A comprehensive view of M–H addition across the RC≡CH bond: frustration culminating in ultimate union

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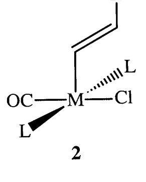
The reaction of $MHCl(CO)L_2$ ($L = P^iPr_3$; M = Ru or Os) with more than a dozen terminal alkynes RC≡CH has been studied at variable temperatures and for a variety of R groups representing a wide range of steric and electronic effects. This *sometimes* reveals (for the slower osmium examples) formation of an η^2-alkyne adduct, then the vinylidene $OsHCl(C{=}CHR)(CO)L_2$ and finally the η^1-vinyl complex $OsCl(CH{=}CHR)(CO)L_2$. The rate of formation of the vinyl complex decreases with R according to the series primary > tertiary > secondary and electron-withdrawing > electron-donating. Deuterium labeling of $OsHCl(CO)L_2$ at either Os or the alkyne sp carbons shows that isotope exchange between these two sites can be competitive with vinylidene and vinyl product formation, and thus can confuse some attempts to trace the fate of the hydride. When this complication is absent, conventional *syn* addition of Os–D to HC≡CR is established, to give Os(*E*-CH=CDR). The rate of conversion to the vinyl product is not suppressed by added free P^iPr_3. Taken together, these results are consistent with a mechanism of vinyl complex formation involving neither the adduct with H *trans* to RC≡CH, nor the vinylidene, but rather with direct alkyne attack *cis* to the hydride, which is also consistent with the considerable steric influence on the rate of vinyl formation. DFT (B3PW91) calculations show that the vinyl complex is the thermodynamically most stable product and thus is always the final observed product. The calculations also show that the "direct" addition of the alkyne occurs *via* approach of the alkyne *cis* to M–H inside the H–M–Cl quadrant. This direct route is in fact calculated to be a multistep process with an alkyne intermediate that is not in a deep well and thus cannot be observed experimentally. Calculations also agree with the fact that the vinylidene and the vinyl complexes are obtained through two independent routes.

This paper considers the following question: how does a terminal acetylene react with an unsaturated metal hydride complex in which the shape of the LUMO would favor addition of the alkyne *trans* to the hydride?

The five-coordinate, 16-electron square-pyramidal complexes $MHCl(CO)L_2$ ($L = PR_3$; M = Ru and Os) provide a rich variety of reactions with unsaturated hydrocarbons.[1–4] Among these, the seemingly simple addition of M–H across the C≡C bond of terminal alkynes for $MHCl(CO)L_2$ is lacking in some mechanistic detail.[5] Both Ru and Os complexes with $L = P^iPr_3$ (**1** for Os) and P^tBu_2Me add M–H rapidly across the RC≡CH bond for R = H, Me and Ph, to give unsaturated vinyl complexes **2**.[3,4] According to the authors: "Addition of the alkyne to the metal first occurs, followed by rapid migration of the hydride from the metal to the carbon atom".[4] These workers recently called this an "unexpected insertion".[6] Such a mechanism should also apply to the reaction with alkenes. However, alkenes seem to give only adducts with these metal fragments,[2] although formation of ethyl from ethylene has been very recently reported[7] for Ru and $L = PCy_3$ (Cy = cyclohexyl). The rarity of M–H addition to C=C but rapid addition to C≡C is not only paradoxical, but it emphasizes how much is unknown about these reactions. The structure of the reactant is a square pyramid with apical hydride (**3**).[8] The LUMO is thus directed away from the hydride and any unsaturated ligand should form an adduct [eqn. (1)] with stereochemistry unsuitable (*i.e.*, H and the reducible ligand mutually *trans*) for easy H transfer to carbon.



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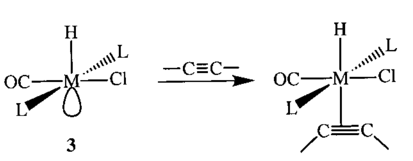

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(1)

Two other observations demand explanation. First, $^tBuC{\equiv}CH$ is stated to be completely unreactive at 25 °C with $MHCl(CO)(P^tBu_2Me)_2$, which was attributed to "steric influence".[2] Additionally, $OsHCl(CO)(P^iPr_3)_2$, **1**, reacts with CyC≡CH within 30 min at 25 °C to give a uniquely persistent vinylidene complex with the proposed isomeric structure **4**.[9] Only after 3 days in solution does **4** isomerize to a vinyl complex [eqn. (2)]. While it can be stated that there are no generalizations regarding how R in RC≡CH influences the rate of the M–H addition or isomerization to vinylidene, this behavior of CyC≡CH is so unique as to attract further attention. There has been intense scrutiny of the η^2-acetylene/

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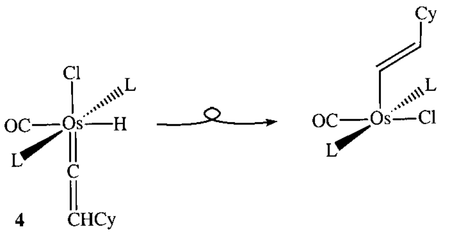

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vinylidene equilibrium, but no general conclusions have emerged.[10–14] In this work, we have studied the reactivity of a large number of terminal alkynes with $MHCl(CO)L_2$ (M = Os, Ru; L = $^iPr_3P$). The purpose is to detect species that appear prior to formation of the final vinyl products and to draw some mechanistic conclusions from their occurrence. In parallel, DFT (B3PW91) calculations were carried out to determine the relative energies of the possible intermediates and products and the mechanism(s) of their formation.

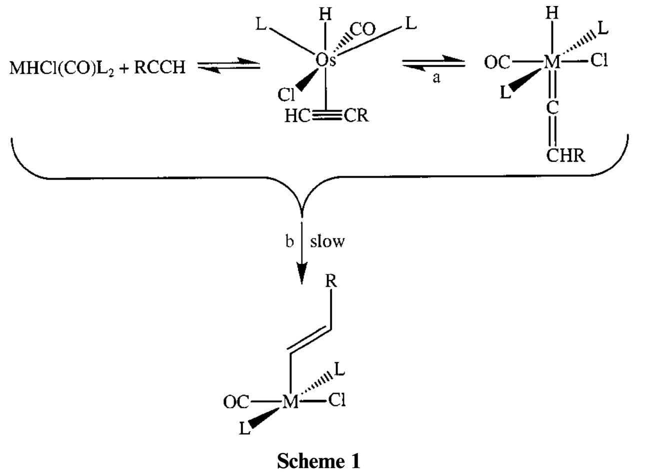
Results

We report results here that implicate a reaction sequence, for *at least* certain of these reactions, which is shown in Scheme 1. This Scheme rests upon direct detection of each intermediate for at least some R, made possible because the unsaturated complex $OsHCl(CO)L_2$ forms an alkyne adduct at a very low temperature, where the rate of subsequent steps is slow. Finally, steps a and, only *slowly*, b occur, both apparently because the hexacoordinate complex resists any intramolecular migration that would bring the hydride *cis* to the acetylene-derived ligand. These observations satisfactorily resolve the two points raised in the preceding paragraph. Note that the hydride/vinylidene stereochemistry in Scheme 1 (*trans*) differs from that proposed in **4**. That in Scheme 1 is chosen as resulting from a least-motion rearrangement from $MHCl(\eta^2\text{-}HCCR)(CO)L_2$.

Detection of intermediates in the reaction of $OsHCl(CO)(P^iPr_3)_2$

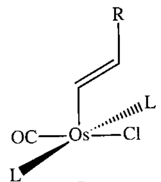
The various alkynes studied differ significantly in their rate of reaction and thus give complementary views of different reaction intermediates. All reactions were carried out with a 1 : 2 Os : alkyne ratio in d_8-toluene.

Identification of the reactive species described here relies on a combination of the presence or absence of Os–H, ≡C–H, =C=CHR and OsCH=CHR ^1H NMR signals at distinctive chemical shifts, as well as an empirical correlation that these analogs, for varying R, have closely grouped ^{31}P NMR chemical shifts: *ca.* 20 ppm for $OsHCl(HCCR)(CO)L_2$, *ca.* 40 ppm for the vinylidene and *ca.* 23 ppm for the vinyl isomers. The time evolution of the *ca.* 20 and *ca.* 23 ppm signals assists in their assignment. The *E* structure around the C=C bond in the OsCH=CHR fragment is based on the observation of a 'large' coupling constant (12–15 Hz) between these hydrogens. In cases of well-resolved ^1H NMR spectra (*i.e.*, narrow lines, observed at only moderately low temperatures), the diastereotopic nature of the P^iPr methyl protons was confirmed experimentally.



Scheme 1

Certain of the R groups permit detection of two ^1H and/or ^{31}P NMR resonances for their vinyl complexes. Specifically, when R = CF_3, CH_2Ph and 2-pentyl, broad signals for the H on C_β are seen; moreover, all vinyl complexes show broad $^{31}P\{^1H\}$ NMR signals. It is clear that the vinyl plane should lie near or in the plane of the Os, C, O, Cl and C_α (vinyl) atoms, to minimize steric repulsion with the bulky L and for electronic reasons, as shown for hexacoordinate complexes and in this work; this is supported by the available[15] crystal structures.[4] Two isomers then exist as shown in **5** and **6**. In certain cases, there may be only one of these, either for thermodynamic or kinetic selectivity reasons. This point must be recognized in analyzing the NMR spectra of evolving reaction mixtures.



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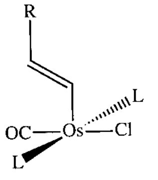

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Detailed observations for individual R groups will now be described. Table 1 is useful for following the descriptions below. A ' + ' entry indicates that the species was detected.

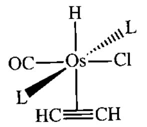
R = Ph, *p*-tolyl. For R = Ph, at the lowest temperature (−60 °C), only the *E*-2-phenylvinyl complex is seen, in a very fast and selective reaction; no adduct or vinylidene is observed. This product assignment is confirmed by ^{31}P and ^1H NMR assays at −60 °C. Visually, there is an immediate color change at −60 °C from the red of the reagent hydride to the violet of the *unsaturated* vinyl complex, whereas alkynes that give *saturated* adducts and vinylidenes immediately become colorless upon addition of alkyne to the solution of $OsHCl(CO)(P^iPr_3)_2$. *p*-Tolylacetylene reacts analogously, so fast that no intermediates are detected, and the only product observed at −60 °C is the vinyl complex.

Table 1 Observed products for different R in reactions of $OsHCl(CO)(P^iPr_3)_2$ with RC≡CH

R	η^2-Adduct	Vinylidene	Vinyl
H	+		+
Me	+	+	+
Ph			+
p-MeC_6H_4			+
CF_3	+		+
^tBu	+[a]	+	+
$SiMe_3$	+[a]	+	+
2-Methylbutyl	+	+	+
1-Cyclohexenyl			+
$PhCH_2$		+ (trace)	+

[a] Not directly observed, but implicated by line broadening/coalescence of its ^{31}P NMR signal and that of $OsHCl(CO)(P^iPr_3)_2$.

R = H. When acetylene is condensed onto a frozen solution of **1** and the cold NMR tube is inserted into a pre-cooled NMR probe at −60 °C, complete conversion of **1** to one product is seen by ^{31}P and ^{1}H NMR spectroscopy. The product is a hydride and its hydride resonance (−4.2 ppm) is significantly downfield of that for **1** (−32.5 ppm), which is an empirical indication of the site *trans* to hydride being occupied. Moreover, this chemical shift is within 1 ppm of the value reported for the ethylene adduct of **1**.[2] The hydrogens of coordinated HC_2H appear as a triplet (coupling to ^{31}P) at 6.46 ppm, indicating that the C≡C bond of the coordinated alkyne is either (i) parallel to the Cl–Os–CO fragment and rotating rapidly around the Os–H axis (**7**) or (ii) coplanar with P–Os–P (**8**) and virtually coupled to the *two* phosphines (*i.e.*, $J_{HP} \ll J_{PP}$). The latter will be seen as more consistent with the behavior observed when $R = CF_3$ and corresponds to the most stable calculated alkyne adduct **Ia**. The ^{13}C{^{1}H} chemical shift for the coordinated alkyne peak is inconsistent with a four-electron donor alkyne, but is consistent with a two-electron donor.[16] Although this value (75.8 ppm) is significantly upfield of those reported for most η^2-alkyne adducts,[17a] there are precedents where this is observed,[17b] specifically when the alkyne is *trans* to a ligand with strong *trans*-influence, thus supporting structure **8** for the adduct, in which the hydride and the η^2-alkyne are mutually *trans*. That is, weak alkyne binding correlates with an upfield δ (^{13}C) value. Gradually, upon warming towards +20 °C, the equilibrium corresponding to the η^2-HCCH adduct formation shifts towards the reactants, best indicated by broadening and disappearance of the ^{1}H NMR peak for η^2-bound acetylenic hydrogens. At +20 °C, the only product observed is the vinyl complex; no evidence for the vinylidene complex is seen at any temperature.



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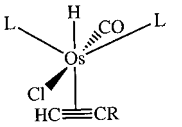

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R = Me. When OsHCl(CO)L$_2$ is reacted with propyne under conditions identical to those above, several species are observed (manifested by several hydride and ^{31}P signals very close to each other): these are η^2-$CH_3C≡CH$ adducts and hydrido-vinylidene complexes. The observation of multiple propyne adducts can most reasonably be attributed to isomeric structures (*i.e.*, methyl orientation) due to the less symmetric structure of η^2-propyne in comparison to acetylene; this also indicates that interconversion of these isomers is slow at −60 °C. Upon warming, hydride peaks of isomers within a given C_3 ligand type merge due to their fast interconversion. The first evidence of the vinyl product is seen at −20 °C. At +20 °C, the reaction mixture consists of some persistent vinylidene, but also vinyl complexes in an approximately 2 : 1 ratio. It requires 80 h at +20 °C to completely convert the vinylidene complex to the vinyl.

R = ^{t}Bu and SiMe$_3$. Combining OsHCl(CO)L$_2$ (L = P^{i}Pr$_3$) with 2 equiv. of ^{t}BuC≡CH in d$_8$-toluene at −60 °C gives several major products (^{31}P{^{1}H} NMR evidence). *tert*-Butylacetylene binds more weakly to the osmium than the previous alkynes, and so, between −60 and −40 °C, a single broad signal is observed due to OsHCl(CO)L$_2$ coalesced together with OsHCl(^{t}BuC≡CH)(CO)L$_2$. The ^{31}P NMR chemical shift of this averaged signal moves in the direction of that of OsHCl(CO)L$_2$ as the temperature is raised, which is indicative of an increase in the mol fraction of OsHCl(CO)L$_2$. As the temperature is raised from −60 to +20 °C, there is an increase in the amount of the species giving a ^{31}P signal at 40.1 ppm [the vinylidene complex OsHCl(CO)(=C=CH^{t}Bu)L$_2$, which was also assigned by its ^{13}C NMR signals]; this becomes the only species present at +20 °C. The mol fraction of this complex evolves over time, and, after 16 h at 25 °C, the vinyl complex Os(*E*-CH=CH^{t}Bu)Cl(CO)L$_2$ (22.5 ppm in ^{31}P{^{1}H} NMR) is the only one observed. Similar behavior is observed for the reaction of OsHCl(CO)L$_2$ with Me$_3$SiC≡CH (see Experimental). This result is in remarkable contrast to the previous report in which *tert*-butylacetylene was found to be completely unreactive towards MHCl(CO)L$_2$ (M = Ru, Os; L = P^{t}Bu$_2$Me).[1,2] This may be an indication of more complete inhibition of the alkyne binding to the metal by more sterically demanding phosphine ^{t}Bu substituents, although the possibility that the previous study did not monitor this slow reaction long enough to observe the formation of vinylidene and vinyl complexes in detectable quantities should also be considered.

R = CF$_3$. The influence of a strongly electron-withdrawing substituent has been studied by reacting OsHCl(CO)L$_2$ with CF$_3$C≡CH. When they are combined at −60 °C in d$_8$-toluene, the solution becomes colorless and NMR shows complete conversion to the η^2-adduct. The ^{31}P{^{1}H} NMR spectrum at this temperature displays an AB pattern with $J_{AB} = 128$ Hz, indicating inequivalence of the two phosphines in the product. This requires structure **8** for this product. The value of the coupling constant is significantly smaller than 273 Hz, observed in similar Ru complexes[18] where ∠P–M–P is close to 180°, which is indicative of a substantial decrease in this angle. Upon warming, the AB pattern is transformed into a broad peak, probably due to the beginning of dissociation of alkyne from Os, or to rotation of the alkyne around the Os–H axis. After 10 h at +20 °C, the only product observed by NMR is the vinyl complex Os(*E*-CH=CHCF$_3$)Cl(CO)(P^{i}Pr$_3$)$_2$. No vinylidene is seen at any temperatures/times. Based on ^{31}P and ^{13}C NMR spectroscopic data (the latter shows that the two alkyne carbon resonances are only modestly shifted by coordination to Os), the conclusion is that the alkyne adduct has a structure in which the C≡C bond is in the plane of the P–M–P fragment. This corresponds to the optimal structure, **Ia**, calculated for OsH(Cl)(CO)(PH$_3$)$_2$(HC≡CH). The strong decrease in the P–Os–P angle (151°) is already present for non-bulky phosphine ligands. This angular deformation is also found in the alkene adduct as shown by the X-ray structure of OsH(OH)[H$_2$C=CHCO$_2$Me](CO)(P^{i}Pr$_3$)$_2$ in that the C=C vector eclipses the P–Os–P fragment.[19] This molecule shows an unusually small P–Os–P angle (144°), with the two phosphines being bent towards the hydride.

R = 1-methylbutyl. The reactivity of OsHCl(CO)L$_2$ with 3-methyl-1-hexyne, bearing a secondary alkyl substituent at the triple bond, has been examined to compare to that previously reported for the sterically and electronically similar cyclohexylacetylene. After 10 min at +20 °C, NMR analysis of the reaction mixture shows the presence of vinylidene and vinyl complexes in a 9 : 1 ratio; complete conversion to the vinyl complex occurs after 100 h. Thus, this result is in agreement with that for cyclohexylacetylene; it also establishes that the formation of this vinyl complex occurs at a slightly slower rate than for methylacetylene and significantly slower than for *tert*-butylacetylene.

Reaction of OsHCl(CO)L$_2$ and 3-methyl-1-hexyne was also studied by combining the reagents in d$_8$-toluene at −60 °C. At −60 °C, there is less than 5% production of an adduct (by ^{31}P and ^{1}H NMR spectroscopy) and no vinyl product evident. At −40 °C, the peaks due to OsHCl(CO)L$_2$ and the η^2-alkyne adduct are broader, suggesting they are connected by a kinetic process. The first evidence for a vinylidene complex is seen at −20 °C (Fig. 1) by both ^{31}P and ^{1}H NMR (hydride signal); a trace of vinyl product is also seen and the resonances arising from OsHCl(CO)L$_2$ and its η^2-alkyne adduct are now

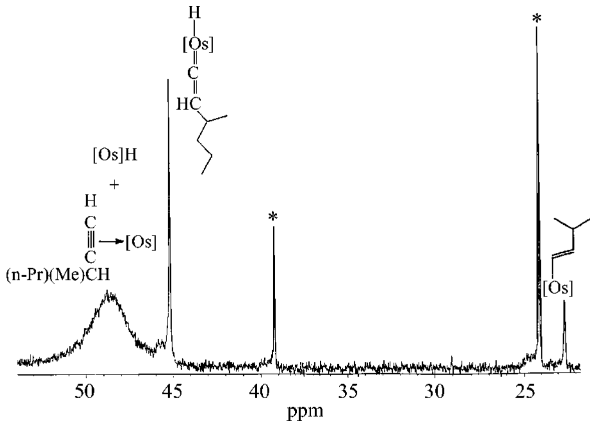


Fig. 1 $^{31}P\{^1H\}$ NMR spectrum (121 MHz, d_8-toluene, −20 °C) of the products of reaction of $OsHCl(CO)(P^iPr_3)_2$ and HC≡CCH(Me)-(*n*-Pr). * indicates impurity in $OsHCl(CO)(P^iPr_3)_2$ reagent.

coalesced, near 49 ppm. At 0 °C, there is still more vinylidene and the vinyl complex ^{31}P NMR signal is strong enough to reveal that it is a doublet, an AB pattern due to the chiral carbon of the vinyl substituent. At this temperature, the coalesced signal of $OsHCl(CO)L_2$ and $OsHCl(\eta^2\text{-}RCCH)(CO)\text{-}L_2$ is nearer the chemical shift of the former, showing it to be the dominant populated species, but its signal is extremely broad (see also Fig. 1). Its short lifetime is due to rapid collisions with free alkyne, to give the adduct. At 20 °C, there are vinylidene and vinyl species, and the equilibrium forming an η^2-alkyne adduct has further broadened the coalesced $^{31}P\{^1H\}$ NMR signal. The vinylidene $^{31}P\{^1H\}$ NMR signal remains sharp. This means that any equilibrium between the vinylidene and the $\eta^2\text{-}RC_2H$ adduct is slower than that between $\eta^2\text{-}RC_2H$ and free alkyne. It also means that the observed (rapid) collisions between $OsHCl(CO)L_2$ and RC_2H do not *directly* produce the vinyl product at a significant rate. After 15 h at 20 °C, the reaction has proceeded further, but not to completion; vinylidene is still evident, as is the final product vinyl complex. These observations are fully consistent with the observations above, all made at +20 °C.

$R = PhCH_2$. Reaction of benzylacetylene with OsHCl-(CO)L_2 is closer in rate to R = Ph than it is to $R = CH_3$. The reaction is nearly complete after 15 min at 25 °C. A trace of vinylidene complex is seen by both ^{31}P and ^1H NMR, and $OsHCl(CO)L_2$ has been completely consumed.

An enyne (R = 1-cyclohexenyl). Reaction with 1-ethynylcyclohexene, seemingly sterically similar to the slow reactant cyclohexylacetylene, has been investigated. However, it was found to react much faster than any alkylacetylene: NMR shows essentially complete conversion to the corresponding vinyl complex within 10 min at +20 °C.

Internal alkynes. In an attempt to observe stable η^2-adducts that could not form a vinylidene by H migration, the reactivity of $OsHCl(CO)L_2$ with two different internal alkynes, MeC≡CMe and $PhC≡CSiMe_3$, was studied. No evidence for adduct formation or insertion in either case was observed from −60 to +20 °C, indicating the necessity of employing terminal alkynes, even merely to obtain an adduct.

The ruthenium analog. We studied a few analogous ruthenium reactions, but using a terminal alkyne that falls into the 'slow reacting' category, to search for possible intermediates. Reaction of $RuHCl(CO)L_2$ ($L = P^tBu_2Me$) with 3-methyl-1-hexyne at 25 °C gives, after 10 min, no evidence of an adduct and only a trace amount of the vinyl complex. After 11 h, there is 93% conversion to one product, that being the vinyl complex. The chiral carbon leads to (minutely) inequivalent phosphine ligands. After 19 h, all the reagent complex is gone and the yield of vinyl complex is >99%. There is no evidence of an alkyne adduct (or a vinylidene complex) at 11 or 19 h. It thus appears that the formation constant for any adduct is much smaller for ruthenium than for osmium and it is this feature that makes study of the osmium chemistry more informative. The DFT calculations have shown that the binding dissociation energy is greatly reduced on going from Os to Ru. The value calculated for Ru (10.6 kcal mol^{-1}) is sufficiently small to reach a zero or negligible value in the presence of bulky phosphine ligands.

Reaction of $RuHCl(CO)(P^tBu_2Me)_2$ and propyne in d_8-toluene gives no new NMR signals at −60 °C, with slow growth of $Ru(CH{=}CHMe)Cl(CO)(P^tBu_2Me)_2$ (but no other species) at 25 °C. Complete conversion requires 1 h at 25 °C.

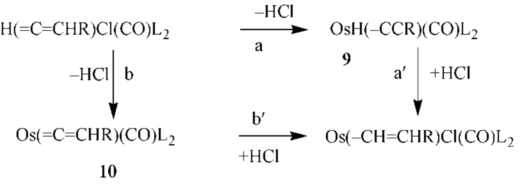
This ruthenium complex reacts with 1-ethynylcyclohexene at 20 °C to give only the β-cyclohexenylvinyl product (99% conversion) within 10 min. The ruthenium complex and $Me_3SiC≡CH$ gives no product over 30 min at 25 °C, but 3 h at 70 °C gives 75% vinyl product and 25% $RuHCl(CO)(P^tBu_2Me)_2$.

Summary of observations. Table 1 summarizes the complex set of observations on the R group dependence of vinyl formation. A species that was not detected could be so for either kinetic or thermodynamic reasons.

To this point, the *observed* species have been identified, together with some semi-quantitative indication of their time evolution. We next deal with the question of which of these are (and are *not*) on the path to the final η^1-vinyl product. In the present reaction, this is not as straightforward as might be anticipated.

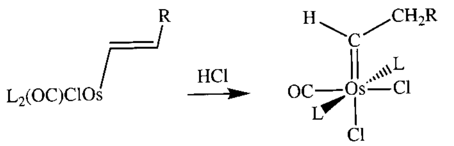
Is the hydrido/vinylidene complex an intermediate in forming the vinyl product?

Alternative isomerization mechanisms. How might hydride and vinylidene ligands, which are mutually *trans*, convert to a vinyl ligand? In particular, is there an alternative to unimolecular isomerization in an octahedral osmium complex? Two alternative (dehydrohalogenation) hypotheses can be considered for the conversion of vinylidene to vinyl (Scheme 2).



Scheme 2

Dehydrohalogenation was considered because we observed that the slower reactions, those where the vinylidene accumulates and persists for a considerable time at 25 °C (R = H, CH_3), show some formation of **11**, a known[20] product [eqn. (3)] of HCl addition to the vinyl complex.



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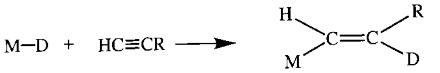
The implication is that HCl may be somehow produced under the reaction conditions. The HCl source might be the vinylidene complex, with the implication of species **9** or **10** as the dehydrohalogenated co-product. Here, HCl *elimination* avoids the intramolecular 'barrier' of the $MCl(CO)L_2$ plane separating the hydride from the vinylidene. Species **9** and **10** differ in that reaction a removes the H from C_β while reaction b removes H from Os. To complete the cycle, an alternative to the microscopic reverse of reactions a and b, involves return of HCl (a′ or b′) to protonate a carbon, yielding the vinyl complex. These mechanisms were tested experimentally by adding a threefold excess of HCl scavengers Et_3N or 1,8-bis-(dimethylamino)naphthalene prior to the reaction of $OsHCl(CO)L_2$ with HCCH or with 3-methylhexyne; however, no new products and no suppression of the rate of vinyl complex formation were observed. Thus, we must conclude that HCl elimination is not operating.

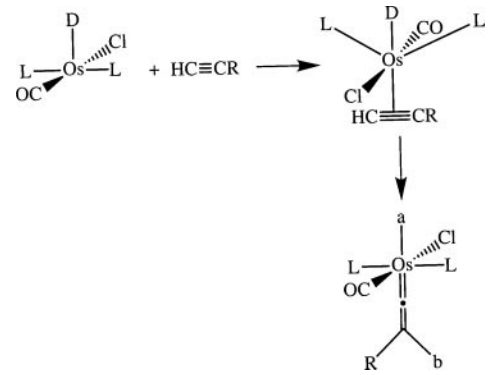
Another possibility which brings the hydride and vinylidene ligands mutually *cis* is dissociation of one phosphine ligand, implicated in recent work on a related hydrido-carbene complex.[21] A fluxional five-coordinate transient can then isomerize to an isomer with H *cis* to vinylidene, followed by insertion of vinylidene into the Os–H bond. Experimental testing of this hypothesis was performed using a 2- to 10-fold excess of P^iPr_3 in reactions of $OsHCl(CO)(P^iPr_3)_2$ with $^tBuC{\equiv}CH$ or $Me_3SiC{\equiv}CH$: no suppression of the rate of formation of the vinylidene or the vinyl complex was observed. This result is in agreement with that obtained[21] in the study of hydrido-carbene/methyl isomerization: P^iPr_3 is insufficiently large (in contrast to P^tBu_2Me, which does dissociate) and, therefore, fails to dissociate from the six-coordinate complex.

Deuterium labeling experiments. The conventional *syn* addition of M–H across a C≡C π-bond predicts the outcome shown in eqn. (4). When this was tested experimentally



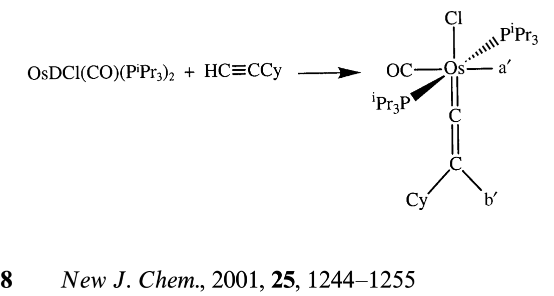
(4)

via eqn. (5) (R = ^tBu or $SiMe_3$, 1 : 2 or 1 : 0.67 mol ratio), there was equal occupancy of H (^1H NMR evidence) in both sites a and b after only 5 min at 25 °C. Free ^tBuCCD was evident by ^2H NMR. After 16 h (R = ^tBu), the vinyl complex that had formed of course also had hydrogen equally at C_α and C_β of the vinyl group. The implication of this is that there is rapid rupture of the Os–D and C–H bonds during or before formation of the η^2-alkyne adduct. The label is lost before vinylidene or vinyl formation takes place.

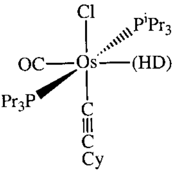


(5)

This has the unfortunate consequence of making impossible the isotopic verification of hydride transfer from the metal to C_β [eqn. (4)]. However, it has implications for the results reported[9] in eqn. (6). The conclusion from that work (*i.e.*, equal D at sites a′ and b′), where the first NMR assay was made when the vinylidene complex was fully formed and no η^2-alkyne complex had been detected, was that the reaction proceeded through species **12**. While this is certainly *one* attractive structure to accomplish the H/D scrambling that we report here, it is only peripheral to the formation of the vinylidene complex, since our deuterium study shows that it collapses back to the η^2-alkyne adduct faster than it transforms to the vinylidene complex. Thus, the implication of eqn. (5) is shown in eqn. (7); H/D exchange is the fastest reaction between these two reagents. For comparison, it has been shown that PhCCD exchanges D with the hydrides of $Fe(H)_2(Me_2PC_2H_4PMe_2)_2$ "rapidly" at 0 °C in aprotic solvent.[22] It has also been argued that PhCCH initially interacts with 18-electron (anionic) hydride complexes *via* **13** (in contrast to the way in which **12** makes H and D equivalent), which collapses to the product as shown in eqn. (8).[23]

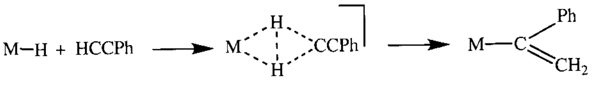


(6)



12

$$OsDCl(CO)L_2 + RCCH \rightleftharpoons OsHCl(CO)L_2 + RCCD \quad (7)$$



13

(8)

To clarify whether this H/D scrambling is general for the M–H additions to RC≡CH under study here, reaction of $OsHCl(CO)L_2$ with PhC≡CD (the alkyne observed to insert fastest into the M–H bond) was monitored by ^1H and ^2H NMR. The result was completely different: D was found to be exclusively on C_α of the vinyl complex, consistent with *syn* addition and *inconsistent* with the involvement of a vinylidene as an essential intermediate. When the location of the isotope is reversed, reaction of $OsDCl(CO)L_2$ with PhCCH gives D only at C_β of the resulting vinyl complex (^2H assay). This isotopic labeling experiment is thus definitive and not significantly influenced by any D isotope effect. This result is fully consistent with the isotopic outcome of the reaction of $RuDCl(CO)(P^tBu_2Me)_2$ with PhCCH.[24]

A labeling study using $OsDCl(CO)L_2$ also has been carried out at 25 °C for an alkyne reacting slightly slower than PhCCH: 1-ethynylcyclohexene. ^1H and ^2H NMR of the reaction mixture after 10 min (complete conversion to vinyl product) showed that the C_α : C_β distribution of deuterium in the vinyl complex is *ca.* 1 : 3. This is consistent with slower insertion of the (bulkier) alkyne into M–H than in the case of phenylacetylene, so there is sufficient time for partial H/D scrambling to occur between the free alkyne and metal complex prior to vinyl complex formation. Free alkyne is also seen, deuterated at the terminal carbon.

Suggested mechanism. On the basis of all these observations, a hypothesis can be suggested: vinylidene formation may be a side process, irrelevant for M–H addition across RC≡CH, but an observable *competing* reaction for the slower reacting alkynes. The absence of observable vinylidene formation for R = Ph, CF_3 might be attributed to (i) unfavorable thermodynamics for vinylidene formation (since electron-donating substituents at the vinylidene C_β apparently have a stabilizing effect on the energy of these species and electron-withdrawing substituents destabilize them);[25] or (ii) more favorable kinetics for hydride transfer from Os to C_β of the alkyne due to the electron-withdrawing effect of these substituents, increasing the electrophilicity of this carbon. On the other hand, for R = Me, ^{t}Bu, $SiMe_3$ and 1-methylbutyl: (i) the vinylidene is stabilized by the electron-donating effect of R and (ii) insertion is inhibited due to both the lesser electrophilicity of C_β of the alkyne and steric hindrance (in the last three cases).

The metastability of the η^2-adducts for both $CH_3C{\equiv}CH$ and $CF_3C{\equiv}CH$, which are very different electronically, can be explained by the influence of different factors contributing to the bonding in these two cases: for relatively electron-rich $CH_3C{\equiv}CH$, the major contributor is alkyne-to-metal electron donation *via* interaction of the filled π-bonding alkyne orbital with the LUMO of the unsaturated metal complex; for very electron-poor $CF_3C{\equiv}CH$, the major contributor could be electron back-donation from a filled metal d-orbital into the π* of the alkyne.

Computational overview

In order to obtain an independent measure of the thermodynamics of the various isomeric structures, DFT (B3PW91) calculations of the products of the reaction of HCCH with $MHCl(CO)(PH_3)_2$ [M = Ru, Os (**I**)] were carried out. The structures and relative energies are shown schematically in Fig. 2.

The full search for various isomers was only carried out at the Os center. The alkyne adds to the metal fragment **I** to give an octahedral η^2-coordinated alkyne complex. Assuming that the PH_3 ligands remain *trans*, three coordination sites are possible for acetylene, *trans* to H (**IIa**), *trans* to CO (**IIb**) or *trans* to Cl (**IIc**) (Fig. 2). All complexes are found to have C_s symmetry and HCCH is bonded to the metal with essentially equal M–C distances. The three isomers have noticeably different stabilities. The most stable isomer, **IIa**, has an HCCH/Os bond dissociation energy (BDE) of 19.2 kcal mol^{-1} (calculated as the difference in energy from the separated fragments in their optimized structures). The CC vector eclipses the Os–P bonds, which results in a decrease in the P–Os–P angle (to 151°) in order to maximize back donation to the alkyne.[26] Ligand arrangement as well as the acetylene orientation found are consistent with the experimental observation for R = H and CF_3. The strong bending of the phosphine is thus not only due to the bulky phosphine ligands. The orientation in **IIc** is similar and results in a similar P–Os–P angle (151.4°) but the BDE in **IIc** is very small and probably tends to zero for more bulky phosphines and substituted alkynes. Two possible orientations were found for **IIb**, the most stable having the CC axis eclipsing the Os–H bond. **IIb** is only slightly higher in energy (5.1 kcal mol^{-1}) than **IIa** and is thus a viable intermediate. The energy of the acetylene adducts is thus not determined by maximizing the back donation in the incoming ligand, which would make the isomer having acetylene *trans* to Cl (that is **IIc**) most stable. It is determined in the most part by the intrinsic stability of the metal fragment $OsHCl(CO)(PH_3)_2$, which favors the strongest σ-donor ligand (H or CO) *trans* to the empty site.

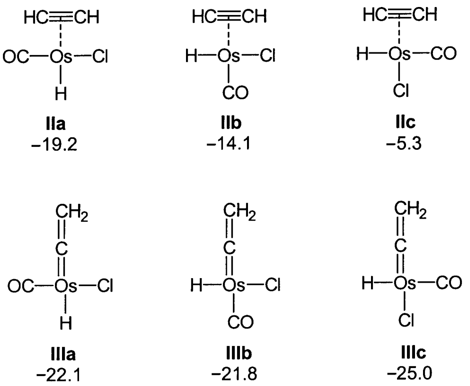


Fig. 2 Schematic representation of structures and energies (kcal mol^{-1}) relative to separated optimized $OsHCl(CO)(PH_3)_2$ and $HC{\equiv}CH$ of acetylene adducts (**II**) and vinylidene isomers (**III**).

The energies and structures of isomeric vinylidene species, **III**, are shown in Fig. 2 with the same notation for the site of coordination of $C{=}CH_2$ as for the alkyne complex and with the same energy reference. In contrast to the alkyne complexes, the energies of the three isomeric species (**IIIa**, **IIIb** and **IIIc**) are very close, with **IIIc** being the most stable. Since the exothermicity is no larger than 6 kcal mol^{-1}, the transformation should be viewed as essentially thermoneutral. This result highlights the importance of the metal fragment in making this transformation feasible, since the isomerization of free HCCH into free CCH_2 is highly endothermic (42.9 kcal mol^{-1}). In the vinylidene series, H, CO and $C{=}CH_2$ all have a large *trans* influence. Since each of the isomers has two of these ligands *trans* to each other, they are relatively close in energy (Fig. 2). Push/pull effects come from Cl and CO in **IIIa**, and Cl and CCH_2 in **IIIc**. Only **IIIb** puts Cl *trans* to a non-π-acceptor (H) and the two π-acceptors (CO and CCH_2) *trans* to each other and is thus the least stable. Note that the H and Cl placement on the vinylidene isomer in Scheme 1 corresponds to **IIIa**, not the (slightly) more stable **IIIc**.

The most stable vinyl isomer **IVa** (Fig. 3) is a square-pyramidal complex with the vinyl group at the apical site eclipsing the CO bond. This conformation agrees with that observed in vinyl pentacarbonyl complexes, suggesting that the occupied d orbital that is not stabilized by π^*_{CO} overlaps with the π and π* orbitals of the vinyl group.[15] This interaction, which is similar to that found in the π-system of $CH_2{=}CHX$, increases the π-electron density on the non-substituted carbon by 0.1 electron (NBO value). Isomer **IV** is calculated to be 40.2 kcal mol^{-1} below separated $OsHCl(CO)(PH_3)_2$ and HCCH and 21.0 kcal mol^{-1} below the most stable HCCH adduct, **IIa**. There is thus a significant thermodynamic drive to form the *unsaturated* vinyl complex in preference to the 18-electron alkyne or vinylidene complex.

The complexes with Ru in place of Os have been calculated for isomers of type **IIa**, **IIIa** and **IVa**. Acetylene is less strongly

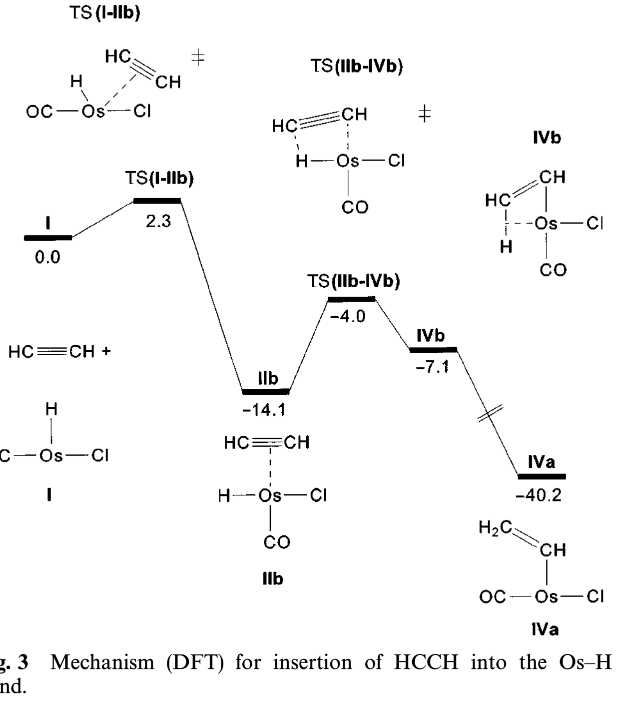
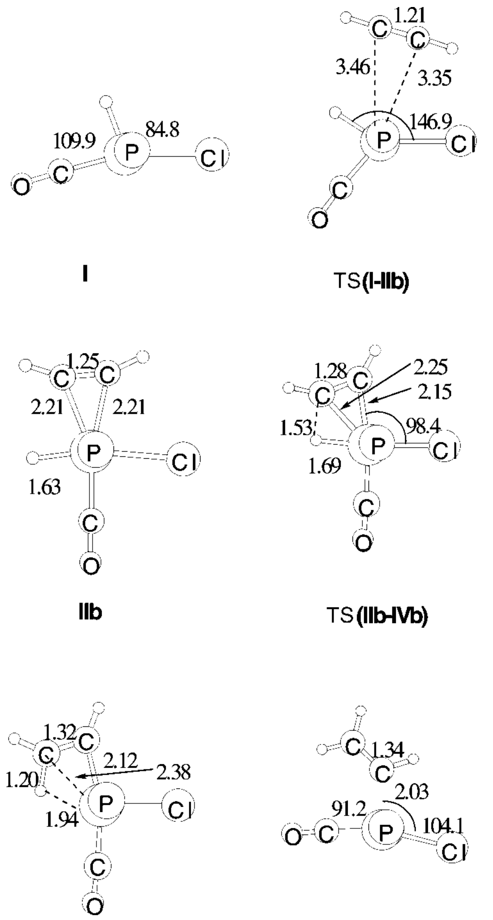


Fig. 3 Mechanism (DFT) for insertion of HCCH into the Os–H bond.

bonded to Ru (10.6 kcal mol^{-1}) than to Os (19.2 kcal mol^{-1}) in an isomer of type **IIa**. The lesser lengthening of CC with Ru (1.23 Å) than with Os (1.25 Å) also illustrates this. Considering the lack of steric effects in our calculated model, substituted alkyne is probably only very weakly bonded to RuHCl(CO)$(PR_3)_2$. This is consistent with the absence of any observed alkyne adduct in the case of the Ru analog. The vinylidene isomer is higher in energy than the HCCH adduct (+5.3 kcal mol^{-1}) in the case of Ru. These results stem from the lesser electron-donating ability of a 5d metal with respect to a 6d one. This is also consistent with the lack of observation of a Ru–vinylidene complex. The Ru–vinyl complex is calculated to be 29.1 kcal mol^{-1} more stable than the HCCH adduct, which is larger than for Os (21.0 kcal mol^{-1}). Using the separated fragments MHCl(CO)$(PH_3)_2$ and HCCH as an energy reference, the exothermicity is calculated to be similar for Ru (39.7 kcal mol^{-1}) and Os (40.2 kcal mol^{-1}).

The mechanism for vinyl formation was sought *via* direct insertion of the alkyne in the Os–H bond from a trajectory *cis* to H, not *trans* to H. Two choices of approach are available, *cis* to Cl and *cis* to CO. Since, in both cases, the angles between the two *cis* ligands must open as the alkyne approaches, we used previous knowledge of the calculated (HF level) relative energy cost for H–Ru–Cl *vs.* H–Ru–CO opening in RuHCl(CO)$(PH_3)_2$ in selecting the approach in the H–Os–Cl quadrant.[24] A transition state [TS(**I–IIb**), Fig. 3 and 4] was located only 2.3 kcal mol^{-1} above the energy of the separated reagents. In this transition state, the alkyne is hardly pertubed from the free alkyne geometry. It is still essentially linear and the CC bond distance is 1.21 Å (identical to that calculated in free C_2H_2). The average of the two Os–C bonds is 3.40 Å, which indicates a very early transition state. The major geometrical changes from the reactants are the opening of the H–Os–Cl angle from 109 to 146.9°. This large angular change at modest energy cost confirms the initial hypothesis that the preferred approach would occur in the most easily distorted quadrant *cis* to the Os–H bond.



I

TS(**I-IIb**)

IIb

TS(**IIb-IVb**)

IVb

IVa

Fig. 4 Calculated (DFT) geometries.

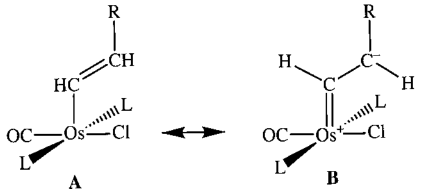
Relaxing the geometry of this transition state along the normal mode of the imaginary frequency leads to the acetylene adduct (discussed earlier) bonded *trans* to CO, **IIb**. In the η^2-adduct **IIb** the acetylene CC bond is only marginally elongated (1.25 Å) from free acetylene and the Os–C bonds are both equal to 2.21 Å. Alkyne insertion into the Os–H bond is thus not one step but a multistep process. In forming the vinyl product, a transition state for the insertion into the Os–H bond was located 10.1 kcal mol^{-1} above the adduct **IIb** (Fig. 3 and 4). The energy of this transition structure is thus 4.0 kcal mol^{-1} below the energy of the separated reagents. Its geometry has the features expected for an insertion: the Os–C_α bond is already mostly formed (2.15 Å) but Os–C_β is only slightly elongated (2.25 Å). The CO ligand remains *trans* to the bond-forming vinyl C_α and *cis* to Cl. Consequently, the insertion product, **IVb**, is essentially a square-based pyramid with an axial Cl group. Since the vinyl group is at the basal site, an agostic interaction with the β C–H is geometrically feasible and the calculation shows severe geometrical distortions of the vinyl group to establish this interaction. The Os–C_α–C_β angle is only 84.3°, which is remarkable for an sp^2 carbon and the C_β–H agostic bond is as long as 1.20 Å. The large elongation of the C_β–H bond is due to the nature of the *trans* ligand, Cl, which has poor σ-donating ability and large π-donating effect. Both factors favor a strong agostic interaction. The agostic interaction is also evident through the rather short Os···H distance, 1.94 Å. In this intermediate **IVb**, the C_α–C_β distance is slightly shorter (1.32 Å) than the CC double bond in the previously discussed vinyl complex **IVa** (1.34 Å). The geometry of **IVb** is close to that of the transition state for insertion. The coordination around Os remains square pyramidal with a transoid C_α–Os–C(O) angle equal to 163.9°.

The vinyl complex **IVb** is 33.1 kcal mol^{-1} less stable than the vinyl complex **IVa** in which the vinyl occupies the apical site of the square-based pyramid and has no agostic interaction. It has been established that the preferred square pyramid has the strongest σ-donating ligand *trans* to the empty site. Despite numerous attempts, no transition state could be located for the transformation of **IVb** into **IVa**. In view of the large energy difference between the two isomers, the Hammond postulate would suggest a transition state close in geometry and energy to **IVb**. Therefore the transformation of **IVb** into **IVa** should occur with almost no activation energy, in agreement with the well-known high fluxionality of d^6 ML_5 species.

The theoretical study shows that the final vinyl complex can form from approach of the alkyne *cis* to the Os–H. In contrast to what was concluded from the experimental results, an adduct **IIb** is formed prior to the final vinyl product **IVa**. However, the relatively low activation energy required for the alkyne to insert into the Os–H bond suggests **IIb** cannot be observed experimentally. The calculations also account for the fact that vinylidene and vinyl are not on the same reaction path. The addition of an alkyne *trans* to H should occur with essentially no activation energy and leads to the most stable alkyne adduct **IIa**. **IIa** could undergo the widely reported alkyne/vinylidene rearrangement.[27,28] The route for formation of the vinyl goes through intermediates **IIb** and **IVb**, which are at higher energy than that involved in the formation of the vinylidene and requires moderate activation energy (alkyne insertion into Os–H). This route leads to the formation of the globally most stable product. These two routes are in competition and it is thus understandable that changes in alkyne substituent can induce dramatic changes in product distribution, although the vinyl is always the final product.

Discussion

Fig. 5 is a semiquantitative potential energy diagram that attempts to represent the R group dependence of energy minima and transition states to account for the observations in Table 1. Where relative energies cannot be estimated, we simply enclose the species in a vertical box or in brackets. It should, however, be noticed that the ordering of the transition states for vinyl formation are given by the rates determined qualitatively in this work. While no quantitative features of relative energies could be incorporated, the diagram shows how unobserved η^2-adduct or vinylidene species (from reaction coordinate RC1) can be due to a low barrier for direct formation of the vinyl (reaction coordinate RC2).



It has been proposed[29] that **B**, a carbene/carbanion structure, is a resonance contributor to the η^1-vinyl structures under study here. As already mentioned, in **B** the overlap of one occupied d orbital of Os with the vinyl π-system results in a polarization of the π-system so as to develop electron density at C_β (0.1 electrons larger than on C_α for Os). The basis for this suggestion is the fact that these vinyl complexes are protonated [by HCl; see eqn. (3)] at the vinyl C_β, consistent with **B**. The contribution of **B** should be enhanced by electron-withdrawing R groups. We have shown[30] that R = ester or acyl does indeed enhance the "carbenoid" ^{13}C chemical shift of C_α, as predicted by **B**, but this is additionally favored because the resulting structure has the ester or acyl oxygens coordinated to the Group VIII metal (in this case Ru). We sought a test of the carbenoid resonance contributor **B** that was less perturbing, and thus more relevant. As shown in Table 2, there is a correlation of the downfield chemical shift of the proton on C_α with the electron-withdrawing character of R. These chemical shifts are considerably larger than merely the effect of the same substituent on the chemical shift of the corresponding olefin.[31] The limiting case here would be the numerous purely carbene $L_nM{=}CHR$ complexes (M = Ru or Os), where the α-proton resonance is in the range 16–20 ppm, a *very* distinctive region. The ^{1}H δ value for R = Ph is already slightly downfield (8.4 ppm). For this purpose, we synthesized the *p*-nitrophenyl analog and found that this electron-withdrawing substituent moves the $C_\alpha H$ δ value an additional 1.0 ppm downfield. This supports the reality of the carbenoid/carbanion resonance contributor **B**, albeit to a small extent, as judged by ^{1}H NMR. Participation by structure **B** is perhaps also the reason why the β-aryl vinyl complexes have low energy electronic transitions: they are violet.

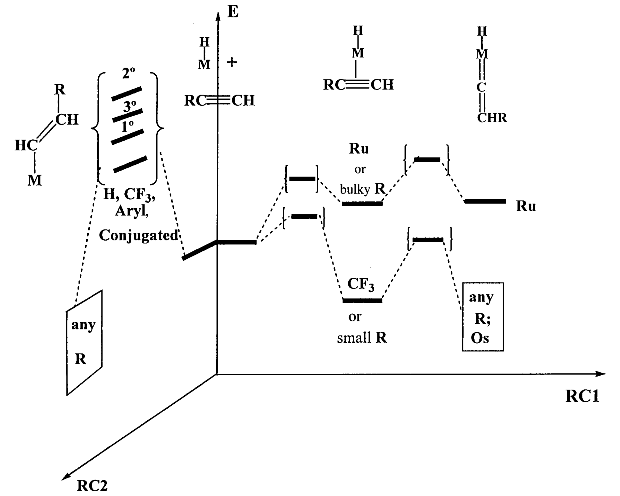


Fig. 5 Schematic 2-D representation of the paths that connect alkyne adducts to vinylidene and vinyl products. Energies are represented qualitatively to indicate the experimental relative rates of reactions. The relative activation energies for vinyl formation have been suggested by the experimental results.

Table 2 ^{1}H NMR chemical shifts of H_α and H_β for complexes Os(*E*-CH=CHR)Cl(CO)(P^{i}Pr$_3$)$_2$ in d_8-toluene

R	H_α	H_β	T/°C
Me	6.55	4.59	0
^{t}Bu	6.60	4.40	+20
1-Methylbutyl[a]	6.72	4.52	+20
H	7.51	4.55	+20
1-Cyclohexenyl[a]	7.63	5.83	+20
SiMe$_3$	8.12	5.10	+20
p-$CH_3C_6H_4$	8.40	5.86	−60
Ph	8.42	5.80	−60
CF_3[b]	8.80	4.76	+20
p-$O_2NC_6H_4$[a]	9.41	5.87	+20

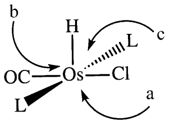
[a] In C_6D_6. [b] In CD_2Cl_2.

While the mechanism of isomerization from η^2-acetylene to vinylidene remains uncertain in the reactions reported here, the idea that it is *not* unimolecular, but rather base catalyzed, seems less likely in these reactions of uncharged complexes in nonpolar solvent where the potential for adventitious base (*i.e.*, water or counterion) seems lacking.

The results studying the influence of the R group identity in RCCH has revealed some surprising and potentially confusing side reactions, in particular the pre-equilibrium scrambling of OsH and RCCD or OsD with RCCH as events prior to (*i.e.*, faster than) formation of even the vinylidene isomer (*vis-à-vis* the final vinyl product). This reaction only becomes detectable (and thus potentially confusing) when the vinylidene or vinyl formation is relatively slow; in the case of the fast production of OsCH=CHPh, the H/D isotope scrambling is ineffectual and thus the isotope experiment successfully reveals that H from Os is delivered exclusively to the vinyl C_β.

The R group dependence study has also revealed the following. (i) The fastest reaction of OsHCl(CO)L$_2$ with terminal alkynes is along the 'least motion' path where the alkyne binds to the free coordination site. This demands minimal reorganization of the metal coordination geometry, but it puts the alkyne in the site *trans* to hydride. However, at this site, the formation constant is not high. This is evident from the examples [R = H, CH$_3$, ^{t}Bu, SiMe$_3$, CH(Me)C$_3$H$_7$] in which the η^2-alkyne adduct mol fraction is demonstrably higher at low temperature, where a small negative $\Delta H°$ will be less offset by a negative $\Delta S°$. Moreover, there will be cases where vinyl formation is slow, but η^2-alkyne binding constants are so small that such species are not detected. (ii) In spite of numerous observations of η^2-alkyne and vinylidene complexes, it is premature to call these intermediates for formation of the vinyl product: we have no firm connection between these alkyne and vinylidene species and the vinyl products. This conclusion is forced on us since the η^2-alkyne and vinylidene species have hydride *trans* to the alkyne-derived ligand, and thus seem no closer to uniting Os–H with RCCH moieties than are the separated molecules OsHCl(CO)L$_2$ and RCCH. An attempt to show an inverse phosphine dependence of the isomerization of vinylidene to vinyl showed *none*, and this could be interpreted as follows. (iii) Certain of the D labeling studies show that the η^2-acetylene species with alkyne *trans* to

H, and the derived vinylidene, are mechanistic dead ends and that the real mechanism to the vinyl product occurs by bimolecular attack, see **14**, of alkyne in quadrant c, rather than b,[32] and leads to the product with no detectable intermediates.



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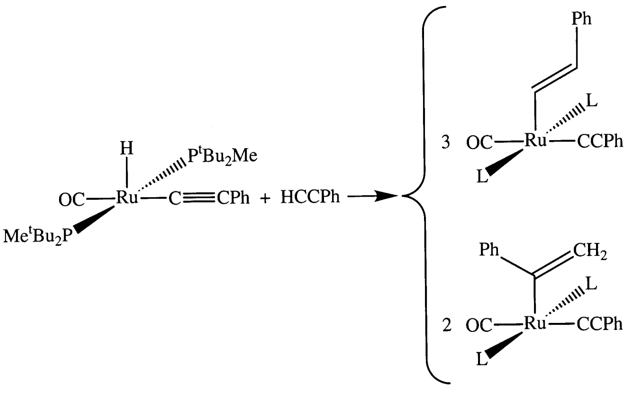
The conclusions from this work fall in two general categories. The first simply relates to the behavior of a terminal acetylene with an unsaturated metal center; this follows since the LUMO of $MHCl(CO)L_2$ is remote from the hydride. It is observed that alkyne coordination is generally weak and rapidly reversible since it occurs *trans* to H and is prevented by steric effects. In addition, replacing Os with Ru reduces the alkyne binding energy even more. With an activation energy only slightly higher than alkyne loss, isomerization to a vinylidene occurs.

The second category of conclusion relates to the reaction of the M–H bond with the C≡C bond. The weight of evidence here is that this, the slowest reaction observed, shows no direct dependence on the species discussed above, where the hydride is *trans* to alkyne or vinylidene. The deuterium labeling experiments, when they are not compromised by scrambling side reactions, show that the vinylidene complex is *not* an intermediate to forming the vinyl group. Since the vinylidene/η^2-alkyne reaction can be reversible,[33] this is not a problem. Apparently there is no facile intramolecular way for hydride to migrate to become *cis* to the η^2-alkyne or the vinylidene ligand.

The fact that *saturated* $RuHCl(CO)_2(PMe_2Ph)_2$ only reacts[34] with phenylacetylene slowly (over 5 days at 25 °C) can be interpreted as reflecting the greater facility of 'outer sphere' attack of alkyne on the hydride ligand when the chloride *can* migrate to the open coordination site of $RuHCl(CO)L_2$. Indeed, calculations show that the bending to increase the H–Ru–Cl angle of $RuHCl(CO)(PH_3)_2$ costs very little energy (<10 kcal mol^{-1}), while increasing the H–Ru–CO angle is very difficult (*ca.* 60 kcal mol^{-1}).[32]

The reactions of $MHX(CO)L_2$ with RC≡CR′ are clearly very sensitive to changes in M, (Ru, Os), X (F, Cl, I), L (P^iPr_3 or P^tBu_2Me) and R/R′ (one being hydrogen, or not). This speaks for a potential energy surface with numerous *competing* pathways (*e.g.*, directions of addition to the RC≡CR′ bond and the identity of the final product) and thus numerous activation energies, which are of similar magnitude but whose inequalities can be reversed by a change of reactant in a way that might ordinarily be considered to be 'small'. The absence of any detectable $M(CR{=}CH_2)$ product in the results we report here may originate from steric control in bringing the bulkier RC end of the alkyne to the crowded (two P^iPr_3) small H–M–Cl angle. However, a somewhat distantly related exception is eqn. (9),[24] which serves to reinforce the idea that quite small changes in the reagents can alter the activation energies to make certain products absent, or to cause them to appear in the system studied here. In an even more relevant example, $RuHF(CO)(P^tBu_2Me)_2$ adds to PhC≡CH with *both* regiochemistries.

In a reaction seemingly immune to steric suppression, MeC≡CMe reacts with $RuHI(CO)(P^tBu_2Me)_2$ (but *not* the F, Cl, $OSiPh_3$, OCH_2CF_3 and OPh analogs) to give $Ru(CMeCHMe)(CO)I(P^tBu_2Me)_2$.[24] *However*, this reaction is much slower (24 h to completion) than those of $RuHCl(CO)(P^iPr_3)_2$ with terminal alkynes; moreover, no intermediate is detected (^1H and ^{31}P NMR), at either 25 or −80 °C. Perhaps this reaction proceeds *via* I^- dissociation.



(9)

Conclusions

The combined experimental and theoretical approach to the understanding of the reaction path for vinyl formation from $MHCl(CO)L_2$ and primary alkynes is complicated because the reaction often begins with frustrating 'dead end' reactions. However, answers on several aspects of the reaction have been unequivocally obtained. The DFT calculations have shown that the unsaturated vinyl complex is a deep thermodynamic well for Os and Ru. This suggests that all alkynes that have the ability (*i.e.*, if steric factors permit) to interact with the unsaturated Os or Ru hydride complex would form the vinyl product although at different rates. The experimental results have shown that the rate of reaction varies according to primary > tertiary > secondary and electron-withdrawing > electron-donating. Calculations also show that the binding energy of the alkyne is not very large (and considerably smaller for Ru than for Os). This suggests that the alkyne adduct may not be observed, depending on the nature of the substituent, and can, in particular, be prevented by steric factors (not included in the model calculations). Experimental results confirm this point. The calculations and experimental results show that the alkyne coordinates *trans* to the hydride, which is certainly a location poorly suited to reaction of the M–H bond with the alkyne. The vinylidene complexes are calculated to be very close in energy to the best alkyne adduct and significantly above the vinyl product. This vinylidene product may thus not be observed if the substituents and steric effects play any destabilizing role. When scrambling of the isotopic label does not confuse the situation, the fate of the label shows that the vinylidene cannot be on the path to form the vinyl product. A new mechanism for formation of the vinyl product was found through the computational study. It involves coordination of the alkyne to M *cis* to the hydride and in the H–M–Cl quadrant. This addition leads to an alkyne adduct that is at 5 kcal mol^{-1} higher energy than the most stable alkyne adduct. This less stable isomer cannot be observed experimentally since it transforms, by insertion of the alkyne into the M–H bond, into a vinyl product *via* a transition state at very moderate energy above the alkyne adduct. The vinyl product thus formed should transform with no expected activation energy into the considerably more stable vinyl product. This route was found to be distinct from that of the formation of vinylidene, which is formed from least motion addition of the alkyne *trans* to H, followed by a 1,2 shift of H in the coordinated alkyne. Thus, the reactivity of the unsaturated $MHCl(CO)L_2$ fragments cannot be understood through a single reactivity channel.

Experimental

All reactions and manipulations were conducted using standard Schlenk and glovebox techniques under prepurified argon. Solvents were dried and distilled under argon, and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred and stored in a glovebox. ^{1}H, ^{13}C, ^{31}P and ^{2}H NMR spectra were recorded on Varian Gemini 300 and Inova 400 instruments. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{2}H, ^{13}C) or external H_3PO_4 (^{31}P). OsHCl(CO)(P^{i}Pr$_3$)$_2$[2] and OsDCl(CO)(P^{i}Pr$_3$)$_2$[1] were synthesized according to published procedures. Liquid reagents were freeze–pump–thaw degassed; gaseous reagents were used as received from the manufacturers.

Variable-temperature NMR experiments

In a general technique, NMR tubes were charged with OsHCl(CO)(P^{i}Pr$_3$)$_2$ (15 mg, 0.026 mmol) and d$_8$-toluene (0.5 mL). These solutions were degassed by three freeze–pump–thaw cycles, then the reaction tubes were cooled to −196 °C and gaseous alkynes were introduced at 1 atm pressure; liquid alkynes (2 : 1 molar ratio alkyne : osmium complex was used) were vacuum transferred into reaction NMR tubes. After the tubes had been shaken several times to allow mixing of the reagents, they were immediately transferred to a pre-cooled NMR probe. Detailed observations and spectral data follow.

Reactions

Reaction with HCCH. The reaction solution turned colorless immediately upon mixing at −60 °C. Complete conversion to the η^2-alkyne adduct OsHCl(HCCH)(CO)(P^{i}Pr$_3$)$_2$ was observed by NMR spectroscopy: ^{1}H NMR (C$_7$D$_8$, −60 °C) δ: −4.17 (t, J_{HP} = 20, Os–H), 1.10 (br, PCCH$_3$), 2.74 (br, PCH), 6.46 (apparent t, J_{HP} = 8.4 Hz, η^2-HCCH); ^{31}P{^{1}H} NMR (C$_7$D$_8$, −60 °C): δ 20.7. ^{13}C{^{1}H} NMR (C$_7$D$_8$, −60 °C): δ 75.8 (br, η^2-HCCH). Upon warming to −20 °C, the triplet at 6.55 ppm in the ^{1}H NMR spectrum corresponding to the adduct was transformed to a broad peak that disappeared completely at +20 °C. The only product observed at +20 °C was Os(CH=CH$_2$)(CO)Cl(P^{i}Pr$_3$)$_2$: ^{1}H NMR (C$_7$D$_8$, 20 °C): δ 1.18, 1.21 (dvt, J_{HH} = 6, J_{HH} = 12.4, PCCH$_3$), 2.80 (m, PCH), 4.55 [d, J_{HH} = 13.6, OsCH=CH*H* (*trans*)], 5.14 [m, OsCH=C*H*H (*cis*)], 7.51 (dd, J_{HH} = 6.4, J_{HH} = 13.6 Hz, OsC*H*=CH$_2$). ^{31}P{^{1}H} NMR (C$_7$D$_8$, +20 °C): δ 23.8 (s).

Reaction with propyne. The reaction solution turned colorless immediately upon mixing at −60 °C. NMR spectroscopy at this temperature indicated formation of the η^2-adduct OsHCl(MeCCH)(CO)(P^{i}Pr$_3$)$_2$ (70%) and the vinylidene complex OsH(=C=CHMe)Cl(CO)(P^{i}Pr$_3$)$_2$ (30%). Based on the number of triplets in the hydride region of the ^{1}H NMR spectrum, the η^2-adduct is present as a mixture of two isomers. ^{1}H NMR (C$_7$D$_8$, −60 °C): δ −4.86 and −4.62 [t, t, J_{PH} = 28 and 26, Os*H*(=C=CHMe)Cl(CO)(P^{i}Pr$_3$)$_2$ isomers], −4.28 and −4.21 [t, t, J_{PH} = 26 and 27 Hz, Os*H*Cl(MeCCH)(CO)(P^{i}Pr$_3$)$_2$ conformers], 1.10 (m, br, PCCH$_3$), 2.00 (br, =C=CHMe), 2.70 (m, br, PCH), 2.94 (br, =C=C*H*Me), 5.47 and 6.38 (br, m, η^2-MeCC*H*). ^{31}P{^{1}H} NMR (C$_7$D$_8$, 60 °C): δ 46.0 [br, OsH(=C=CHMe)Cl(CO)(P^{i}Pr$_3$)$_2$ isomers], 20.8 and 20.4 [br, OsHCl(MeCCH)(CO)(P^{i}Pr$_3$)$_2$ conformers]. At 0 °C, the amount of adduct in the reaction mixture decreased to 13% and the corresponding ^{31}P NMR peaks became very broad; the conformers are no longer resolved, while the amount of vinylidene increased to 42% with no isomers resolved. The vinyl complex Os(*E*-CH=CHMe)Cl(CO)(P^{i}Pr$_3$)$_2$ accounts for 45% of the reaction mixture: ^{1}H NMR (C$_7$D$_8$, 0 °C): δ 1.11 (m, br, PCCH$_3$), 1.98 (m, br, Os-*E*-CH=CH*Me*), 2.71 (m, br, PCH), 4.50 (m, br, Os-*E*-CH=C*H*Me), 6.55 (m, br, Os-*E*-C*H*=CHMe). ^{31}P{^{1}H} NMR (C$_7$D$_8$, 0 °C): δ 22.7. Signals for the adduct disappear completely at +20 °C.

Reactions with phenylacetylene and *p*-tolylacetylene. The reaction solutions turned violet immediately upon mixing at −60 °C, giving complete conversion to the vinyl complexes. Os(*E*-CH=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$: ^{1}H NMR (C$_7$D$_8$, −60 °C): δ 1.10 (m, PCCH$_3$), 2.65 (m, PCH), 5.80 (d, J_{HH} = 12.4, Os-*E*-CH=C*H*Ph), 6.84–7.28 (m, Os-*E*-CH=CH*Ph*), 8.42 (d, J_{HH} = 12.4 Hz, Os-*E*-C*H*=CHPh); ^{31}P{^{1}H} NMR (C$_7$D$_8$, −60 °C): δ 24.4. Os(*E*-CH=CH-*p*-C$_6$H$_4$CH$_3$)Cl(CO)(P^{i}Pr$_3$)$_2$: ^{1}H NMR (C$_7$D$_8$, −60 °C): δ 1.10 (m, PCCH$_3$), 2.08 (s, Os-*E*-CH=CH-*p*-C$_6$H$_4$C*H*$_3$), 2.68 (m, PCH), 5.86 (d, J_{HH} = 13.5,Os-*E*-CH=C*H*-*p*-C$_6$H$_4$CH$_3$), 6.72 and 7.30 (each a d, J_{HH} = 8.1,Os-*E*-CH=CH-*p*-C$_6$*H*$_4$CH$_3$), 8.40 (d, J_{HH} = 13.5Hz, Os-*E*-C*H*=CH-*p*-C$_6$H$_4$CH$_3$); ^{31}P{^{1}H} NMR (C$_7$D$_8$, −60 °C): δ 24.8.

Reactions with 2-butyne and trimethylsilyl(phenyl)acetylene. No color change was observed upon mixing at −60 °C or at room temperature. NMR spectroscopy showed only the presence of OsHCl(CO)(P^{i}Pr$_3$)$_2$ and the free alkynes MeCCMe or Me$_3$SiCCPh at temperatures between −60 and +20 °C, even after 24 h at 20 °C.

Reaction with *tert*-butylacetylene. The reaction solution turned colorless immediately upon mixing at −60 °C. NMR data at −60 °C showed the presence of the vinylidene complex OsHCl(=C=CH^{t}Bu)(CO)(P^{i}Pr$_3$)$_2$. ^{1}H NMR (C$_7$D$_8$, −60 °C): δ −5.22 (t, J_{PH} = 29.2 Hz, OsH), 1.10 (br, PCCH$_3$), 1.12 (br, =C=CH^t*Bu*), 2.43 (br, PCH), 2.90 (m, =C=C*H*^{t}Bu); ^{31}P{^{1}H} NMR (C$_7$D$_8$, 60 °C): δ 40.4 [OsHCl(=C=CH^{t}Bu)(CO)(P^{i}Pr$_3$)$_2$], 44.7 [OsHCl(CO)(P^{i}Pr$_3$)$_2$] and 20.0 [br, OsHCl(η^2-^{t}BuCCH)(CO)(P^{i}Pr$_3$)$_2$ in equilibrium with OsHCl(CO)(P^{i}Pr$_3$)$_2$]. The presence of the vinylidene complex as a major product at low temperature was additionally confirmed by observation of the characteristic signature of the vinylidene ligand in ^{13}C{^{1}H} NMR (C$_7$D$_8$, −40 °C): δ 336.3 (br, Os=*C*=CH^{t}Bu), 130.0 (br, Os=C–*C*H^{t}Bu), the vinylidene : η^2-adduct ratio at −60 °C is *ca.* 1 : 1 (from ^{31}P{^{1}H} NMR data). When the temperature was raised, the position of the peak at 44.7 ppm moved toward the chemical shift corresponding to OsHCl(CO)(P^{i}Pr$_3$)$_2$ (measured independently at −40 °C: 46.1 ppm, −20 °C: 47.4 ppm, +20 °C: 48.0 ppm), indicating a shift of the equilibrium toward the starting material. The ^{31}P{^{1}H} NMR spectrum at +20 °C showed only traces of OsHCl(CO)(P^{i}Pr$_3$)$_2$ and OsHCl(η^2-^{t}BuCCH)(CO)(P^{i}Pr$_3$)$_2$, indicating complete conversion to the vinylidene complex. After 16 h at room temperature, the reaction mixture had changed color to violet; the NMR data showed the vinyl complex Os(*E*-CH=CH^{t}Bu)Cl(CO)(P^{i}Pr$_3$)$_2$ as the only product: ^{1}H NMR (C$_7$D$_8$, 20 °C): δ 1.06 (s, –CH=CH^t*Bu*), 1.12 (m, PCCH$_3$), 2.73 (m, PCH), 4.40 (d, J_{HH} = 12.4; Os-*E*-CH=C*H*^{t}Bu), 6.60 (d, J_{HH} = 12.4 Hz, Os-*E*-C*H*=CH^{t}Bu); ^{31}P{^{1}H}NMR (C$_7$D$_8$, +20 °C): δ 22.5.

Reaction with benzylacetylene. The reaction solution turned violet immediately upon mixing at +20 °C. Complete conversion to Os(*E*-CH=CHCH$_2$Ph)Cl(CO)(P^{i}Pr$_3$)$_2$ was observed after 15 min by NMR. ^{1}H NMR (C$_6$D$_6$, +20 °C): δ 1.21 (m, PCCH$_3$), 2.80 (m, PCH), 3.62 (br, –C*H*$_2$Ph), 4.88 (m, Os–CH=C*H*), 7.02–7.60 (m, –C$_6$H$_5$), 7.80 (m, Os–C*H*=). ^{31}P{^{1}H} NMR (C$_7$D$_8$, +20 °C): δ 23.4.

Reaction with trimethylsilylacetylene. The observations for this reaction are similar to those for the reaction with ^{t}BuCCH, however: (i) at −60 °C the equilibrium between the hydrido chloride complex and the η^2-adduct is shifted more toward the adduct than in the case of ^{t}BuCCH, which is indicated by the position of an equilibrium peak for OsHCl(CO)(P^{i}Pr$_3$)$_2$ at 44.0 ppm in the ^{31}P{^{1}H} NMR spectrum; (ii) upon warming, this equilibrium shifts faster toward the five-coordinate starting material than in the previous case, which is indicated by the positions of the same peak: 47.7

ppm at $-40\,°C$, 48.8 ppm at $-20\,°C$ and complete disappearance of this peak at $0\,°C$ and higher temperatures. The vinylidene complex $\mathrm{OsH({=}C{=}CHSiMe_3)(CO)(P^iPr_3)_2}$ is formed at $-60\,°C$ and is the only product at $0\,°C$ and higher temperatures: ^{1}H NMR (C_7D_8, $-60\,°C$): δ -5.75 (t, $J_{PH} = 30$, OsH), 0.24 (s, $\mathrm{SiMe_3}$), 1.10 (m, $\mathrm{PCCH_3}$), 2.55 (br, PCH), 2.79 (t, $J_{PH} = 6$ Hz, $\mathrm{{=}C{=}C\mathit{H}SiMe_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_7D_8, $-60\,°C$): δ 40.4. This vinylidene complex is longer-lived than that formed in the reaction with $\mathrm{^tBuCCH}$: after 16 h, the reaction mixture contained 50% of the vinylidene complex and 50% of the vinyl complex $\mathrm{Os(\mathit{E}\text{-}CH{=}CHSiMe_3)Cl(CO)(P^iPr_3)_2}$: ^{1}H NMR ($C_7D_8$, $+20\,°C$): δ 0.23 (s, $\mathrm{SiMe_3}$), 1.23 (m, $\mathrm{PCCH_3}$), 2.80 (m, PCH), 5.10 (m, Os-E-CH=CHSiMe$_3$), 8.12 (d, $J_{HH} = 13$ Hz, Os-E-CH=CHSiMe$_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (C_7D_8, $+20\,°C$): δ 23.9. After 72 h, the vinylidene complex was completely converted to the vinyl complex (based on disappearance of the 40.4 ppm signal from the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum).

Reaction with 3,3,3-trifluoropropyne. The reaction solution turned colorless immediately upon mixing at $-60\,°C$. According to the NMR data, the only product formed at $-60\,°C$ is the adduct $\mathrm{OsHCl(\eta^2\text{-}CF_3CCH)(CO)(P^iPr_3)_2}$. ^{1}H NMR ($C_7D_8$, $-60\,°C$): δ -3.51 (t, $J_{PH} = 25$ Hz, Os–H), 1.01 (br, $\mathrm{PCCH_3}$), 2.98 (br, PCH), 7.61 (m, η^2-$\mathrm{CF_3CC\mathit{H}}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.5 Hz, C_7D_8, $-60\,°C$): δ 26.18, 25.40, 20.80, 20.02 (AB); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (C_7D_8, $-60\,°C$): δ 99.4 (m, $\mathrm{\mathit{C}F_3CCH}$), 94.4 ($\mathrm{CF_3C\mathit{C}H}$), 87.7 ($\mathrm{CF_3\mathit{C}CH}$). After 10 h at room temperature, the solution turned brown and the only product observed by NMR was the vinyl complex $\mathrm{Os(\mathit{E}\text{-}CH{=}CHCF_3)Cl(CO)(P^iPr_3)_2}$. ^{1}H NMR ($CD_2Cl_2$, $+20\,°C$): δ 1.30 (m, $\mathrm{PCCH_3}$), 2.94 (m, PCH), 4.76 (m, Os-E-CH=CHCF$_3$), 8.80 (d, $J_{HH} = 14.7$ Hz, Os-E-CH=CHCF$_3$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (C_7D_8, $+20\,°C$): δ 27.3.

Reaction with 3-methyl-1-Hexyne. The reaction solution turned brown immediately upon mixing at room temperature. After 10 min, NMR spectroscopy indicated the presence of complexes $\mathrm{OsH[{=}C{=}CHCH(CH_3)CH_2CH_2CH_3]Cl(CO)(P^iPr_3)_2}$ and $\mathrm{Os[\mathit{E}\text{-}CH{=}CHCH(CH_3)CH_2CH_2CH_3]Cl(CO)(P^iPr_3)_2}$ as the two products of the reaction. The vinylidene : vinyl complex ratio after 10 min was 9 : 1, after 18 h it was 7 : 3, after 80 h it was 1 : 7 (from $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectral data). ^{1}H NMR (C_6D_6, $+20\,°C$): δ -4.70 (t, $J_{PH} = 30$, OsH), 0.8 (m, $\mathrm{C\mathit{H}_3CH_2}$–), 1.03 (m, $\mathrm{C\mathit{H}_3CH}$), 1.15–1.70 (m, $\mathrm{CH_3C\mathit{H}_2C\mathit{H}_2}$–, $\mathrm{PCCH_3}$), 2.40–2.55 (m, $\mathrm{CH_3C\mathit{H}}$), 2.56 {m, PCH of $\mathrm{OsH[{=}C{=}CHCH(CH_3)CH_2CH_2CH_3]Cl(CO)(P^iPr_3)_2}$}, 2.85 {m, PCH of $\mathrm{Os[\mathit{E}\text{-}CH{=}CHCH(CH_3)CH_2CH_2CH_3]Cl(CO)(P^iPr_3)_2}$}, 2.96 [m, $\mathrm{Os{=}C{=}C\mathit{H}CH(CH_3)CH_2CH_2CH_3}$], 4.52 [m, Os-$E$-CH=C$H$CH(CH$_3$)CH$_2CH_2CH_3$], 6.72 [d, $J_{HH} = 13.6$ Hz, Os-E-CH=CHCH(CH$_3$)CH$_2$CH$_2$CH$_3$]; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_7D_8, $+20\,°C$): δ 22.6, 22.7, {$\mathrm{Os[\mathit{E}\text{-}CH{=}CHCH(CH_3)CH_2CH_2CH_3]Cl(CO)(P^iPr_3)_2}$, the two peaks are due to the inequivalence of the two phosphorus atoms resulting from the presence of a chiral center in the vinyl fragment}, 45.0 {$\mathrm{OsH[{=}C{=}CHCH(CH_3)CH_2CH_2CH_3]Cl(CO)(P^iPr_3)_2}$}.

Variable-temperature study with $\mathrm{OsHCl(CO)L_2}$: alkyne ratio of 1 : 1. The reaction solution did not change color upon mixing at $-60\,°C$. Five percent conversion to the η^2-adduct $\mathrm{OsHCl[\eta^2\text{-}HCCCH(CH_3)(CH_2)_2CH_3](CO)(P^iPr_3)_2}$ was indicated by a new peak in the ^{31}P NMR spectrum at 23.3 ppm. There were also two new broad ^{1}H NMR peaks at -17.00 and 5.63 ppm, corresponding to the hydride and to the η^2-alkyne hydrogen, respectively, which is evidence for an equilibrium between $\mathrm{OsHCl(CO)(P^iPr_3)_2}$ and the η^2-adduct. At $-40\,°C$, along with these two complexes, ^{1}H and ^{31}P NMR spectra showed the presence of a trace amount of the vinylidene complex $\mathrm{OsHCl(CO)[{=}C{=}CHCH(CH_3)(CH_2)_2CH_3](P^iPr_3)_2}$. At $-20\,°C$, the amount of the vinylidene complex in the mixture grew to 5% and the formation of a trace amount of the vinyl complex $\mathrm{Os[\mathit{E}\text{-}CH{=}CHCH(CH_3)(CH_2)_2CH_3](CO)Cl(P^iPr_3)_2}$ was observed. At $0\,°C$, the adduct signals were no longer seen in the ^{1}H NMR spectrum, although the ^{31}P NMR spectrum showed an extremely broad signal close to the chemical shift of $\mathrm{OsHCl(CO)(P^iPr_3)_2}$, indicating that the exchange process involving the adduct was still present; the vinylidene and the vinyl contents grew to 18 and 4%, respectively. At $+20\,°C$, the vinylidene and the vinyl complex contents were 22 and 7%, respectively. After 15 h at $+20\,°C$, these amounts changed to 45 and 35%; the rest of the mixture was the unreacted starting material in equilibrium with the adduct.

Reaction with 1-ethynylcyclohexene. The reaction solution turned violet immediately upon mixing at $+20\,°C$. After 10 min, NMR spectroscopy showed the presence of the vinyl complex $\mathrm{Os(\mathit{E}\text{-}CH{=}CH\text{–}C_6H_9)(CO)Cl(P^iPr_3)_2}$ as the only product. ^{1}H NMR (C_6D_6, $+20\,°C$): δ 1.20 (m, $\mathrm{PCCH_3}$), 1.44, 1.54, 1.70 (m, –CH$_2$– of cyclohexene ring aliphatic hydrogens), 2.82 (m, PCH), 5.35 (Os–CH=CH–C=CH–), 5.83 (d, $J_{HH} =$ 15.0, Os–CH=CH–), 7.63 (d, $J_{HH} = 12.6$ Hz, Os–CH=); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_6D_6, $+20\,°C$): δ 23.1 (s).

Reaction with *p*-nitrophenylacetylene. The reaction solution turned violet immediately upon mixing at $+20\,°C$. NMR spectroscopy showed complete conversion to $\mathrm{Os(\mathit{E}\text{-}CH{=}CH\text{–}C_6H_4NO_2)Cl(CO)(P^iPr_3)_2}$. ^{1}H NMR ($C_6D_6$, $+20\,°C$): δ 1.18 (m, $\mathrm{PCCH_3}$), 2.72 (br, PCH), 5.87 (m, Os–CH=CH–), 6.92–7.19 (m, $-\mathrm{C_6H_4NO_2}$), 9.41 (d, $J_{HH} = 12.6$ Hz, Os–CH=); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_6D_6, $+20\,°C$): δ 31.4.

Reaction of $\mathbf{RuHCl(CO)(P^tBu_2Me)_2}$ with 3-methyl-1-hexyne. The reaction solution became red several hours after mixing at $+20\,°C$. Complete conversion to $\mathrm{Ru[\mathit{E}\text{-}CH{=}CH\text{–}CH(Me)C_3H_7]Cl(CO)(P^tBu_2Me)_2}$ was observed after 16 h by NMR. ^{1}H NMR (C_6D_6, $+20\,°C$): δ 0.81 (t, $J_{HH} = 6.9$, CH_3–CH$_2$–), 1.04 (d, $J_{HH} = 6.0$, CH_3–CH–), 1.20–1.42 (m, $\mathrm{CH_3C\mathit{H}_2C\mathit{H}_2}$, $\mathrm{CCH_3}$, $\mathrm{PCH_3}$), 2.23–2.33 (m, $\mathrm{CH_3C\mathit{H}}$–), 4.90 (m, Ru–CH=CH–) 7.34 (d, $J_{HH} = 12.0$ Hz, Ru–CH=); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_6D_6, $+20\,°C$): 34.7.

Reaction of $\mathbf{RuHCl(CO)(P^tBu_2Me)_2}$ with propyne. The reaction solution did not change color immediately upon mixing at $-60\,°C$. NMR spectroscopy showed no reaction at this temperature. Upon warming to $-40\,°C$, 7% conversion to $\mathrm{Ru(\mathit{E}\text{-}CH{=}CHMe)Cl(CO)(P^tBu_2Me)_2}$ was observed. At $0\,°C$, it grew to 52%. Complete conversion to the vinyl complex occured within 1 h at $+20\,°C$. ^{1}H NMR (C_7D_8, $0\,°C$): δ 1.15–1.32 (m, $\mathrm{P^tBu}$, $\mathrm{PCH_3}$), 1.88 (d, $J_{HH} = 6.6$, Ru–CH=CHMe), 4.91 (m, Ru–CH=CH–), 7.24 (d, $J_{HH} = 12.9$ Hz, Ru–CH=); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_7D_8, $0\,°C$): δ 34.6.

Reaction of $\mathbf{RuHCl(CO)(P^tBu_2Me)_2}$ with 1-ethynylcyclohexene. The reaction solution turned red immediately upon mixing at $+20\,°C$. NMR spectra showed 99% conversion to the vinyl complex $\mathrm{Ru(\mathit{E}\text{-}CH{=}CHC_6H_9)Cl(CO)(P^tBu_2Me)_2}$ after 10 min at $+20\,°C$. ^{1}H NMR (C_6D_6, $+20\,°C$): δ 1.19 (vt, $\mathrm{P^tBu}$), 1.27 (vt, $\mathrm{P^tBu}$), 1.36 (vt, $\mathrm{PCH_3}$), 1.42, 1.55, 1.69 (m, –CH$_2$– of the cyclohexene ring), 5.48 (br, Ru–CH=CH–C=CH–), 5.99 (d, $J_{HH} = 13.8$, Ru–CH=CH–), 8.09 (d, $J_{HH} = 12.9$ Hz, Ru–CH=); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (C_6D_6, $+20\,°C$): δ 35.1.

Reaction of $\mathbf{RuHCl(CO)(P^tBu_2Me)_2}$ with trimethylsilylacetylene. The reaction solution did not change color immediately upon mixing at $+20\,°C$. NMR spectroscopy showed no reaction after 30 min at $+20\,°C$. After heating the reaction mixture at +70 °C for 3 h, 75% conversion to the vinyl complex Ru(E-CH=CHSiMe$_3$)Cl(CO)(P^{t}Bu$_2$Me)$_2$ was observed. ^{1}H NMR (C$_6$D$_6$, +20 °C): δ 0.13 (–SiMe$_3$), 1.16 (vt, P^{t}Bu), 1.25 (vt, P^{t}Bu), 1.34 (vt, PMe), 5.54 (m, Ru–CH=CH–), 8.80 (d, J_{HH} = 13.5 Hz, Ru–CH=): ^{31}P{^{1}H} NMR (C$_6$D$_6$, +20 °C): 35.8.

Mechanistic study using OsDCl(CO)(P^{i}Pr$_3$)$_2$

OsDCl(CO)(P^{i}Pr$_3$)$_2$ (18 mg, 0.031 mmol) in C$_6$D$_6$ was combined with a deficiency of ^{t}BuCCH (2.5 μL, 0.020 mmol) in an NMR tube at room temperature and the progress of the reaction was followed by ^{1}H, ^{31}P{^{1}H} and ^{2}H{^{1}H} NMR spectroscopy. After 10 min, the ^{2}H{^{1}H} spectrum showed the presence of free ^{t}BuCCD, indicated by the peak at 1.85 ppm. After 60 min, ^{2}H{^{1}H}NMR showed the presence of deuterated complexes OsD(=C=CH^{t}Bu)Cl(CO)(P^{i}Pr$_3$)$_2$ (m, −5.0 ppm), OsH(=C=CD^{t}Bu)Cl(CO)(P^{i}Pr$_3$)$_2$ (m, 3.0 ppm), Os(E-CH=CD^{t}Bu)(CO)Cl(P^{i}Pr$_3$)$_2$ (4.5 ppm) and Os(E-CD=CH^{t}Bu)(CO)Cl(P^{i}Pr$_3$)$_2$ (6.8 ppm); the protons on Os and the vinyl carbons indicated above were observed concurrently by ^{1}H NMR.

Test of phosphine dissociation mechanistic hypothesis

P^{i}Pr$_3$ was injected into reaction tubes containing 15 mg OsHCl(CO)(P^{i}Pr$_3$)$_2$ in C$_6$D$_6$ (2 : 1, 5 : 1 and 10 : 1 molar ratios of these reagents were used) at room temperature. Then, 2 equiv. of ^{t}BuCCH or Me$_3$SiCCH were introduced into the two separate NMR tubes and the progress of the reaction was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. No suppression of the qualitative rate of vinylidene and vinyl complex formation, in comparison to the experiments without P^{i}Pr$_3$ present, was observed in any of these cases.

Computational details

The calculations were carried out using the GAUSSIAN 98 set of programs[35] within the framework of DFT at the B3PW91 level.[36,37] LANL2DZ effective core potentials (quasi-relativistic for the metal center) were used to replace the 28 innermost electrons of Ru and the 60 innermost electrons of Os,[38] as well as the 10 core electrons of Cl and P.[39] The associated double ξ basis set[38,39] was used and was augmented by a d polarization function for Cl and P.[40] The other atoms were represented by a 6-31(d,p) basis set (5d).[41] Full geometry optimization was performed with no symmetry restriction. The nature of extrema as transition states was assigned through analytical calculation of frequencies. To verify that transition states led to products, the structure of the transition state was perturbed along the normal mode of the imaginary frequency and optimization of the geometry was carried out.

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