Facile C(sp^2)/OR Bond Cleavage by Ru or Os

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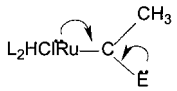
$Os(H)_3ClL_2$ (L = P^iPr_3 or P^tBu_2Me) are shown to be useful "precursors" to "$OsHClL_2$", which react with vinyl ethers to form first an η^2-olefin adduct and then isomerize to the carbenes, $OsHCl[CMe(OR)]L_2$. Subsequent R- and L-dependent reactions involve C(sp^2)−OR bond cleavage, to make either 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 $[RuHClL_2]_2$ (L = P^iPr_3) and a variety of olefins with donor substituents H_2C═CHE (E = OR, RNC(O)R′) are the carbene complexes L_2HClRu═C(E)CH_3. We have analyzed the thermodynamics of this reaction in terms of the carbene carbon being stabilized by *two* π-donor substituents, E and $RuHClL_2$ (**1**).[1,2]



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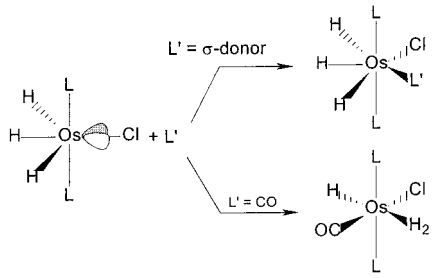
We are interested in studying the analogous chemistry for osmium, particularly since there is considerable accumulated evidence[2−5] that, in the same ligand environment, Os is considerably more π basic (i.e., reducing) than Ru. Since the necessary "$OsHClL_2$" reagent is unavailable for such a study, 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 $[RuHClL_2]_2$ employs dehydrohalogenation of $Ru(H)_2Cl_2L_2$. Attempts to dehydrohalogenate $Os(H)_2Cl_2L_2$ analogously in C_6D_6 at 25 °C with LiMe, $LiCH_2CMe_3$ (also in Et_2O-d_{10}), or Li 2,2,6,6-tetramethyl piperidide (LiTMP) were generally unsatisfactory, even under mild conditions; only mixtures of products were obtained.

Scheme 1



Synthetic Alternatives. We therefore turned to $Os(H)_3ClL_2$ as a possible "functional equivalent" of $OsHClL_2$, provided the equimolar H_2 could somehow be removed. In a general sense, we hoped to render the H_2 innocuous by carrying out reactions with *two* moles of olefin, thereby scavenging the H_2 into alkane (eq 1).

$$Os(H)_3ClL_2 + 2\ H_2C{=}CHE \xrightarrow{?} \text{product} + H_3C{-}CH_2E \quad (1)$$

The low-temperature ligand addition chemistry of $Os(H)_3ClL_2$ has already been reported[6] and is summarized in Scheme 1, where the LUMO of $Os(H)_3ClL_2$ is sketched. The σ donors L′ are THF, MeCN, MeOH, NH_3, and PEt_3. 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, H_2, trans to the potent trans effect hydride. Prior to studies with vinyl ethers, we studied the case of L′ = C_2H_4.

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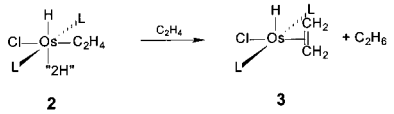
Reaction of $Os(H)_3ClL_2$ with Ethylene (L = P^tBu_2Me). These reagents react within 10 min in toluene to give an adduct. Especially remarkable is that this molecule shows *two* Os/H signals at 25 °C: −4.1 (triplet J_{HP} = 21 Hz, intensity 1) and −14.6 (t, J_{HP} = 13 Hz, intensity 2). The signals of coordinated C_2H_4 are broad, but that of free dissolved C_2H_4 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 η^2-H_2. 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 H_2. As the temperature is raised (eq 2), ethane is produced (^{1}H NMR evidence) and excess ethylene binds to give **3**.



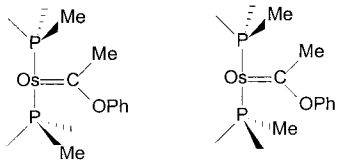
2 **3** (2)

Key spectroscopic features of **3** are two ^{t}Bu methyl chemical shifts (i.e., they are diastereotopic), virtual coupling for ^{t}Bu 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 ^{13}C 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 ^{13}C and ^{1}H 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 $OsHCl(CO)L_2$, where the double-faced π acid CO occupies the site of the single-faced olefin. It is also the structure observed for $RuHCl(olefin)L_2$. The olefin orientation minimizes steric repulsion with the bulky phosphines.

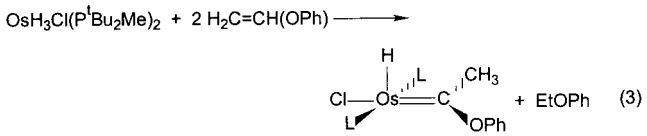
$OsHCl(C_2H_4)(P^tBu_2Me)_2$ adds H_2 at or below 25 °C to give the same 1:1 adduct **2** observed above; over a longer period of time (2 h), the reaction proceeds further to give $OsH_5Cl(P^tBu_2Me)_2$ and C_2H_6. If $OsHCl(C_2H_4)(P^tBu_2Me)_2$ is reacted with D_2 at −80 °C, D is detected in both negative 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 $Os(D)_3Cl(P^tBu_2Me)_2$.

Reaction of $Os(H)_3Cl(P^tBu_2Me)_2$ with H_2C═CH(OPh). (A) First Step. This reaction proceeds already at −80 °C in toluene-d_8 to give a 1:1 adduct, $OsH_3Cl[H_2C$═$CH(OPh)]L_2$. 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 $^{31}P\{^1H\}$ NMR spectrum shows an AB pattern with J_{AB} = 167 Hz. This value is smaller than the 250−350 Hz found when ∠P−M−P ≈ 180° and indicates that this angle is significantly bent in this adduct. Analogous to $OsH_3Cl(C_2H_4)$-L_2, the hydride region of $OsH_3Cl[H_2C$═$CH(OPh)]L_2$ shows a 1:2 ^{1}H 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 two hydrides with an H−Os−H angle ∼72° (i.e., planar pentagon) or a molecular H_2 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 $Os(H)_3Cl(P^tBu_2Me)_2$.

Scheme 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).



(3)

This carbene, $OsHCl[C(OPh)Me]L_2$, is the anticipated result of the $OsHClL_2$ 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 $^{31}P\{^1H\}$ 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 ^{31}P 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 $OsHCl[C(OPh)Me](P^tBu_2Me)_2$ is unusual, first because it is not true of $RuHCl[C(OR)Me](P^iPr_3)_2$ (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 ^{1}H and by ^{31}P NMR spectroscopies) at 25 °C; only at low temperatures are the two conformational isomers, **4a** and **4b**, decoalesced (eq 4, R = Et).

4a **4b** (4)

When $OsHCl[C(Me)OPh](P^tBu_2Me)_2$ was heated for 1 h at 80 °C in benzene, the carbene complex was totally consumed during this period, but the ^{1}H and ^{31}P NMR spectra show an

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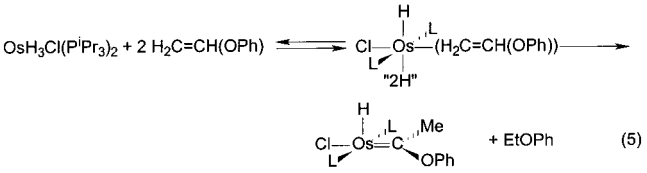
unappealing mixture of products, none of which is a carbyne complex (see below). The growth of free P^tBu_2Me is symptomatic of unselective decomposition.

The Effect of Changing the Phosphine: P^iPr_3. (A) First Step. $OsH_3Cl(P^iPr_3)_2$ reacts with phenyl vinyl ether (1:2 mole ratio) in toluene-d_8 at −78 °C to form the adduct $OsH_3Cl[H_2C{=}CH(OPh)](P^iPr_3)_2$. This shows three NMR peaks for coordinated vinyl hydrogen shifted upfield from free olefin values, and these integrate against ^{i}Pr hydrogens to show that one olefin is coordinated. The ^{i}Pr 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 $^{31}P\{^1H\}$ NMR singlet from −78 to −40 °C, and must be due to an AB spin system where $J_{AB} > \nu_A - \nu_B$. 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 $J_{HP} = 11$ Hz. At 0 °C, ^1H NMR signals of both free and coordinated phenyl vinyl ether broaden, as do the hydride peaks.

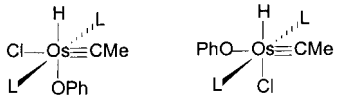
(B) Second Step. At 0 °C, ethyl phenyl ether and a new $^{31}P\{^1H\}$ NMR AB pattern are observed; the J_{AB} value, 291 Hz, indicates a trans stereochemistry. A new hydride resonance grows simultaneously (−26 ppm, broad), as does a methyl (on a carbene C) signal at 2.9 ppm (eq 5). Peaks due to $OsH_3Cl(P^iPr_3)_2$ also appear at 0 °C, showing an entropically controlled equilibrium shift.



(5)

(C) Third Step. C/O Cleavage Reaction. $OsHCl[C(OPh)Me](P^iPr_3)_2$ is a metastable species, in contrast to its (persistent) Ru analogue. Within 5 h of initiating the reaction of $Os(H)_3ClL_2$ and $H_2C{=}CH(OPh)$ at 25 °C, the carbene product has isomerized to form $OsHCl(OPh)(CMe)L_2$. 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, Os*CMe*; both in C_6D_6), which are very similar to the values found for $OsHCl_2(CMe)L_2$.[8]

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



5a **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 ^{i}Pr 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.

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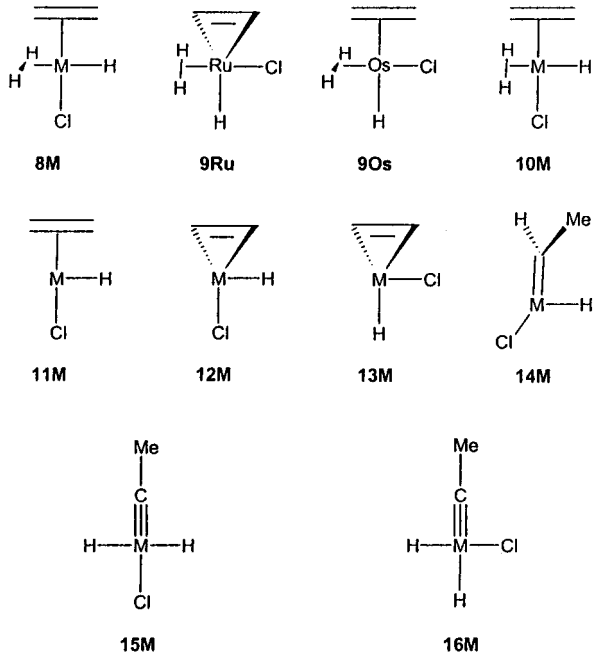
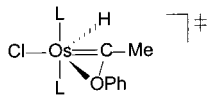


Figure 1. Schematic representation of the DFT (B3PW91) optimized structures for **8M**−**16M** (M = Os, Ru). For clarity, phosphines (PH_3) are not shown and are pointing toward and away from the plane displayed. All structures are minima except for **10Os**, which is a transition state for H_2 rotation.

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 $OsHCl[C(OPh)Me](P^iPr_3)_2$. We therefore considered several alternative mechanisms.



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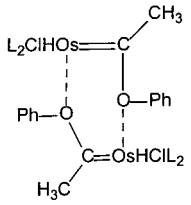
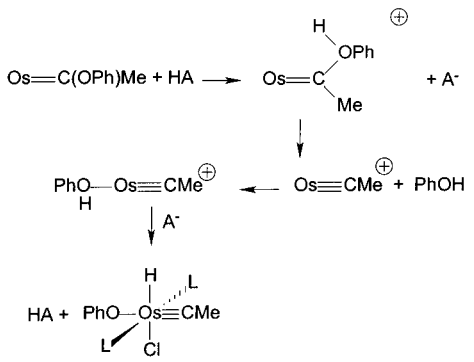


7

The rate of isomerization of $OsHCl[C(OPh)(Me)](P^iPr_3)_2$ 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 $[Et_3NH]Cl$ is sufficient to convert $OsHCl[C(OPh)Me]L_2$ to $OsHCl_2(CMe)L_2$, 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

Scheme 3

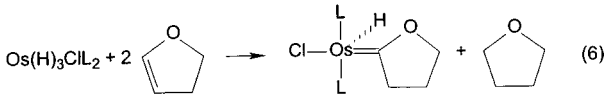


migration reaction by adding a scavenger for an acid catalyst. To test for an acid-catalyzed mechanism, the reaction rate was studied in the presence of added proton sponge (1,8-bisNMe$_2$-naphthalene), which was shown independently to not complex directly to reactant or product. Rates were again first-order 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 OsH$_3$Cl(P^{i}Pr$_3$)$_2$ and vinyl phenoxide was, therefore, carried out in the presence of 2 equiv of the isomeric phosphine, P^{t}Bu$_2$Me. 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 OsH$_3$Cl(η^2-H$_2$C=CH(OPh))(P^{i}Pr$_3$)$_2$ 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)(CCH$_3$)(P^{i}Pr$_3$)$_2$, 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^{t}Bu$_2$Me)(P^{i}Pr$_3$); 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 P^{i}Pr$_3$.

Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ + 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)$_3$ClL$_2$ (L = P^{i}Pr$_3$) reacts with two moles of this dihydrofuran at 25 °C in 22 h to produce THF (identified by ^{1}H NMR after vacuum transfer of the volatiles).

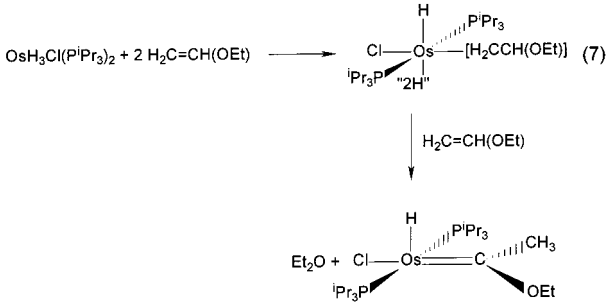


The major product remaining after vacuum transfer is the cyclic carbene complex. The product shows a hydride (triplet) chemical shift of −21.9 ppm and two diastereotopic P/CH$_3$ virtual triplets, indicating transoid phosphines. The ^{31}P{^{1}H} NMR spectrum is an AB pattern, indicating that the carbene plane eclipses in the P−Os−P direction. The ring CH$_2$ 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 ^{31}P NMR time scale, where an AB pattern is observed, but fast on the ^{1}H NMR time scale.

An Electron-Rich Ether Substituent: Reaction of OsH$_3$Cl(P^{t}Bu$_2$Me)$_2$ with Ethyl Vinyl Ether. Ethyl vinyl ether reacts to completion in benzene over 48 h at 25 °C with Os(H)$_3$Cl(P^{t}Bu$_2$Me) (2:1 mole ratio) to give OsHCl[CMe(OEt)](P^{t}Bu$_2$Me)$_2$. This reaction is thus distinctly slower than the analogous reaction with [RuHCl(P^{i}Pr$_3$)$_2$]$_2$.[2] The far upfield hydride chemical shift (−28 ppm) is consistent with a square-pyramidal structure with hydride trans to the empty site. The ^{t}Bu groups show diastereotopic inequivalences by ^{1}H NMR. The ^{31}P{^{1}H} NMR spectrum of the carbene complex is a singlet. Steady growth of Et$_2$O is observed (^{1}H NMR) during the reaction, thus establishing this as the fate of two of the three reagent hydride ligands. No intermediates are detected by ^{1}H or ^{31}P NMR spectroscopy at 25 °C during the reaction, although the hydride signal of OsH$_3$Cl(P^{t}Bu$_2$Me)$_2$ 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.

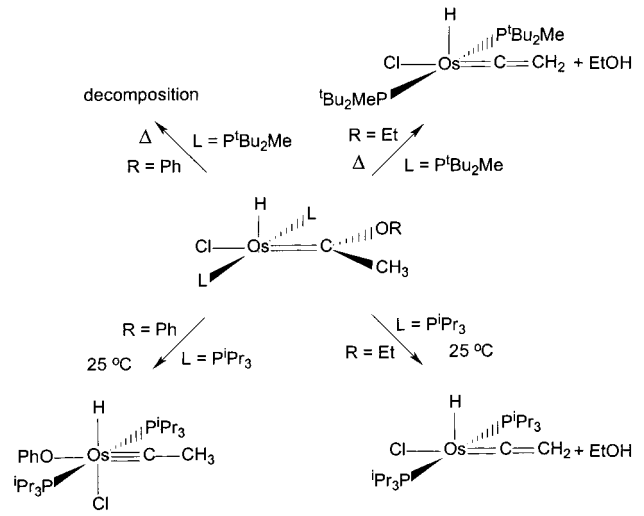
When OsHCl[C(Me)OEt](P^{t}Bu$_2$Me)$_2$ is heated at 80 °C for 1.5 h in benzene, the carbene intensity declines, with formation of approximately equimolar amounts of the two known compounds, OsHCl(CCH$_2$)(P^{t}Bu$_2$Me)$_2$ and OsHCl(CO)(P^{t}Bu$_2$Me)$_2$. Further heating of this benzene solution causes further progress of this same conversion.

Reaction of OsH$_3$Cl(P^{i}Pr$_3$)$_2$ with Ethyl Vinyl Ether. (A) Initial Stages. This reaction proceeds through the intermediate η^2-olefin adduct analogous to the phenyl analogue, although at a slower rate of conversion of adduct to carbene, as shown in eq 7.



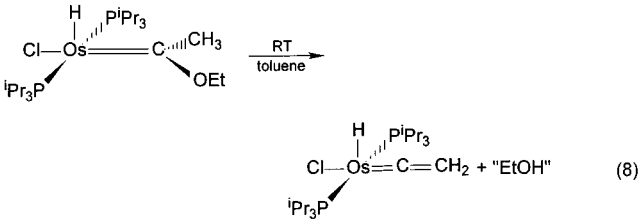
After 3 h at 25 °C, the η^2-olefin adduct and the carbene (and Et$_2$O) are present. All observed resonances are consistent with analogues reported earlier here. In particular, the ^{31}P{^{1}H} NMR spectrum is an AB pattern at 25 °C, which is consistent with the carbene plane alignment illustrated and with the OPh analogue. The expected diastereotopic inequivalence of the OCH$_2$ proton is not observed at 25 °C, indicating either

Scheme 4



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

(B) Subsequent Reaction. This carbene is metastable, and the following reaction is C(sp^2)/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^{t}Bu$_2$Me analogue is known.[9]



(8)

No hydride carbyne OsHCl(OEt)(CCH$_3$)(P^{i}Pr$_3$)$_2$ is observed by ^{1}H or ^{13}C{^{1}H} NMR spectra. Such elimination contrasts to the more typical addition[10] of the RO−H bond across a vinylidene C=C bond. Vacuum transfer of the reaction volatiles shows unreacted olefin and Et$_2$O (from the initial reaction of OsH$_3$ClL$_2$ with EtOCHCH$_2$), but no EtOH. Since a secondary product in this reaction (40% yield) is OsHCl(CO)L$_2$, we presume that decarbonylation of liberated ethanol to CO, CH$_4$, and H$_2$ occurs, and CO is trapped to give OsHCl(CO)L$_2$, 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^{t}Bu$_2$Me do react, but more slowly than the P^{i}Pr$_3$ analogues. For P^{t}Bu$_2$Me, 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 P^{i}Pr$_3$ analogue. Although the NMR evidence of hindered phosphine rotation indicates that the P^{t}Bu$_2$Me analogues are more crowded than those of P^{i}Pr$_3$, 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^{t}Bu$_2$Me examples is consistent with the associative step involved in acid catalysis. These rate differences do not alter the general conclusion that OsHCl[CMe(OR)]L$_2$ species are only metastable toward further reaction.

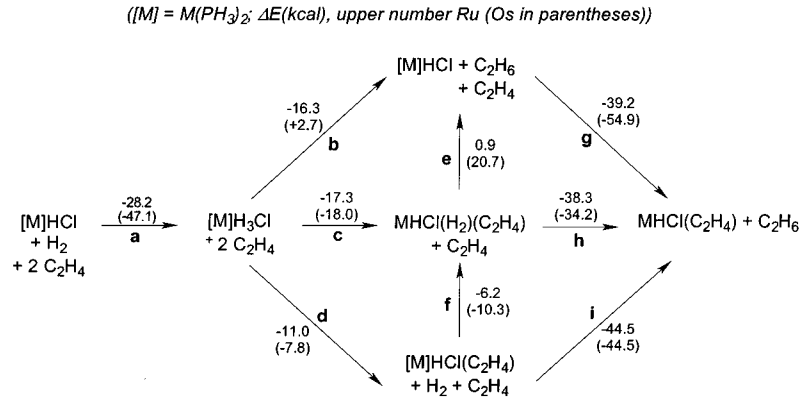
Computational Studies. Scheme 5 (energies in kcal mol^{-1} for the most stable isomer of each species, without ZPE correction) provides a convenient summary of a variety of calculated energy differences for both Ru and Os. The calculations show that RuH$_3$ClL$_2$ and OsH$_3$ClL$_2$ have, respectively, a dihydrogen Ru(H)(H$_2$)ClL$_2$ and an osmium trihydride structure; these results are in agreement with previous experimental and theoretical studies.[11,12] Removing H$_2$ 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.

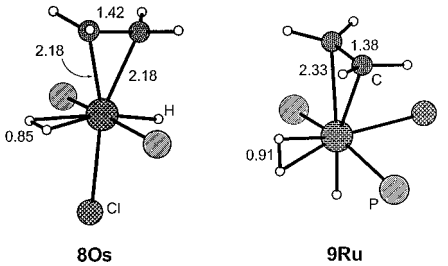
The Ethylene Reaction Products. (A) The Ethylene Adducts. All structures are schematically represented in Figure 1. Only selected structures will be shown accurately in Figure 2. For clarity, both such drawings have identical labels. Coordination of C$_2$H$_4$ to the unsaturated 16-electron complex MH$_3$(Cl)L$_2$ (M=Ru, Os, L=PH$_3$) yields, in both cases, a dihydrogen complex. Structures with C$_2$H$_4$ 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. H$_2$ 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. C$_2$H$_4$ is found to be coplanar with the M−H bonds in **8M**. In **9M**, the orientation preference for H$_2$ 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 H$_2$ is trans to chloride (**9Os**), with a much shorter M−H bond length (1.69 (**9Ru**); 1.63 (**9Os**)). Whatever the binding and H$_2$ orientation, the P−M−P angle is significantly bent: 168.2−155.0°. This increases back-donation to the H$_2$ 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 complexes[13] 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 H$_2$ 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 H$_2$ adduct complexes (H$_2$ trans to H), a noteworthy result which underlines the small degree to which the bound H$_2$ perturbs the MHCl(C$_2$H$_4$)(PH$_3$)$_2$ 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)L$_2$ (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





8Os **9Ru**

Figure 2. Selected structural parameters for the most stable DFT (B3PW91) optimized structure for $MHCl(H_2)(C_2H_4)(PH_3)_2$. M = Os (left), Ru (right). Distances are in Å. For clarity, H of PH_3 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/H_2 complexes, loss of either H_2 or of ethylene is energetically facile. In the case of Ru, the BDE of H_2 (Scheme 5, eq **f**) is 6.2 kcal mol^{-1} and that of C_2H_4 (eq **c**) is 17.2 kcal mol^{-1}. For Os, the corresponding values are 10.3 (H_2) and 18.0 (C_2H_4). As expected, dihydrogen is the less strongly bonded ligand (e.g., Scheme 5, eq **d**). The BDE of H_2 to Ru is small enough to suggest that an H_2/ethylene complex should not be thermally stable. In the case of Os, reversible binding could be observed for H_2, although the two acceptor ligands are more equally bonded. To determine the role of ΔS, calculations of ΔG at 298 °C were carried out. They show that H_2 is calculated to be almost nonbonded for Os ($\Delta G = -1.2$ kcal mol^{-1}), whereas the corresponding value for ethylene is 2.6 kcal mol^{-1}. This accounts for the thermal loss of H_2 from $OsH(H_2)(Cl)(C_2H_4)L_2$.

(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 ΔE of hydrogenation of ethylene itself (Scheme 5, eq **i**), −44.5 kcal mol^{-1}, makes the dehydrogenation of $MH_3Cl(PH_3)_2$ 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 H_2 in six-coordinated $MHCl(H_2)(C_2H_4)(PH_3)_2$, to give 14 electron $MHCl(PH_3)_2$, is quite unfavorable for Os. Thus, without that second olefin (i.e., for the 1:1:1 reaction of $MHCl(PH_3)_2/H_2/C_2H_4$), the global minimum is $MHCl(H_2)(C_2H_4)(PH_3)_2$.

(C) The Isomeric $MHCl(CHMe)(PH_3)_2$ and $MH_2Cl(CMe)(PH_3)_2$ Complexes. The 16 electron carbene MHCl(CHMe)$(PH_3)_2$ (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 $OsHCl(C_2H_4)L_2$ 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 d^6 ML_5 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 OsH_3XL_2 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 $MHCl(PH_3)_2$ (**17M** and **18M**). The case where H_2 also coordinated was not studied.

Optimization of the $MHCl(PH_3)_2$ (CH_2=CH(OMe)) gives results similar, for geometry and BDE, to that for C_2H_4. 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.

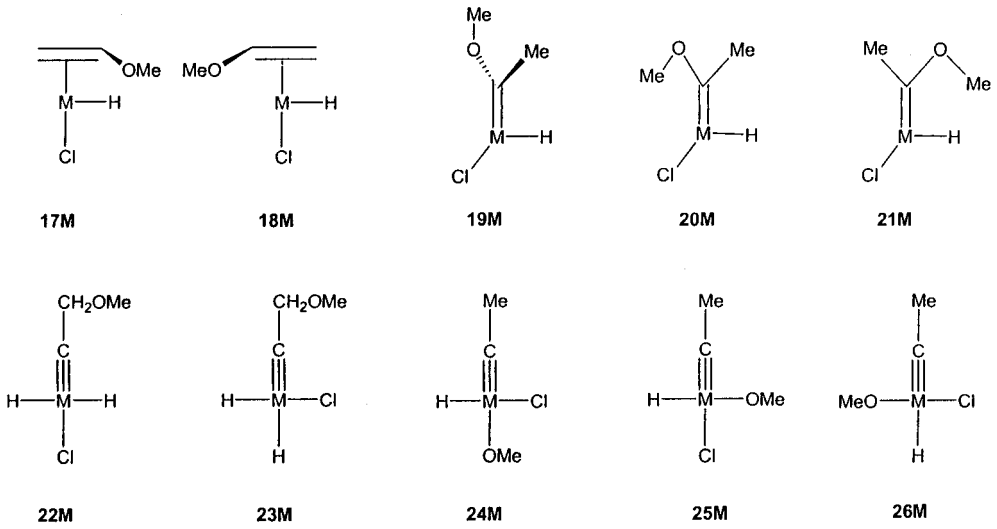


Figure 3. Schematic representation of the DFT (B3PW91) optimized structures for **17M**−**26M** (M = Os, Ru). For clarity, phosphines (PH_3) are not shown and are pointing toward and away from the plane shown. All structures are minima.

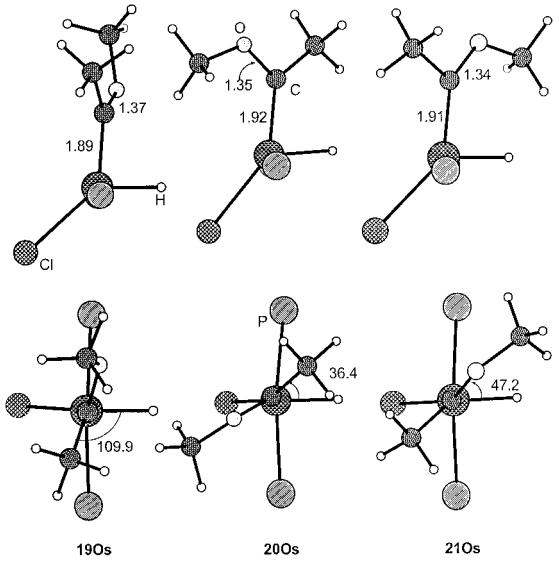


Figure 4. Selected structural parameters for all DFT (B3PW91) optimized conformers for $OsHCl(CMe(OMe))(PH_3)_2$, **19Os**−**21Os**. Structures are given viewed along the P−P direction (top) and along the C═Os bond (bottom). Distances are in Å and angles in degrees. For clarity, H of PH_3 have been omitted.

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═[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 $CH(CH_3)$, 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 $OsHCl(PH_3)_2$ was more efficient than its Ru equivalent in diminishing the difference in energy between the C_2H_4 and CH(Me) isomers, this is not the case for CH_2═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 Os═C bond of the carbene group in $OsHCl(CMe(OMe))(PH_3)_2$ 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 Os≡CCH_2OMe 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 carbyne 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 carbyne (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 carbyne) 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, PH_3 was next replaced by PMe_3. The endothermicity is also notably diminished, and the preferred carbyne is only 7.3 kcal mol^{-1} above the carbene complex (i.e., PMe_3 alone on the OMe species stabilizes the carbyne by 17.1−7.3 = 9.8 kcal mol^{-1} versus PH_3). Combining the energy increments caused individually by the two substituents PMe_3 (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).

$$\mathrm{MeOH} + \mathrm{C(Me)(OPh)} \rightarrow \mathrm{PhOH} + \mathrm{C(Me)(OMe)} \qquad \Delta E = -14.5\ \mathrm{Kcal\ mol^{-1}} \quad (9)$$

$$\mathrm{CH_3CH_2(OMe)} + \mathrm{C(Me)(OPh)} \rightarrow \mathrm{CH_3CH_2(OPh)} + \mathrm{C(Me)(OMe)} \qquad \Delta E = -10.4\ \mathrm{Kcal\ mol^{-1}} \quad (10)$$

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.

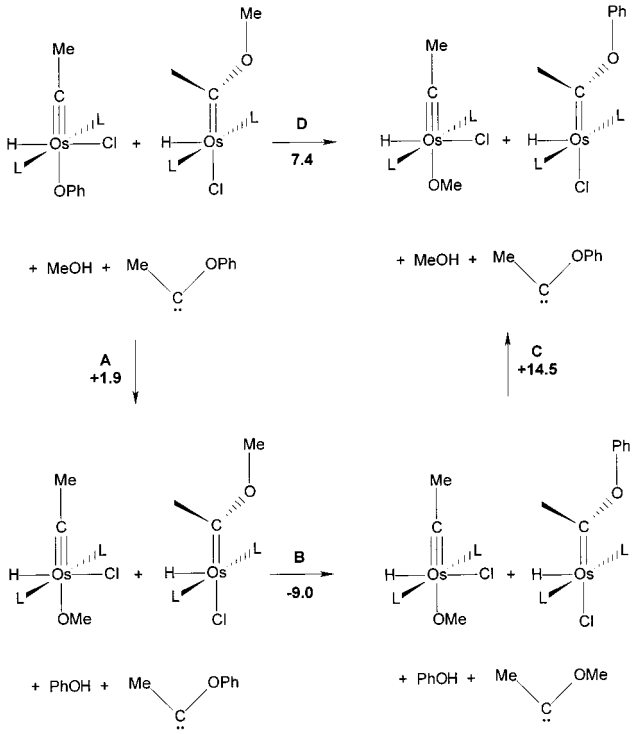
The differential effect of the metal fragment ([Os] = Os-$(PH_3)_2$) on the relative stability of the two carbenes (cf. eqs 9 or 10) is to diminish the exothermicity of the transformation of eq 11,

$$\mathrm{[Os](OMe)HCl(CMe)} + \mathrm{[Os]HCl[CMe(OPh)]} \rightarrow \mathrm{[Os](OPh)HCl(CMe)} + \mathrm{[Os]HCl[CMe(OMe)]} \qquad \Delta E = -7.4\ \mathrm{Kcal\ mol^{-1}} \quad (11)$$

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 carbyne 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=CH_2)$(PH_3)_2$ and RuHCl(=C=CH_2)$(PH_3)_2$ are essentially identical and have been previously discussed.[9,17] The energy difference for the transformation shown in eq 12

$$\mathrm{[M]HCl[(=C(Me)(OR)]} \rightarrow \mathrm{ROH} + \mathrm{[M]HCl(=C=CH_2)} \quad (12)$$

(where [M]= M$(PH_3)_2$) 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 PH_3 (23.6 kcal mol^{-1}) by PMe_3 (15.7 kcal mol^{-1}). Assuming similar entropy effects for the two phosphine ligands indicate that eq 12 is thermodynamically feasible.

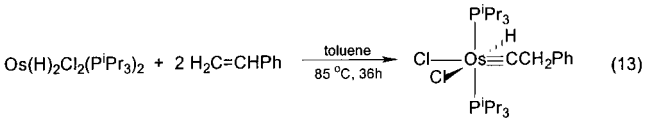
Experimental Evidence for HCl as a Participant in Related Reactions. We reported earlier[18] the following reactivity (eq 13), which differs from the present work in using (1) a

(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.



(13)

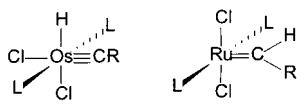
The analogous reaction occurs for the Ru analogue in CD_2Cl_2, giving $RuCl_2$(carbene)L_2, but in poor yield (50%) for styrene and only 15% yield for ethylene. While both $MH_2Cl_2(P^iPr_3)_2$ reagents suffer from very low solubility in all available solvents, the reactions in eq 13 are significantly slower than those of MH_3ClL_2 with vinyl ethers. When $OsH_2Cl_2L_2$ and 3 equiv of CH_2=CH(O^tBu) in C_7D_8 were heated at 115 °C for 24 h, $OsHCl_2(CCH_3)L_2$ was the only osmium−phosphine complex formed (as determined by $^{31}P\{^1H\}$ NMR spectroscopy). The ^1H NMR spectrum of the same solution confirmed signals of $OsHCl_2(CCH_3)L_2$, unreacted CH_2=CH(O^tBu), and also showed $CH_3CH_2O^tBu$. Monitoring the $^{31}P\{^1H\}$ 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 $OsH_2Cl_2L_2$ and a concomitant increase in concentration of the carbyne $OsHCl_2(CCH_3)L_2$ ($OsH_2Cl_2L_2$ 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 $OsHCl_2(CCH_3)L_2$. Scaling up the reaction between $OsH_2Cl_2L_2$ and CH_2=CH(O^tBu) led to the isolation of pale yellow $OsHCl_2(CCH_3)L_2$.

When $OsH_2Cl_2L_2$ was heated for 10 h at 110 °C in the presence of 3 equiv of CH_2=CH(OEt) in C_7D_8, the carbyne $OsHCl_2(CCH_3)L_2$ was produced, along with free phosphine and $(CH_3CH_2)_2O$, as determined by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy ($OsH_2Cl_2L_2$ and CH_2=CH(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 $OsH_2Cl_2L_2$ with H_2C=CH(OR) is slow, as it is for H_2C=CHR, the high activation energy must be characteristic of the $M(H)_2Cl_2L_2$ unit. Since the (unusual, nonoctahedral) structure of $M(H)_2Cl_2L_2$ 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 $Ru(H)_2Cl_2L_2$ reacting with nucleophiles, due to the +4 oxidation being uncharacteristically high for Ru. Coupled with the determination that free HX converts OsHCl[C(OR)Me]L_2 to OsHClX(CMe)L_2, this further supports the idea that even trace elimination of HCl is the cause of C/O cleavage in reactions employing $M(H)_2Cl_2L_2$.

Discussion

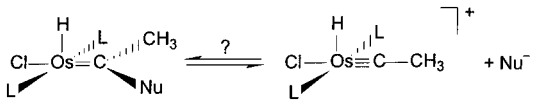
This report reinforces the idea that osmium in this ligand environment (i.e., one where no strong π acid carbonyl coligand depletes metal electron density) prefers the hydride carbyne redox isomer over the carbene. Thus, saturated high-valent osmium (**27**) contrasts to unsaturated lower valent ruthenium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



27 **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).



(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.

(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^{-1} 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 M=C(OR)R′ bond would be the same for M = Ru and M = Os. In fact, it is not. Various conformers around the M=C (and C−OMe) bonds were found computationally, but no strong conformational preference exists. In fact, these complexes exhibit a strong coupling between the Ru=C and the C−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 Ru=C and the C−OMe conformation also implies subtle steric and electronic effects. This behavior is noticeably different from that of the C(H)(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 M(H)(Cl) (carbene carbon) plane adopts a shape (either Y-shaped or T-shaped) that allows for best back-donation

(19) Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 281.
(20) Maseras, F.; Eisenstein, O. *New J. Chem.* **1998**, *22*, 5.

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, P_2O_5, CaH_2, 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 OsH_3ClL_2 (L = P^tBu_2Me, P^iPr_3) were synthesized according to published procedures.[12,17] Traces of $[Et_3NH]Cl$ which are retained as an impurity in OsH_3ClL_2 will rapidly transform $OsHCl(OPh)(CMe)L_2$ to $OsHCl_2(CMe)L_2$, 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 H_3PO_4 (^{31}P), external $CFCl_3$ (^{19}F), or natural abundance ^{13}C peaks of the solvent (^{13}C). NMR spectra were obtained on a Varian Gemini 2000 (300 MHz ^1H, 121.4 MHz ^{31}P, 75 MHz ^{13}C, 282 MHz ^{19}F), a Varian Unity Inova instrument (400 MHz ^1H, 162 MHz ^{31}P), or a Bruker AM spectrometer (500 MHz ^1H, 125.6 MHz ^{13}C). All T_1 measurements were made at 300 MHz. The NOE experiment was performed at 400 MHz.

Reaction of $OsH_3Cl(P^iPr_3)_2$ with 4-(Dimethylamino)pyridine. In an NMR tube, $OsH_3Cl(P^iPr_3)_2$ (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, C_6D_6, 20 °C): δ −12.8 (t, $J_{(HP)}$ = 12.5 Hz, Os-*H*), 1.18 (dvt, N = 12.3 Hz, Os−P(CH(C*H*$_3$)$_2$)$_3$, 1.36 (dvt, N = 12.9 Hz, Os−P(CH(C*H*$_3$)$_2$)$_3$, 2.05 (s, Os−((NC$_5$*H*$_4$)-(N(C*H*$_3$)$_2$))), 2.22 (m, Os−P(C*H*(CH$_3$)$_2$)$_3$, 5.83, 9.45 (m, Os−((NC$_5$*H*$_4$)-(N(CH$_3$)$_2$))). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 20 °C): 25.7.

Synthesis of $OsHCl(C_2H_4)(P^tBu_2Me)_2$. The complex $OsH_3Cl(P^tBu_2Me)_2$ (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, C_7D_8, 20 °C): δ −35.4 (t, $J_{(HP)}$= 11 Hz), 0.6 (s, P^{t}Bu$_2$*Me*), 1.2 (vt, N = 12.9 Hz, P^{t}Bu$_2$Me), 1.3 (vt, N = 12.9 Hz, P^{t}Bu$_2$Me), 2.7 (br, Os(C$_2$*H*$_4$)). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, 20 °C): 12.3. $^{13}C\{^1H\}$ NMR (75.4 MHz, C_7D_8, 20 °C): −5.0 (vt, $J_{(CP)}$=10.5 Hz, P^t*Bu*$_2$*C*H3), 29.0 (s, P(C(*C*H$_3$)$_3$)$_2$Me), 30.6 (vt, $J_{(CP)}$= 2.4 Hz, P(C(*C*H$_3$)$_3$)$_2$Me), 35.8 (vt, $J_{(CP)}$=11 Hz, P(*C*(CH$_3$)$_3$)$_2$Me), 40.1 (vt, $J_{(CP)}$=10 Hz, P(*C*(CH$_3$)$_3$)$_2$Me)), 23.9 (br, Os(*C*$_2$H$_4$)). ^1H NMR (300 MHz, C_7D_8, −80 °C): δ 2.5, 3.15 (br, Os(C$_2$*H*$_4$)). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_7D_8, −80 °C): 23.0, 25.5 (br, Os(*C*$_2$H$_4$)).

Reaction of $OsH_3Cl(P^tBu_2Me)_2$ and Ethylene. In an NMR tube, $OsH_3Cl(P^tBu_2Me)_2$ (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 $^{31}P\{^1H\}$ NMR. After 10 min, the main product is the "adduct" $OsH_3Cl(\eta^2\text{-}C_2H_4)(P^tBu_2Me)_2$. Only diagnostic data are provided. ^1H NMR (300 MHz, C_7D_8, 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-(C$_2$*H*$_4$), 4H). ^1H NMR (300 MHz, C_7D_8, −70 °C): δ −14.6 (t, $J_{(HP)}$ = 12 Hz, Os-*H*, 2H, T_1 77 ms).

$OsHCl(C_2H_4)(P^tBu_2Me)_2$ with D_2. In an NMR tube, $OsHCl(C_2H_4)(P^tBu_2Me)_2$ (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 D_2 (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.

$OsHCl(C_2H_4)(P^tBu_2Me)_2$ with H_2. In an NMR tube, $OsHCl(C_2H_4)(P^tBu_2Me)_2$ (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 H_2 (700 mm Hg). After 2 h, the main product is $OsH_5Cl(P^tBu_2Me)_2$.[21] Upon vacuum removal of the volatiles, $OsH_3Cl(P^tBu_2Me)_2$[12] is recovered.

CH_2=CH(OC_6H_5)-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, C_6D_6): δ 4.18 (d, $^3J_{H-H}$ = 6 Hz, 1H, C*H*$_2$=CH(OPh)), 4.74 (d, $^3J_{H-H}$ = 14 Hz, 1H, C*H*$_2$=CH(Ph)), 6.37 (dd, $^3J_{H-H}$ = 14 Hz, $^3J_{H-H}$ = 6 Hz, 1H, CH$_2$=C*H*(OPh)), 6.82 (t, $^3J_{H-H}$ = 8 Hz, 1H, *o*-C$_6$H$_5$), 6.85 (d, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C$_6$H$_5$), 7.00 (apparent t, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C$_6$H$_5$).

Synthesis of $OsHCl(=C(OPh)(CH_3))(P^tBu_2Me)_2$. In an NMR tube, $OsH_3Cl(P^tBu_2Me)_2$ (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, C_7D_8, −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)(C*H*$_3$), A), 2.87 (s, Os=C(OPh)(C*H*$_3$), B). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, −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, C_7D_8, 25 °C): δ −29.9 (br, Os−H, A), −33.1 (br, Os−H, B), 2.35 (s, Os=C(OPh)(C*H*$_3$), A), 2.87 (s, Os=C(OPh)(C*H*$_3$), B). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, 25 °C): 10.7, 13.2, 18.3, 20.9 (br, center lines of the two AB pattern, A + B overlapped). $^{13}C\{^1H\}$ NMR (125.6 MHz, C_6D_6, 25 °C): 4.3 (vt, N = 28 Hz, Os−P(*C*H$_3$)(C(CH$_3$)$_3$)$_2$), A + B), 29.4 (s, Os−P(CH$_3$)(C(*C*H$_3$)$_3$)$_2$), B), 29.8 (s, Os−P(CH$_3$)-(C(*C*H$_3$)$_3$)$_2$), A + B), 30.2 (s, Os−P(CH$_3$)(C(*C*H$_3$)$_3$)$_2$) A), 36.8 (vt, N = 23 Hz, Os−P(CH$_3$)(*C*(CH$_3$)$_3$)$_2$) A), 37.3 (vt, N = 22 Hz, Os−P(CH$_3$)-(*C*(CH$_3$)$_3$)$_2$) B), 63.0 (s, Os=C(OPh)(*C*H$_3$), A + B), 94.9, 108.9, 121.2, 122.7, 157.3, 159.9 (s, Os=C(O*Ph*)(CH$_3$), B), 114.7, 117.4, 120.7, 123.2, 142.3, 148.5 (s, Os=C(O*Ph*)(CH$_3$), A), 254.3 (t, $J_{(C-P)}$ = 5.1 Hz, Os=*C*, A + B).

Reaction of $OsH_3Cl(P^tBu_2Me)_2$ 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 $OsH_3Cl(P^tBu_2Me)_2$ (0.0100 g, 0.018 mmol) and stored in liquid N_2. 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, C_7D_8, −80 °C): δ −14.02 (br, Os−*H*, 2H, T_1 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−(H$_2$C=C*H*(OPh))), 3.0, 2.7 (br, Os−(*H*$_2$C=CH(OPh))). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, −80 °C): 20.6, 15.3 (AB pattern, $J_{(A-B)}$= 167 Hz).

Reaction of $OsH_3Cl(P^iPr_3)_2$ and Vinyl Phenoxide. In an NMR tube, the complex $OsH_3Cl(P^iPr_3)_2$ (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 $^{31}P\{^1H\}$ 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, C_6D_6, 20 °C): δ −26.0 (br, Os−H), 2.9 (m, Os=C(C*H*$_3$)(OPh)). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 20 °C): 16.6, 24.2 (δ_A and δ_B of an AB pattern, $J_{(P-P')}$ = 291 Hz).

Reaction of $OsH_3Cl(P^iPr_3)_2$ and Vinyl Phenoxide at Low Temperatures. The procedure is analogous to the one described above using $OsH_3Cl(P^iPr_3)_2$ (0.0100 g, 0.018 mmol). Only diagnostic data are provided. ^1H NMR (300 MHz, C_7D_8, −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),

(21) Laurer, W. M.; Spielman, M. A. *J. Org. Chem.* **1990**, *55*, 1572.

5.91(br, Os−(H_2C═C*H*(OPh))), 2.6, 2.1 (br, Os−(*H_2*C═CH(OPh))). ^{31}P{^{1}H} NMR (121.4 MHz, C_7D_8, −80 °C): 16.2.

Synthesis of OsHCl(OPh)(CCH$_3$)(P^{i}Pr$_3$)$_2$. In an NMR tube, the complex $OsH_3Cl(P^iPr_3)_2$ (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. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −7.18 (t, $J_{(H-P)}$ = 15 Hz, Os-*H*), 0.63 (t, $J_{(H-P)}$ = 2.4 Hz, Os═C−C*H*$_3$), 1.03 (dvt, N = 13.0 Hz, Os−P(CH(C*H*$_3$)$_2$)), 1.28 (dvt, N = 15.0 Hz, Os−P(CH(C*H*$_3$)$_2$)), 2.38 (m, Os−P(C*H*(CH$_3$)$_2$)), 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). ^{31}P {^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): 31.2. ^{13}C {^{1}H} NMR (125.6 MHz, C_6D_6, 25 °C): 19.2 (s, Os−P(CH(*C*H$_3$)$_2$)), 21.0 (s, Os−P(CH(*C*H$_3$)$_2$)), 23.2 (vt, N = 30 Hz, Os−P(*C*H(CH$_3$)$_2$)), 40.4 (s, Os≡C−*C*H$_3$), 114.7, 120.9, 129.0, 165.4 (s, Os−O−*C*$_6$H$_5$), 269.7 (t, $J_{(C-P)}$ = 13 Hz, Os≡*C*).

Kinetic Studies. (A) General. Rates were determined by disappearance of the hydride ^{1}H 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 $OsH_3Cl(P^iPr_3)_2$ and vinyl phenoxide. Approximately 10 min after the two reagents were mixed, at which point the main product of the reaction is observed by ^{1}H 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 OsH$_3$Cl(P^{i}Pr$_3$)$_2$ and Vinyl Phenoxide in the Presence of Free P^{t}Bu$_2$Me. 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)(CCH$_3$)(P^{i}Pr$_3$)(P^{t}Bu$_2$Me), in addition to OsHCl(OPh)(CCH$_3$)(P^{i}Pr$_3$)$_2$ as the major product. The ^{1}H NMR spectrum showed a slightly broadened triplet (dd) at −6.92 ppm, free P^{i}Pr$_3$, and a ^{31}P{^{1}H} NMR AB pattern with lines at 31.7, 29.8, 27.0, and 25.3 ppm. The amount of this mixed-phosphine carbyne 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)(CCH$_3$)(P^{i}Pr$_3$)$_2$ with free P^{t}Bu$_2$Me.

Synthesis of OsHCl[═C(CH$_3$)(OEt)](P^{t}Bu$_2$Me)$_2$. In an NMR tube, the complex $OsH_3Cl(P^tBu_2Me)_2$ (0.0200 g, 0.0364 mmol) was dissolved in 2 mL of benzene-d_6, and ethyl vinyl ether (7μL, 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. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −28.1 (t, $J_{(HP)}$ = 17.4 Hz, Os-*H*), 1.2 (vt, N = 3.6 Hz, P^{t}Bu$_2$*Me*), 1.30 (vt, N = 12.4 Hz, P^t*Bu*$_2$Me), 1.37 (vt, N = 12.6 Hz, P^t*Bu*$_2$Me), 2.052 (s, Os═C(C*H*$_3$)(OEt)), 1.50 (t, $J_{(H-H)}$ = 6.3 Hz, Os═C(CH$_3$)(OCH$_2$C*H*$_3$)), 4.09 (q, $J_{(H-H)}$ = 7.0 Hz, Os═C(CH$_3$)(OC*H*$_2$CH$_3$)). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): 36.9. ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 20 °C): 11.1 (vt, N = 25.8 Hz, P^{t}Bu$_2$*C*H$_3$), 29.7 (s, P(C(*C*H$_3$)$_3$)$_2$Me), 30.8 (s, P(C(*C*H$_3$)$_3$)$_2$Me), 35.6 (vt, N = 23.5 Hz, P(*C*(CH$_3$)$_3$)$_2$Me), 38.1 (vt, N = 17.4 Hz, P(*C*(CH$_3$)$_3$)$_2$Me)), 14.2 (s, Os═C(CH$_3$)(OCH$_2$*C*H$_3$)), 49.6 (s, Os═C(*C*H$_3$)(OCH$_2$CH$_3$)), 67.3 (s, Os═C(CH$_3$)(O*C*H$_2$CH$_3$)), 243.9 (br, Os═*C*).

Reaction of OsH$_3$Cl(P^{i}Pr$_3$)$_2$ and Ethyl Vinyl Ether. In an NMR tube, $OsH_3Cl(P^iPr_3)_2$ (0.010 g, 0.018 mmol) was disolved 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 ^{1}H and ^{31}P{^{1}H} 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. ^{1}H NMR (300 MHz, C_7D_8, 20 °C): δ −19.29 (br. Os-*H*), 2.24 (m, Os−P(C*H*(CH$_3$)$_2$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_7D_8, 20 °C): 59.1 (very br). ^{1}H NMR (300 MHz, C_7D_8, −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−(*H_2*C═CH(OEt))), 6.2 (br, Os−(H_2C═C*H*(OEt))). ^{31}P{^{1}H} NMR (121.4 MHz, C_7D_8, −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═CH$_2$)(P^{i}Pr$_3$)$_2$. Only diagnostic data for the carbene are provided. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −27.66 (t, $J_{(H-P)}$ = 17 Hz, Os−H), 2.31 (s, Os═C(C*H*$_3$)(OEt)), 2.52 (m, Os−P(C*H*(CH$_3$)$_2$)$_3$), 4.25 (q, $J_{(H-H)}$ = 7.2 Hz, Os═C(CH$_3$)(OC*H*$_2$CH$_3$))). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 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^{i}Pr$_3$)$_2$.[22] The volatiles are removed under vacuo, and the solid is washed with pentane (2 × 2 mL). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −18.12 (t, $J_{(H-P)}$ = 14 Hz, Os−*H*), 0.23 (t, $J_{(H-P)}$ = 3 Hz, Os═C═C*H*$_2$), 1.23 (m, Os−P(CH(C*H*$_3$)$_2$)), 1.29 (m, Os−P(CH(C*H*$_3$)$_2$)), 2.84 (m, Os−P(C*H*(CH$_3$)$_2$)). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): 38.2. ^{13}C{^{1}H} NMR (125.6 MHz, C_6D_6, 25 °C): 19.7 (s, Os−P(CH(*C*H$_3$)$_2$)), 20.6 (s, Os−P(CH(*C*H$_3$)$_2$)), 25.4 (vt, N = 30 Hz, Os−P(*C*H(CH$_3$)$_2$)), 86.2 (s, Os═C═*C*H$_2$), 281.9 (br, Os═*C*).

Synthesis of OsHCl[═C(CH$_2$)$_3$O](P^{i}Pr$_3$)$_2$. In an NMR tube, the complex $OsH_3Cl(P^iPr_3)_2$ (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. ^{1}H NMR (300 MHz, C_6D_6, 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(C*H*$_3$)$_2$)), 1.44 (dvt, $J_{(H-H)}$ = 7.2 Hz, N = 12.8 Hz, Os−P(CH(C*H*$_3$)$_2$)), 1.46 (m, Os-[═C(CH$_2$−C*H*$_2$−CH$_2$−O)]), 1.99 (t, $J_{(H-H)}$ = 7.5 Hz, Os[═C(C*H*$_2$−CH$_2$−CH$_2$−O)]), 2.53 (m, Os−P(C*H*(CH$_3$)$_2$)), 3.46 (t, $J_{(H-H)}$ = 7.5 Hz, Os[═C(CH$_2$−CH$_2$−C*H*$_2$−O)]). ^{31}P {^{1}H} NMR (162 MHz, C_6D_6, 20 °C): 44.9 (two lines separated by 0.098 ppm; AB pattern with outer lines undetected). ^{13}C{^{1}H} NMR (125.6 MHz, C_6D_6, 25 °C): 20.1 (Os−P(CH(*C*H$_3$)$_2$)), 20.7 (Os−P(CH(*C*H$_3$)$_2$)), 24.8 (Os[═C(CH$_2$-*C*H$_2$−CH$_2$−O)]), 25.7 (vt, N = 22.4 Hz, Os−P(*C*H(CH$_3$)$_2$)), 56.7 (Os[═C(*C*H$_2$−CH$_2$−CH$_2$−O)]), 74.9 (Os[═C(CH$_2$−CH$_2$-*C*H$_2$−O)]), 235.5 (br, Os═*C*).

Synthesis of OsHCl$_2$(CCH$_3$)(P^{i}Pr$_3$)$_2$. (a) Under Ar, a suspension of $OsH_2Cl_2(P^iPr_3)_2$ (0.0750 g, 0.129 mmol) in toluene (15 mL) was treated with excess CH$_2$═CH(O^{t}Bu) (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%). ^{1}H NMR (300 MHz, $CDCl_3$): −7.49 (t, J(PH) = 16 Hz, 1 H, Os−*H*), 0.98 (br, 3H, OsCC*H*$_3$), 1.40 (dvt, N = 14.1, J(HH) = 7.2 Hz, 18 H, PCHC*H*$_3$), 1.45 (dvt, N = 13.8, J(HH) = 6.8 Hz, 18 H, PCHC*H*$_3$), 2.72 (m, 6H, PC*H*CH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): 21.92 (s, P^{i}Pr$_3$).

(b) In a similar manner as that outlined in (a) above, a suspension of $OsH_2Cl_2(P^iPr_3)_2$ (0.050 g, 0.086 mmol) in toluene (10 mL) was treated with excess CH$_2$CH(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 produce of this reaction were the same as that for (a) above.

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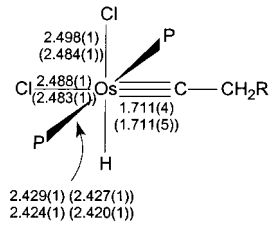
X-ray Structure Determination of $OsHCl_2(CCH_3)(P^iPr_3)_2$. The crystal was affixed to a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to −158 °C using a gas−flow cooling system of local design. Standard inert atmosphere techniques were used during the handling 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 $OsHCl_2(CCH_2R)(P^iPr_3)_2$ are identical within 2σ for R = H and = Ph (see **29**).



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

29

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 98[23] 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 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.

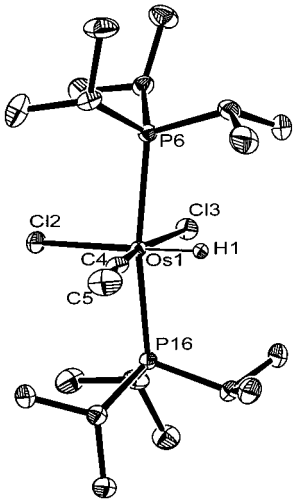


Figure 5. ORTEP drawing of $OsHCl_2(CCH_3)(P^iPr_3)_2$, omitting H on carbon. Selected bond lengths: Os−Cl2 = 2.484(1) Å; Os−Cl3 = 2.481(1); Os−P6 = 2.428(1); Os−P16 = 2.419(1); Os−C4 = 1.711-(4); Os−H1 = 1.35(5). Bond angles: Cl2−Os−Cl3 = 87.73(4)°; Cl2−Os−C4 = 103.57(15); Cl3−Os−C4 = 168.68(15); Os−C4−C5 = 174.5(4); Cl2−Os−H1 = 167.5(20); Cl3−Os−H1 = 79.8(20); P6−Os−P16 = 170.03(4).

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Supporting Information Available: Kinetic plots and full crystallographic details for $OsHCl_2(CCH_3)(P^iPr_3)_2$ 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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