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Mini Review

Factors governing the equilibrium between metal–alkyl, alkylidene and alkylidyne: MCX_2R, $X–M=CXR$ and $X_2M\equiv CR$

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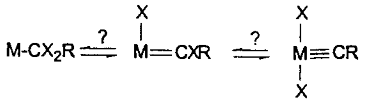
Abstract

The reactions of vinyl ethers, $H_2C=CH(OR)$, with $RuHClL_2$ ($L = P^iPr_3$) furnish the carbene complexes $RuHCl[C(CH_3)(OR)]L_2$ by H migration. $Os(H)_3ClL_2$ serves as a surrogate for unknown $OsHClL_2$, to give the analogous carbene, but this transforms further for R=Ph to give the carbyne $OsHCl(OPh)(CCH_3)L_2$. DFT calculations furnish insight into the relative thermodynamic stability of the various isomeric species, and are consistent with the major influence of π-donation by OR, as well as the preference of Os (versus Ru) for saturation and higher oxidation state. Comparison of the reactivity of $H_2C=CHD_0$ (D_0 = π-donor) towards $MHClL_2$ versus Cp_2ZrHCl shows the dominant influence of metal π-donor power. Ruthenium and osmium complexes containing an MCF_3 subunit show remarkably facile isomerization to $FM=CF_2$ carbenes. © 2001 Published by Elsevier Science B.V.

Keywords: Carbene complexes; Alkylidene; Alkylidyne

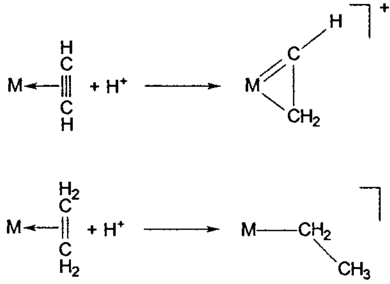
1. Introduction

We deal here with what can hopefully be agreed is a subject that is so elementary that it might otherwise be entirely neglected: the interconversion of an alkyl ligand with a carbene or a carbyne, all by α-substituent migration (Eq. (1)). Although this is rarely thought of as a designed, controllable synthetic route, the mechanistic plausibility of what is simply a 1,2-substituent migration will hopefully be sufficient to induce the reader to proceed further! Clearly, the two conversions in Eq. (1) will depend heavily on the identity of M and of X. The factors that require consideration are of course both thermodynamic and kinetic. As will be seen, the identities of M and X will influence both of these factors. We choose to focus initially on M, being a late transition metal, and will exploit the comparison of 4d and 5d representatives of the same group to better understand the thermodynamic influence of M. The migration has not yet been observed for X = alkyl, but X = H and X = OR, O_2CR and F will all be described. Given the considerable migratory aptitude of SiR_3, it should be profitable to seek such examples, but they have not yet been observed.



$$M\text{-}CX_2R \overset{?}{\rightleftharpoons} \overset{X}{\overset{|}{M}}{=}CXR \overset{?}{\rightleftharpoons} \underset{X}{\underset{|}{\overset{X}{\overset{|}{M}}}}{\equiv}CR \qquad (1)$$

From the earliest days of organometallic chemistry, one observation of practitioners of the trade was that hydrocarbyl groups which were short-lived in the free state were ‘stabilized’ (i.e. were persistent) when attached to a metal: cyclobutadiene, carbene, carbyne, etc. Moreover, by stabilizing the product, reactions that were highly improbable (e.g. endergonic) for the free hydrocarbon (e.g. acetylene or ethylene) became possible (Eq. (2)).



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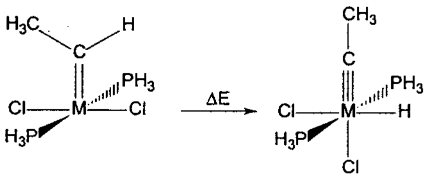
2. Historical background

2.1. Hydrocarbon carbenes and carbynes

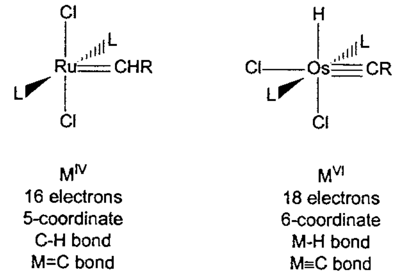
Our entry into this subject was with a surprising observation [1]. Reaction of $Os(H)_2Cl_2L_2$ ($L = P^iPr_3$) with styrene (1:2 mole ratio) produced the carbyne complex $OsHCl_2(CCH_2Ph)L_2$, together with equimolar PhEt, the product of hydrogenation of styrene. The H and $\equiv CCH_2Ph$ ligands on Os represent the formal rearrangement products of styrene: double dehydrogenation of the styrene C_α, with migration of one H to Os and the other H to C_β. This same compound was made earlier by the reaction of $Os(H)_2Cl_2L_2$ with equimolar $HC\equiv CPh$ [2]. The similar product from reagents with different carbon oxidation levels, we feel, is due to $OsHCl_2(carbyne)L_2$ being in a particularly deep thermodynamic well.

The synthesis of a carbyne from an olefin is an exceptionally easy route to such a ligand. What was especially remarkable, in our view, is that $OsHCl_2(CR)L_2$ is an isomer of the well-studied class of molecules $RuCl_2(CHR)L_2$. Irrespective of the charge attributed to carbene and carbyne ligands, we proposed to call these 'redox isomers'; with the charge assignments RC^{3-} and RHC^{2-}, these compounds contain Os^{VI} and Ru^{IV}. Are these contrasting redox isomers thermodynamic products, or could it be that one is a kinetic product? We attempted isomerization of each molecule to its redox isomer by reflux in hydrocarbon solvent for many hours, but recovered unaltered reagent; this permits the tentative conclusion that the distinct isomeric Os and Ru species are in fact thermodynamic products. If true, why do Os and Ru have different preferred ground states? Distinguishing features of the two structures (Scheme 1) can be interpreted as the 5d metal being more reducing, and also preferring coordinative saturation. Given the generally greater strength of metal/ligand bonds for 5d versus 4d metals, it might also be argued that Os prefers the redox isomer with more metal/ligand bonds. This qualitative, after-the-fact rationalization, was given objective support by DFT (density functional theory) calculations of ΔE for this 1,2-H migration reaction (Eq. (3)). ΔE for forming hydrido carbyne



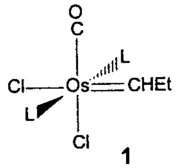
(3)

from carbene is over 20 kcal mol^{-1} less favorable for M = Ru than for M = Os. On a confessional note, the DFT calculations with PH_3 as a model of P^iPr_3, leave ΔE positive (by 6.4 kcal mol^{-1}) even for M = Os, but calculation with a more electron-donating PR_3 would presumably move towards a negative calculated ΔE. We routinely emphasize the application of DFT for comparison, rather than for absolute numbers. Alternatively stated, we do not believe calculated ΔE values for transition metal complexes carried out at our level of computation to better than approximately ±5 kcal mol^{-1}. Calculated structures can be more accurate, however.



Scheme 1.

Can hydrogen migration in $OsHCl_2(CR)L_2$, from Os to carbon, be induced? The π-acid CO (1 atm) reacts [3] with $OsHCl_2(CEt)L_2$ within 14 h at 20°C. This represents rather mild conditions for CO addition to an 18-electron 5d metal. The product, **1**, has the hydride ligand now attached



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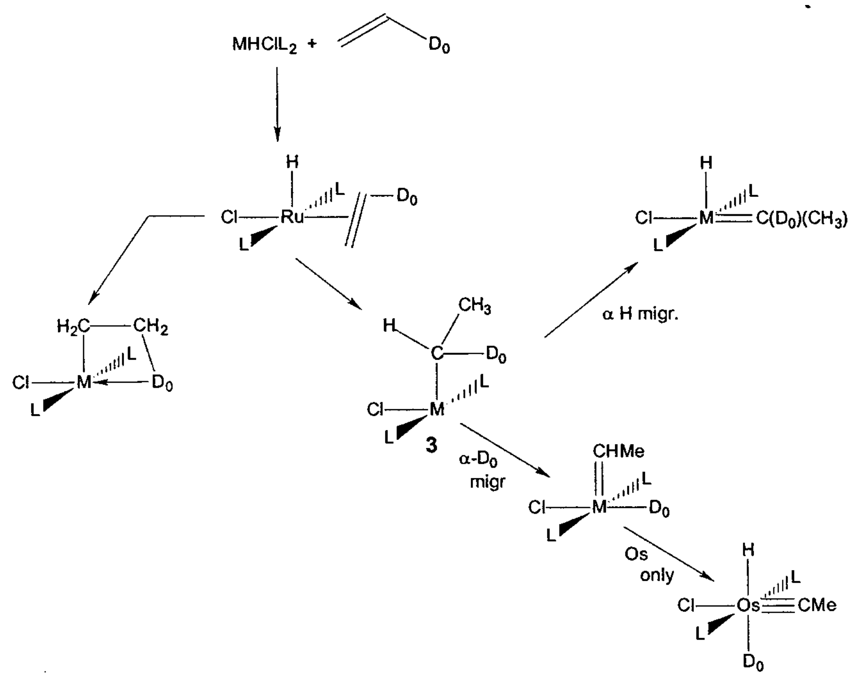
to the former carbyne carbon, so migration is indeed possible. A pre-equilibrium migration of the hydride (Eq. (4)) can be ruled out as the mechanism for this CO addition because the calculated

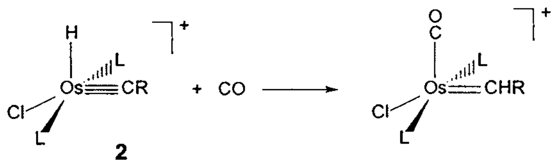
$$OsHCl_2(CEt)(PH_3)_2 \rightarrow OsCl_2(CHEt)(PH_3)_2 \qquad (4)$$

energy for the transition state is 27.2 kcal mol^{-1} above the hydrido/carbyne reagent, a value too large to be consistent with the observed reaction rate. The reaction must therefore be associative in CO. This demonstrates a valuable application of DFT computations: quantitative evaluation of unimolecular transition state energies can be a unique mechanistic tool.

The sodium electrophile in $NaBAr^F_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) effects chloride abstraction from $OsHCl_2(CR)L_2$ to give the unsaturated species **2**, which retain the separate hydride and carbyne ligands. However, addition of CO to this effects H migration, to give a carbene complex (Eq. (5)). Since this 1,2-H migration is formally a reduction of Os, the arrival of the π-acidic CO ligand must be thought of as effecting reductive coupling of H^- and CR^{3-}, to give CHR^{2-}, and reduced Os, which is then better able to back bond to CO. This need to adjust the π-basicity of Os is especially great in a cationic species, and one containing two π-acid ligands, carbene and CO.



Scheme 2.



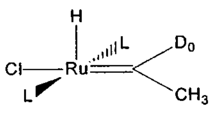
2 (5)

3. Heteroatom-stabilized carbene complexes from olefins

3.1. Ruthenium

Dehydrohalogenation of $Ru(H)_2Cl_2L_2$ ($L = P^iPr_3$) with a strong base gives [4] a compound of empirical formula $RuHClL_2$. Although this exists in hydrocarbon solvents as the dimer $[RuH(\mu{-}Cl)L_2]_2$, it is a source of the *cis*-divacant octahedral fragment $RuHClL_2$. This structure has the property of binding π-acid fragments *cis* to hydride, and thus enabling facile reaction between hydride and substrate. The variety of such reactions is shown in Scheme 2. When the substrate is an olefin bearing a π-donor substituent (i.e. vinyl ethers, amines, amides, esters), hydrogen migration from Ru to an sp^2 carbon is facile. Although both H-migration regiochemistries are detected, only **3** leads to the thermodynamically-preferred carbene ligand, with hydride back on Ru. We have analyzed the DFT energies of the various isomers, and studied various substituents D_o and established the following:

1. Both computation and experiment show that the isomerization of olefin to coordinated carbene does not occur if $D_o = H$; purely hydrocarbon olefins are not isomerized, for thermodynamic reasons;
2. D_o stabilizes both the free carbene and the coordinated carbene;
3. π-donation from Ru also stabilizes the carbene;
4. If the π-donor ability of Ru is diminished by replacing the chloride ligand by CO, the isomer preference is reversed, and the alkyl form **5**, further stabilized by β-D_o donation to the metal, becomes the ground state. Apparently the carbene **4** is stabilized by Cl → Ru π-donation, while the absence of this makes the carbonyl analog favor the alkyl [5,6]. It is nevertheless important to recognize that these several isomers are all within easy reach (i.e. ∼ + 5 kcal/mol) on the potential energy surface, and a modest perturbation can lead to the formation of an alternative isomer. Thus, $RuH(CO)L_2^+$ reacts with 2,3-dihydrofuran (Eq. (6)) beyond the η^2-olefin product, to give a carbene complex. In this vinyl ether, where four-membered ring formation in the alkyl isomer is sterically precluded by the ring constraint, the carbene isomer is preferred to the η^2-vinyl ether alternative.



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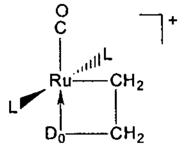
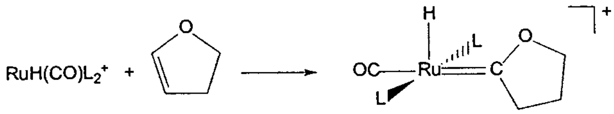
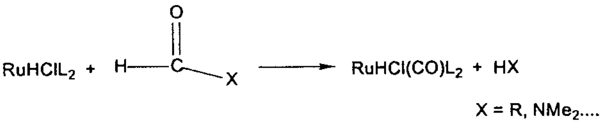


4 **5**


(6)

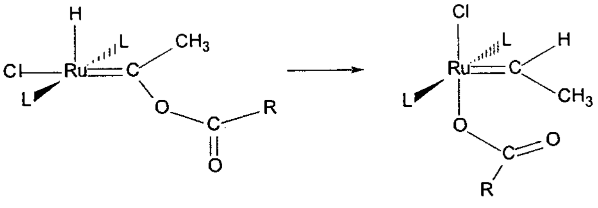
The preference for the heteroatom-stabilized carbene alternative of the ligand is so strongly developed that it can even be used [7] to effect geminal double dehydrogenation of an sp^3 carbon (Scheme 3). We propose to think of all these reactions as oxidation of $RuHClL_2$, enabled by the extensive π-donor power of Ru(II) devoid of any π-donor ligands and enhanced by $Cl \rightarrow Ru$ π-donation. Since the products all contain a π-acid ligand, this provides the thermodynamic driving force. This is further supported by the ability of $RuHClL_2$ to abstract [8] the π-acid ligand CO from aldehydes and amides (Eq. (7)) and to abstract isonitriles from aldimines (Eq. (8)). In short, the reactions of $RuHClL_2$ occur to create π-acid ligands on Ru, be they carbenes, isonitriles, or CO.



(7)

$$RuHClL_2 + R'HC{=}NR \rightarrow RuHCl(CNR) + R'H \quad (8)$$

When D_o is a good leaving group, that is, a weaker nucleophile, this substituent in fact leaves the carbene carbon. Thus, acetate migrates to Ru and hydride migrates to carbon, leaving an unsaturated Ru and a non-heteroatom-stabilized carbene (Eq. (9)). This shows clearly that donor stabilization of the carbene ligand is finally insufficient with carboxylate, and such a weak donor (perhaps bidentate on Ru?) is preferred on the metal, with hydride on the carbene.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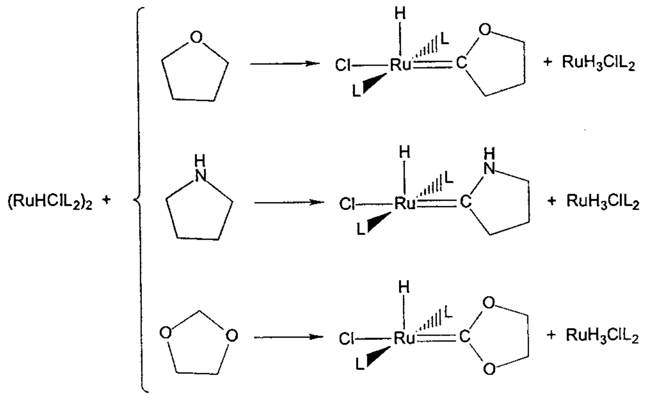
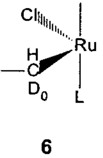

Scheme 3.

It is of interest that deuterium isotope label is observed to be scrambled during the time evolution of carbene complex formation, which proves that the H migration from Ru to olefinic carbon is *not* highly regioselective. It is the thermodynamic preference for the donor substituent on the carbene carbon that causes all products to derive from species **6**. In support of this claim, an alkyl intermediate has been observed in several cases. The inequivalences observed for the two phosphorus nuclei in this low temperature transient confirm the presence of a chiral carbon, which excludes the alternative regioisomer **7**. Indeed, DFT calculations reveal the less stable β-OMe isomer to be only 5.6 kcal mol^{-1} higher in energy.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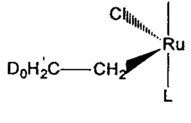
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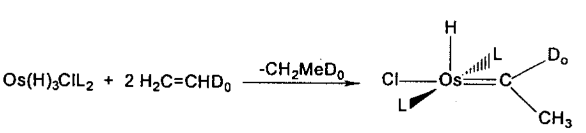
3.2. Osmium

Although '$OsHClL_2$' is not an available reagent, $Os(H)_3ClL_2$ serves as an alternative source of this fragment, after 2H are removed by reaction with a sacrificial olefin (i.e. olefin hydrogenation). Vinyl ethers react analogously to Ru to give a heteroatom-substituted carbene complex (Eq. (10)), but here the apparently greater electrophilicity of Os (see above) subsequently leads to migration of D_o = phenoxide to Os, to give the carbyne redox isomer of the Ru analogs [9]. Thus, the 2:1 reaction of phenyl vinyl ether with $Os(H)_3ClL_2$ ($L = P^iPr_3$) proceeds smoothly to give equimolar PhOEt and carbene complex **8**. However, this molecule is metastable and transforms (Eq. (11)) at 25°C by phenoxy migration to Os to give carbyne complex **9**. This clearly establishes the carbyne complex as thermodynamically more stable than the carbene redox isomer, consistent with what we surmised above about the $OsHCl_2(CR)L_2/OsCl_2(CHR)L_2$



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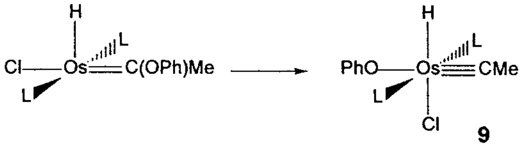
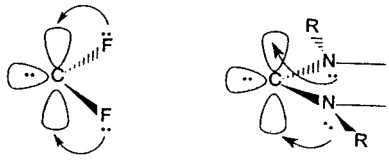


(11)

pair which led us into this chemistry. DFT calculations reveal that the (non-least motion) product **9**, with PhO

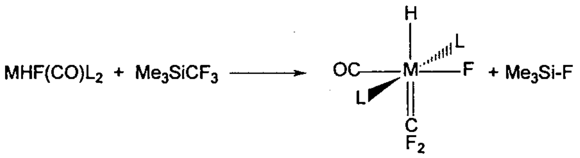


Scheme 4.

trans, not *cis*, to the carbyne is in fact the more stable stereoisomer. This is presumably because it has a better (trans) push/pull stabilization between PhO and carbyne. Although this is a formal 1,2-OPh migration, the location of OPh trans to CMe makes it likely that this is not an intramolecular reaction. Kinetic studies revealed that this migration is acid catalyzed; the rate can be slowed by adding proton sponge. This can then account for the lack of observation of the expected intramolecular migration product, that with PhO cis to carbyne.

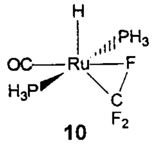
4. Migrations on Ru(II) and Os(II)

Some dramatic examples of migration involving an alkyl involve the rather atypical group CF_3. The reagent Me_3SiCF_3 is a formal source of nucleophilic CF_3. It is expected to react with M–F bonds to produce M–CF_3 and the thermodynamic driving force, Me_3Si–F. In fact, we have observed [10] (Eq. 12, M = Ru or Os) that the reaction proceeds further to give F–M=CF_2.



(12)

We proposed that this does indeed proceed through the intermediacy of the expected product $MH(CF_3)(CO)L_2$, but that this rearranges rapidly to the fluoro/carbene alternative.



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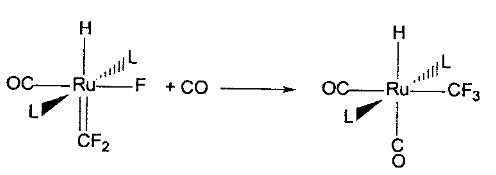
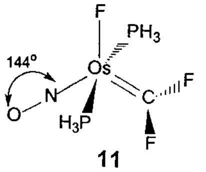
Quantum computations reveal that the (undetected) CF_3 complex should have an α-agostic structure, **10**, which would certainly facilitate rearrangement to the fluoro/carbene complex. Using the spin saturation transfer technique in the ^{19}F NMR spectrum of $RuHF(CF_2)(CO)L_2$, it was possible to show that, at 60°C, there is exchange between Ru–F and CF_2 fluorines on the timescale of 1 s^{-1}. A plausible physical mechanism for accomplishing this is to have an equilibrium reformation of an Ru–CF_3 isomer, which shows the close energetic proximity of this form, as well as the accessibly low barrier to the 1,2-F migration. This hypothesis simultaneously explains how it is possible for $RuHF(CF_2)(CO)L_2$ to react within minutes at 20°C to add CO (Eq. (13)), with reformation of CF_3. Low activation energy addition of a nucleophile 'to an 18-electron complex' can be understood if the CO actually attacks the Ru–CF_3 isomer, which either has an empty valence orbital or can form one by breaking the α-agostic fluorine link in **10**.



(13)

5. Migrations on Os(0)

Reaction of Me_3Si–CF_3 with $OsF(NO)L_2$ proceeds slowly (many hours at 25°C) to give the product of C–F bond scission, $OsF(CF_2)(NO)L_2$, together with Me_3SiF. DFT calculations establish that this carbene complex is indeed more stable than the $Os(CF_3)(NO)(PH_3)_2$ alternative, and give a product with geometry **11** which



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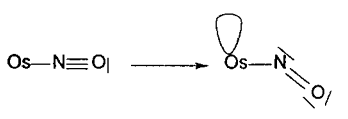
resembles a trigonal bipyramid. The modest bending of the OsNO unit suggests an NO^+ formulation, and thus, if CF_2 is taken as a neutral ligand, this is a complex of Os(0). Although the CF_2 conformation shown, with the CF_2 plane eclipsing the Os–P bonds, is the more stable one, the rotational barrier around this Os/C bond is low. This might be interpreted as indicating (Scheme 4) that $F \rightarrow C$ π-donation significantly diminishes the π-acidity of CF_2 'directed towards' the metal, since the carbon p_π orbital is nearly saturated by the fluorine lone pairs. This indicates a close relationship between CF_2 and the Arduengo carbenes, the latter now generally recognized [11] to approach in character a pure σ-donor to a metal, with very little π-acidity due to saturation of the carbon pure p_π orbital by amine lone pairs. Because strong π back bonding from metal to ligand is in effect the oxidation of a metal by a carbene ligand (i.e. $CR_2 \rightarrow CR_2^{2-}$), this supports the above supposition that CF_2 (and Arduengo carbenes) be assigned zero charge for the purpose of determining metal formation oxidation number. Note that this contradicts what would be predicted simply from considering the electronegativity of F, which is, of course, primarily a σ effect.

In contrast to $RuHF(CF_2)(CO)L_2$, where the angle F–Ru–CF_2 is about 90°, the F–Os–CF_2 angle in $OsF(CF_2)(NO)L_2$ is nearly 137°, which could make more difficult the achieving of an unsaturated isomeric Os–CF_3 structure. However, in the present case, a valuable application of computational chemistry is possible. It is possible to calculate the energetic cost of a geometric distortion from the ground state structure to open up F–Os–CF_2 angle so as to accommodate the approach of an arriving reagent. This 'rearrangement energy', essentially a tracing of the vibrational energy curve, can be evaluated by calculating the energy of changing the angle F–Os–CF_2 while holding all other structural parameters fixed; this thus gives an upper limit (due to the 'frozen' constraint) to the cost of changing this bond angle from its preferred value in $OsF(CF_2)(NO)(PH_3)_2$ itself. As shown in Fig. 1, a large increase (up to 30°) costs less than 3 kcal mol^{-1}. Also shown in this figure is the cost of bending the Os–N–O angle, while keeping all other structural parameters frozen. Here again, decreasing the angle by up to 25° costs less than 3 kcal mol^{-1}. The importance of this latter bending is that it is, simplistically said, a two-electron oxidation of the metal: those two electrons 'appear' on the nitrogen and thus an empty orbital is created on Os (Eq. (14)). This phenomenon has been studied computationally for reaction of $W(CO)_4(NO)Cl + PMe_3$ [12]. In sum, DFT calculations show that the presence of a nitrosyl ligand can facilitate nucleophilic addition to this CF_2 complex even without direct participation by an Os–CF_3 transient.



(14)

6. A unique spectroscopic characteristic

A signature feature of molecules of the type $Ru[C(H)X]Cl_2L_2$ is the ^1H NMR chemical shift of the hydrogen on the alpha (carbene) carbon: 16–20 ppm. This greatly facilitates detection of such carbenes. While the origin of this far downfield chemical shift is not clear, some empirical correlations are possible. Similar downfield chemical shifts are known for the M ← N(H)O [13] and M ← N(H)=NR [14] ligands, which clearly destroys any hypothesis that the downfield shift derives simply from an M=C bond. Metal formyl, M–C(H)=O, chemical shifts are also downfield (~ 12 ppm). The common feature might be sp^2 hybridization at the ligand α atom, although M–C(H)=CR_2 has a chemical shift only downfield to ~ 10 ppm. Moreover, since free aldehydes and even formate esters, HC(O)OR, have chemical shifts of 9–12 ppm, markedly downfield chemical shifts are not even uniquely derived from the presence of a transition metal. We suggest a provisional correlation of these

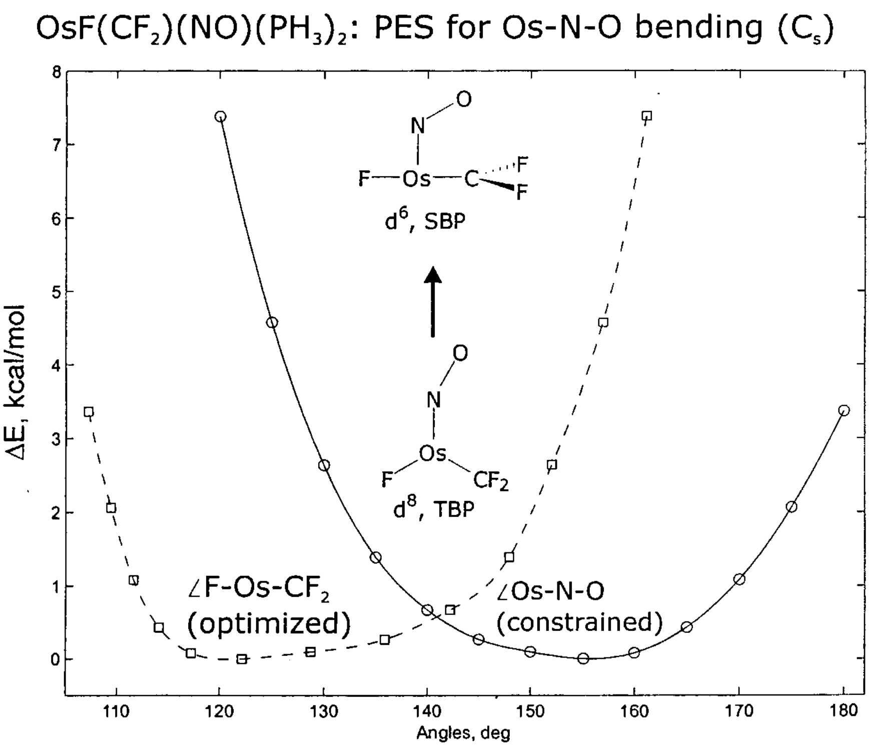
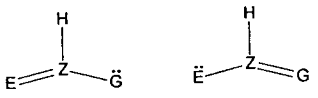


Fig. 1. Calculated DFT energies for selected angular deformations of $OsF(NO)(CF_2)(PH_3)_2$.



Scheme 5.

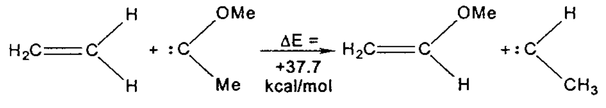
downfield chemical shifts with the presence of allylic resonance alternatives (Scheme 5), but the case where $E = Cl_2L_2Ru$ is clearly special in reaching the most downfield chemical shifts. Note that unsaturation at the metal is *not* a factor, since $OsCl_2[CHEt](CO)L_2$ has a carbene ^1H δ value [3] of 18.6.

7. Evaluation of bonding to these carbene carbons

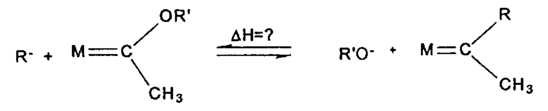
We are often asked if $RuHCl[C(D_o)Me]L_2$ are 'Fischer carbenes' or 'Schrock carbenes'. The presence of the heteroatom substituent on the carbene carbon gives them a formal resemblance to Fischer carbenes, but the fact that we can have analogs where D_o is H confuses the issue. In fact, analyses of wave functions for our molecules by a number of different criteria reveal [4] that while $RuHCl[C(OCH_3)CH_3](PH_3)_2$ are prototypical Fischer carbenes, $RuHCl[CH(CH_3)](PH_3)_2$ has characteristics between a Fischer and a Schrock carbene. For comparison, $RuCl_2[CH(CH_3)](PH_3)_2$ has typical Schrock carbene wave function characteristics.

Indeed, the terms Fischer and Schrock carbene convey the false impression that these are purely properties of the ligand. In fact, their existence is generally for a *distinct* metal/ancillary ligand environment: Fischer for middle- and late-transition metals in low oxidation states (often with very π-acidic carbonyl ancillary ligands) and Schrock for high oxidation state early transition metals which are often unsaturated. In this situation, any differences clearly cannot be attributed purely to the nonmetal carbene substituents. We have argued that reactivity is likewise not to be attributed purely to a ligand type (i.e. Fischer versus Schrock) and in fact olefin metathesis, a late-metal accomplishment, has never been causally associated with either carbene type.

One might like to pose the question, 'which is more reactive (or more stable), Fischer or Schrock carbenes?' A donor substituent significantly stabilizes a *free* carbene, as is clear from the thermodynamic comparison in Eq. (15). Here, we attribute most of the energy cost to the relative stability of the two carbenes.

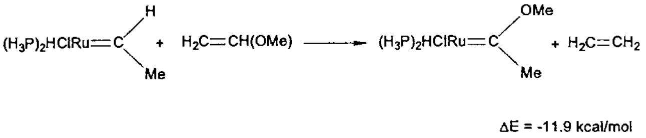


(15)

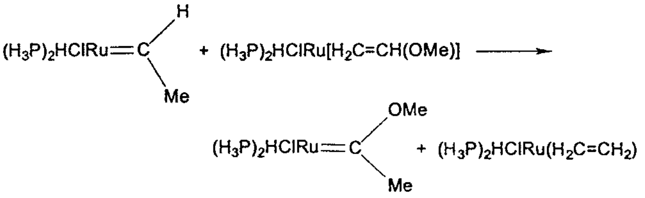


(16)

For metal/carbene complexes, any claim of heteroatom stabilization has been impossible to verify quantitatively because there is no experimental system where a comparison (e.g. Eq. (16)) can be made. The reaction that converts free (or coordinated) olefin to carbene now offers such a possibility. Experimentally, we have established that $RuHClL_2$ and $H_2C{=}CH(D_0)$ will not form a carbene complex for $D_0 = H$ but will do so for $D_0 = OR$. The DFT calculations permit a quantitative evaluation of a situation analogous to Eq. (16), and thus enable the desired comparison of heteroatom stabilization. A direct comparison of the two carbene complexes is also possible with respect to the two free olefins (Eq. (17)). A final comparison of these two carbene complexes is with reference to the coordinated olefins (Eq. (18)) for which $\Delta E = -13.9$ kcal mol^{-1}.



(17)



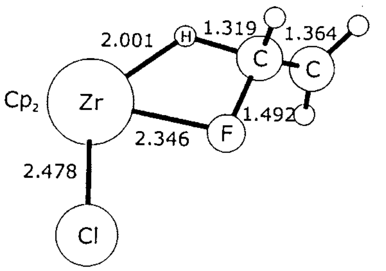
(18)

In summary, all of these comparisons indicate that the non-heteroatom-bearing carbene complex is less stable and thus more reactive.

8. A carbene of Zr(IV)?

It is generally considered that the heteroatom 'stabilizes' a carbene ligand relative to its purely hydrocarbon analogue. This is attributed to $D_0 \rightarrow C$ π donation. Indeed, it is for this reason that a heteroatom-stabilized carbene ligand will have less M/C π bond character than a hydrocarbyl carbene ligand, and the latter, because it *depends* on $M \rightarrow C$ carbene donation, is more oxidizing of the metal: back bonding is oxidation of the metal.

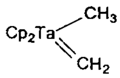
We have therefore turned to explore a very different part of carbene chemistry, indeed one that is without precedent. Those molecules termed 'Schrock carbenes' all have requisite metal electrons to complete the formation of a double bond between the metal and the



TS_A

Fig. 2. Calculated DFT transition state structure for Zr–H/C–F sigma bond metathesis.

carbene carbon, e.g. **12**. We are interested in a situation where L_nM has no d electrons, and thus L_nMCR_2 can only have a carbon-to-metal σ bond. We were drawn to this subject because our unsaturated monohydride $RuHClL_2$ (d^6) isomerizes $H_2C{=}CHD_0$ into the carbene ligand $C(Me)D_0$. Will a similar rearrangement occur with the d^0 unsaturated monohydride Cp_2ZrHCl?

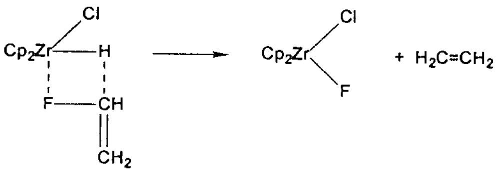


12

In fact, Cp_2ZrHCl reacts with vinyl ethers to give $Cp_2ZrCl(OR)$ and C_2H_4. Even the strong C–F bond of vinyl fluoride is cleaved (Eq. (19)). These reactions look like they could be:

$$Cp_2ZrHCl + H_2C{=}CHF \rightarrow Cp_2ZrFCl + H_2C{=}CH_2 \qquad (19)$$

effected by a sigma bond metathesis mechanism (Eq. (20)). After all, it was for the d^0 electron configuration that the σ-bond metathesis mechanism was initially conceived.



(20)

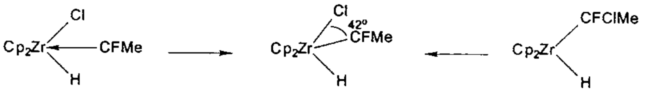
What then is the mechanism of this reaction? Because the insolubility of Cp_2ZrHCl causes the reaction rate to be diffusion-controlled, kinetic studies would not be informative about molecular encounters leading to the transition state. This is an ideal situation to supplement our understanding with a computational study. As will be seen, this allows learning not only the lowest energy path to product, but also structural details of higher energy species: the carbene.

Density functional theory (DFT) calculations reveal the transition state for σ-bond metathesis (Fig. 2) lies 13.0 kcal mol^{-1} higher than that for addition of Zr–H across the C=C double bond. From this latter transition state, β-F migration to Zr is facile, forming the product Zr–F bond concurrent with liberation of ethylene. Nowhere in the mechanism is there an η^2-olefin intermediate, neither of vinyl fluoride nor of ethylene. This is consistent with a d^0 electronic configuration lacking the ability to contribute to η^2-olefin intermediate stabilization by back donation. If true, then carbene species are anticipated to also be high energy structures.

13

(21)

Geometry optimization beginning with carbene **13** leads to a structure (Fig. 3) where the carbene has inserted Eq. (21) into the Zr–Cl bond. Therefore, **13** is not a minimum. Geometry optimization beginning with carbene **14** does lead to an apparent carbene (Fig. 3) as an energy minimum. However, the Cl–Zr–C angle is so small as to indicate some interaction, although the C/Cl separation is a long 2.09 Å (which is nevertheless below the sum of the van der Waals radii). Geometry optimization from a tetrahedral alkyl **15** (not a minimum)



14 **16** **15**

leads to the same odd geometry **16**. We therefore conclude that **16** has an unsatisfied CFMe carbene

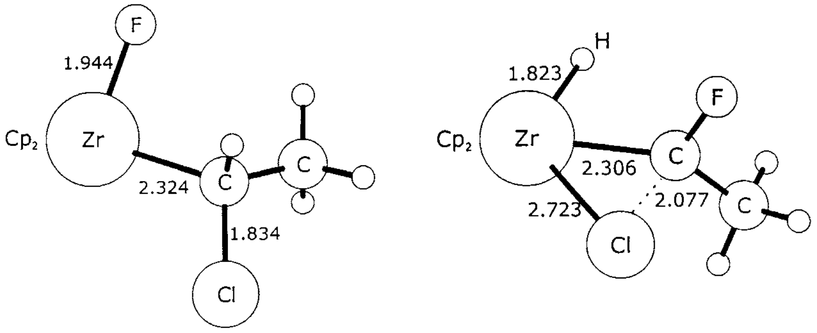
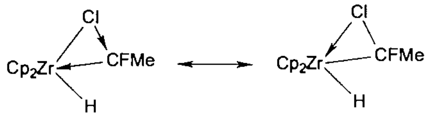


Fig. 3. Calculated DFT structures of haloethyl isomers.

ligand, and, in the absence of Zr → carbene donation, a lone pair of chlorine on Zr donates to the carbene p orbital (**17**). This unconventional bonding, which is a sort of mirror image of an agostic Cl **18**, is a symptom of an unstable carbene, and the energy of **16**, 20.3 kcal mol^{-1} above $Cp_2ZrHCl + H_2C{=}CHF$, reflects this also. However, the energy of dissociation of the carbene CFMe from structure **16** (Eq. (22)), 33.1 kcal mol^{-1}, shows that the carbene does bind significantly to the d^0 metal center.



17 **18**

16 (22)

9. Conclusions

The thermodynamic preferences of organometallic molecules to ‘simple’ transformations such as hydrogen migration, or even to more complex insertion/migration reactions are often difficult to understand, or even rationalize once the truth is experimentally established. In other cases, there is the question of whether an observed product is a kinetic or a thermodynamic one. Finally, there are cases (e.g. the insolubility of Cp_2ZrHCl) where kinetic studies are frustrated for technical reasons. These are all situations where density functional theory, when judiciously (i.e. skeptically) applied for learning general energetic and structural *trends*, can be a useful adjunct to the routinely-employed experimental laboratory instrumentation and techniques. You are invited to test this claim in your own research area!

Acknowledgements

This work is a tribute to the tremendous skills and intellect of the young colleagues whose names appear in the references. Special thanks are due to Professors Odile Eisenstein and Ernest R. Davidson for the computational studies and their insightful analysis of the resulting energies. Their efforts, and those of the French co-workers named in the references, helped reveal the essential determining factors behind the experimental observations.

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