Facile C(sp²)/O₂CR bond cleavage by Ru or Os†

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$[RuHClL_2]_2$, $L = P^iPr_3$, reacts with $H_2C=CH(O_2CR)$ ($R = CH_3$, CF_3, C_6H_5) during mixing at 20 °C, *via* two observable intermediates, to give $RuCl(O_2CR)(CHMe)L_2$; this carbene complex then redistributes the Cl and O_2CR groups. Vinyl tosylate gives $RuCl(OTs)(CHMe)L_2$ already at −60 °C. Vinyl chloroformate, $H_2C=CH(O_2CCl)$ reacts rapidly with $[RuHClL_2]_2$ to give the olefin metathesis catalyst $RuCl_2(CHMe)L_2$ and CO_2. $Os(H)_3ClL_2$ ($L = P^iPr_3$ or P^tBu_2Me) reacts with vinyl esters $H_2C=CHE$ ($E = O_2CR$) to form first an η^2-olefin adduct. This is followed by C/O bond cleavage, giving the *carbyne* $OsHCl(O_2CCF_3)(CMe)L_2$. Vinyl chloroformate and $Os(H)_3ClL_2$ gives $OsHCl_2(CMe)L_2$ and CO_2. $RuHCl(PPh_3)_3$ reacts with vinyl chloroformate, *via* $RuCl(O_2CCl)(CHMe)(PPh_3)_2$, to give $RuCl_2(CHMe)(PPh_3)_2$ while $OsHCl(PPh_3)_3$ reacts analogously, through observable $OsCl_2(CHMe)(PPh_3)_2$, to form $OsHCl_2(CMe)(PPh_3)_2$. Vinyl trifluoroacetate converts $OsHCl(PPh_3)_3$, to $OsHCl(O_2CCF_3)(CMe)(PPh_3)_2$. The less π-basic metal in $OsH(CO)(P^tBu_2Me)_2^+$ reacts with vinyl esters to give only an olefin adduct; detectable binding of the ester oxygen to Os in this adduct suggests a mechanism for carboxylate migration from carbene carbon to metal. The mechanisms of these reactions are explored, and the thermodynamic disparity between Ru and Os is discussed. DFT (B3PW91) calculations have been carried out to establish the energy pattern of possible products. The thermodynamic preference for cleaving the C–O_2CR bond is shown to have a thermodynamic origin associated with the energy of the formed Ru–O_2CR bond. The calculations also indicate the very large thermodynamic driving force for loss of CO_2 in the case of $H_2C=CH(O_2CCl)$. The corresponding loss of CO_2 is shown to be thermodynamically unfavorable in the case of $H_2C=CH(O_2CR)$. The energy of the Ru-R bond is a key factor.

Introduction

$[RuHClL_2]_2$ and $Os(H)_3ClL_2$ (L = bulky phosphine) have both been shown[1] to be sources of the reactive, nonplanar fragment $MHClL_2$, which react (Scheme 1) with vinyl ethers at $\leq$20 °C to form first an alkyl, then, by α-H migration to M, a hydrido carbene. This is effectively an isomerization of a vinyl ether to a heteroatom-substituted carbene, and the favorable thermodynamics for this remarkably easy carbene

Scheme 1

synthesis depends in part on π-donation of an OR lone pair to the carbene carbon. When M=Os, the reaction proceeds further (Scheme 1) because this metal has a preference (*vs.* Ru) for higher oxidation states and for an 18-electron configuration; OR migrates to Os, to leave behind a carbyne ligand.

Vinyl *esters*, $H_2C=CH[OC(O)R]$, have a better leaving group as substituent on the vinyl carbon. We also report here that *chloro*formates, $H_2C=CHOC(O)Cl$, furnish a very convenient synthesis of one Grubbs olefin metathesis catalyst, and have studied the Os analog of this reaction. Finally, we have studied the reaction of several vinyl esters with an osmium analog reagent, $OsH(CO)(P^tBu_2Me)_2^+$, where the π-acidity of Os is much reduced by formal replacement of a π-donor Cl^- by the π-acid CO. This provides a useful mechanistic insight.

Results

1. Reaction of $[RuHCl(P^iPr_3)_2]_2$ with vinyl esters

A) Products. Reaction of $[RuHCl(P^iPr_3)_2]_2$ with equimolar (ester : Ru), $CH_2=CH(O_2CR)$ (R = Me, CF_3, Ph) at room temperature in arene solvent forms the ethylidene complex, $RuCl(O_2CR)(P^iPr_3)_2(=CHMe)$ in the time of mixing (Scheme 2). After 1 hour, however, anionic ligand redistribution leads to 50 mole % conversion to $RuCl_2(P^iPr_3)_2(=CHMe)$, with the balance degrading to intractable materials. Though complexes similar to the second expected redistribution product, $Ru(O_2CR)_2(P^iPr_3)_2(=CHMe)$ have been reported,[2] we find no spectroscopic evidence for their persistence here.

Scheme 2

B) Mechanism. Combining [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ and vinyl acetate in toluene-d$_8$ at −60 °C and warming to room temperature with periodic spectroscopic monitoring reveals initial conversion to an adduct, (**I**)

 with inequivalent

I   **II**
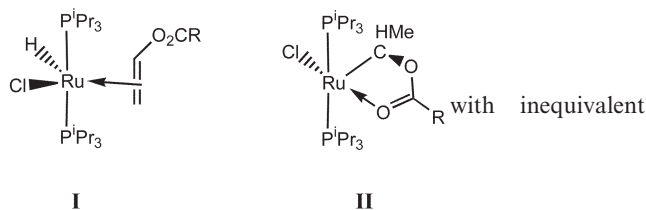
phosphines (32 and 54 ppm; $^2J_{P-P'} = 283$ Hz) by ^{31}P{^{1}H} NMR and a hydride doublet of doublets at −18.3 ppm (^{1}H NMR). Based on the correlation of hydride chemical shift with the donor power of the ligand *trans* to itself, the similar hydride chemical shift of this adduct to that of [RuHCl-(P^{i}Pr$_3$)$_2$]$_2$ with CH$_2$=CH(OEt)[1] suggests that the adduct involves coordination through only the olefinic portion of the molecule (coordination η^1 through oxygen would render the phosphines equivalent). Warming the sample to −30 °C shows the appearance of a second intermediate with inequivalent phosphines at 34 and 48 ppm (^{31}P{^{1}H} NMR; signals too broad to determine $J_{P-P'}$) and no corresponding hydride peak. We assign this species as having olefin inserted in the Ru–H bond, which could be stabilized by intramolecular coordination of the acetate carbonyl oxygen to the otherwise 14e$^-$ ruthenium center (**II**). The asymmetric carbon renders the phosphines inequivalent (this would not be true if the insertion created a Ru(CH$_2$CH$_2$O$_2$CMe) ligand), and the bulk of the secondary alkyl and/or η^2 binding mode causes hindered rotation around Ru–P bonds[3] and the broad phosphine resonances. Above this temperature, two carbene products form with ^{31}P{^{1}H} singlets at 46.4 and 35.5 ppm and corresponding ^{1}H NMR quartets in the 19–20 ppm range. The first to appear we attribute to the new, mixed anionic species, RuCl(O$_2$CR)(P^{i}Pr$_3$)$_2$(=CHMe), and the second is RuCl$_2$-(P^{i}Pr$_3$)$_2$(=CHMe),[4] by comparison to literature data. The propensity for coordinated acetates to adopt multiple coordination modes (*e.g.* η^1, η^2, μ$^{2-4}$) is likely the mechanism for the decomposition of the mono/bis(acetato) ruthenium species *via* acetate aggregates. No evidence for butenes (*i.e.*, coupled ethylidenes) was seen, although a small amount of ethylene in addition to free phosphine was observed in several of the samples.

Possible reaction mechanisms of vinyl carboxylates with metal hydrides have been discussed previously[5] as C–O oxidative addition (eqn. 1) or M–H addition to olefin, followed by migration of X to M from either C$_\alpha$ or C$_\beta$ (eqn. 2). The oxidative addition

$$L_nHM + \text{\Large \diagup\!\!\!\diagdown} OC(O)R \longrightarrow L_nHM \diagdown\!\!\diagup OC(O)R \qquad (1)$$
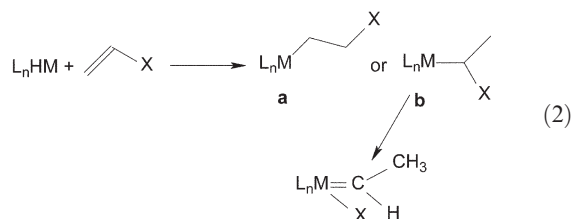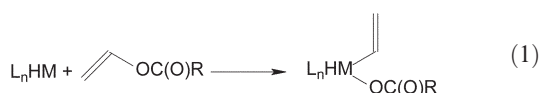
mechanism is less attractive here since we begin with Ru(II) and with a paucity (14) of valence electrons. Concerning the mechanism of the transformation in Scheme 2, we have shown earlier that Ru–H addition to a *triple* bond is faster than oxidative addition of the (acidic) CH bond of terminal alkynes (*i.e.*, the reaction of RuH(H$_2$)XL$_2$ with RC≡CH[6]), so this is more consistent with the occurrence of eqn. 2 *vs.* eqn. 1. β-alkoxide migration analogous to (eqn. 2a) has been demonstrated[7] on Pt(II). Nevertheless, because the reaction of vinyl ethers goes *via* the regiochemistry of eqn. 2b, the simplest (*i.e.*, unified) logic would propose the analogous alkyl intermediate for vinyl carboxylate reactions as for vinyl ethers.

C) A faster leaving group: vinyl tosylate. Use of vinyl tosylate in place of vinyl acetate for this isomerization allows a more detailed examination of the decomposition of RuCl(X)(P^{i}Pr$_3$)$_2$(=CHMe), since with this olefin, carbene formation is much more rapid than anionic ligand redistribution. When these reagents are combined at −60 °C in toluene-d$_8$, quantitative formation of RuCl(OTs)(P^{i}Pr$_3$)$_2$(=CHMe) is observed with no redistribution to the dichloro ethylidene complex. However, as the temperature approaches −20 °C, the formation of RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe) (*i.e.*, halide redistribution) is substantial, and again, the resulting tosylate complexes were not identified.

A recent report[8] shows, in an only partially relevant example, how a carboxylate ligand can be responsible for a significant change in product type. Reaction of RuCl$_2$-(CHPh)(PCy$_3$)$_2$ with 2 AgO$_2$CCF$_3$ does not give Ru-(O$_2$CCF$_3$)$_2$(CHPh)(PCy$_3$)$_2$,   but   instead   **III**.
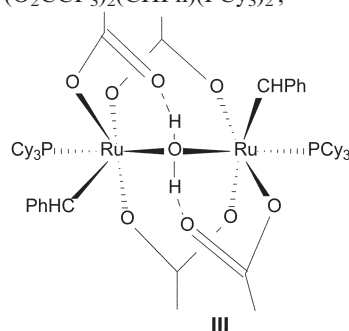
 Thus, one phosphine is

III

lost, and the bidentate potential of carboxylate is realized, by *bridging* two metals. Adventitious water then occupies a bridging site, and hydrogen bonds to two η^1-carboxylates. It is noteworthy that the carbene ligands persist, and in terminal sites. There have also been brief references to RuCl(X)-(=CHCH$_2$R)(PCy$_3$)$_2$ for X = CF$_3$CO$_2$ or CN[9] and to bis(trifluoroacetato) ruthenium carbenes bearing triaryl phosphines.[2]

D) A vinyl ester also containing a reactive C–Cl bond. The ability of a pendant donor to bind in the intermediate of addition of Ru–H across the olefin double bond can also be seen in reaction of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ with vinyl chloroformate,


(3)
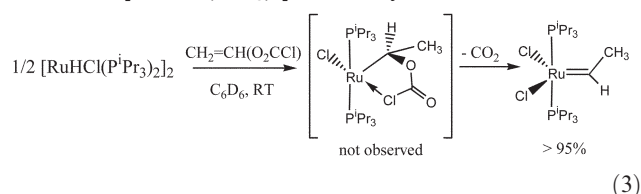
CH_2=CH(O$_2$CCl). The combination of these reagents at room temperature (RT) results (eqn. 3) in the immediate, quantitative formation of dichloro carbene, RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe) and vigorous CO_2 evolution. We believe this represents a convenient synthesis of this molecule.

Computational studies

The variety of compounds that can be obtained when reacting substituted alkenes CH_2=CHG with [RuHClL$_2$]$_2$ or OsH$_3$ClL$_2$ can be better understood through a computational study of the relative energies of possible products. Such study is thus informative of the thermodynamic control of the reactions but not of the mechanisms that could lead to the products. The mechanism described in Scheme 1 has been suggested for RO-substituted olefins[1] and can be reasonably applied for substituted systems. For these reasons, olefin, alkyl, and carbene structures with the O$_2$CR group in various possible sites have been calculated. As in previous studies, MHCl(P^{i}Pr$_3$)$_2$ (M = Ru, Os) is modeled by MHCl(PH$_3$)$_2$ which will be denoted as [M]. The relative energy schemes of most relevant minima are shown in Fig. 1 (O$_2$CMe) and Fig. 2 (O$_2$CCl).

CH_2=CH(O$_2$CMe) and RuHCl(PH$_3$)$_2$

The olefin adducts. The geometry of selected complexes is given in Fig. 3. The coordination of CH_2=CH(O$_2$CMe) to [Ru] occurs preferably *trans* to Cl with the acetate group towards the empty site, **1Ru**. The metal is in a square-pyramidal environment as found for previous olefin complexes of the same [Ru] fragment.[1,10] The complex, **1'Ru**, in which the acetate group is towards the hydride and thus with no possible interaction with Ru is 4.0 kcal mol^{-1} higher in energy. In **1Ru**, an interaction is established between Ru and the carbonyl oxygen of O$_2$CMe as shown by the Ru...O distance, 2.387 Å. This distance is longer by 0.17 Å in comparison to the Ru–ether bond distance but is still compatible with weak bonding. A proof of this interaction is given by the change in the orientation of the olefin. In **1'Ru**, the C=C bond is parallel to Ru–H. The geometrical constraint of the Ru...O interaction in **1Ru** results in the C=C bond being neither parallel to Ru–H nor to Ru–P (dihedral angle HRuCC ~40°). Another consequence of the Ru...O interaction in **1Ru** is that the plane of the acetate group is essentially perpendicular to the plane of the coordinated olefin. However the Ru...O bonding interaction does not greatly influence the binding energy of the olefin. The binding energy of CH_2=CH(O$_2$CMe) in **1Ru** is equal to 39.3 kcal mol^{-1} which is similar to that calculated[1] for various CH_2=CHG (G=H 39.2 kcal mol^{-1}, OMe 36.6 kcal mol^{-1}, N(H)C(O)Me 39.5 kcal mol^{-1}).
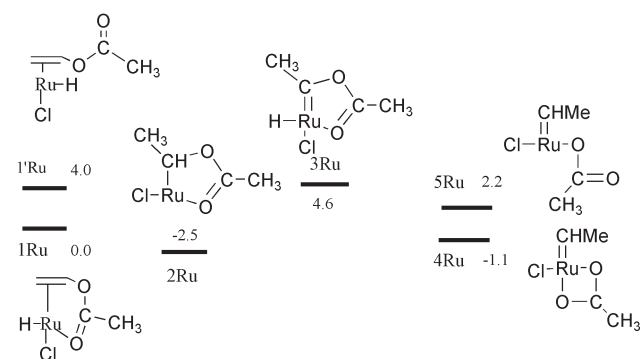
The alkyl complex. The alkyl complex **2Ru** with the acetate group on the α carbon is calculated to be 2.5 kcal mol^{-1} more stable than **1Ru**. The geometry is similar to that of other Ru(alk)ClL$_2$ complexes in that it has an angle of Cl–Ru–C = 105.9°. In contrast to the ethyl analog where only an agostic C–H interaction could provide some additional stabilization to the highly unsaturated metal center, the O$_2$CMe group can give additional electron density to the metal *via* the terminal oxygen. Thus, the Ru...O distance is short, 2.135 Å. The C$_\alpha$–O bond is significantly elongated (1.519 Å). The two C–O bonds of the acetate group are not equal, 1.244 Å for the oxygen bonded to the metal and 1.301 for the oxygen bonded to C$_\alpha$. The angles at the C$_\alpha$ center are also somewhat distorted (Ru–C–C = 118.9° and Ru–C–H = 111.3°) but not sufficiently to suggest that C$_\alpha$ is already an sp^2 center. The acetate group is bridging across the Ru–C bond and the complex is best viewed as a square-pyramidal 16-electron complex with an apical alkyl group. The stability of **2Ru** relative to the olefin complex **1Ru** is however not entirely due to the Ru–O interaction. Previous studies on substitution at the alkyl group of the same metallic fragment have shown the stabilizing influence of an electron acceptor group on C$_\alpha$. The same effect applies here. The complex with the acetate group on the β carbon was not calculated. Previous studies for the vinyl ether with the same fragment have shown a preference for the OMe group to be on C$_\alpha$.[10]

The carbene complexes. The alkyl complex can give several products depending on which atom or group migrates to Ru. From the α substituted alkyl complex, migration of H gives the (MeCO$_2$)CMe complex. Several structures have been found for this complex. The most stable structure, **3Ru**, 4.6 kcal mol^{-1} above the most stable olefin complex, **1Ru**, has a square-pyramidal geometry with the carbene group coplanar with Ru–H and the acetate group towards the Ru vacant coordination site to form an Ru...O bond. It is interesting to compare the metric parameters of the Ru...O interaction in **3Ru** to that[11] of the cationic [RuCl(P^{i}Pr$_3$)$_2$(C(CH$_2$Ph)OC(O)R)]$^+$. The Ru...O distance (2.346 Å) in **3Ru** is significantly longer than in the cationic complex (2.108Å). In the cationic complex, the incipient Ru...O bond is *trans* to a chloride ligand. In **3Ru**, the same bond is *trans* to a hydride ligand and in addition the system is neutral. These conditions are responsible for a longer Ru...O distance. This additional Ru...O bond in **3Ru** brings some significant stabilization, since the minimum deprived of the Ru...O interaction (acetate group away from the empty coordination site) is 11.1 kcal mol^{-1} higher in energy, and it is thus mechanistically irrelevant.

Migration of the acetate group from **2Ru** leads to a CHMe complex **4Ru**, which is calculated to be more stable than **3Ru** and is 1.1 kcal mol^{-1} below the olefin complex **1Ru**. In **4Ru**, the acetate is bidentate with one O pseudo *trans* to the carbene group. This causes the acetate group to have unequal Ru–O bonds, 2.125 Å for O *trans* to Cl and 2.398 Å for O pseudo *trans* to the carbene (the group with the larger *trans* influence). The two CO bond lengths are not very different (1.256 and 1.284 Å). The carbene group is parallel to the Ru–P bond. The η^1–O$_2$CMe isomer **5Ru** lies only 3.4 kcal mol^{-1} above **4Ru**. In **5Ru**, the acetate group plays the role of a strong π donor as shown by the shortening of the Ru–O bond by 0.09 Å. In going from the dihapto to the monohapto geometry, the acetate has compensated for the loss of the Ru–O bond by being a strong π donor through the remaining Ru–O bond.
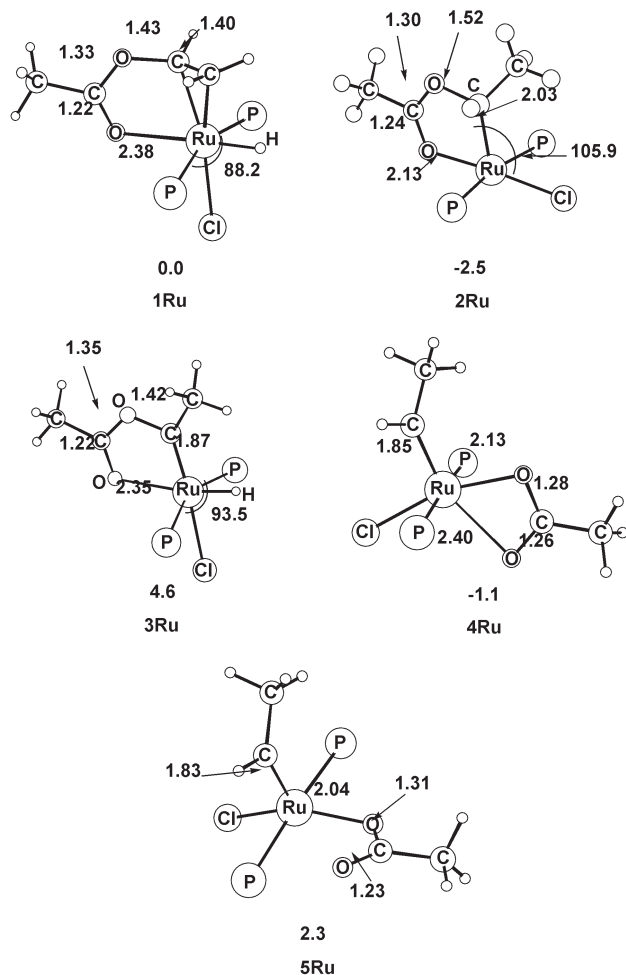
b) CH_2=CH(O$_2$CCl)

The olefin adducts. The structure of selected products obtained from CH_2=CH(O$_2$CCl) are given in Fig. 4. Many results are analogous to those obtained with the acetate group. The vinyl chloroformate coordinates preferably *trans* to Cl

Fig. 1 Calculated (DFT) energies (kcal mol^{-1}) of isomeric structures derived from RuHCl (PH$_3$)$_2$ and H$_2$C=CH(O$_2$CMe). For clarity, the two PH$_3$ groups equidistant from the RuHCl plane are not drawn.
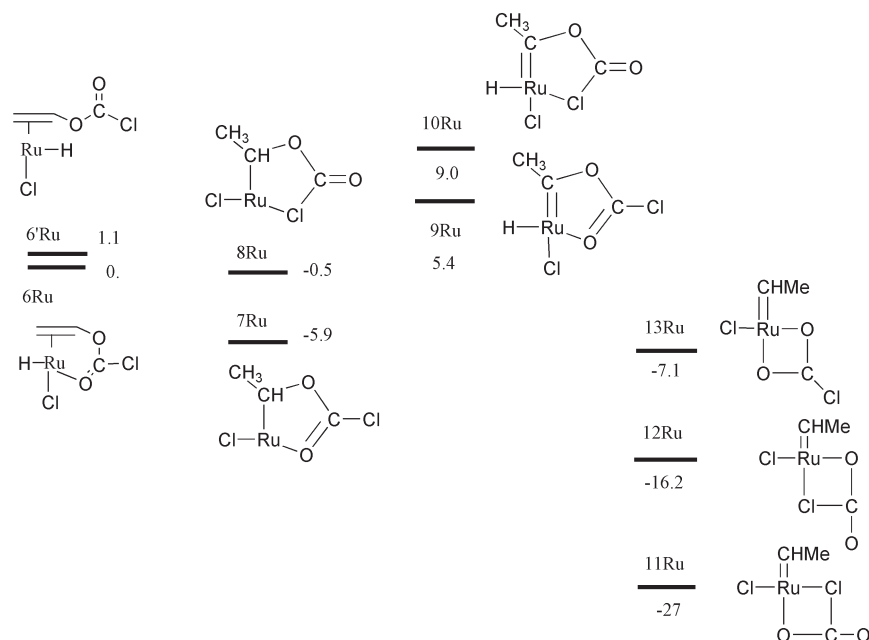
Fig. 2 Calculated (DFT) energies (kcal mol^{-1}) of isomeric structures derived from RuHCl (PH$_3$)$_2$ and H$_2$C=CH(O$_2$CCl). For clarity, the two PH$_3$ groups equidistant from the RuHCl plane are not drawn.

with the oxygen towards the empty coordination site of Ru (Ru...O = 2.518 Å), **6Ru**. However the complex **6′Ru** deprived of the Ru...O interaction is only 1.1 kcal mol^{-1} higher in energy. The Ru...O interaction is weaker than with O$_2$CMe

as expected from an oxygen with lesser donating ability due to the presence of the electron withdrawing Cl atom. The binding energy of CH$_2$=CH(O$_2$CCl) to [Ru] is 40.8 kcal mol^{-1} which is very similar to the values given above for several different G groups. This reiterates that the G group has only a modest influence on the binding ability of the starting olefin to the metal fragment and also that the G group does not create significant Ru..G interaction that would turn a 16-electron in a 18-electron complex.

The alkyl complexes. The alkyl complex with the chloroformate group on the α carbon needs to be stabilized by additional bonding from the chloroformate group in order not to be a highly unsaturated 14 electron complex. As expected, the alkyl complex with an Ru...O bond (2.165 Å), **7Ru**, is preferred (5.9 kcal mol^{-1} below **6Ru**) followed by a complex with an Ru..Cl interaction (2.451 Å), **8Ru** (0.5 kcal mol^{-1} below **6Ru**) and followed by a complex (not illustrated) with a β C–H agostic bond from the Me group, (7.6 kcal mol^{-1} above **6Ru**). This order follows the electron donating ability of the atom or group interacting with the metal in this formal 14-electron complex. In the most stable alkyl complex, **7Ru**, the C$_\alpha$–O bond is significantly elongated (1.551 Å), which is even slightly longer than in the case of the acetate (1.519 Å). The overall geometry of **7Ru** is similar to that obtained for the acetate group. The slightly longer Ru...O and C–O distances for O$_2$CCl compared to O$_2$CMe reflects the electron withdrawing property of the chloroformate group compared to the acetate.

The carbene complexes. The carbene complexes could result from the migration of H or the migration of the chloroformate group to the metal. The carbene complexes in which H has migrated to the metal are above **6Ru** in energy and the preferred such complex **9Ru**, 5.4 kcal mol^{-1} above **6Ru**, has an Ru...O bonding interaction. The Ru...O distance in **9Ru** is 2.421 Å, which is longer than that obtained in the acetate analog **3Ru** (2.346 Å) in agreement with chemical intuition. The carbene complex **10Ru** with an Ru..Cl interaction (2.621 Å) is as expected even higher in energy, 9 kcal mol^{-1} above **6Ru**.

Fig. 3 Detailed geometry (Å and degrees) of species from Fig. 1.
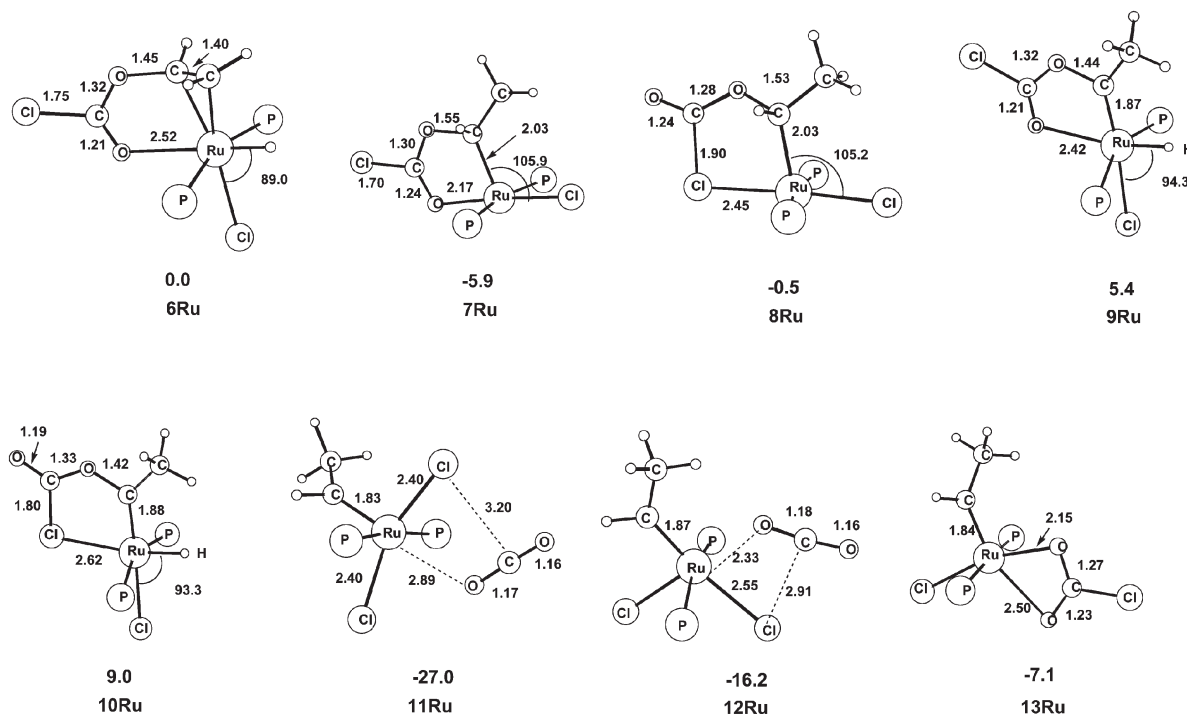
Fig. 4 Detailed geometry (Å and degrees) of species in Fig. 2.

All complexes resulting from the cleavage of the C_α–O bond are energetically more stable than those resulting from the migration of H. The most stable carbene complex, **11Ru**, 27 kcal below **6Ru** is best viewed as a weak complex of $RuCl_2(PH_3)_2(CHMe)$ and fully formed CO_2. In **11Ru**, the square-pyramidal $RuCl_2(PH_3)_2(CHMe)$ complex with an apical carbene coordinates CO_2 with O adjacent to Ru (Ru...O = 2.889 Å) and C adjacent to Cl (3.199 Å). The linear geometry of the CO_2 unit (O–C–O = 177.5°) confirms that the chloroformate group has been dismantled. The CO_2 group is in fact very weakly bonded (2.3 kcal mol^{-1}) to Ru. Inclusion of the entropy factor, which favors dissociation of CO_2, should account for the observed spontaneous loss of CO_2. The other isomeric carbene complexes are significantly higher in energy than **11Ru**. We have located another complex of CO_2 and $RuCl_2(PH_3)_2(CHMe)$, **12Ru**, in which Cl occupies the apical site of the square pyramidal structure (16.2 kcal mol^{-1} below **6Ru**). An even less stable species, **13Ru**, is the 18-electron complex in which the chloroformate is dihapto through both its oxygens and is therefore comparable structurally to **4Ru**. **13Ru** is 19.9 kcal mol^{-1} above **11Ru**. As in **4 Ru**, the two Ru–O bond lengths are different (2.145 and 2.500 Å), the longer one being *trans* to the carbene ligand. It should be kept in mind that **13Ru** is 7.1 kcal mol^{-1} below the corresponding olefin complex while in the case of the acetate group the corresponding complex **4Ru** is only 1.1 kcal mol^{-1} below its corresponding olefin complex **1Ru**. Thus chloroformate favors even more than acetate the coordination of the O_2CCl group to the metal fragment. However, there is an even more stable product that results from the loss of CO_2. The extreme stability of CO_2 is most likely the determining parameter for this strong thermodynamic preference. The factors favoring loss of CO_2 in the chloroformate and not in the acetate case will be addressed later in this work, but the calculations are in agreement with the observed loss of CO_2.

c) The H/G migrating ability: cleaving α C–H *versus* α C–G

The calculations reproduce well the experimental observations, *i.e.* the preference for the migration of the acetate group to the metal center and the decarboxylation of the chloroformate. In order to better understand the factors that control this result, we have calculated the relative energies of products which would result from the migration of H (formation of a CGMe complex) or the migration of G (formation of a CHMe complex) for various CH_2=CHG (G = OMe, NHC(O)Me, O_2CMe), in which G represents groups with variable π donating ability. The difference in energy between $RuHCl(PH_3)_2(CGMe)$ and $RuClG(PH_3)_2(CHMe)$ decreases in the order OMe (12.8 kcal mol^{-1}), N(H)C(O)Me (9 kcal mol^{-1}), OC(O)Me (−5.7 kcal mol^{-1}). Thus only the acetate clearly favors migration to the metal center. All other ligands favor the migration of H over that of G in agreement with experiment. The chloroformate favors it even more as evidenced by the relative energy of **13Ru** *versus* **9Ru** ($\Delta E = -12.5$ kcal mol^{-1}) but it should be kept in mind that another product of reaction is even more preferred (contrast Figs. 1 and 2).

An interpretation of the results can be obtained from the thermodynamic cycles shown in Fig. 5. The H/G exchange

G	E(b)	E(c)	E(a)
OMe	20.5	-7.7	12.8
N(H)C(O)Me	21.6	-12.5	9.0
OC(O)Me	17.3	-23.0	-5.7
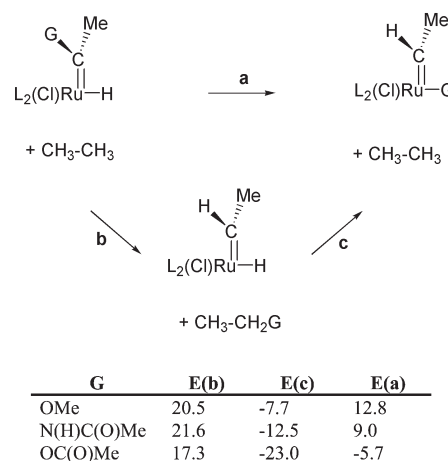
Fig. 5 Thermodynamic cycle and DFT energies for isomerization of variable groups G from carbene carbon to Ru.

(step a) is decomposed into a step b which exchanges G between the sp^2 C of the carbene complex and the sp^3 C of CH$_3$–CH$_3$ and a step c which exchanges G between the sp^3 carbon of CH$_3$CH$_2$G and the metal center. In this manner the donating ability of G (vs. H) towards an unsaturated carbon (step b) and the unsaturated Ru center (step c) is approximately separated. The energy associated with each step for each group G is given in Fig. 5.The positive character of the values for step b show that all groups G are more favorable on the sp^2 carbon. Although the values vary by 3–4 kcal mol^{-1}, such variation is small compared to the overall trend in step a. The negative energies for step c indicate that G is also preferred on Ru vs. on the sp^3 carbon but the variation is large, with the largest value for the acetate group. The ability to become a dihapto coordinated G group is not determining since our studies (above) have shown that the $\eta^2 \rightarrow \eta^1$ change of the acetate is energetically easy.

The calculations clearly show that the strength of the Ru–G bond (E(c)) is an important criterion in the ability for the G group to migrate to the metal. It is remarkable that the Ru–O binding energies are significantly different for the methoxy and acetate ligands. This can reflect the larger electron affinity of the acetate group that better stabilizes a partially ionic M–O bond.

d) Discussion of the decarboxylation thermodynamics and mechanism

The thermodynamics of decarboxylation can be addressed through the thermodynamic cycle (Fig. 6) that compares the acetate and chloroformate groups. Step a illustrates the strong preference for the chloroformate to lose CO$_2$ and form RuCl$_2$L$_2$(CHMe) from the olefin complex. The analogous reaction with the acetate group, leading to RuCl(Me)L$_2$(CH-Me) + CO$_2$, is calculated to be endothermic. The formation of the very stable CO$_2$ molecule (which was responsible for the great stability of **11Ru** and **12Ru** over **13Ru**) is not sufficient to balance other factors in the acetate case. The decomposition of step a into several consecutive steps shows (Fig. 6) that the single step which dominates the overall reaction involves exchange of H and Cl between an sp^2 carbon and the metal center. This step (d) is strongly exothermic for the transformation of Ru–H and C–Cl bonds into Ru–Cl and C–H bonds while it is endothermic for the transformation of Ru–H and C–Me bonds into Ru–Me and C–H bonds. The

decarboxylation reaction can only be thermodynamically favorable if the R group of O$_2$CR also makes a stable Ru–R bond (Cl vs. CH$_3$).

Since we have not conducted a study of the reaction path, we can only discuss the decarboxylation *mechanism* through the energy and structures of energy minima. The loss of CO$_2$ can in principle occur from the alkyl complexes or from the carbene complexes. In the Ru=CHMe species, the calculations for both O$_2$CMe and O$_2$CCl show that the stabilization derived from taking η^1-carboxylate to the η^2- alternative is only 2–3 kcal mol^{-1}. This additional Ru...O bond is thus not very strong, perhaps because it is trans to the carbene. In any event, it shows that an unsaturated complex with η^1-carboxylate is thermally accessible; a pendant carboxylate is also a candidate for the carboxylate/chloride ligand redistribution observed experimentally and reported above. In the alkyl species, the Ru..Cl interaction provides significant stabilization and the Cl bonded chloroformate (**8Ru**) is energetically accessible (about 5 kcal mol^{-1} above the Ru...O bonded **7Ru** species). The alkyl and the carbene complexes are all within 5 kcal mol^{-1} of the olefin adduct and this provides intermediates to departure of CO$_2$. As shown by the energy minima **11Ru** and **12Ru**, which are very separated-product-like, the formation of a CO$_2$ ligand is so very exothermic compared to all other products calculated (16 and 27 kcal mol^{-1} more stable than the olefin adduct) that the energy gain must rest mainly on nearly complete formation of the very stable CO$_2$ molecule. A very similar binding energy and geometry pattern has been calculated[12] for the interaction of RuH$_2$(PH$_3$)$_3$ with CO$_2$.

Experimental study of Os analogs. Since OsHClL$_2$ is unknown, we have employed Os(H)$_3$ClL$_2$, with the hope that two H can be removed, either as H$_2$, or by hydrogenation of equimolar vinyl ester.

a) Os(H)$_3$ClL$_2$ + vinyl trifluoroacetate. Reaction of Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ and vinyl trifluoroacetate in a 1 : 1 mole ratio in toluene-d$_8$ at 25 °C gives an immediate color change from brown to green-yellow and gas evolution (presumably H$_2$), but the ^{31}P NMR spectrum indicates a variety of products, only a minor one of which is a *carbyne*; OsH$_5$Cl(P^{i}Pr$_3$)$_2$,[13] a product of Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ scavenging released H$_2$, is observed, as is free ethylene. The reaction was therefore studied with excess vinyl trifluoroacetate, to more effectively capture all Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ with the vinyl ester rather than be confused with the reaction of ester and OsH$_5$Cl(P^{i}Pr$_3$)$_2$. Combining Os(H)$_3$ClL$_2$ with 4 moles of H$_2$C=CH(O$_2$CCF$_3$) gives, within short time of observation in toluene-d$_8$, OsH-Cl(O$_2$CCF$_3$)(CCH$_3$)L$_2$.

To elucidate the mechanism of this reaction, we combined Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ (**IV**) and vinyl trifluoroacetate at −80 °C in 1 : 1 stoichiometry in toluene-d$_8$ and slowly warmed the mixture to room temperature to identify the intermediates by ^{1}H and ^{31}P {^{1}H} NMR. At −80 °C, we observe (Scheme 3, where "2H" indicates either dihydride or H$_2$) the presence of the reagent Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ (**IV**), the final product OsH-Cl(O$_2$CCF$_3$)($\equiv$CCH$_3$)(P^{i}Pr$_3$)$_2$ (**IX**, two isomers), free H$_2$ (^{1}H NMR), and several intermediates. The intermediates observed are the olefin adduct, OsH$_3$Cl(H$_2$C=CH(O$_2$CCF$_3$))(P^{i}Pr$_3$)$_2$ (**V**), the chiral alkyl intermediate OsCl(CH(CH$_3$)(O$_2$CCF$_3$))-(P^{i}Pr$_3$)$_2$ (**VII**, with or without an Os–O bond), and the ethylidene intermediate due to carboxylate migration to the metal OsCl(O$_2$CCF$_3$)(=CH(CH$_3$))(P^{i}Pr$_3$)$_2$ (**VIII**). The olefin adduct is characterized in the ^{1}H NMR spectrum by the two signals (intensity 1 : 2) of H attached to Os. Analogous decoalesced hydrides have been observed previously with vinyl ether adducts of Os(H)$_3$ClL$_2$. The hydride signals resonate as a triplet at −4.05 ppm with $J_{(H-P)} = 20$ Hz and a broad peak at −14.78 ppm in 1 : 2 intensity ratio. The signals due to the
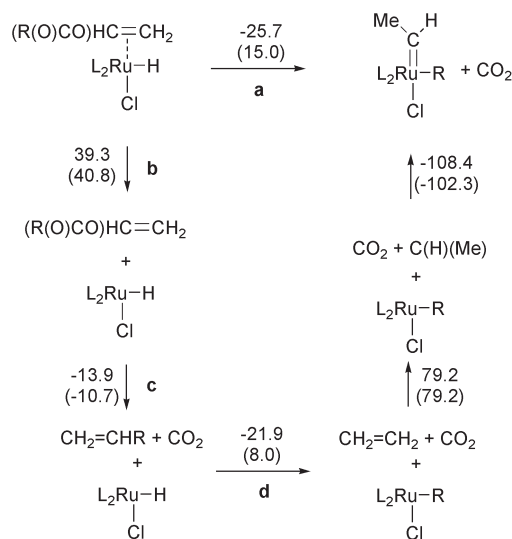
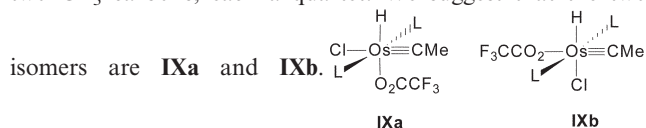**Fig. 6** DFT energies for the reactions shown, contrasting R = Cl with R = CH$_3$ (in parentheses).
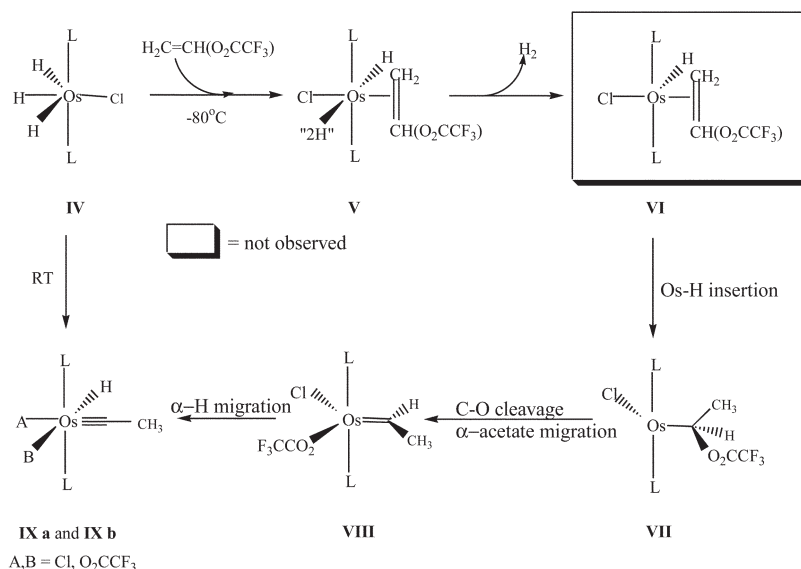
Scheme 3

coordinated olefin are a broad AB pattern at 2.75, 2.87 and a broad peak at 3.97 ppm. Surprisingly, the ^{31}P $\{^1\text{H}\}$ NMR spectrum of **V** displays a sharp singlet at 37.8 ppm, instead of the AB pattern expected in the presence of a prochiral olefin. This can only be explained if the value of $J_{P–P'}$ is much larger than the value of Δv. The olefin adduct liberates H_2 leading to the undetected 16 e$^-$ $OsHCl(H_2C=CH(O_2CCF_3))(P^iPr_3)_2$ (**VI**), which undergoes insertion of the olefin into the Os–H bond to give the chiral 14 e$^-$ alkyl $OsCl(CH(CH_3)(O_2CCF_3))$-$(P^iPr_3)_2$ (**VII**). Given the calculated structure of the ruthenium analog, **2Ru**, it is likely that **VII** has the carboxylate oxygen bound to Os. This alkyl compound displays two characteristic multiplets in the ^{1}H NMR: a methyl doublet at 1.60 ppm with $J_{(H–H)} = 6.6$ Hz, and a quartet at 0.77 ppm with $J_{(H–H)} = 6.6$ Hz, corresponding to the α proton. Again, the $J_{P–P'}$ must be much larger than the value of Δv, which explains the sharp ^{31}P $\{^1\text{H}\}$ NMR singlet at 28.9 ppm. The H_2 liberated by **V** is trapped by unreacted $Os(H)_3Cl(P^iPr_3)_2$ (**IV**) forming the known $OsH_5Cl(P^iPr_3)_2$. At this point, the C–O bond is cleaved and the acetate group migrates to the metal, forming the 16 e$^-$ mixed-halide ethylidene $OsCl(O_2CCF_3)(=CH(CH_3))(P^iPr_3)_2$ (**VIII**), best detected by a broad signal far downfield in the ^{1}H NMR spectrum (18.5 ppm). In addition, another broad peak is observed at 1.68 ppm, which corresponds to the methyl substituent on the carbene carbon. The ^{31}P $\{^1\text{H}\}$ NMR spectrum displays a sharp singlet for **VIII** at 20.2 ppm.

At $-60\,°$C all $Os(H)_3Cl(P^iPr_3)_2$ (**IV**) has already reacted. Formation of more hydrido-carbyne is observed when warming the sample to $-40\,°$C. At this temperature, the major species are the two hydrido-carbyne isomers, as well as some olefin adduct **V**. Minor quantities of the carbene **VIII** are still present, whereas the alkyl species **VII** has already disappeared. The carbene disappears at $-30\,°$C, but the olefin adduct does not disappear until room temperature is achieved, at which point only the two isomeric carbynes remain.

The hydrido carbyne species **IX** exists as two isomers in a 3 : 1 ratio, as seen by ^{1}H and ^{31}P$\{^1\text{H}\}$ NMR spectroscopies. Observed are hydrides (-8.9 and -5.8 ppm, both triplets) and OsC–CH_3 (singlets at 0.7 and 0.4 ppm) and two ^{i}Pr methine hydrogens (3 : 1 ratio), as well as two ^{31}P$\{^1\text{H}\}$ NMR singlets (31.0 and 32.6 ppm). Two ^{13}C$\{^1\text{H}\}$ carbyne carbon triplets (266.7 and 276.5 ppm) of intensity 3:1 have similar $J_{C–P}$ values (11 Hz); two carbyne methyl carbons are also seen. The O_2CCF_3 carbonyl carbons are seen at 161.7 and 159.9 ppm; each is a quartet (C/F coupling). Also observed are

two CF_3 carbons, each a quartet. We suggest that the two isomers are **IXa** and **IXb**.

These undergo no change (*e.g.*, population) or redistribution to $OsCl_2H(CMe)L_2$ and $Os(O_2CCF_3)_2H(CMe)L_2$ upon heating at $70\,°$C for 24 h in toluene.

b) Vinyl chloroformate. Vinyl chloroformate is a bifunctional substrate, and this is evident in its reaction with an osmium reagent. Reaction of $Os(H)_3Cl(P^tBu_2Me)_2$ with vinyl chloroformate (1 : 2 mole ratio) in toluene proceeds to complete consumption of the trihydride (eqn. 4) in less than 5 min at $20\,°$C to give $OsHCl_2(CCH_3)(P^tBu_2Me)_2$ (80% yield), H_2 (^{1}H NMR evidence) and CO_2 (visible gas evolution). Some ethylene and some vinyl chloride are also detected (^{1}H NMR). This reaction is apparently fast enough that

$$Os(H)_3ClL_2 + H_2C=CH(O_2CCl) \rightarrow$$
$$OsHCl_2(CCH_3)L_2 + CO_2 + H_2 \quad (4)$$
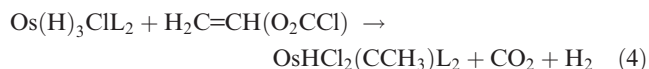
the released hydrogen does not hydrogenate the C=C bond of the vinyl reagent, or of ethylene; there is no evidence of ethane or ethyl groups. If the reaction stoichiometry is changed to 1:1, accompanying the carbyne product (within 5 min) are $OsH(H_2)Cl(C_2H_4)(P^tBu_2Me)_2$, which is the product of $Os(H)_3Cl(P^tBu_2Me)_2$ reacting with ethylene, and free C_2H_4 (vinyl chloride is absent); all vinyl chloroformate is gone at this time. The production of ethylene from vinyl chloroformate in this reaction depletes the $Os(H)_3ClL_2$ reagent of one H and adds to it one Cl, in effect creating $OsH_2Cl_2L_2$. In fact, some of this dichloride complex is observed within 5 min when the reaction stoichiometry is 1 : 1; we have shown independently that $OsH_2Cl_2L_2$ reacts promptly with vinyl chloroformate to give some $OsHCl_2(CCH_3)L_2$, but also an unappealing array of other phosphine complexes. Because some vinyl chloroformate is converted to ethylene, and ethylene binds to $Os(H)_3Cl(P^tBu_2Me)_2$, thereby diminishing its reactivity, consumption of vinyl chloroformate slows, and its complete consumption depends on equilibrium 5 shifting to the right. In general, using $Os(H)_3ClL_2$ as a substitute for the unknown $OsHClL_2$ demands consideration of the consequences of the released H_2. The side reactions which begin with ethylene

production thus deplete $Os(H)_3ClL_2$

$$OsH_3Cl(C_2H_4)(P^tBu_2Me)_2 \rightleftharpoons Os(H)_3Cl(P^tBu_2Me)_2 + C_2H_4$$

$$OsHCl_2(CCH_3)(P^tBu_2Me)_2 + H_2 + CO_2 \quad (5)$$
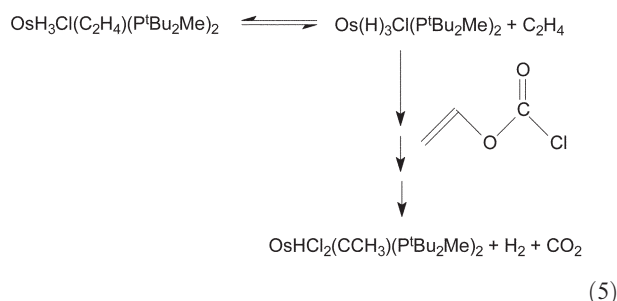
consumption according to the primary reaction (eqn. 4), and lead to the slower reaction completion and inexact stoichiometry.

The bifunctional nature of vinyl chloroformate permits a second, competitive reaction, oxidative addition of the C–Cl bond to some osmium species (*e.g.*, eqn. 6).
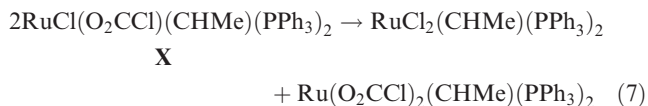
$$(6)$$
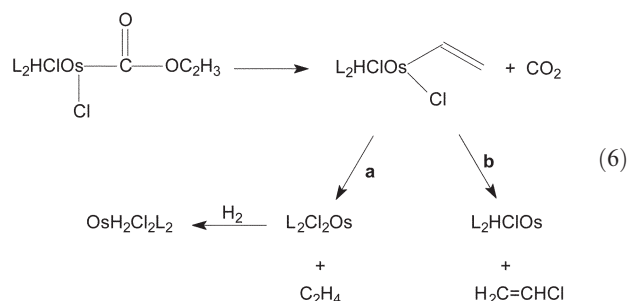
Reductive elimination of ethylene (**a**) or vinyl chloride (**b**) then completes this side reaction.

Influence of phosphine identity: reactions of vinyl chloroformate with $MHCl(PPh_3)_3$ (M = Ru, Os)

a) M = Ru. These reagents were employed in the hope that one PPh_3 will serve as a leaving group, and thus provide a functional source of $MHCl(PPh_3)_2$. This would diminish the side reactions resulting from the H_2 released by $Os(H)_3ClL_2$. Valuable information regarding the mechanism of carbene delivery was indeed obtained by reaction of vinylchloroformate with the monohydride $RuHCl(PPh_3)_3$[14] in 1:1 stoichiometry in benzene-d_6 at 20 °C. The first product observed is a carbene, characterized by a downfield resonance in the ^1H NMR at 16.7 ppm, due to the carbenic proton. This signal displays an apparent triplet of quartets with $^3J_{H-P} = 13.5$ Hz and $^3J_{H-H} = 6$ Hz. The triplet indicates that there are only two phosphines bound to the metal center, whereas the quartet indicates that the other substituent in the carbene carbon is a methyl group. This assignment is confirmed by the presence of a doublet in the ^1H NMR spectrum, corresponding to the methyl substituent on the carbene carbon, at 2.12 ppm with the same coupling constant. Free triphenylphosphine is observed by $^{31}P\{^1H\}$ NMR. Comparison of these values with those in the literature for $RuCl_2L_2(=CHMe)$ (L = PPh_3)[15] shows that the product is *not* this one. We propose this carbene to be the mixed halide-carboxylate six coordinate compound $RuCl(\eta^2-O_2CCl)(=CHMe)L_2(\mathbf{X})$. The corresponding $^{31}P\{^1H\}$ NMR displays an AB pattern with $^2J_{P-P'} = 430$ Hz. The AB pattern can be due to either mutually *cis* phosphines or orientation of the carbene substituents along the P–Ru–P vector. A *cis* disposition of the phosphines is eliminated by the large value of the coupling constant. Therefore, the inequivalent phosphines must be due to the configuration of the carbene ligand. This is particularly intriguing since most of the related 16 electron dihalide ethylidene compounds

show essentially free rotation around the Ru=C bond[16] on the NMR timescale. However, in these dihalide compounds there is no possibility of η^2 ligand coordination, which we assume enhances a push-pull interaction between the carboxylic group and the carbene, increasing back donation from Ru to the empty p-orbital of the carbene carbon. As a consequence, the bond order of the Ru=C bond increases along with its rotational barrier. Compound **X** is the major product of the reaction 2 h after mixing the reagents, but it slowly disappears and disproportionates (eqn. 7) to the known dichloride carbene.[15] After 24 h at 20 °C the

$$2RuCl(O_2CCl)(CHMe)(PPh_3)_2 \rightarrow RuCl_2(CHMe)(PPh_3)_2$$
$$\mathbf{X}$$
$$+ Ru(O_2CCl)_2(CHMe)(PPh_3)_2 \quad (7)$$

reaction is not yet complete; small quantities of unreacted vinylchloroformate and species **X** are still present. At this time, a third product appears in the ^1H NMR spectrum, displaying a multiplet at 17.12 ppm thus confirming its ethylidene nature. This species is assigned as $Ru(O_2CCl)_2(=CHMe)L_2$, the corresponding disproportionation product.

b) M=Os. The analogous reaction with $OsHCl(PPh_3)_3$[17] was studied in benzene-d_6 at 20 °C. Upon combining the reagents, strong effervescence is observed, indicative of CO_2 release. Only one ethylidene fragment is observed in the ^1H NMR spectrum. The signal corresponding to the carbenic proton appears at 19.76 ppm, displaying the characteristic triplet of quartets with $^3J_{H-P} = 11$ Hz and $^3J_{H-H} = 5.5$ Hz. The ethylidene formulation is confirmed by the appearance of a doublet at 1.70 ppm with $^3J_{H-H} = 5.5$ Hz, corresponding to the methyl substituent on the carbene carbon. The $^{31}P\{^1H\}$ NMR spectrum is a sharp singlet at 8.1 ppm. We attribute this to the carbene $OsCl_2(=CHMe)L_2$(**XI**). This carbene is metastable and over a period of 2 days isomerizes to the carbyne $OsHCl_2$-$(CMe)L_2$ (**XII**).
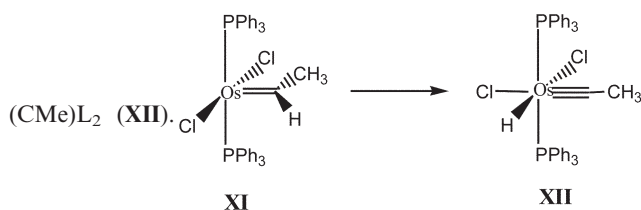
At this time the isomerization is not yet complete. Carbyne **XII** displays a triplet at -5.60 ppm with $^2J_{H-P} = 15$ Hz and a triplet at -0.59 ppm with $^3J_{H-P} = 2.4$ Hz in the ^1H NMR spectrum, corresponding to the hydride and the methyl carbyne ligands respectively. The $^{13}C\{^1H\}$ NMR spectrum displays a triplet at 278.2 ppm with $^2J_{C-P} = 12$ Hz, corresponding to the carbyne carbon, and a singlet at 34.8 ppm corresponding to the methyl carbon, thus confirming the hydrido-carbyne formulation. The hydrido-carbyne displays a sharp singlet in the $^{31}P\{^1H\}$ NMR at 4.6 ppm.

c) Reaction of $OsHCl(PPh_3)_3$ with vinyl trifluoroacetate. In an attempt to strengthen the C–X bond (thus avoiding a subsequent chloroformate decarboxylation process) in the carboxylate substituent XCO_2, we chose vinyl trifluoroacetate as the vinyl reagent. The products first observed (2.5 h after combining these reagents in C_6D_6) are the dichloride ethylidene **XI**, the mixed chloride-carboxylate carbene $OsCl(O_2CCF_3)$-$(=CHMe)L_2$ (**XIII**), and its isomeric hydrido-carbyne as a result of α–H migration $OsHCl(O_2CCF_3)(CMe)L_2$ (**XIV**), all of them present in very small quantities. The carbene **XIII** is identified in the ^1H NMR spectrum by a downfield multiplet at 21.1 ppm and a doublet at 1.65 ppm with $^3J_{H-H} = 6.6$ Hz, whereas its isomeric hydrido-carbyne **XIVa** displays a triplet at -4.24 ppm with $^2J_{H-P} = 15$ Hz and a triplet at -0.13 ppm

with $^4J_{H-P}$ = 2.4 Hz, corresponding to the hydride ligand and the methyl substituent on the carbyne carbon respectively. The ^{31}P {^{1}H} NMR signal for the hydrido-carbyne **XIVa** is a singlet at 18.1 ppm.

XIII **XIVa** and **XIVb**
A,B = Cl⁻,⁻O₂CCF₃
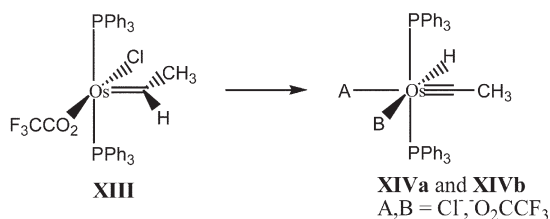
The dichloro-carbene species **XI** spontaneously transforms to its isomeric hydrido-carbyne **XII** analogously to the behavior observed in the reaction between OsHCl(PPh₃)₃ and vinylchloroformate. The carbyne species **XIVa** then transforms partially to isomeric **XIVb**. The isomer **XIVb** is characterized by a triplet in the hydride region at −7.45 ppm with a $^2J_{H-P}$ = 16 Hz and a singlet for the carbyne methyl at −0.28 ppm.

The influence of CO on Os. The influence of metal π-basicity on the C/O bond cleavage reaction is also shown by employing OsH(CO)(P^{t}Bu₂Me)₂$^+$ as the unsaturated monohydride.[18] The cationic charge and the carbonyl ligand (*cf.* Cl⁻ in OsHClL₂) greatly diminish the reducing ability in spite of the general reducing character of a 5d metal. This cation was synthesized by abstraction of triflate from OsH(OTf)(CO)L₂ using NaBAr^F (Ar^F = 3,5(CF₃)₂C₆H₃) in CH₂Cl₂. This cation reacts with equimolar vinyl trifluoroacetate within 5 min in CD₂Cl₂ at 25 °C to give an olefin adduct with inequivalent ^{31}P nuclei, whose $J_{PP'}$ = 112 Hz indicates extreme P–Os–P bending, to increase π donation to the olefin.[19–21] The hydride resonance is a doublet of doublets (J_{PH} = 28 and 33 Hz), consistent with inequivalent phosphines, and its chemical shift, −1.9 ppm, suggests a strong

ligand *trans* to itself: olefin (see **XV**). This

XV
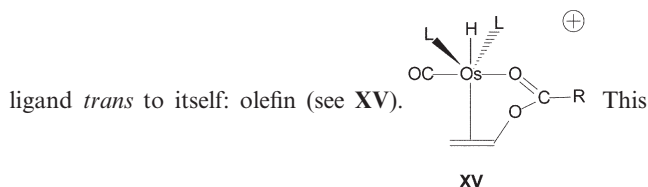
chemical shift contrasts to the values −23.7 ppm for the water adduct OsH(OTf)(H₂O)(CO)(P^{t}Bu₂Me)₂ and −27.5 ppm for[18] OsH(CD₂Cl₂)(CO)(P^{t}Bu₂Me)₂$^+$. A vinylic ^{1}H NMR signal at 7.09 ppm shows coupling to phosphines, confirming olefin/Os binding. Vinyl acetate gives an analogous adduct under the same conditions. Evidence that the keto oxygen also binds to Os is the large (136 cm^{-1}) reduction of $v_{C=O}$ for coordinated vinyl acetate (to 1619 cm^{-1}) from its value (1755 cm^{-1}) for free vinyl acetate.

The vinyl trifluoroacetate adduct is unchanged after 2 h at 80 °C in benzene. This less-reducing osmium thus shows no tendency for C–O bond cleavage.

Discussion

The present work reveals the previously-reported tendency of ruthenium to prefer the carbene form, while osmium prefers the isomeric carbyne, formed by transfer a carbene substituent to the metal. Osmium thus "benefits" from higher coordination number and oxidation state, as well as from 18-valence electrons.

This report also shows the relative stability of isomeric ruthenium carbenes, **XVI** *vs.* **XVII**. For E = *alkoxide*, the final product has E on carbon (**XVI**). As E becomes less electron donating (*e.g.*, E = OTs or O₂CR), the thermodynamic isomer

has E on Ru (**XVII**).
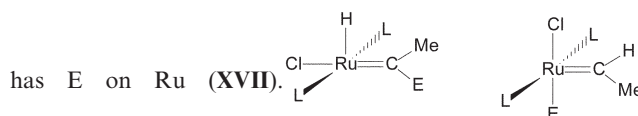
Finally, a CO ligand in place of Cl⁻ decreases the reducing power of osmium to the point where olefin binding, but neither carbene nor carbyne ligand formation occurs.

These studies are the first to observe, at a detectable rate, the transformation from osmium carbene to hydrido osmium carbyne by a formal α-H migration (for Ru, this reaction is not observed because it is endergonic). What is remarkable is that this reaction is quite fast (minutes at −30 °C) for L = P^{i}Pr₃ yet slow (hours at 25 °C) for
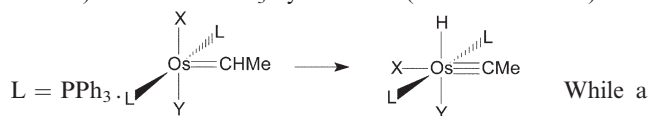
unimolecular 1,2-H migration from C to Os seems an "obvious" mechanism, DFT calculations showed this mechanism to be precluded by a large activation energy (27.2 kcal mol^{-1}) in the case where X = Y = Cl.[17]

The experimental observations, together with the energies calculated for observed and postulated intermediates have defined the general features by which the O–C bond of vinyl esters is cleaved easily by (electron-rich) Ru and Os complexes devoid of π-acid ligands. As shown in Fig. 1, all necessary intermediates lie within easy energetic reach. Because of the energetic proximity of both the alkyl (**2Ru**) and the carbene (**3Ru**) with the ester oxygen bonded to Ru, each is a viable intermediate for intramolecular O₂CMe transfer from carbon to metal. This contrasts to vinyl ethers, where observations are consistent with an acid-catalyzed mechanism. The greater "reach" of an ester than an ether functionality (five- *vs.* three-membered ring) accounts for this difference.
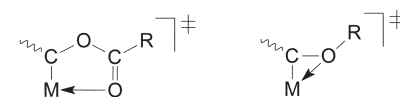
Experimental

General procedure

All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox. Solvents were dried, degassed or distilled under argon from Na, Na/benzophenone, P₂O₅, CaH₂, and/or 4 Å molecular sieves and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in a glovebox. Complexes OsH₃ClL₂ (L = P^{t}Bu₂Me, P^{i}Pr₃) were synthesized according to published procedures.[13] The synthesis of OsH₃Cl(P^{i}Pr₃)₂ from OsH₂Cl₂(P^{i}Pr₃)₂ and NEt₃ can leave variable small amounts of [HNEt₃]Cl as an impurity which is difficult to remove by recrystallization. When present, this can lead to the production of OsH₂Cl₂L₂ as a by product of the dehydrogenation reactions reported here; this product is thus not derived from the ester reaction, but from the available "HCl". [RuHCl(P^{i}Pr₃)₂]₂,[1,22] was prepared according to published procedures. Commercially available vinyl esters were used as received after drying and degassing when applicable. Chemical shifts are referenced to residual protio solvent peaks (^{1}H), external H₃PO₄ (^{31}P), external CFCl₃ (^{19}F), or natural abundance ^{13}C peaks of the solvent (^{13}C). NMR spectra were obtained on a Varian Gemini 2000 (300 MHz ^{1}H; 121.4 MHz ^{31}P, 75 MHz ^{13}C, 282 MHz ^{19}F), a Varian Unity Inova

instrument (400 MHz ^{1}H; 162 MHz ^{31}P), or a Bruker AM spectrometer (500 MHz ^{1}H, 125.6 MHz ^{13}C). "N" is the spacing (Hz) of the sharp outer liner in a virtual triplet ("vt").

RuCl(O$_2$CCH$_3$)(P^{i}Pr$_3$)$_2$(=CHMe)

15.0 mg (0.016 mmol) [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in 0.5 mL C$_6$D$_6$ and added to an NMR tube with a septum cap. Via syringe, 3.0 μL (0.033 mmol) vinyl acetate was added and the sample mixed. ^{1}H and ^{31}P NMR spectra taken immediately reveal signals of the title compound, in addition to those of RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe).[4] Selected spectroscopic data for the title compound: ^{1}H NMR (25 °C, 300 MHz, C$_6$D$_6$): δ 1.76 (s, 3H, Ru(O$_2$CCH_3)), δ 2.48 (d, $^3J_{H-H}$ = 7 Hz, 3H, Ru=CH(CH_3)), δ 19.67 (q, $^3J_{H-H}$ = 7 Hz, 1H, Ru=CHMe). ^{31}P NMR (25 °C, 121 MHz, C$_6$D$_6$): δ 37.2 (s).

RuCl(O$_2$CCF$_3$)(P^{i}Pr$_3$)$_2$(=CHMe)

15.0 mg (0.016 mmol) [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in 0.5 mL C$_6$D$_6$ and added to an NMR tube with a septum cap. Via syringe, 3.7 μL (0.032 mmol) vinyl trifluoroacetate was added and the tube shaken. ^{1}H, ^{31}P, and ^{19}F NMR spectra taken immediately reveal predominately signals of the title compound, in addition to those of RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe).[4] Selected spectroscopic data follows: ^{1}H NMR (25 °C, 400 MHz, C$_6$D$_6$): δ 2.49 (d, $^3J_{H-H}$ = 5 Hz, 3H, Ru=CH(CH_3)), δ 19.88 (q, $^3J_{H-H}$ = 5 Hz, 1H, Ru=CHMe). ^{31}P NMR (25 °C, 162 MHz, C$_6$D$_6$): δ 44.3 (s). ^{19}F NMR (25 °C, 121 MHz, C$_6$D$_6$): δ −76.7 (s).

RuC(O$_2$CPh)(P^{i}Pr$_3$)$_2$(=CHMe)

15.0 mg (0.016 mmol) [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in 0.5 mL C$_6$D$_6$ and added to an NMR tube with a septum cap. Via syringe, 4.4 μL (0.032 mmol) vinyl benzoate was added and the sample mixed. ^{1}H and ^{31}P NMR spectra taken immediately reveal signals of the title compound, in addition to those of RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe).[4] Selected spectroscopic data for the title compound: ^{1}H NMR (25 °C, 300 MHz, C$_6$D$_6$): δ 2.61 (d, $^3J_{H-H}$ = 6 Hz, 3H, Ru=CH(CH_3); overlaps with those of RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe)), δ 7.01 (t, $^3J_{H-H}$ = 5 Hz, 1H, Ru(O$_2$CC$_6$H$_5$)), δ 7.12 (apparent t, $^3J_{H-H}$ = 5 Hz, 2H, Ru(O$_2$CC$_6$H$_5$)), δ 8.25 (d, $^3J_{H-H}$ = 5 Hz, 2H, Ru(O$_2$CC$_6$H$_5$)), δ 19.75 (q, $^3J_{H-H}$ = 7 Hz, 1H, Ru=CHMe). ^{31}P NMR (25 °C, 121 MHz, C$_6$D$_6$): δ 51.3 (s).

Reaction of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ with CH$_2$=CH(O$_2$CCl)–vinyl chloroformate

15.0 mg (0.016 mmol) [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in 0.5 mL C$_6$D$_6$ and added to an NMR tube with a septum cap. Via syringe, 2.8 μL (0.033 mmol) vinyl chloroformate was added and the sample mixed. Gas evolution was observed immediately and the solution turned deep purple. ^{1}H and ^{31}P NMR spectra taken immediately show quantitative conversion to RuCl$_2$(P^{i}Pr$_3$)$_2$(=CHMe).[4]

CH$_2$=CH(OSO$_2$C$_6$H$_4$CH$_3$)–vinyl tosylate

Vinyl tosylate was prepared with a slightly modified procedure from the original literature reference.[23] Anhydrous *p*-tolylsulfonic acid was prepared by heating the monohydrate *in vacuo* (60 °C, 0.01 torr) for 12 hours. 10.0 g (58 mmol) anhydrous *p*-tolylsulfonic acid and 0.67 g (3.1 mmol) yellow HgO were charged in a glass pressure reaction vessel. 20 mL ether was added, the vessel sealed, cooled to −50 °C, and the headspace gasses evacuated. The flask was filled to 80 psi with acetylene and re-pressurized as needed. After initial gas uptake had ceased (2 hours), the mixture was heated at 50 °C for 1 hour (vessel pressure increased to 120 psi -caution!). After cooling

and filtering in air, the ether solution was added to a separating funnel, washed with dilute aqueous K$_2$CO$_3$ (6 × 50 mL), and dried over MgSO$_4$. After removal of the solvent *in vacuo*, the resulting brown liquid was vacuum distilled, collecting the colorless fraction boiling at 96–97 °C (0.3 torr). Yield: approximately 3 g (26%). ^{1}H NMR (25 °C, 400 MHz, C$_6$D$_6$): δ 1.77 (s, 3H, OSO$_2$C$_6$H$_4$CH_3), δ 4.08 (dd, $^3J_{H-H}$ = 6 Hz, $^2J_{H-H}$ = 2 Hz, 1H, CH_2=CH(OTs)), δ 4.52 (dd, $^3J_{H-H}$ = 11 Hz, $^2J_{H-H}$ = 2 Hz, 1H, CH_2=CH(OTs)), δ 6.47 (dd, $^3J_{H-H}$ = 11 Hz, $^3J_{H-H}$ = 6 Hz, 1H, CH$_2$=CH(OTs)), δ 6.61 (d, $^3J_{H-H}$ = 8 Hz, 2H, OSO$_2$C$_6$H$_4$CH$_3$), δ 7.63 (d, $^3J_{H-H}$ = 8 Hz, 2H, OSO$_2$C$_6$H$_4$CH$_3$).

RuCl(OSO$_2$C$_6$H$_4$CH$_3$)(P^{i}Pr$_3$)$_2$(=CHMe)

15.0 mg (0.016 mmol) [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in 0.5 mL C$_7$D$_8$ and added to an NMR tube equipped with a Teflon seal. Via syringe, 5.4 μL (0.032 mmol) vinyl tosylate was added so that the reagents did not mix and the tube was sealed. The sample was cooled in a dry ice–acetone bath, shaken vigorously, and then placed in a pre-cooled NMR probe (−60 °C). ^{1}H and ^{31}P NMR spectra taken at this temperature reveal quantitative conversion to the title compound. Selected spectroscopic data follows: ^{1}H NMR (−60 °C, 400 MHz, C$_7$D$_8$): δ 1.97 (s, 3H, Ru(OSO$_2$C$_6$H$_4$CH_3)), δ 2.59 (d, $^3J_{H-H}$ = 4 Hz, 3H, Ru=CH(CH_3)), δ 6.78 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ru(O-SO$_2$C$_6$H$_4$CH$_3$)), δ 7.87 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ru(O-SO$_2$C$_6$H$_4$CH$_3$)), δ 20.08 (q, $^3J_{H-H}$ = 4 Hz, 1H, Ru=CHMe). ^{31}P NMR (−60 °C, 162 MHz, C$_7$D$_8$): δ 51.3 (s).

Synthesis of OsHCl(η^1-O$_2$CCF$_3$)(CCH$_3$)(P^{i}Pr$_3$)$_2$, IX

In an NMR tube, OsH$_3$Cl(P^{i}Pr$_3$)$_2$ (0.0100 g, 0.018 mmol) was dissolved in 0.8 ml of toluene-d$_8$ and vinyl trifluoroacetate (8.48 μL, 0.072 mmol) was added to the solution. The reaction proceeds with strong effervescence and is complete in 10 min. The volatiles were removed *under vacuo* and the yellowish residue recovered. The solid residue consists of a mixture of two carbyne products in a 3:1 intensity ratio. Major isomer will be noted as isomer A, whereas the minor isomer will be noted as B. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): −8.90 (t, $J_{(H-P)}$ = 16 Hz, Os–H, A), −5.88 (t, $J_{(HP)}$ = 15 Hz, Os–H, B), 0.39 (s, Os≡C–CH_3, B), 0.72 (s, Os≡C–CH_3, A), 1.12 (dvt, N = 13.5 Hz, Os–P(CH(CH_3)$_2$), A + B overlapped), 1.22 (dvt, N = 13.5 Hz, Os–P(CH(CH_3)$_2$), A + B overlapped), 2.25 (m, Os–P(CH(CH$_3$)$_2$), B), 2.44 (m, Os–P(CH(CH$_3$)$_2$), A). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 31.0 (A), 32.6 (B). ^{13}C{^{1}H} NMR (125.6 MHz, C$_6$D$_6$, 25 °C): 19.1 (s, Os–P(CH(CH_3)$_2$), A), 19.2 (s, Os–P(CH(CH_3)$_2$), B), 19.6 (s, Os–P(CH(CH_3)$_2$), A), 19.7 (s, Os–P(CH(CH_3)$_2$), B), 24.3 (t, $J_{(C-P)}$ = 12 Hz, Os–P(CH(CH$_3$)$_2$), B), 25.3 (t, $J_{(C-P)}$ = 13 Hz, Os–P(CH(CH$_3$)$_2$), A), 38.1 (s, Os≡C–CH_3, A), 39.4 (s, Os≡C–CH_3, B), 116.1 (q, $J_{(C-F)}$ = 291 Hz, Os–OCO(CF_3), A + B overlapped), 159.9 (q, $J_{(C-F)}$ = 45 Hz, Os–OCO(CF$_3$), B), 161.7 (q, $J_{(C-F)}$ = 45 Hz, Os–OCO(CF$_3$), A), 266.7 (t, $J_{(C-P)}$ = 11 Hz, Os≡C–CH$_3$, A), 276.5 (t, $J_{(C-P)}$ = 11 Hz, Os≡C–CH$_3$, B).

Reaction of OsH$_3$Cl(P^{i}Pr$_3$)$_2$ and vinyl trifluoroacetate at low temperatures

Vinyl trifluoroacetate (2.12 μL, 0.018 mmol) was dissolved in 0.8 ml of toluene-d^8. The solution was vacuum transferred into an NMR tube charged with OsH$_3$Cl(P^{i}Pr$_3$)$_2$ (0.0100 g, 0.018 mmol) and frozen at 78 K. The NMR tube was thawed and shaken for one second prior inserting it into a precooled NMR probe at −80 °C. The temperature of the probe was raised to room temperature in 10 °C intervals and the solution was allowed to react for 5 min prior to acquiring the ^{1}H NMR and ^{31}P {^{1}H} NMR spectra. Only diagnostic data is provided

for the identified compounds. Data for the compound $OsH_3Cl(H_2C=CH(O_2CCF_3))(P^iPr_3)_2$, **V**: ^1H NMR (300 MHz, C_7D_8, $-70\,^{\circ}C$): -4.05 (t, $J_{(H-P)} = 20$ Hz, Os–H, H), -14.78 (br Os–H, 2H), 2.75, 2.87 (br AB, Os(H_2C=CH-(O_2CCF_3)), 2H), 3.97 (br AB, Os(H_2C=C$H(O_2CCF_3)$), H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_7D_8, $-70\,^{\circ}C$): 37.8. Data for the compound $OsCl(CH(CH_3)(O_2CCF_3))(P^iPr_3)_2$, **VII**: ^1H NMR (300 MHz, C_7D_8, $-70\,^{\circ}C$): 1.60 (d, $J_{(H-H)} = 6.6$ Hz, Os–$CH(CH_3)(O_2CCF_3)$, 3H), 0.77 (q, $J_{(H-H)} = 6.6$ Hz, Os–$CH(CH_3)(O_2CCF_3)$, H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_7D_8, $-70\,^{\circ}C$): 28.9. Data for the compound $OsCl(O_2-CCF_3)(=CH(CH_3))(P^iPr_3)_2$, **VIII**: ^1H NMR (300 MHz, C_7D_8, $-60\,^{\circ}C$): 18.5 (br Os=C$H(CH_3)$, H), 1.68 (br, Os=CH-(CH_3), 3H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_7D_8, $-60\,^{\circ}C$): 20.2.

Synthesis of $OsHCl_2(CMe)(PPh_3)_2$, XII

In an NMR tube $OsHCl(PPh_3)_3$ (0.0100 g, 0.01 mmol) was dissolved in 0.8 mL of benzene-d_6 and vinyl chloroformate (0.9 μL, 0.01 mmol) was added to the solution. The reaction was allowed to proceed for 2 days at room temperature. At this point the hydrido-carbyne is the major species. The volatiles were removed *under vacuo* and a brown solid is obtained. The solid is redissolved in benzene-d_6. Only diagnostic data is provided for the carbene and the title product. Data for the carbene, **XI**: ^1H NMR (300 MHz, C_6D_6, $20\,^{\circ}C$): 19.76 (tq, $J_{(H-P)} = 11$ Hz, $J_{(H-H)} = 5$ Hz, Os=C$H(CH_3)$, H), 1.70 (d, $J_{(H-H)} = 5.5$ Hz, Os=CH(CH_3), 3H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_6D_6, $20\,^{\circ}C$): 8.1. Data for the title compound: ^1H NMR (300 MHz, C_6D_6, $20\,^{\circ}C$): -5.60 (t, $J_{(H-P)} = 15$ Hz, Os–H, H), -0.59 (t, $J_{(H-P)} = 2.4$ Hz, Os≡C–CH_3, 3H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_6D_6, $20\,^{\circ}C$): 4.6. ^{13}C $\{^1H\}$ NMR (100 MHz, C_6D_6, $20\,^{\circ}C$): 34.8 (s, Os≡C–CH_3), 278.2 (t, $J_{(H-P)} = 12$ Hz, Os≡C).

Synthesis of $OsHCl(O_2CCF_3)(CMe)(PPh_3)_2$ isomers, XIV

In an NMR tube $OsHCl(PPh_3)_3$ (0.0100 g, 0.01 mmol) was dissolved in 0.8 mL of benzene-d_6 and vinyl trifluoroacetate (1.1 μL, 0.01 mmol) was added to the solution. The reaction was allowed to proceed for 2 days at room temperature. At this point the two hydrido-carbyne isomers are the major species. The volatiles were removed *under vacuo* and a brown solid is obtained. The solid is redissolved in benzene-d_6. The major isomer will be noted as **A**, whereas the minor isomer will be noted as **B**. Only diagnostic data is provided for the carbene intermediate and the title compound. Data for the carbene intermediate, **XIII**: ^1H NMR (300 MHz, C_6D_6, $20\,^{\circ}C$): 21.1 (m, Os=C$H(CH_3)$, H), 1.65 (d, $J_{(H-H)} = 6.6$ Hz, Os=CH(CH_3), 3H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_6D_6, $20\,^{\circ}C$): 5.5. Data for the carbyne isomers: ^1H NMR (300 MHz, C_6D_6, $20\,^{\circ}C$): -4.24 (t, $J_{(H-P)} = 15$ Hz, Os–H, H,**A**), -7.45 (t, $J_{(H-P)} = 16$ Hz, Os–H, H, **B**), -0.13 (t, $J_{(H-P)} = 2.4$ Hz, Os≡C–CH_3, 3H, **A**), -0.28 (s, Os≡C–CH_3, 3H, **B**). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_6D_6, $20\,^{\circ}C$): 18.1 (**A**), 11.7(**B**).

Synthesis of $RuCl_2(=CHMe)(PPh_3)_2$

In an NMR tube, $RuHCl(PPh_3)_3$ (0.0100 g, 0.011 mmol) was dissolved in 0.8 ml of benzene-d_6 and vinyl chloroformate (1 μl, 0.011 mmol) was added to the solution. The reaction was allowed to proceed for 1 day at room temperature. The volatiles were removed *under vacuo* and a brown solid is obtained. The solid is redissolved in benzene-d_6. Its spectroscopic data (^1H NMR and ^{31}P $\{^1H\}$ NMR) compares to that reported in the literature[15] within experimental error. only diagnostic data for the intermediate $RuCl(O_2CCl)(=CHMe)(PPh_3)_2$ is provided: ^1H NMR (300 MHz, C_6D_6, $20\,^{\circ}C$): 16.7 (tq, $J_{(H-P)} = 13.5$ Hz, $J_{(H-H)} = 6$ Hz, Ru = C$H(CH_3)$, H), 2.12

(d, $J_{(H-H)} = 6$ Hz, Ru = CH(CH_3), 3H). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_6D_6, $20\,^{\circ}C$): 37.7, 48.1 (AB, $J_{(P-P')} = 430$ Hz)

Synthesis of $OsHCl_2(CMe)(P^tBu_2Me)_2$

In an NMR tube $OsH_3Cl(P^tBu_2Me)_2$ (0.0100 g, 0.018 mmol) was dissolved in 0.8 mL of benzene-d_6 and vinyl chloroformate (3.25 μL, 0.036 mmol) was added to the solution. The reaction was allowed to proceed for 15 min at room temperature. At this point the hydrido-carbyne is the major species. Some ethylene and vinyl chloride are observed in the solution. The volatiles were removed *under vacuo* and a brown solid is obtained. The solid is redissolved in benzene-d_6. ^1H NMR (300 MHz, C_6D_6, $20\,^{\circ}C$): -8.96 (t, $J_{(H-P)} = 15$ Hz, Os–H, H), 0.78 (s, Os≡C–CH_3, 3H), 1.26 (vt, $J_{(H-P)} = 6.3$ Hz, Os–(PCH$_3$-$(C(CH_3)_3)$), 1.30 (vt, $J_{(H-P)} = 5.5$ Hz, Os–(PCH$_3$(C(CH_3)$_3$)), 1.86 (vt, $J_{(H-P)} = 11.1$ Hz, Os–(PCH_3(C(CH$_3$)$_3$)). ^{31}P $\{^1H\}$ NMR (121.4 MHz, C_6D_6, $20\,^{\circ}C$): 28.6. ^{13}C $\{^1H\}$ NMR (75 MHz, C_6D_6, $20\,^{\circ}C$): 3.7 (t, $J_{(C-P)} = 14$ Hz, Os–(PCH_3-$(C(CH_3)_3)$), 29.5 (s, Os–(PCH$_3$(C(CH_3)$_3$)), 31.1 (s, Os–(PCH$_3$-$(C(CH_3)_3)$), 36.7 (t, $J_{(C-P)} = 11$ Hz, Os–(PCH$_3$(C(CH$_3$)$_3$)), 38.3 (t, $J_{(C-P)} = 11$ Hz, Os–(PCH$_3$(C(CH$_3$)$_3$)), 40.8 (s, Os≡C–CH_3), 271.2 (t, $J_{(H-P)} = 13$ Hz, Os≡C).

$OsH(OTf)(CO)(P^tBu_2Me)_2$

Me_3SiOTf (70 μl, 0.36 mmol) was added dropwise to benzene (5 mL) solution of $OsHF(CO)L_2$ (200 mg, 0.36 mmol; L = P^tBu_2Me). The solution color changed to dark red after stirring for 10 min at $20\,^{\circ}C$. after evaporation of volatiles, the residue was dissolved in 2 mL toluene and cooled to $-40\,^{\circ}C$ for 24 h to afford orange crystals, which were filtered at $-78\,^{\circ}C$, washed with pentane and dried. Yield 100 mg (40%). Anal. Calcd for $C_{20}H_{43}F_3O_4OsP_2S$: C, 34.89; H, 6.29. Found: C, 34.93; HHHHh, 5.99. ^1H NMR (360 MHz, $20\,^{\circ}C$): 1.60 (br s, 6H, PCH_3), 1.15 (vt, N = 13.3 Hz, 18H, PC(CH_3)$_3$), 1.04 (vt, N = 12.6 Hz, PC(CH_3)$_3$), -35.6 (t, $J_{PH} = 13.7$ Hz, 1H, Os–H). $^{31}P\{^1H\}$ NMR (146 MHz): 49.5 (s). IR (C_6D_6, cm^{-1}): 1908 ($v(CO)$)

$OsH(OTf)(OH_2)(CO)(P^tBu_2Me)_2$

Water (*ca.* 0.3 μL) was added to $OsH(OTf)(CO)L_2$ (10 mg, 0.018 mmol) in CD_2Cl_2 (0.5 mL) to yield a light yellow solution. ^1H NMR (300 MHz, $20\,^{\circ}C$): 2.87 (br s, coordinated H_2O), 1.37 (vt, N = 12.6 Hz, 24 H, PC(CH_3)$_3$ and overlapping with PCH_3), 1.30 (vt, N = 12.9, 18 H, PC(CH_3)$_3$), -23.7 (t, $J = 14.4$, Os–H). $^{31}P\{^1H\}$ NMR: 39.7 (s). IR (CD_2Cl_2): 1896 ($v(CO)$).

$[OsH(\eta^2–CD_2Cl_2)(CO)(P^tBu_2Me)_2]BAr'_4$

$OsH(OTf)(CO)L_2$ (10 mg, 0.014 mmol) and $NaBAr'_4$ (12.9 mg) was mixed in CD_2Cl_2 (0.5 ml). Thirty minutes after the mixing, NMR spectra reveals clean formation of a complex. ^1H NMR (300 MHz, $20\,^{\circ}C$): 1.61 (br, 6H, PCH_3), 1.32 (vt, N = 13.5 Hz, 18H, PC(CH_3)$_3$), 1.18 (vt, N = 13.2 Hz, 18H, PC(CH_3)$_3$), -27.5 (br, 1 H, $w_{1/2} = 486$ Hz, Os–H). ^{19}F NMR (282 MHz): -61.9 (s, BAr'$_4$). $^{31}P\{^1H\}$ NMR: 42.9 (s)

$[OsH(\eta^3–CH_2=CHOC(O)CF_3)(CO)(P^tBu_2Me)_2]BAr'_4$, XV

$OsH(OTf)(CO)L_2$ (10 mg, 0.018 mmol) and $NaBAr'_4$ (12.9 mg, 0.018 mmol) was dissolved in CD_2Cl_2 (0.5 mL). To the solution, $CH_2=CHOC(O)CF_3$ (1.5 μL) was added. The solution color changed to light yellow immediately. NMR spectral analysis show exclusive formation of $OsH(\eta^3–CH_2=CHOC(O)-CF_3)(CO)L_2]BAr'_4$. ^1H NMR (300 MHz, $20\,^{\circ}C$): 7.09 (dtd, $J_{HH} = 13.5$ Hz, $J_{PH} = 5.1$ Hz, $J_{HH} = 2.1$ Hz, 1H, =CH–O), 2.58 (m, 1H, CH_2=), 2.51 (m, 1H, CH_2=), 1.84 (d, $J_{PH} = 8.4$ Hz, 3H, PCH_3), 1.49 (d, $J_{PH} = 10$ Hz, 3H, PCH_3), 1.45 (d,

J_{PH} = 14.4 Hz, 9H, PC(CH$_3$)$_3$), 1.34 (d, J_{PH} = 14.1 Hz, 18H, PC(CH$_3$)$_3$), 1.23 (d, J_{PH} = 13.5 Hz, 9H, PC(CH$_3$)$_3$), −1.92 (dd, 1 H, J_{PP} = 27.6, 33 Hz, Os–H). ^{31}P{^{1}H} NMR (121 MHz): 27.6 (d, J_{PP} = 112 Hz, Os–P), 25.6 (d, J_{PP} = 112 Hz, Os–P).

[OsH(η^3–CH$_2$=CHOC(O)CH$_3$)(CO)(P^{t}Bu$_2$Me)$_2$]BAr$'_4$

Same procedure as above was followed except CH$_2$=CHO-C(O)CH$_3$ was used. ^{1}H NMR (300 MHz, 20 °C): 6.73 (ddt, J_{PH} = 5.4 Hz, J_{HH} = 6 Hz, J_{HH} = 11.7 Hz, 1H, CHO), 2.48 (m, CH$_2$), 2.36 (t, J = 5.7 Hz, 1H, CH$_2$), 2.17 (s, 3H, CH$_3$CO), 1.77 (vt, 3H, N = 6.9 Hz, PCH$_3$), 1.48 (vt, 3H, N = 6.9 Hz, PCH$_3$), 1.41 (vt, 9H, N = 14.4 Hz, PC(CH$_3$)$_3$), 1.34 (vt, 9H, N = 14.4 Hz, PC(CH$_3$)$_3$), 1.24 (vt, 9H, N = 14.1 Hz, PC(CH$_3$)$_3$), 1.26 (vt, 9H, N = 14.1 Hz, PC(CH$_3$)$_3$), -2.39 (t, 1 H, J_{PH} = 30 Hz, Os–H). ^{31}P{^{1}H} NMR (121 MHz): 25.9 (s). IR (CD$_2$Cl$_2$): 1959 (v(CO), 1619 (v(C=O)).

Computational details

The calculations were carried out using the Gaussian 98 set of programs[24] within the framework of DFT at the B3PW91 level.[25,26] LANL2DQ effective core potentials (quasi-relativistic for the metal centers) were used to replace the 28 innermost electrons of Ru[27] and the ten core electrons of Cl, and P.[28] The associated double-basis set was used[27,28] and was augmented by a d polarization function for Cl, and P.[29] The other atoms were represented by a 6-31 (d,p) basis set (5d).[30] Full geometry optimization was performed with no symmetry restriction, and the nature of the minima was assigned by analytical frequency calculations.

Acknowledgements

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