

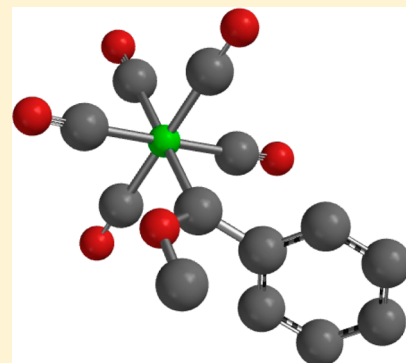
Fischer and Schrock Carbene Complexes: A Molecular Modeling Exercise

Craig D. Montgomery*

Department of Chemistry, Trinity Western University, 7600 Glover Road, Langley, BC, Canada V2Y 1Y1

S Supporting Information

ABSTRACT: An exercise in molecular modeling that demonstrates the distinctive features of Fischer and Schrock carbene complexes is presented. Semi-empirical calculations (PM3) demonstrate the singlet ground electronic state, restricted rotation about the C–Y bond, the positive charge on the carbon atom, and hence, the electrophilic nature of the Fischer carbene complex. Likewise, the triplet ground state of the Schrock carbene complex, along with the negative charge on the carbon atom and nucleophilic behavior, is also demonstrated.



KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Computer-Based Learning, Molecular Modeling, Organometallics, Coordination Compounds

INTRODUCTION

Transition metal carbene complexes, organometallic compounds possessing a $M=C$ double bond, represent a class of compounds of increasing significance in organic synthesis and as such are a topic of great importance in organometallic chemistry courses. Two types of transition metal carbene complexes can be identified and distinguished: Fischer carbene complexes and Schrock carbene complexes, as shown in Figure 1.

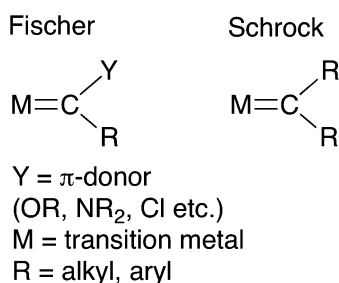


Figure 1. Fischer- and Schrock-type carbenes.

Fischer carbene complexes are now used extensively in organic synthesis, such as in cycloaddition reactions as well as the addition of amines and alcohols to photogenerated ketenes,¹ while Schrock carbene complexes find application most significantly in olefin metathesis.² Indeed the 2005 Nobel Prize in Chemistry was awarded to Chauvin, Grubbs and Schrock for “development of the metathesis method in organic synthesis”.³ As such, this *Journal* has included a number of lab

experiments involving the preparation and application of carbene complexes^{4,5} including *N*-heterocyclic carbenes.^{6,7} In addition, quantum mechanical studies have been undertaken on the bonding in Fischer and Schrock carbene complexes.⁸ Commonly, both Fischer- and Schrock-type carbenes are considered in undergraduate organometallic chemistry courses, along with the differences between these two subclasses of carbenes.

Accompanying the increase in the role of molecular modeling and computational methods in chemical research has been a parallel increase in the use of modeling in chemical education.^{9–14} Molecular modeling is important not merely as an aid in visualization, as important as that is, but also as a hands-on experience that leads to a deeper conceptual understanding.^{15–20} To that end, this paper presents an exercise in molecular modeling of Fischer and Schrock carbene complexes that allows the student not only to visualize these compounds, but also to understand in a hands-on manner the interplay of factors that bring about the differences between these two classes of organometallic compounds.

The author has employed this exercise in an upper level course in advanced inorganic chemistry (Advanced Inorganic Chemistry II) dealing with organometallic chemistry. The prerequisites for this course include second year inorganic chemistry and Advanced Inorganic Chemistry I, and therefore, a student who is completing this assignment would understand MO theory, including as applied to transition metal complexes. Additionally in Advanced Inorganic Chemistry II, the student

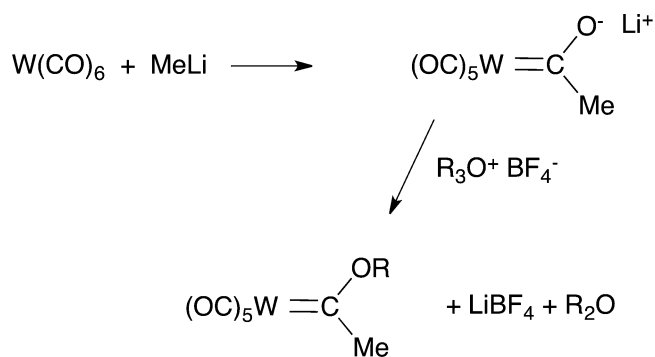
learns the synthesis, bonding features and reactivity for various ligands observed in organometallic chemistry, including the comparative features of Fischer vs Schrock carbenes. Obviously, it would be very difficult to supply the student with an accompanying lab experience that would illustrate the various points of comparison between these two types of complexes; such a lab would be very time-consuming. However, by assigning this exercise, the students have been provided with an opportunity to see these features demonstrated vividly in the molecular models. Student response has indicated that the exercise is successful in achieving this goal. The exercise is assessed based on the accuracy of the computations and the level of comprehension as displayed in the discussion points (see Procedure step 5 and the student instructions handout supplied in the [Supporting Information](#)).

RESULTS AND DISCUSSION

Evaluating the Precision of the Models

Fischer carbene complexes are generally prepared as shown in [Scheme 1](#), by nucleophilic attack at the carbon of a metal carbonyl complex, followed by alkylation using a trialkyl oxonium salt.²¹

Scheme 1. Synthetic Route to Fischer-Type Carbene Complexes



In this exercise, the Fischer carbene complex that we have chosen to model is $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$, the chromium analogue to the tungsten complex from [Scheme 1](#). This particular complex was chosen because it is among the first such compounds prepared and is relatively easily modeled. Initially, it is important to compare the optimized structure of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ with the experimental crystal structure of the same compound.²² In so doing, one can evaluate the validity of the modeling results and the suitability of PM3 calculations for this study. Selected bond lengths are shown in [Table 1](#).

The calculated structural features compare quite favorably with those from the crystal structure, especially when one bears in mind that additional packing forces can be at work in the case of the latter. The largest difference between experimental and calculated bond distances is 0.08 Å for the Cr–CO(trans) distance which suggests that this method is sufficiently accurate for the purpose of demonstrating the features of the two types of carbene ligands.

The Ground and Electronic States of Fischer and Schrock Carbene Ligands

To begin the actual comparison of Fischer and Schrock carbene complexes, one may first consider the ligands themselves. As

Table 1. Comparison of Calculated and Experimental Bond Lengths for *syn*- $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$

Complex	Calculated and Experimental Results for Bond Length, Å	
	$[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$, PM3 Model	$[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$, X-ray Crystal Structure ^a
Cr–C(OMe)Ph	2.02	2.05(3)
C–OMe	1.34	1.33(2)
O–Me	1.42	1.43(3)
Cr–CO(trans)	1.92	1.84

^aReference 22.

illustrated in [Figure 1](#), Fischer-type carbenes feature a substituent Y that is a π -donor (by virtue of having a lone pair of electrons available to donate to the carbon atom), such as OR, NR₂ or Cl. In addition, the tendency for such carbenes is to bind to low oxidation state transition metals with π -acceptor coligands (having an empty d-orbital such as on a phosphine, or an empty π^* orbital as on a CO ligand).²³ The $=\text{C}(\text{Y})\text{R}$ moiety is regarded as a neutral two-electron donor in a singlet electronic ground state.

Conversely, Schrock carbenes are lacking a π -donor substituent Y and, as ligands, are considered to be four electron donors with a charge of –2 for purposes of formal electron counting and having a triplet electronic ground state. The metals to which these ligands bind are generally early transition metals in higher oxidation states and with coligands that are non- π -acceptors.²³

The models of C(OMe)Me and CH₂ as shown in [Figure 2](#) with certain highlighted results in [Table 2](#). These two ligands were chosen as very simple representatives of each class.

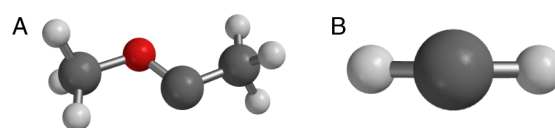


Figure 2. Fischer carbene ligand C(OMe)Me and Schrock carbene ligand CH₂. (A) C(OMe)Me; (B) CH₂.

Table 2. Comparison of C(OMe)Me and CH₂ Ligands

Energy Status	C(OMe)Me	CH ₂
Singlet State, kJ/mol	+24	+474
Triplet State, kJ/mol	+33	+300
π -orbital, eV	+0.4	–10.4
σ -orbital, eV	–9.0	–10.9

These results indicate that the singlet state is preferable for the Fischer carbene, whereas the triplet state is more stable in the case of the Schrock carbene, as illustrated in [Figure 3](#). The stability of the triplet state in the Schrock carbene ligand is due to the near-degeneracy of the σ - and π -orbitals (see [Table 2](#)). Conversely, the larger difference in energy between the σ - and π -orbitals of the Fischer carbene ligand destabilizes the triplet state relative to the singlet state.

Molecular Orbitals in Fischer and Schrock Carbenes

Furthermore, one may compare the ligand orbitals involved in bonding for the two species. Both ligands serve as σ -donors and π -acceptors, and students doing this exercise have been able to identify the orbitals that are so utilized. In the case of the singlet Fischer carbene ligand, σ -donation is done through the HOMO

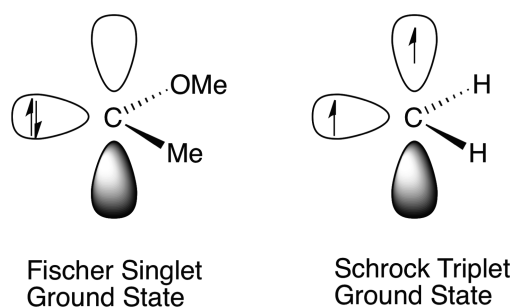


Figure 3. Ground electronic states for $\text{C}(\text{OMe})\text{Me}$ and CH_2 .

and π -back bonding occurs with the LUMO, whereas for the triplet Schrock ligand, σ - and π -bonding utilizes the HOMO – 1 and HOMO, respectively (Figure 4). In the case of the triplet Schrock ligand, the orbitals shown are α -spin.

Figure 5 plots out the σ and π orbitals of the Fischer and Schrock carbenes with the energies of the orbitals. This further illustrates the cause of the singlet ground state and the triplet ground state for the free Fischer and Schrock carbene ligands, respectively; that is, the large difference between the σ and π orbitals of the Fischer carbene gives rise to a singlet state, whereas the opposite is true of the Schrock carbene.

The figure also shows how the free carbene orbitals can then interact with the metal d-orbitals (of either σ - or π -symmetry, as is appropriate) to form the molecular orbitals of the carbene complex. In the case of the Fischer carbene ligand $\text{C}(\text{OMe})\text{Me}$, the π -orbital on the carbon atom is rather high in energy (+0.4 eV) as a result of the electronegative π -donor substituent $\text{Y} = \text{OMe}$; alternately, in the case of the Schrock carbene, the π -orbital is relatively low in energy (–10.4 eV). This gives rise to the corresponding schemes in Figure 5.

Additionally, the two bonding schemes result in the Fischer carbene complex having a pair of electrons in the π -bonding MO that resides more on the metal, while in the Schrock carbene complex, the pair of electrons in the π -bonding MO resides more on the carbon atom. This difference is a factor in the contrasting reactivities of the two types of carbenes, as discussed below.

Resonance Structures for the Fischer Carbene Complex

The π -donor ability of the Y substituent in a Fischer carbene complex also allows for two resonance structures as shown in

Figure 6, with form B being the dominant resonance form. As a result the M–C bond order, while greater than a single bond, is less than a true $\text{M}=\text{C}$ double bond. Evidence for the $\text{C}=\text{Y}$ double bond as in resonance structure B would include a shortening of the C–Y bond as well as restricted rotation about the C–Y bond. Indeed, both of these phenomena are observed in the modeling of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$. The C–OMe bond length is calculated to be 1.34 Å (compared to the experimental length of 1.33(2) Å), which is midway between a C–O single bond (1.43 Å) and a double bond (1.23 Å).²⁴

In addition, rotation about both the C–OMe and the Cr–C bonds is restricted. In the case of the C–OMe bond, this results in *syn* and *anti*-isomers, whereas in the case of the Cr–C bond, the restricted rotation results in two rotamers, one with the plane of the $\text{Cr}=\text{C}(\text{OMe})$ moiety eclipsed with the $\text{OC}–\text{Cr}–\text{CO}$ group and one where the two groups are staggered. Furthermore, it may be noted that the phenyl group is in a different orientation in Figure 7D. This is due to the fact that the C–Ph bond allows for free rotation and the phenyl substituent rotates to find the lowest energy conformation. The result of this restricted rotation is then four possible isomers *eclipsed, syn*–; *staggered, syn*–; *eclipsed, anti*–; and *staggered, anti*– (see Figure 7). By constraining dihedral angles, it is possible to optimize each of these isomers. In each case, once the model of the isomer is optimized, one may then remove the constraint on the dihedral angle and the model remains in that conformation; this is again consistent with the restricted rotation about the Cr–C and C–O bonds. The results of these calculations are shown in Table 3.

The *syn*-conformers are thermodynamically preferred over the two *anti*-conformers. This again compares well with the experimental crystal structure of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$, which adopts this same geometry.²² In the case of the *anti*-isomers, the eclipsed conformation is preferred, whereas in the case of the *syn*-isomers, the difference in energy is not sufficiently large to allow for differentiating between the eclipsed and staggered conformations. (The energy difference of 2 kJ/mol is within the error of the semiempirical method that was employed.) Nevertheless, the critical point to be observed in these calculations is that it is possible to optimize models for all four conformers. This indicates that both Cr–C and C–O bonds exhibit restricted rotation, consistent with the

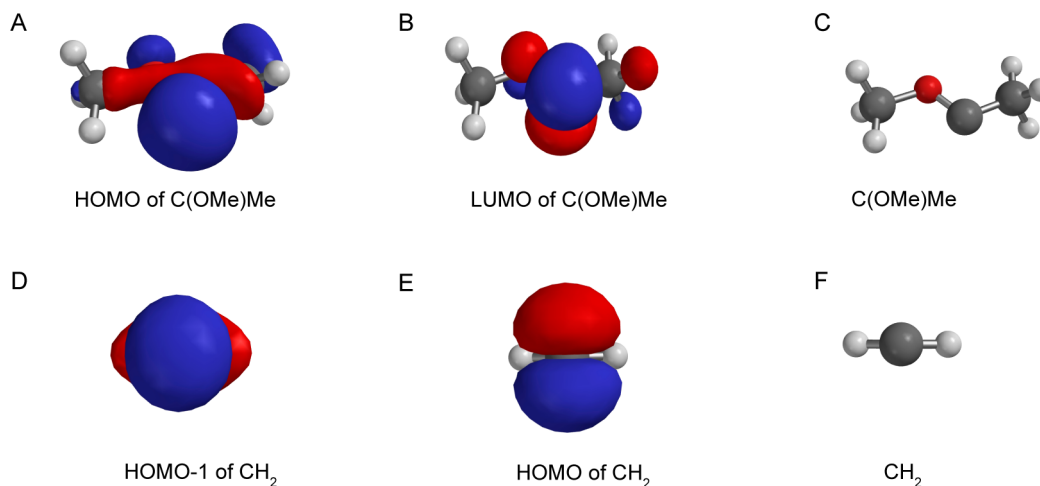


Figure 4. σ -donor and π -acceptor orbitals of Fischer and Schrock carbenes.

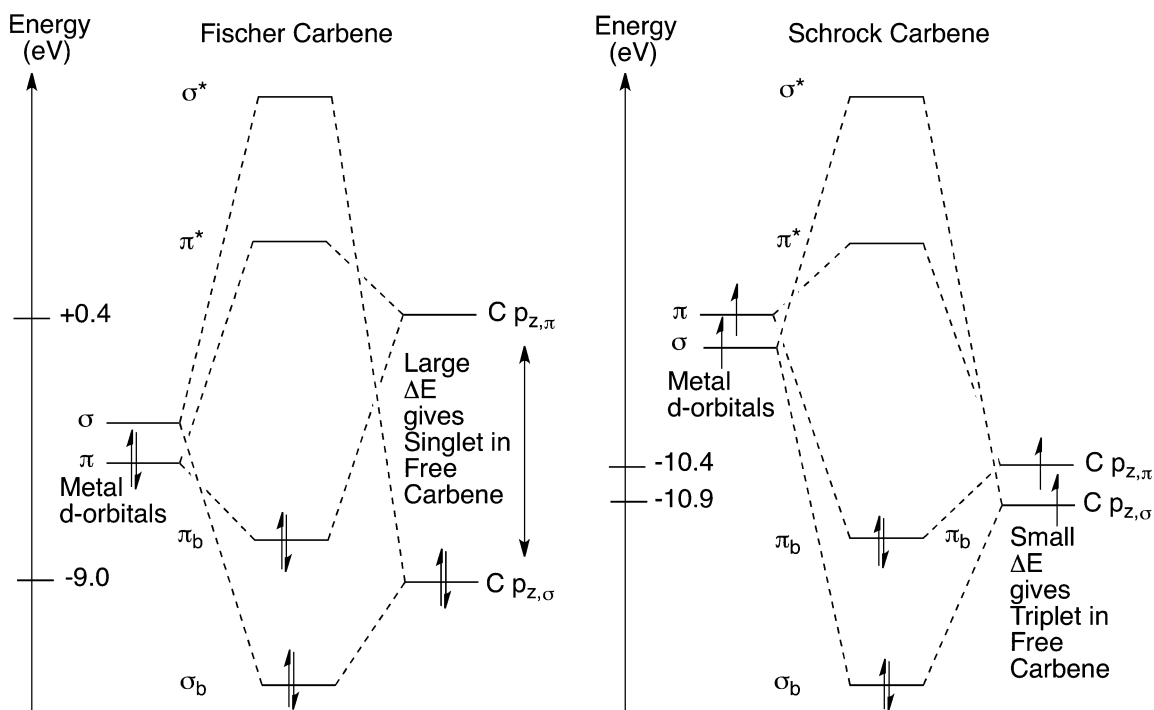


Figure 5. π -bonding in Fischer vs Schrock carbene complexes.

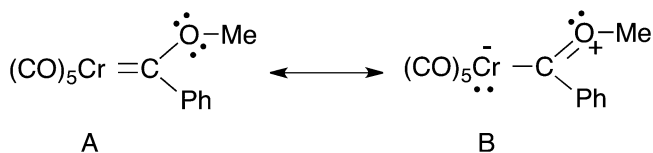


Figure 6. Resonance structures for the Fischer carbene complex, $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$.

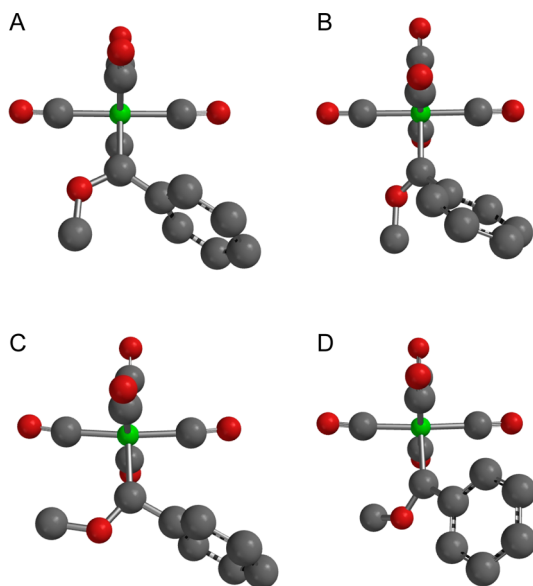


Figure 7. Four conformations of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ obtained by constraining dihedral angles (A) *syn*, *eclipsed*; (B) *syn*, *staggered*; (C) *anti*, *eclipsed*; (D) *anti*, *staggered*. (H atoms omitted for clarity.)

resonance structures suggested for a Fischer carbene complex (Figure 6).

Table 3. Energies of Isomers of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$

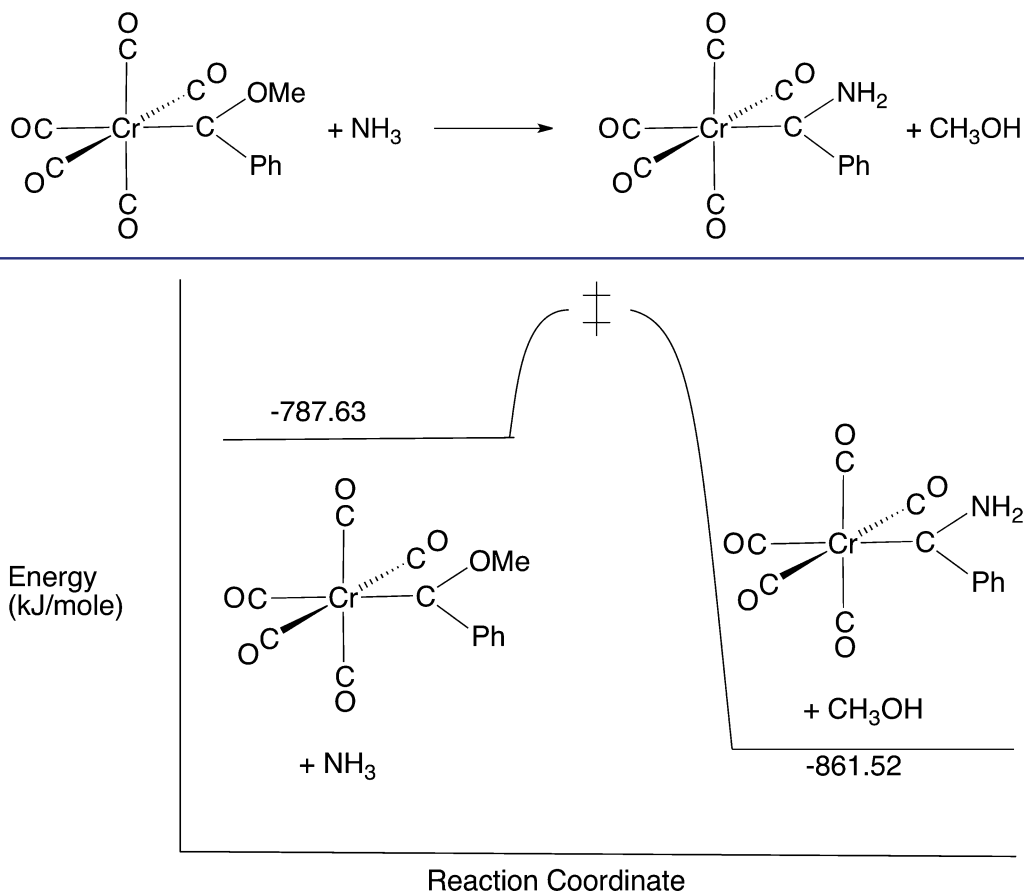
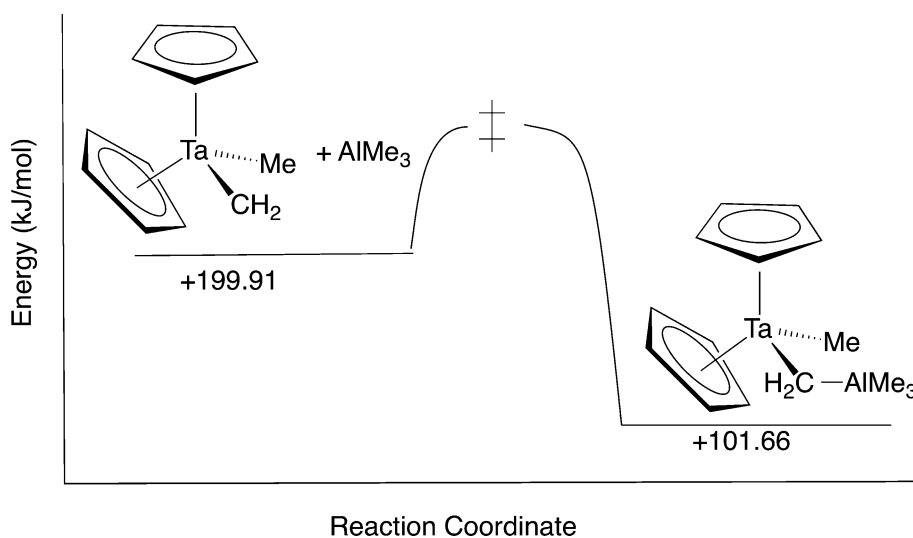
C–O–C–Ph Dihedral Angle	Energy of Eclipsed Isomer (kJ/mol)	Energy of Staggered Isomer (kJ/mol)
0° (<i>syn</i>)	−775	−773
180° (<i>anti</i>)	−752	−726

Different Reactivities of Fischer and Schrock Carbene Complexes

Additionally, in the case of both Fischer and Schrock carbene complexes, π -bonding between the metal center and the carbon atom exists. However, in the case of the Fischer carbene complex, the pair of electrons in the π -bonding MO resides more on the metal, as in Figure 6. This, along with the electronegative nature of the Y substituent, has the effect of generating a positive charge on the carbon atom. As a result of the positive charge on the carbon atom, Fischer carbenes in coordination complexes tend to be electrophilic.

Not possessing the electronegative substituent Y and having a π -acceptor orbital on the carbon atom that is lower in an energy than the π -orbital on the metal (opposite to the situation observed in a Fischer carbene complex) means that carbon atom of a Schrock carbene complex possesses a negative charge, leading to nucleophilic behavior.

By calculating the atomic charges, one may compare the charge on the carbon atom in a Fischer carbene complex and a Schrock carbene complex and thus make predictions as to the relative reactivity. In the case of the Fischer carbene complex *eclipsed*, *syn*- $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$, the electrostatic atomic charge on the carbon atom (bonded to the metal) was calculated to be +0.65, whereas in the case of the Schrock carbene complex, the corresponding charge was −0.97. Thus, one would predict electrophilic behavior in the case of the Fischer carbene complex and nucleophilic behavior in the case of the Schrock carbene complex. This is consistent with the observed reactivities.²³

Scheme 2. Electrophilic Reactivity of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ with NH_3 Figure 8. Reaction profile for reaction of electrophilic $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ with NH_3 .Figure 9. Reaction profile for the reaction of nucleophilic $[\text{TaCp}_2\text{Me}(\text{CH}_2)]$ with AlMe_3 .

The complex $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ has been shown to react as an electrophile with ammonia^{25–30} as shown in Scheme 2.

The energetics of this reaction can be modeled and the reaction profile shown in Figure 8 is obtained. (The presence of an energy barrier and transition state are recognized in the diagram but are not calculated as part of this exercise.)

The product of this reaction is of course also a Fischer carbene complex where the π -donor substituent Y is now $-\text{NH}_2$ instead of $-\text{OMe}$. It is of interest to compare the carbene electrophilicity in these two species by considering the calculated positive charge on the carbon atom of the Fischer carbene. With Y now being the more strongly π -donating $-\text{NH}_2$, the charge on the carbon atom has decreased to +0.31 (from +0.65 when Y = OMe). This result is consistent with the

Table 4. Feature Comparison of Fischer and Schrock Carbenes

Features	Fischer Carbene	Schrock Carbene
M tends to be	Late-Transition Metal, Low Ox. State, π -Acceptor Co-Ligands	Early-Transition Metal, Higher Ox. State
Charge	0	−2
No. of e [−] donated	2	4
Ground state	Singlet	Triplet
Charge on carbon atom	Positive	Negative
Chemical behavior	Electrophilic	Nucleophilic
Example	[Cr(CO) ₅ (C(OMe)Ph)]; Cr(0); d ⁶	[TaCp ₂ Me(CH ₂)]; Ta(V); d ⁰

previous suggestion by Cases et al.³¹ that the electrophilicity of the Fischer carbene complex decreases with increasing π -donating ability of Y.

In addition to considering the positive charge, there is a second means of predicting the relative electrophilicity of Fischer carbene complexes and that is by calculating the electrophilicity index,³² ω , as expressed by

$$\omega = \mu^2/2\eta$$

where

$$\mu \text{ (electronegativity)} = (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}})/2$$

and

$$\eta \text{ (hardness)} = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})/2$$

(and ϵ_{LUMO} , ϵ_{HOMO} are given in eV)

Cases et al.³¹ report ω values of 4.606 and 3.651 for [Cr(CO)₅(C(OMe)Ph)] and [Cr(CO)₅(C(NH₂)Ph)], respectively, using DFT calculations. In this study, using PM3 calculations, the corresponding ω values are 2.68 and 2.46, respectively. While these values deviate significantly from the values of Cases et al., nevertheless, they do again demonstrate the decrease in carbene electrophilicity with increasing π -donor ability of Y. In addition, more accurate values of 4.00 and 3.26 are obtained in this study when DFT single point molecular orbital calculations (B3LYP/6-31G*) are performed on the models already optimized by PM3 methods.

In a similar fashion, the predicted nucleophilic behavior of the Schrock carbene complex can be modeled in the reaction of [TaCp₂Me(CH₂)] with AlMe₃. As in the case of the Fischer carbene example, we have chosen [TaCp₂Me(CH₂)] as the example of a Schrock carbene complex because it is modeled with relative ease. Electrophiles such as AlMe₃ have been shown to react in this manner with [TaCp₂Me(CH₂)]^{33,34} as in Figure 9; this reaction illustrates the nucleophilic behavior of Schrock carbene complexes.

A summary of this comparison of Fischer and Schrock carbene complexes appears in Table 4.

PROCEDURE

Herein, the modeling software that is employed is Spartan Student version 5.0.1;³⁵ however, various other modeling programs would be suitable. It is assumed that the student has a basic understanding of the software and molecular modeling. (At the author's institution, students are required to purchase the modeling software in their second year and then use it in various exercises.) The actual student handout is supplied in the Supporting Information with more detailed descriptions of the required steps.

Step 1

The following molecules are built and then optimized first with molecular mechanics, followed by semiempirical methods (PM3). (The final PM3 optimization should include the calculation of molecular orbitals and atomic charges.)

C(OMe)Me; CH₂ (For these two molecules, optimize the structure in both the singlet and triplet states.)

[Cr(CO)₅(C(OMe)Ph)] (Make four models of this complex with the Me groups of the C(OMe)Ph carbene moiety *syn* and *anti*, and with the plane of the C(OMe)Ph moiety eclipsed and staggered with respect to the Cr(CO)₄ plane. Do this by constraining the appropriate dihedral angles, C(Me)–O–C–C(Ph) to 0° and 180° and OC–Cr–C(carbene)–O(carbene) to 0° and 45°. These four models for [Cr(CO)₅(C(OMe)Ph)] are shown in Figure 7. It should be noted that in each case the phenyl ring is allowed to rotate freely about the C–Ph bond.)

[Ta(η^5 -C₅H₅)₂Me(CH₂)]; NH₃; [Cr(CO)₅(C(NH₂)Ph)]; CH₃OH; [Ta(η^5 -C₅H₅)₂Me(CH₂AlMe₃)].

Save the model and output of the calculation in each case.

Step 2

Note the energy of each molecule (in kJ/mol).

Step 3

DFT single point energy calculations (B3LYP/6-31G*; include calculation of molecular orbitals) can also be done on *syn*, *eclipsed*-[Cr(CO)₅(C(OMe)Ph)] and [Cr(CO)₅(C(NH₂)Ph)] (previously optimized above by semiempirical PM3 calculations). Record the energy (in eV) of the LUMO and HOMO of each model. [Note: Obviously, these two DFT calculations are the lengthiest in the exercise; when the author performed these calculations, the time required was approximately 90 min for each. Other calculations (PM3) generally require less than a minute. Therefore, the DFT calculations can be omitted at the discretion of the instructor.]

Step 4

The students record the results in a series of tables as in this paper (Tables 1–3). In addition, include in the results: figures of the σ -donor and π -acceptor orbitals of both C(OMe)Me and CH₂; the charges on the carbon atom of the carbene ligand in [Cr(CO)₅(C(OMe)Ph)], [Cr(CO)₅(C(NH₂)Ph)] and Ta(η^5 -C₅H₅)₂Me(CH₂); and reaction profiles for both the reaction of [Cr(CO)₅(C(OMe)Ph)] with NH₃ and the reaction of Ta(η^5 -C₅H₅)₂Me(CH₂) with AlMe₃.

Step 5

The results of the calculations are then employed in order to

- determine the ground electronic state of the Fischer (–C(OMe)Me) and Schrock (–CH₂) carbene ligands from the results recorded in Table 2;
- determine the molecular orbitals used by the Fischer (–C(OMe)Me) and Schrock (–CH₂) carbene ligands for σ -donation and π -accepting and plot these orbitals;

- c. explain the π -bonding schemes of Figure 5 using the energies of these ligand orbitals (from Table 2);
- d. suggest evidence for restricted rotation about the C–Y bond;
- e. determine which of the two resonance forms of Figure 6 most accurately describes the nature of the C–O bond;
- f. predict the chemical reactivity of the Fischer and Schrock carbene complexes based on the charge on the carbon atom;
- g. draw a reaction profile diagram depicting the reaction of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ with NH_3 and of $[\text{TaCp}_2\text{Me}(\text{CH}_2)]$ with AlMe_3 ;
- h. calculate the electrophilicity index ω of $[\text{Cr}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$ and $[\text{Cr}(\text{CO})_5(\text{C}(\text{NH}_2)\text{Ph})]$ and discuss the results.

CONCLUSIONS

The molecular modeling exercise described herein uses PM3 calculations to demonstrate the distinctive features of Fischer and Schrock carbene complexes. These distinctive features include the ground electronic states, σ -donor and π -acceptor molecular orbitals and reactivity. In addition, the resonance structures and the accompanying restricted rotation in the C–Y bond of the Fischer carbene complex are demonstrated. The exercise provides students with an experience that enhances their understanding of transition metal carbene complexes.

ASSOCIATED CONTENT

Supporting Information

Student handout. The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00036.

AUTHOR INFORMATION

Corresponding Author

*E-mail: montgome@twu.ca.

Notes

The authors declare no competing financial interest.

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