh)). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 20 °C): 16.6, 24.2 (δ_A and δ_B of an AB pattern, J_(P-P) = 291 Hz).

Reaction of OsH₃Cl(P^rPr₃)₂ and Vinyl Phenoxide at Low Temperatures. The procedure is analogous to the one described above using OsH₃Cl(P^rPr₃)₂ (0.0100 g, 0.018 mmol). Only diagnostic data are provided. ¹H NMR (300 MHz, C₇D₈, -80 °C): δ -14.03 (br, Os-H, 2H, T_{1(min)} 45 ms at -60 °C), -4.18 (t, J_(H-P) = 22 Hz, Os-H, 1H),

5.91(br, Os-(H₂C=CH(OPh))), 2.6, 2.1 (br, Os-(H₂C=CH(OPh))). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, -80 °C): 16.2.

Synthesis of OsHCl(OPh)(CCH₃)(P^tPr₃)₂. In an NMR tube, the complex OsH₃Cl(P^tPr₃)₂ (0.010 g, 0.018 mmol) was dissolved in 0.8 mL of benzene-*d*₆, and vinyl phenoxide (4.37 μL, 0.036 mmol) was added to the solution. The reaction was allowed to proceed for 5 h, and the volatiles were removed in vacuo. The residue was washed with benzene-*d*₆ (0.8 mL), and a brown solid was obtained. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -7.18 (t, *J*_(H-P) = 15 Hz, Os-H), 0.63 (t, *J*_(H-P) = 2.4 Hz, Os=C-CH₃), 1.03 (dvt, N = 13.0 Hz, Os-P(CH(CH₃)₂)), 1.28 (dvt, N = 15.0 Hz, Os-P(CH(CH₃)₂)), 2.38 (m, Os-P(CH(CH₃)₂)), 6.67 (t, *J*_(H-H) = 7.2 Hz, Os-O-Ph, H_{para}, 1H), 7.00 (d, *J*_(H-H) = 7.2 Hz, Os-O-Ph, H_{ortho}, 2H), 7.28 (t, *J*_(H-H) = 7.2 Hz, Os-O-Ph, H_{meta}, 2H). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 20 °C): 31.2. ¹³C{¹H} NMR (125.6 MHz, C₆D₆, 25 °C): 19.2 (s, Os-P(CH(CH₃)₂)), 21.0 (s, Os-P(CH(CH₃)₂)), 23.2 (vt, N = 30 Hz, Os-P(CH(CH₃)₂)), 40.4 (s, Os≡C-CH₃), 114.7, 120.9, 129.0, 165.4 (s, Os-O-C₆H₅), 269.7 (t, *J*_(C-P) = 13 Hz, Os≡C).

Kinetic Studies. (A) General. Rates were determined by disappearance of the hydride ¹H NMR signal of the hydride carbene complex. Reactions were followed over approximately four half-lives. Representative kinetic data are included in Supporting Information.

(B) Kinetic Studies with 5 or 10 Equivalents of 1,8-Bisdimethylaminonaphthalene (Proton Sponge). The procedure was analogous to the routine reaction between OsH₃Cl(P^tPr₃)₂ and vinyl phenoxide. Approximately 10 min after the two reagents were mixed, at which point the main product of the reaction is observed by ¹H NMR to be the carbene, proton sponge (0.0195 g, 0.09 mmol) was added to the solution, and the reaction was followed at 25 °C every 30 min to a total of four half-lives. The procedure was repeated, but 0.039 g (0.18 mmol) proton sponge was added.

(C) Kinetic Studies with Added Triisopropylphosphine. The procedure was analogous to that described above. In this case, triisopropylphosphine (2.9 μL, 0.018 mmol) was added 10 min after the two reagents were mixed. The reaction was followed at 25 °C every 30 min to a total of four half-lives.

(D) Reaction of OsH₃Cl(P^tPr₃)₂ and Vinyl Phenoxide in the Presence of Free P^tBu₂Me. The procedure was analogous to that described above. In this case, di(*tert*-butyl)methylphosphine (5.82 μL, 0.036 mmol) was added to a toluene-*d*₈ solution of the reagents 20 min after the two reagents were mixed. The reaction was followed for 5 h at 25 °C and showed NMR peaks attributable to about 5% of OsHCl(OPh)(CCH₃)(P^tPr₃)(P^tBu₂Me), in addition to OsHCl(OPh)(CCH₃)(P^tPr₃)₂ as the major product. The ¹H NMR spectrum showed a slightly broadened triplet (dd) at -6.92 ppm, free P^tPr₃, and a ³¹P{¹H} NMR AB pattern with lines at 31.7, 29.8, 27.0, and 25.3 ppm. The amount of this mixed-phosphine carbene did not increase upon heating the solution at 70 °C for 4 h, indicating that this product is not formed from exchange of OsHCl(OPh)(CCH₃)(P^tPr₃)₂ with free P^tBu₂Me.

Synthesis of OsHCl[=C(CH₃)(OEt)](P^tBu₂Me)₂. In an NMR tube, the complex OsH₃Cl(P^tBu₂Me)₂ (0.0200 g, 0.0364 mmol) was dissolved in 2 mL of benzene-*d*₆, and ethyl vinyl ether (7 μL, 0.0728 mmol) was added to the solution. The reaction mixture was allowed to react at room temperature for 48 h (tumbling). The volatiles were removed under partial vacuum, and a dark-brown solid was obtained. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -28.1 (t, *J*_(HP) = 17.4 Hz, Os-H), 1.2 (vt, N = 3.6 Hz, P^tBu₂Me), 1.30 (vt, N = 12.4 Hz, P^tBu₂Me), 1.37 (vt, N = 12.6 Hz, P^tBu₂Me), 2.052 (s, Os=C(CH₃)(OEt)), 1.50 (t, *J*_(H-H) = 6.3 Hz, Os=C(CH₃)(OCH₂CH₃)), 4.09 (q, *J*_(H-H) = 7.0 Hz, Os=C(CH₃)(OCH₂CH₃)). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 20 °C): 36.9. ¹³C{¹H} NMR (75.4 MHz, C₆D₆, 20 °C): 11.1 (vt, N = 25.8 Hz, P^tBu₂CH₃), 29.7 (s, P(C(CH₃)₂)Me), 30.8 (s, P(C(CH₃)₂)Me), 35.6 (vt, N = 23.5 Hz, P(C(CH₃)₂)Me), 38.1 (vt, N = 17.4 Hz, P(C(CH₃)₂)Me), 14.2 (s, Os=C(CH₃)(OCH₂CH₃)), 49.6 (s, Os=C(CH₃)(OCH₂CH₃)), 67.3 (s, Os=C(CH₃)(OCH₂CH₃)), 243.9 (br, Os=C).

Reaction of OsH₃Cl(P^tPr₃)₂ and Ethyl Vinyl Ether. In an NMR tube, OsH₃Cl(P^tPr₃)₂ (0.010 g, 0.018 mmol) was dissolved in 0.5 mL of toluene-*d*₈, and ethyl vinyl ether (3.5 μL, 0.036 mmol) was added to the solution. The reaction was followed by ¹H and ³¹P{¹H} NMR. After 2.5 h, the olefin adduct is the major product, along with some carbene

and ether (hydrogenated olefin). Only diagnostic data for the olefin adduct are provided. ¹H NMR (300 MHz, C₇D₈, 20 °C): δ -19.29 (br, Os-H), 2.24 (m, Os-P(CH(CH₃)₂)₃). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, 20 °C): 59.1 (very br). ¹H NMR (300 MHz, C₇D₈, -70 °C): δ -14.47 (s, Os-H, 2H), -4.98 (t, *J*_(H-P) = 20 Hz, Os-H), 2.70, 2.86 (br, Os-(H₂C=CH(OEt))), 6.2 (br, Os-(H₂C=CH(OEt))). ³¹P{¹H} NMR (121.4 MHz, C₇D₈, -70 °C): 21.16, 19.18 (δ_A and δ_B of an AB pattern with *J*_(P-P) = 189.2 Hz).

After 7 h, the carbene is the major product, along with some olefin adduct and the final product, vinylidene OsHCl(=C=CH₂)(P^tPr₃)₂. Only diagnostic data for the carbene are provided. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -27.66 (t, *J*_(H-P) = 17 Hz, Os-H), 2.31 (s, Os=C(CH₃)(OEt)), 2.52 (m, Os-P(CH(CH₃)₂)₃), 4.25 (q, *J*_(H-H) = 7.2 Hz, Os=C(CH₃)(OCH₂CH₃)). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 20 °C): 43.3, 43.5 (two inner lines of an AB pattern).

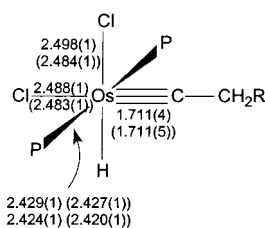
After 48 h, the reaction is complete. The solution consists of vinylidene and the byproduct OsHCl(CO)(P^tPr₃)₂.²² The volatiles are removed under vacuo, and the solid is washed with pentane (2 × 2 mL). ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -18.12 (t, *J*_(H-P) = 14 Hz, Os-H), 0.23 (t, *J*_(H-P) = 3 Hz, Os=C=CH₂), 1.23 (m, Os-P(CH(CH₃)₂)), 1.29 (m, Os-P(CH(CH₃)₂)), 2.84 (m, Os-P(CH(CH₃)₂)). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 20 °C): 38.2. ¹³C{¹H} NMR (125.6 MHz, C₆D₆, 25 °C): 19.7 (s, Os-P(CH(CH₃)₂)), 20.6 (s, Os-P(CH(CH₃)₂)), 25.4 (vt, N = 30 Hz, Os-P(CH(CH₃)₂)), 86.2 (s, Os=C=CH₂), 281.9 (br, Os=C).

Synthesis of OsHCl[=C(CH₂)₃O](P^tPr₃)₂. In an NMR tube, the complex OsH₃Cl(P^tPr₃)₂ (0.015 g, 0.027 mmol) was dissolved in 0.5 mL benzene-*d*₆, and 2,3-dihydrofuran (4.13 μL, 0.054 mmol) was added to the solution. The solution was allowed to react for 17 h, after which time the volatiles are removed under vacuum. The residue was washed with benzene-*d*₆ (2 × 0.8 mL). A brown-red solid was observed. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ -21.90 (t, *J*_(H-P) = 17.4 Hz, Os-H), 1.41 (dvt, *J*_(H-H) = 7.2 Hz, N = 12.8 Hz, Os-P(CH(CH₃)₂)), 1.44 (dvt, *J*_(H-H) = 7.2 Hz, N = 12.8 Hz, Os-P(CH(CH₃)₂)), 1.46 (m, Os=[C(CH₂-CH₂-CH₂-O)]), 1.99 (t, *J*_(H-H) = 7.5 Hz, Os=[C(CH₂-CH₂-O)]), 2.53 (m, Os-P(CH(CH₃)₂)), 3.46 (t, *J*_(H-H) = 7.5 Hz, Os=[C(CH₂-CH₂-O)]). ³¹P{¹H} NMR (162 MHz, C₆D₆, 20 °C): 44.9 (two lines separated by 0.098 ppm; AB pattern with outer lines undetected). ¹³C{¹H} NMR (125.6 MHz, C₆D₆, 25 °C): 20.1 (Os-P(CH(CH₃)₂)), 20.7 (Os-P(CH(CH₃)₂)), 24.8 (Os=[C(CH₂-CH₂-O)]), 25.7 (vt, N = 22.4 Hz, Os-P(CH(CH₃)₂)), 56.7 (Os=[C(CH₂-CH₂-O)]), 74.9 (Os=[C(CH₂-CH₂-O)]), 235.5 (br, Os=C).

Synthesis of OsHCl₂(CCH₃)(P^tPr₃)₂. (a) Under Ar, a suspension of OsH₂Cl₂(P^tPr₃)₂ (0.0750 g, 0.129 mmol) in toluene (15 mL) was treated with excess CH₂=CH(O^tBu) (0.386 mmol, 50.6 μL). The suspension was refluxed for 24 h under Ar, yielding a golden yellow solution. The solution was cooled to room temperature and filtered through Celite to produce a clear yellow solution. The solution was concentrated to 1–2 mL under reduced pressure, and excess pentane (40 mL) was added, precipitating a pale yellow solid. The solid was collected, washed with pentane (10 mL), and dried under reduced pressure. Yield: 0.0211 g (27%). ¹H NMR (300 MHz, CDCl₃): -7.49 (t, *J*(PH) = 16 Hz, 1 H, Os-H), 0.98 (br, 3H, OsCCH₃), 1.40 (dvt, N = 14.1, *J*(HH) = 7.2 Hz, 18 H, PCHCH₃), 1.45 (dvt, N = 13.8, *J*(HH) = 6.8 Hz, 18 H, PCHCH₃), 2.72 (m, 6H, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, C₆D₆): 21.92 (s, P^tPr₃).

(b) In a similar manner as that outlined in (a) above, a suspension of OsH₂Cl₂(P^tPr₃)₂ (0.050 g, 0.086 mmol) in toluene (10 mL) was treated with excess CH₂CH(OEt) (0.28 mmol, 25 μL) under Ar. The mixture was refluxed for 24 h, yielding a dark yellow solution. The solution was concentrated to about 1 mL under reduced pressure, and excess pentane (25 mL) was added, precipitating a pale yellow solid. The reaction flask was placed in an ice bath to complete the precipitation of the product. The solvent was decanted, and the pale yellow solid was dried under reduced pressure. Yield: 0.0193 g (39%). The spectroscopic data for the product of this reaction were the same as that for (a) above.

X-ray Structure Determination of OsHCl₂(CCH₃)(PⁱPr₃)₂. The crystal was affixed to a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to -158 °C using a gas-flow cooling system of local design. Standard inert atmosphere techniques were used during the handling and mounting process. The data were collected using 15 s frames with an ω scan of 0.30° on a Bruker CCD 6000. Data were corrected for Lorentz and polarization effects, and equivalent reflections were averaged using the Bruker SAINT software and utility programs from the XTEL library. An absorption correction was performed using the SADABS program supplied by Bruker AXS. A peak was located in the site where the hydride was expected, and it refined normally, Figure 5. The vast majority of bond lengths and angles for OsHCl₂(CCH₂R)(PⁱPr₃)₂ are identical within 2 σ for R = H and = Ph (see 29).



Bond lengths for R = Ph (R = H in parentheses)

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The most important feature is that both molecules show the chemically inequivalent Os-Cl distances to be, in fact, nearly identical, at 2.48 Å.

Computational Details. The calculations were carried out using the Gaussian 98²³ set of programs within the framework of DFT at the B3PW91 level.^{24,25} LANL2DZ effective core potentials (quasi-relativistic for the metal centers) were used to replace the 28 innermost electrons of Ru,²⁶ the 60 innermost electrons of Os,²⁶ and the 10 core

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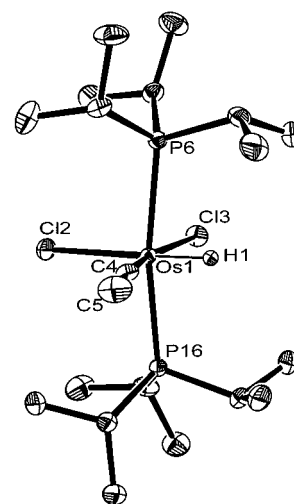


Figure 5. ORTEP drawing of OsHCl₂(CCH₃)(PⁱPr₃)₂, omitting H on carbon. Selected bond lengths: Os-Cl2 = 2.484(1) Å; Os-Cl3 = 2.481(1); Os-P6 = 2.428(1); Os-P16 = 2.419(1); Os-C4 = 1.711(4); Os-H1 = 1.35(5). Bond angles: Cl2-Os-Cl3 = 87.73(4)°; Cl2-Os-C4 = 103.57(15); Cl3-Os-C4 = 168.68(15); Os-C4-C5 = 174.5(4); Cl2-Os-H1 = 167.5(20); Cl3-Os-H1 = 79.8(20); P6-Os-P16 = 170.03(4).

electrons of Cl and P.²⁷ The associated double ζ basis set was used^{26,27} and augmented by a d polarization function for Cl and P.²⁸ The other atoms were represented by a 6-31 (d, p) basis set (5d).²⁹ Full geometry optimization was performed with no symmetry restriction, and the nature of the minima was assigned by analytical frequency calculations.

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Supporting Information Available: Kinetic plots and full crystallographic details for OsHCl₂(CCH₃)(PⁱPr₃)₂ and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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