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Structure and Conformations of Heteroatom-Substituted Free Carbenes and Their Group 6 Transition Metal Analogues

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A systematic density functional theory (DFT) study of free and Cr- and W-coordinated alkoxy-carbenes has been carried out. The structure of the free carbenes and their relative energies remains unaltered by coordination to the metal. A clear bias for the *anti*-isomer is observed in both the free and coordinated carbenes. The exception is complexes having alkynyl substituents. In this case, the metal complex prefers the *syn*-disposition. The theoretical model explains the observed bias for the *anti*-isomer by the stabilizing contribution of a stereoelectronic effect due to the two-electron donation from the σ_{CH} orbital of the O-Me group to the π^*_{CO} orbital of the CO ligand and feedback donation of the π_{CO} orbital to the σ^*_{CH} orbital and the destabilizing repulsion between the groups linked to the carbene carbon. This last factor is the determinant one since the linear triple bond produces a clear bias for the *syn*-isomer only in the coordinated carbene, showing that the steric contribution rather than the electronic repulsion is responsible for the structure of group 6 Fischer carbenes. The *anti*−*syn* isomerization in chromium(0)-carbene complexes has also been studied. This process occurs without affecting either the carbene ligand or the coordination sphere of the metal by rotation of the C(Cr)−O−Me bonds. The developed model is fully applicable to tungsten-carbene complexes.

Introduction

The first tungsten(0)-carbene complex was prepared by Fischer and Maasböl in 1964.[1] Almost 40 years after this seminal discovery, these reagents have a widespread use in organic synthesis.[2] Among them, group 6 metal-carbene complexes are especially well suited for structural and mechanistic studies because of the easiness of their preparation and the amazing number of different reactivities they can experience. The nature of the metal−carbon double bond has attracted a continuous and still unabated interest, from both the experimental and theoretical points of view. In fact, the first crystal and molecular structure of [pentacarbonyl-(methoxyphenyl)chromium(0)]carbene, **2**, was reported in 1968 by Mills and Redhouse[3] showing a partial double-bond character of the [O−C]═Cr bond. This was explained from the interaction between a lone pair on the oxygen and the empty p_z orbital orbital of the carbene carbon. This interaction would be competitive with the back-donation from the metal and therefore would result in the consequent lessening of the double-bond character of the O−[C═Cr] double bond. One remarkable feature of this structure was that the methyl group is directed toward the chromium (an orientation we shall denote *anti* throughout this work; see below).

Since this original crystallographic study, many other structures of group 6 alkoxy metal-carbene complexes have been reported.[4,5] Except for complexes having linear substituents linked to the carbene carbon such as [pentacarbonyl(phenylethynylmethoxy)chromium(0)], **4**,[12] [pentacarbonyl(phenylethynylethoxy)chromium(0)], **5**,[5t] and the allenylethoxy derivative,[5s] the remaining

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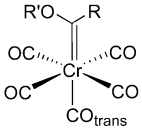
Table 1. Selected Experimental and Calculated Bond Distances (Å) and Angles (deg) for Complexes 1−5



	$(CO)_5Cr{=}C(OR')R^a$	dCr−C	dCr−CO_{trans}	dC−R	dC−O	dO−C_1	$d$$C_1$−$C_2$	C−O−C_1	R−C−O
1	R = Me, R′ = Et[6]	2.053	1.894	1.511	1.314	1.461	1.509	124.1	106.1
		(2.064)	(1.892)	(1.515)	(1.313)	(1.454)	(1.517)	(124.1)	(105.9)
2	R = Ph, R′ = Me[3]	2.04	1.87	1.47	1.33	1.40		121	104
		(2.084)	(1.889)	(1.493)	(1.323)	(1.436)		(124.3)	(105.3)
3	R = CH=CHPh	2.054	1.884	1.478	1.299	1.449	1.452	123.4	108.6
	R′ = Et[b]	(2.057)	(1.896)	(1.483)	(1.322)	(1.435)		(123.4)	(107.5)
4	R = C≡CPh, R′= Me[12]	1.9990	1.897	1.416	1.3233				
		(2.005)	(1.908)	(1.426)	(1.329)	1.447		(121.7)	(115.5)
5	R = C≡CPh, R′ = Et[5t]	2.00	1.86	1.37	1.32	1.51	1.50	121	116

[a] Calculated data are given in parentheses. See text. The C_1 and C_2 atoms refer to the ethoxy groups. [b] Data provided by Prof. Lars K. Hansen (University of Tromsø, Norway). The full crystallographic data for compound **2** will be reported in due time.

alkoxy complexes, whose structures have been reported, systematically have the alkoxy substituent in an *anti*-disposition (Figure 1). Furthermore, the [C−C]−O−C=Cr distance in the crystals is in many cases considerably shorter than expected for a single bond, like for example in CH_3-CH_2-OH. One clear exception to this rule is observed in [pentacarbonyl(ethoxymethyl)chromium(0)]-carbene, **1**,[6] albeit in this case the measurement was effected by neutron diffraction (Table 1).

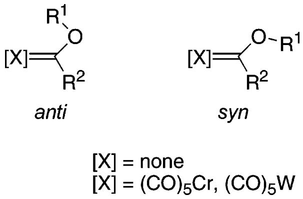


Figure 1. *Syn*- and *anti*-conformations of free and Fischer carbenes.

From a theoretical point of view the nature of the metal−carbene bond has been repeatedly discussed. Early work by Block[7] using semiempirical methods showed a correlation between the site of nucleophilic attack and the location of the LUMO in the metal complexes. In this work the effect of complexation on the electronic distribution of the ligands was also studied by comparison of the nature of the free and coordinated carbenes, although they were directed toward the comparative effect of coordination between CH_3CO^- and CH_3COMe. Subsequently the problem of the nature of the metal−carbon double bond was approached using semiempirical,[8] Hartree−Fock (HF),[9] post-HF,[10] and most recently density functional theory

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(DFT) calculations.[11] A landmark in these works is the study by Wang,[12] who demonstrated by a combination of X-ray diffraction and molecular orbital (MO) calculations that the π-bond character of the metal−carbene can be best represented by a Cr−C−X three-centered four-electron bond, with the π-electron density mainly located at either the d_{yz} orbital of Cr or the p_z orbital of X in the carbene ligand. This makes the carbene an electrophilic site in the p_π direction. An extensive DFT study by Frenking and Solá[13] reported, while this work was under progress, that stronger π-electron donors attached to the carbene carbon lead to larger Cr═C, shorter Cr−CO_{trans}, and larger C−O_{trans} bond distances. An additional effect of these stronger π-electron donors is to produce smaller Cr═C bond dissociation energies. Surprisingly, all these calculations were effected on the *syn* orientation, which is not usually encountered in the solid structures of group 6 alkoxy carbenes.

Despite the extensive studies resumed above no additional effort has been exerted to compare the free and coordinated ligands to extract information about the nature of the M═C bond, except the pioneering work by Block.[7] Reported herein is a systematic DFT study of different conformations of free and Cr- and W-coordinated alkoxy-carbenes that shows that coordination to the metal does not change the structure of the free carbenes and their conformational trends. Furthermore, the preference of the free and coordinated carbenes for the *anti*-geometry is explained by means of a simple model based upon second-order perturbation theory.

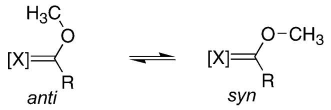
Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 98 suite of programs.[14] Electron correlation has been partially taken into account using the hybrid functional usually denoted as B3LYP[15] and the standard 6-31G* basis set[16] for hydrogen, carbon, oxygen, and nitrogen and the Hay−Wadt small-core effective core potential (ECP) including a double-ξ valence basis set[17] for chromium or tungsten (LanL2DZ keyword). Zero-point vibrational energy (ZPVE) corrections have been computed at the B3LYP/6-31G* level and have not been corrected. Stationary points were characterized by frequency calculations[18] and have positive defined Hessian matrixes. Transition structures (TSs) show only negative eigenvalues in their diagonalized force constant matrixes, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. Nonspecific solvent effects have been taken into account by using the self-consistent reaction field (SCRF) approach.[19] Donor−acceptor interactions and atomic charges have been computed using the natural bond order (NBO)[20] method. The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E_{\phi\phi^*}{}^{(2)} = -n_\phi \frac{\langle \phi^* | \hat{F} | \phi \rangle}{\epsilon_{\phi^*} - \epsilon_\phi} \qquad (1)$$

where $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled natural bond orbitals having ϵ_ϕ and ϵ_{ϕ^*} energies, respectively; n_ϕ stands for the occupation number of the filled orbital.

Table 2. Relative Energies (ΔE,[a,b] kcal mol^{-1}) of *syn*- and *anti*-Conformations of Carbenes 2 and 6−12



[X] = none		[X] = (CO)$_5$Cr	
6, R = Me	+7.3	**10**, R = Me	+1.8
7, R = Ph	+9.7	**2**, R = Ph	+1.3
8, R = CH═CH$_2$	+6.2	**11**, R = CH═CH$_2$	+4.0
9, R = C≡CH	+2.9	**12**, R = C≡CH	−1.6

[a] ΔE values computed as $\Delta E = E_{\text{syn}} - E_{\text{anti}}$. [b] All values have been calculated at the B3LYP/LANL2DZ&6-31G*+ΔZPVE level.

Results and Discussion

Both free carbenes and their organometallic group 6 metal-carbene analogues may exist in two conformations, *syn* and *anti*, interchangeable by rotation through the C−heteroatom bond. Our study was initiated studying the comparative stability of free carbenes **6**−**9** and their pentacarbonylchromium(0) analogues **2**, **10**, **11**, and **12**. Table 2 compiles the calculated energies for both classes of compounds. The optimized geometries of both isomers of complexes **2**, **10**, **11**, and **12** are depicted in Figure 2. Except for the alkynyl-substituted carbene complex **12**, in all cases the *anti*-isomer was the more stable of both isomers. The difference in energies between the *anti*- and *syn*-isomers is considerably higher in the free carbenes **6**−**9** than in the metallacarbenes **2**, **10**, **11**, and **12**. These results are in full agreement with the reported X-ray structural data for complexes **1**−**3** (see Table 1).[4] The calculated preference of alkynyl-substituted carbene complex for the *syn*-isomer form is also concordant with the observed X-ray structure for [pentacarbonyl(phenylethynylmethoxy)-carbene]chromium(0), **4**.[12]

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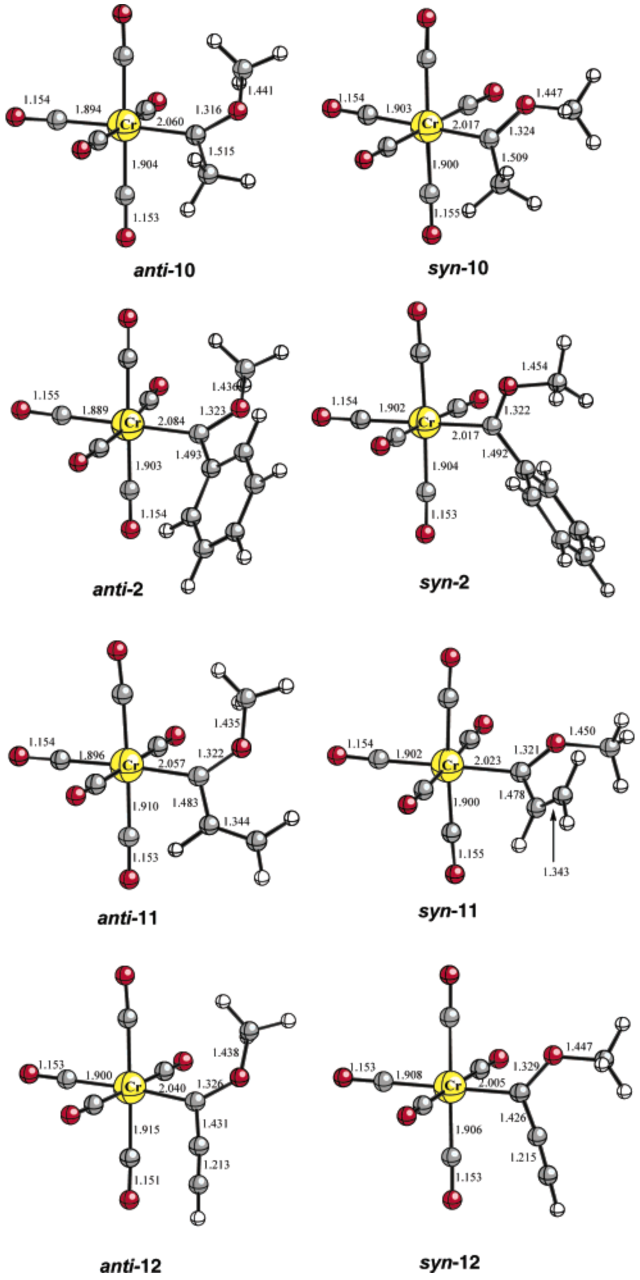

Figure 2. Chief geometrical data (B3LYP/LANL2DZ&6-31G* fully optimized structures) of *syn*- and anti-conformations of Fischer carbenes **2** and **10**−**12**. Bond distances are given in Å. Carbon, oxygen, and hydrogen atoms are represented in gray, red, and white, respectively.

The preference of both free **6**−**9** and complexed carbenes **2**, **10**, and **11** for the *anti*-isomer may be explained on the basis of two additive effects. The *syn*-isomer has two unfavorable interactions. Free carbenes have a staggered interaction between the methyl group bonded to oxygen and the substituent in the carbene carbon. Additionally, free carbenes are also affected by the strong repulsive interaction between the carbene electron pair and the two nonbonding electron pairs of the oxygen (Figure 3). Clearly, this last interaction is not present in complexed carbenes; therefore the difference in energy between both isomers is reduced.

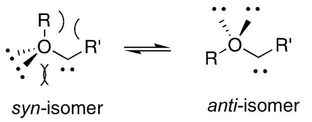

Figure 3. Conformational equilibrium in free singlet carbenes.

This reduction of the energy differences between both isomers would be exacerbated by the repulsive steric interaction that exists between the methyl group and the "CO wall".[21] Nevertheless, there are three factors that minimize this interaction. The first one is the enlargement of the bond distance between the metal and the sp^2-hybridized atom of the carbene in the *anti*-conformation (see Figure 2). The second factor is the staggered disposition of the carbene group and two CO-*cis* ligands flanking it. This staggered disposition is maintained in all complexes studied, independently of the isomer considered with dihedral angles OC−Cr−C−OMe having absolute values between 25.1° (complex ***syn*-11**) and −58.0° (complex ***anti*-2**). The conformational staggering should minimize the steric repulsion. The exception is complex ***syn*-2**, which is in a nearly eclipsed conformation (dihedral angle OC−Cr−C−OMe = 8.4°). In addition, the NBO analysis of compound **10** shows a two-electron stabilizing interaction between the O-Me group hydrogens and the CO ligand *cis* to the carbene moiety. Thus, the two-electron donation from the σ_{CH} orbital of the O-Me group to the π^*_{CO} orbital of the CO ligand (−0.21 kcal mol^{-1}) coupled to the feedback donation of the π_{CO} orbital to the σ^*_{CH} orbital (−0.67 kcal mol^{-1}) results in a significant stabilizing contribution in the *anti*-isomer that is not present in the *cis*-isomer (Figure 4). The additive effect of all the contributions mentioned above (at least two contributions for each interaction mode) renders the *anti*-isomer more favorable than the *syn*-isomer for chromium(0) alkoxy carbenes, in full agreement with experimental X-ray data. Even bulky substituents such as menthyl groups linked to the oxygen maintain the *anti*-disposition despite the expected increased steric destabilization expected in these cases.[5c]

Alkynyl-substituted carbene complex **12** is the exception to the rule. In fact, in this case, according to our calculations, the *syn*-isomer is preferred by 1.6 kcal mol^{-1}. This result is supported by experimental data since complex **4** crystallized as the *syn*-isomer.[12] A considerable decrease in the difference of energies between *syn*- and *anti*-isomers is also observed in the free carbene **9**, but in this case there is still a clear bias favoring the *anti*-isomer. The reasons for this change in behavior should be found in the linear structure of the triple bond. In this case, and according to our model,

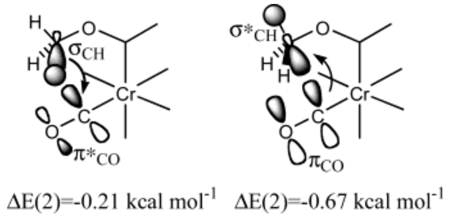

Figure 4. Two-electron interactions and associated second-order perturbational energies between a methyl group and a CO ligand in *syn*-Fischer carbenes.

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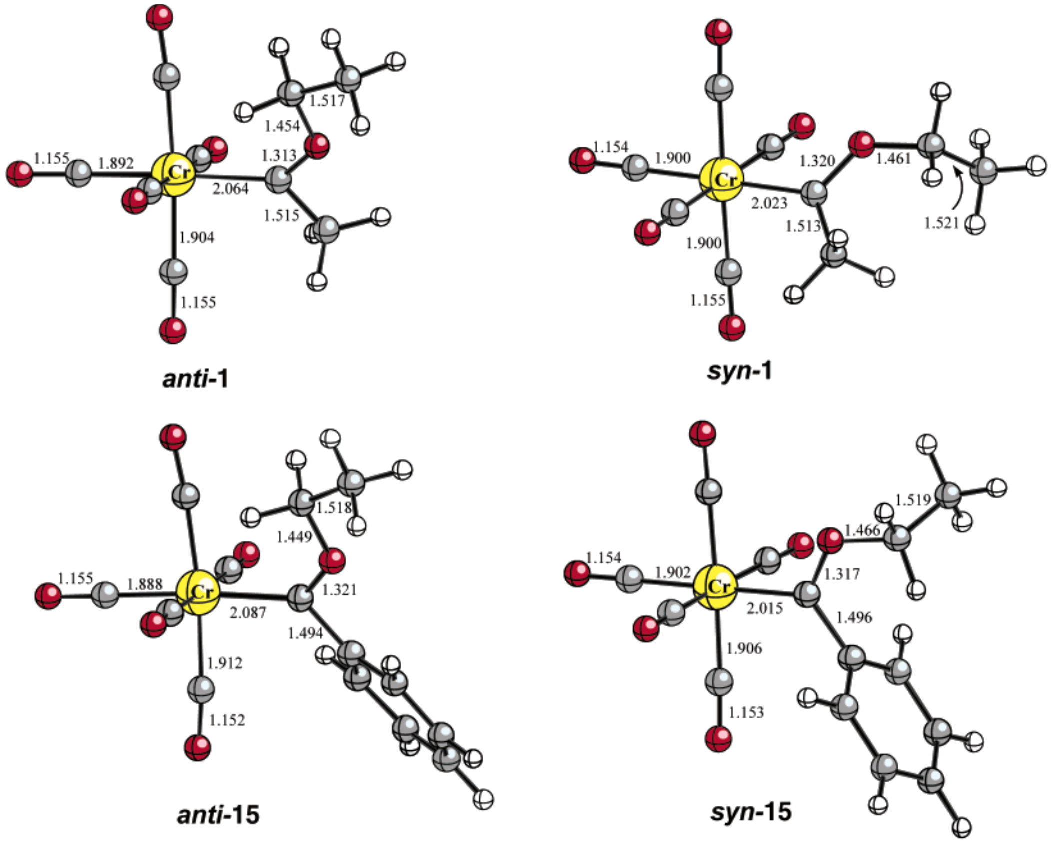
[21] Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Sausalito, CA, 1999.



***anti*-1** ***syn*-1**

***anti*-15** ***syn*-15**

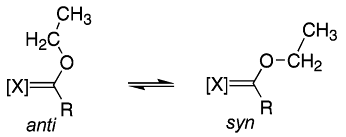
Figure 5. Chief geometrical data (B3LYP/LANL2DZ&6-31G* fully optimized structures) of *syn*- and *anti*-conformations of Fischer carbenes **1** and **15**. See Figure 2 caption for additional details.

the decrease in the steric interaction between the triple bond and the methyl group of the carbene may approach the energies of both isomers. In fact, this may serve as a probe to evaluate the relative participation between the steric repulsion and the electronic destabilization. Clearly, and according to the relative energies shown in Table 1, it is the steric repulsion between the groups attached to the carbene carbon rather than the electronic repulsion that is responsible for the bias toward the *anti*-isomer. This trend is also maintained in compounds having linear allene substitutents linked to the carbene carbon.[5s] Coordination of the triple bond to a $Co_2(CO)_6$ fragment results in the recovery of the usual *anti*-disposition.[4h,5m]

X-ray data for the structures of ethoxy-substituted complexes show in some cases a significant shortening of the [C−C]−O bond that could be as short as 1.45 Å.[5k,n,p] Our calculated optimized structures for *syn*- and *anti*-conformations of complexes **1** and **15** are depicted in Figure 5.

Our model again explains the bias for the *anti*-isomer in both the free and coordinated carbenes (Table 3). These results are also confirmed by neutron diffraction measurements.[6] However, the calculated [C−C]−O distances (1.517 and 1.518 Å for complexes **1** and **15**, respectively) are the expected for a single σ_{C-C} bond. The dihedral angles OC−Cr−C−OEt of complexes **1** and **15** follow the same trend as their methoxy analogues. Again, with the exception of ***syn*-15** (OC−Cr−C−OEt = 4.5°), which is close to an eclipsed conformation, the remaining compounds are in a staggered disposition.

Table 3. Relative Energies ($\Delta E^{a,b}$, kcal mol^{-1}) of *syn*- and *anti*-Conformations of Carbenes 1 and 13−15



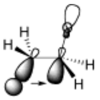
[X] = none		[X] = $(CO)_5Cr$	
13, R = Me	+7.5	**1**, R = Me	+2.9
14, R = Ph	+10.0	**15**, R = Ph	+1.7

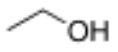
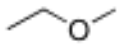
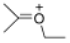
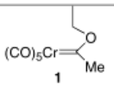
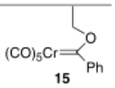
[a] ΔE values computed as $\Delta E = E_{syn} - E_{anti}$. [b] All values have been calculated at the B3LYP/LANL2DZ&6-31G*+ΔZPVE level.

There are, in principle, two alternative hypotheses to explain the shortening effect of the σ_{O-C-C}. It might be a consequence of a stereoelectronic effect involving donation of electron density from the σ_{CH} orbital to the σ^*_{CO} orbital placed in an antiperiplanar disposition (Table 4). This donation would result in the shortening of the [C−C]−O bond while elongating the C−H bond. This model is a simple orbital description of the inductive effect exerted by the oxygen onto the adjacent C−C bond. Within this hypothesis higher positive charges on the oxygen should result in shorter adjacent C−C bonds. The magnitude of this donation was evaluated on the basis of the donor−acceptor interactions in the NBO analysis using ethanol, ethyl methyl ether, *O*-ethylformaldehyde, and complexes **1** and **15**. Table 4 compiles the results obtained in these calculations.

Data in Table 4 show clearly the stronger donation from the ethyl group in formaldehyde with a positive charge on the oxygen ($\Delta E(2) = -7.06$ kcal mol^{-1}) compared to either the alcohol or the ether ($\Delta E(2) =$

Table 4. C−C Bond Distances[a] (d_{C-C}, Å) and Second-Order Perturbational Energies[a,b] ($\Delta E(2)$, kcal mol^{-1}) Associated with Two-Electron Interactions between σ_{CH} and σ^*_{CO} Localized Orbitals in Several Ethoxy Derivatives



				 **1**	 **15**
ΔE(2)	-3.99	-3.91	-7.06	-4.69	-4.65
d_{C-C}	1.519	1.520	1.508	1.517	1.519

[a] Properties computed at the B3LYP/LANL2DZ&6-31G* level. [b] Calculated by means of eq 1.

−3.99 and −3.91 kcal mol^{-1}, respectively). Complexes **1** and **15** are closer in the value of $\Delta E(2)$ to neutral alcohols than to ethylated formaldehyde. In any case, the expected shortening of the [C−C]−O bond was observed. To obtain more accurate geometries, the basis set for the explicit electrons of chromium was augmented with a set of f-polarization functions.[22] The ethoxy [C−C]−O distance remained invariant also in these conditions.

This failure to explain the observed bond shortening by applying an inductive model led us to consider an alternative explanation. In fact, the bond shortening is clearly seen in X-ray diffraction structural determinations,[5] but it is not present in the structure of [pentacarbonyl(ethoxymethyl)carbene]chromium(0) obtained by neutron diffraction.[6] Therefore, it can be thought that the anomalous shortening seen in some ethoxy-carbene complexes may be due to the packing in the crystal. To simulate the condensed phase,[19] we repeated the calculations carried out on complex **15** but now using a dielectric constant $\epsilon = 7$, conditions that would favor the contribution of the corresponding polar hyperconjugative forms. Again, our efforts meet no success. The [C−C]−O was not affected by these new conditions. Therefore, although crystal packing may be responsible for this effect, we have so far been unable to model the shortening of the [C−C]−O bond experimentally observed in some cases.

The question of the *syn*/*anti* isomerization was addressed next. The experimental activation energy for this transformation in the methoxymethylchromium(0)-carbene complex was 12.4 ± 1 kcal mol^{-1}.[23] Figure 6 represents the calculated coordinate of reaction for the ***anti*-10** to ***syn*-10** isomerization. According to our calculations, the activation energy associated with this process has a value of 14.3 kcal mol^{-1} for complex **10** and decreases to 11.1 kcal mol^{-1} for complex **2**. The dihedral angle Me−C(Cr)−O−Me changes from an initial value of −178.2° in the *anti*-isomer to −91.9° in the transition structure **TS1**. It should be noted that the staggered conformation of the carbene moiety and the *cis*-CO ligands is maintained in the transition state. The final dihedral for the *syn*-isomer is 0.0°, which is again in a staggered conformation. The behavior of the phenyl-substituted carbene complex is similar, although in this case the dihedral Ph−C(Cr)−O−Me in the transition state **TS2** is slightly larger (−103.8°) than in the methyl-substituted analogue. This is maintained in the *syn*-isomer. It is worthy to note that the staggered disposition of the carbene is maintained during the *syn*−*anti* isomerization process that occurs by rotation across the C(Cr)−O−Me without affecting the Cr═C bond and therefore the coordination sphere of chromium. Our calculated energies for the *syn*−*anti* isomerization barrier match those experimentally determined by NMR.

Table 5. Calculated ΔE(*anti*−*syn*) for Both Isomers in Different Solvents[a]

ϵ (solvent)	ΔE_a/ kcal mol^{-1}	ΔE(*anti*−*syn*)/ kcal mol^{-1}	relative amounts of *anti*−*syn*[23]
1 (gas phase)	14.3	1.8	
4.9 ($CHCl_3$)	14.5	0.2	90:10
5.621 (chlorobenzene)	14.5	0.1	84:16
20.7 (acetone)	14.6	−0.4	50:50
32.63 (MeOH)	14.6	−0.5	61:39

[a] All values have been calculated at the B3LYP/LANL2DZ&6-31G*+ΔZPVE level.

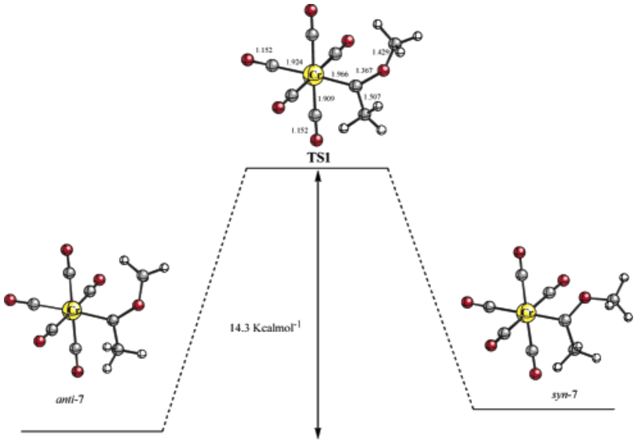


Figure 6. Main geometric features and relative energy of transition structure **TS1** associated with *syn*−*anti* isomerization of Fischer carbene **10**. All values have been obtained at the B3LYP/LANL2DZ&6-31G*(+ΔZPVE) level. See Figure 2 caption for additional details.

Experimentally, the solvent has a strong effect on the *anti*−*syn* isomer ratio of alkoxy Fischer carbenes.[23] Thus, this ratio changes from 50:50 (acetone-d_6) to 90:10 in Cl_3CD in complex **10**. This points to a strong difference in the polarity of both forms, with the *syn*-isomer being more polar. Therefore, this is the preferred isomer in the more polar acetone solvent. The calculated ΔE(*anti*−*syn*) for both isomers in different solvents ranging from gas phase ($\epsilon = 1$) to MeOH ($\epsilon = 32.63$)[24] are compiled in Table 5, together with the ΔE_a for the isomerization process. Clearly, the effect of the solvent change on ΔE_a is not significant. The *syn*-isomer is more stable in polar solvents than in apolar solvents, in full

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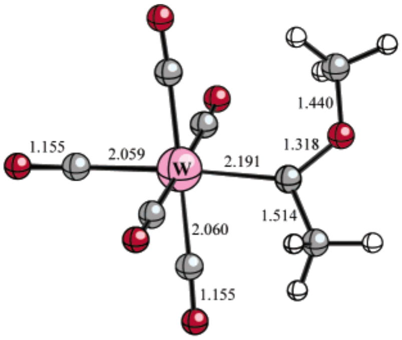
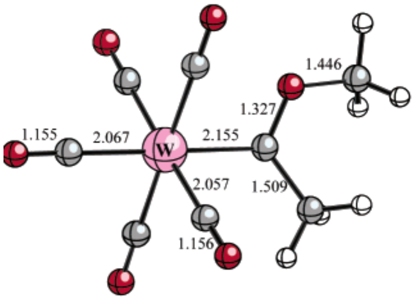
[22] Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

[23] (a) Kreiter, C. G.; Fischer, E. O. *Angew. Chem.* **1969**, *81*, 780; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761. (b) Kreiter, C. G.; Fischer, E. O. *Pure Appl. Chem.* **1971**, *6* 151. A theoretical value of 18.3 kcal mol^{-1} has been previously calculated for this isomerization, see: (c) Marynick, D. S.; Kirkpatrick, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 1993.

[24] Reichardt, C. *Solvents and Solvents Effetcs in Organic Chemistry*; VCH Publishers: Weinheim, 1990.



***anti*-16**



***syn*-16**

Figure 7. Main geometrical features of *syn*- and *anti*-conformations of tungsten Fischer carbene **16**. See Figure 2 caption for additional details.

agreement with the NMR data. Since the calculated dipolar moment of the *anti*-isomer of complex **10** has a value of 4.14 D and that of its *syn*-isomer is 6.36 D, with the value for **TS1** being 3.84 D, the small effect of the polarity on the ΔE_a derives from its decreased polarity compared to the *anti*-isomer, while the preference for the *syn* form in polar solvents may be explained through a Coulombic stabilization of this more polar isomer. Even more, the conditions in the crystal should resemble those of the vacuum since only the *anti*-isomer is mainly observed in the different examples reported in the literature.[4]

To conclude this study, the pentacarbonyl-[methoxymethyltungsten(0)]carbene, **16**, was studied. The optimized structures for both *syn*- and *anti*-isomers are depicted in Figure 7. The bias for the *anti*-isomer (2.8 kcal mol^{-1}), as well as the staggered conformation of the carbene ligand and the *cis*-CO ligands, is maintained also in these cases, thus indicating that the model reported above can be extended to other Fischer carbenes.

Conclusions

A systematic DFT study of free and Cr- and W-coordinated alkoxy-carbenes has shown that the structure of the free carbenes does not vary significantly by coordination to the metal. Although of lower magnitude than in their free analogues, a clear bias for the *anti*-isomer is observed in the free and coordinated carbenes with the exception of complexes having alkynyl substituents. In the latter case, the metal complex prefers the *syn*-disposition. According to our model, the observed bias for the *anti*-conformer in Fischer alkoxy carbenes can be explained in terms of the stabilizing contribution of a stereoelectronic effect due to the two-electron donation from the σ_{CH} orbital of the O-Me group to the π^*_{CO} orbital of the CO ligand and feedback donation of the π_{CO} orbital to the σ^*_{CH} orbital and the destabilizing repulsion between the groups linked to the carbene carbon. This latter factor is the determinant one since the linear triple bond produces a clear bias for the *syn*-isomer only in the coordinated carbene, showing that the steric contribution rather than the electronic repulsion is responsible for the structure of group 6 Fischer carbenes. Finally, the *anti*−*syn* isomerization in chromium(0)-carbene complexes occurred by simple rotation around the C−O bond without affecting the carbene ligand.

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Supporting Information Available: Cartesian coordinates (in Å) and total energies (in au, noncorrected zero-point vibrational energies included) of all the stationary points discussed in the text are available free of charge via the Internet at http://pubs.acs.org.

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