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Steric versus Electronic Effects in the Structure of Heteroatom (S and O)-Substituted Free and Metal (Cr and W)-Complexed Carbenes

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DFT computational energies for free alkoxy- and thio-substitued free carbenes correlate with experimental steric data (Taft parameters) showing the importance of the steric volume at the expense of the electronic interaction in determining the conformation of free carbenes **1**−**14**. The shorter C−O bond distances in the alkoxy derivatives render alkoxycarbene more sensitive to steric effects than thiocarbenes. This strong dependence of the conformation with the steric hindrance is not applicable to metal-complexed carbenes. Thio-substituted carbene complexes exist exclusively as *syn*-isomers due to the combination of an interaction of the sulfur lone pair with two CO ligands and the steric repulsion with the "CO-wall". The stronger $C_{carbene}$−S bond compared to $C_{carbene}$−O is responsible for the increased *syn−anti* rotation barrier observed for the alkylthio-substituted metal carbene complexes compared to their oxygen analogues. The differences of polarity between *syn*- and *anti*-isomers of alkylthio-substituted metal carbene complexes explain also the increment of the isomerization barrier with the polarity of the solvent. The effect of the substituent attached to the carbene carbon is not decisive in the conformation of these compounds.

Introduction

The textbook, classic vision of carbenes as electron-deficient, highly reactive electrophilic intermediates, thence capable of addition to alkenes, C−H insertion, and reaction with heteroatom lone pairs to yield ylides,[1] is only partial. Substitution on the carbene carbon by one or two heteroatoms (e.g., O, N, or S) renders the species nucleophilic. This modulation in reactivity by the heteroatom (which extends also to the stability of the different species) is attributable to the electronic delocalization of the lone pair in the vacant p-orbital of the carbene carbon, which can compensate for the electronic deficiency at the carbene.[2]

Free carbenes may exist in two conformations, *syn* and *anti*, interchangeable by rotation through the C−heteroatom bond (Figure 1). In a recent paper[3] we developed a model explaining a clear bias for the *anti*-isomer in some alkoxy-substituted carbenes. This conformational preference was explained on the basis of two additive effects. The *syn*-isomer has two unfavorable interactions: (a) the steric repulsion between the substituent directly bonded to the hetereoatom and the substituent of the

carbene carbon and (b) the electronic repulsive interaction between the carbene electron pair and the two nonbonding electron pairs of the oxygen (Figure 1).

The model was further extended to Fischer-type carbene complexes.[3] Typically, in these complexes one of the substituents on the carbon linked to the metal acts as a π-donor, allowing for an electronic stabilization of the electron-deficient carbene carbon atom, whereas the other carbene substituent may be either a saturated or unsaturated group. Evidently, these compounds lack the electronic repulsive interaction between the carbene lone electron pair and the two nonbonding electron pairs of the heteroatom (Figure 1). Hence, only steric effects have to be considered in these cases. The decreased difference of energies between the preferred *anti*-isomer and the *syn*-isomer validates the model.
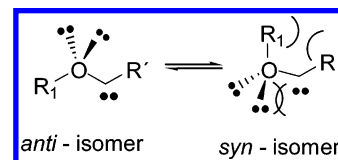
Figure 1. Conformational equilibrium in free singlet carbenes.

The fact that Fischer thiocarbene complexes show a complete conformational bias for the *syn*-isomer[4] strongly contrasts with alkoxy-substituted carbene complexes, which, with the exception of compounds having linear substituents at the carbene carbon, are always *anti*. Therefore, the extension of our study to free thiocarbenes and its comparison with free alkoxycarbenes may allow evaluating the extension of the steric against the electronic

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contribution to the stability of these species. The corresponding metal-complexed species will be useful compounds to validate our model, as well as to determine the importance of the stereoelectronic effect between the substituent attached at the carbene carbon and the metal ligands, compared to the steric repulsion with the "CO-wall". Reported herein is a DFT computational study addressing these aspects of carbene and metal−carbene species.[5]

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 03 suite of programs.[6] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[7] and the standard 6-31+G* basis set[8] for hydrogen, carbon, oxygen, and sulfur and the Hay−Wadt small-core effective core potential (ECP) including a double-ξ valence basis set[9] for chromium and tungsten (LanL2DZ keyword). Zero-point vibrational energy (ZPVE) corrections were computed at the B3LYP/LANL2DZ&6-31+G* level and were not scaled. Reactants and products were characterized by frequency calculations[10] and

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have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method.[11] Nonspecific solvent effects were described by using the self-consistent reaction field (SCRF) approach in its Onsager−Kirkwood formalism.[12] Donor−acceptor interactions have been computed using the natural bond order (NBO)[13] method. The energies associated with these two-electron interactions have been computed according to the following equation:
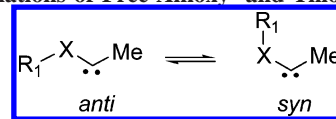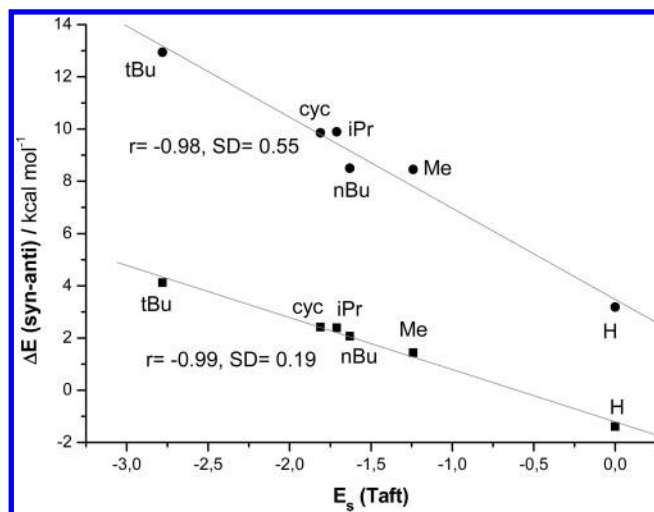
$$\Delta E_{\phi\phi^*}^{(2)} = -n_\phi \frac{\langle \phi^*|\hat{F}|\phi\rangle^2}{\in_{\phi^*} - \in_\phi} \tag{1}$$

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

Results and Discussion

DFT calculations (B3LYP/ 6-31+G*) were carried out starting with the *syn* and *anti* forms of methylcarbenes **1−14**. Data in Table 1 show that the *anti* conformation is the preferred one for both alkoxy- (**1−7**) and thiocarbenes (**9−14**). The exception is complex **8**, which prefers the *syn* conformation. The energy difference between both conformations is in all cases higher for alkoxy carbenes. These results point to a clear steric effect. Since steric repulsion may be responsible for the energy difference between *anti* (preferred) and *syn* (disfavored, see Figure 1), the ΔE between both conformers should correlate with the steric volume of the substituent attached to the heteroatom, measured by the E_s Taft constants.[14] Figure 2 plots the E_s Taft constants of the different substituents against the calculated $\Delta E(syn−anti)$ values for alkoxycarbenes **1−7** (circles)

Table 1. Relative Energies (ΔE,[a,b] kcal mol^{-1}) of *syn* and *anti* Conformations of Free Alkoxy- and Thiocarbenes 1−14

R$_1$	E_s (Taft)[c]	$\Delta E(syn−anti)$ X = O	R$_1$	$\Delta E(syn−anti)$ X = S
1, H	0.00	+3.19	**8**, H	−1.39
2, Me	−1.24	+8.46	**9**, Me	+1.44
3, ^{i}Pr	−1.71	+9.90	**10**, ^{i}Pr	+2.40
4, ^{n}Bu	−1.63	+8.50	**11**, ^{n}Bu	+2.07
5, ^{t}Bu	−2.78	+12.95	**12**, ^{t}Bu	+4.12
6, cyclohexyl	−1.81	+9.86	**13**, cyclohexyl	+2.42
7, phenyl	−	+8.12	**14**, phenyl	+1.93

[a] All values have been calculated at the B3LYP/6-31+G*+ΔZPVE level. [b] $\Delta E(syn−anti)$ values computed as $\Delta E = E(syn) − E(anti)$. [c] E_s values have been taken from ref 14.

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Figure 2. Plot of E_s versus $\Delta E(syn-anti)$ for alkoxy- (circles) and thiocarbenes (squares) **1−13**.

and thiocarbenes **9−14** (squares). Both classes of compounds gave very good linear relationships (correlation coefficient of −0.99 and standard deviation of 0.19 for thiocarbenes; correlation coefficient of −0.98 and standard deviation of 0.55 for alkoxycarbenes). Furthermore, the higher slope found in alkoxycarbenes (−3.49 ± 0.27 kcal/mol) compared to thiocarbenes (−1.99 ± 0.09 kcal/mol) reflects the higher sensitivity of carbenes **1−7** compared to carbenes **9−14**. The lack of steric hindrance in compound **8** (R_1 = H) should be responsible for the bias of this compound for the *syn*-isomer. The reduced steric hindrance should result in a higher conjugation between the heteroatom and the carbene carbon in thiocarbenes compared to alkoxycarbenes. This statement is supported by the higher C−X NBO (Wiberg) bond order values in *syn*-**8** (1.73 au) compared to the alkoxycarbene *syn*-**1** (1.33 au). The resulting effect is that the electronic stabilization factor overcomes the steric effects and simultaneously the electronic repulsions are minimized. As a consequence the *syn*-**8** isomer is more stable than the *anti*-**8** isomer.

The shorter C−heteroatom bond distance in the alkoxy derivatives correlates the higher sensitivity of alkoxycarbenes to the bulkiness of the substituent attached to the carbene carbon, compared to alkythiocarbenes. Thus, the distance between the carbon atoms of the respective methyl groups in the alkoxycarbene *syn*-**2** is 0.414 Å shorter than the same distance in the corresponding thiocarbene *syn*-**9** due to the bulkier sulfur atom. This clearly decreases the value of the steric interaction between the groups attached to the carbene (Table 1), which are considerably smaller in thiocarbenes.

The good correlations obtained between experimental steric (Taft parameters) data and computational energies (Figure 2) show the importance of the steric volume at the expense of the electronic interaction in determining the conformation of free carbenes **1−14**. In accord with our previously proposed model (Figure 1),[3] the coordination of the alkoxycarbene to a pentacarbonylmetal(0) moiety eliminates the electronic repulsion between the electron pairs. Furthermore, the *anti*-isomer of alkoxy (Fischer) carbene complexes (the more stable form of the free carbene) experiences a repulsive steric interaction

between the group attached to the heteroatom and the "CO-wall".[15] The consequence is a decrease in ΔE between both conformers, with the *anti*-isomer being still the preferred form for these compounds.

This situation reverses when alkylthio (Fischer) carbene complexes are considered. Table 2 compiles the relative energies of *syn* and *anti* conformers of complexes **15−26**. All these compounds show a marked bias for the *syn*-isomer, with chromium(0)carbenes **15−20** having higher $\Delta E(syn-anti)$ values than tungsten(0)carbenes. This last result is due to the longer M≡C distance in tungsten complexes (2.175−2.219 Å) compared to Cr (2.053−2.106 Å), which reduces the unfavorable steric interaction of the thioalkyl group with the carbonyl ligands present in the *anti* but not in the *syn* form.

Table 2. Relative Energies (ΔE,[a,b] kcal mol⁻¹) of *syn* and *anti* Conformations of Fischer-Type Thiocarbenes 15−26 and M=C$_{carbene}$ Bond Lengths (in Å, in parentheses; first value corresponds to the *syn*-isomer and the second one to the *anti*-isomer)

		$\Delta E(syn-anti)$		
R	M = Cr(CO)$_5$		R	M = W(CO)$_5$
15, Me	−1.68 (2.053, 2.073)		**21**, Me	−1.03 (2.175, 2.193)
16, ^{i}Pr	−1.34 (2.070, 2.088)		**22**, ^{i}Pr	−0.77 (2.182, 2..207)
17, ^{n}Bu	−1.69 (2.057, 2.078)		**23**, ^{n}Bu	−1.14 (2.179, 2.195)
18, ^{t}Bu	−6.50 (2.078, 2.106)		**24**, ^{t}Bu	−5.44 (2.197, 2.219)
19, cyclohexyl	−1.20 (2.064, 2.096)		**25**, cyclohexyl	−0.78 (2.183, 2.206)
20, phenyl	−3.79 (2.054, 2.063)		**26**, phenyl	−3.13 (2.171, 2.184)

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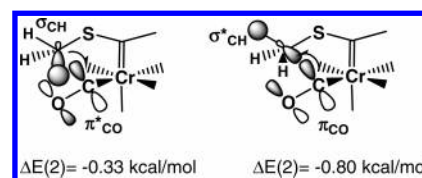

Figure 3. Two-electron interactions and associated second-order perturbational energies between an alkyl group and a CO ligand in *anti*-Fischer carbenes.
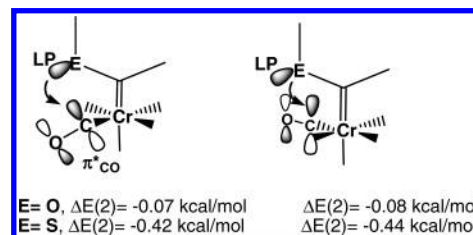
Figure 4. Two-electron interactions and associated second-order perturbational energies between the lone electron pair of the sulfur or oxigen atom and a CO ligand in *syn*-Fischer carbene complexes.

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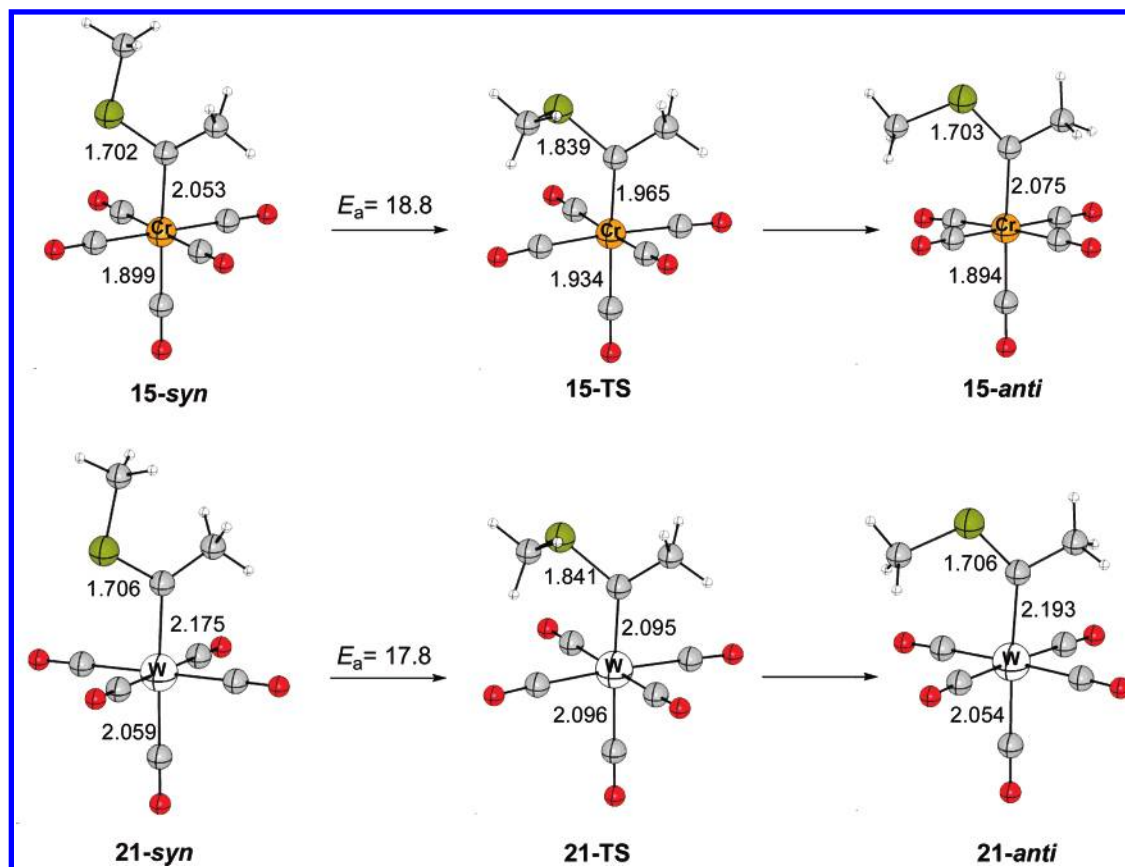
Figure 5. Stationary points found in the isomerization reaction in Fischer carbene complexes *syn*-**15** → *anti*-**15** and *syn*-**21** → *anti*-**21**. All structures correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) geometries. Bond distances and energies are given in Å and kcal/mol, respectively. Numbers over the arrows correspond to the activation energies of the corresponding processes. Zero-point vibrational energy corrections have been included (kcal/mol). Unless otherwise stated, white, gray, red, and yellow colors denote hydrogen, carbon, oxygen, and sulfur atoms, respectively.

The preference of alkylthio(Fischer)carbene complexes for the *syn*-isomers is not explainable on pure steric grounds. The NBO analysis of compound ***anti*-15** shows a two-electron stabilizing interaction between the S−Me group hydrogen atoms and the CO ligand *cis* to the carbene moiety. Thus, the two-electron donation from the σ_{CH}-orbital of the S−Me group to the π^*_{CO}-orbital of the CO ligand (-0.33 kcal mol^{-1}) coupled to the feedback donation of the π_{CO}-orbital to the σ^*_{CH}-orbital (-0.80 kcal mol^{-1}) results in a significant stabilizing contribution in the *anti*-isomer that is not present in the *syn*-isomer (Figure 3), which leads to a lower value of $\Delta E(syn-anti)$. However, alkylthiochromium(0) and tungsten(0) carbenes exist as *syn*-isomers. Obviously, *syn*-isomers lack the steric interaction with the "CO-wall". Nevertheless, the stereoelectronic effect prevails over the steric repulsion in alkoxycarbene complexes, which, as stated above, exist mainly as *anti*-isomers. Therefore, an additional stabilizing effect should be present in alkylthiochromium(0)- and tungsten(0)carbenes. Moreover, this effect should stabilize the *syn*-isomer in alkylthio Fischer carbene complexes but should not be present in the analogous alkoxycarbene complexes.

The stabilizing effect was found in the interaction of the lone pair of electrons in the sulfur atom and the π^*-orbital of the CO ligand (Figure 4). This strong interaction (-0.42 and -0.44 kcal mol^{-1}) with the two CO ligands flanking the sulfur atom is almost negligible with the less polarizable oxygen atom of the metal alkoxycarbenes (-0.07 and -0.08 kcal mol^{-1}). Therefore, both the lack of the steric repulsion with the "CO-wall" and the RS−CO stereoelectronic interaction favor the *syn*-isomer. This explains the bias of thio-substituted carbenes for

the *syn*-isomers. These computational findings fully match the crystallographical data for the few reported X-ray structures of Fischer thiocarbene complexes.[4]

The strong preference for the *syn*-isomer in thio-substituted carbene complexes is also reflected in the dynamic *syn* → *anti* isomerization compared with the process in their alkoxy analogues. Alkoxychromium(0)- or tungsten(0)carbenes show two signals, one for each isomer, in their ^{1}H NMR spectra recorded below -25 °C (average coalescence temperature). In contrast, the ^{1}H NMR spectra of Fischer thiocarbenes show a single signal even at low temperatures, which correspond to the *syn*-isomer.[16] The experimental activation energy for the *anti*−*syn* transformation in the pentacarbonyl[methoxymethyl]-chromium(0)carbene complex is 12.4 ± 1 kcal/mol.[17] The rotation barrier for Fischer thiocarbenes lies in the range 15−18 kcal/mol, with coalescence temperatures from 68 to 84 °C. The stronger $C_{carbene}$−S bond compared to $C_{carbene}$−O is the responsible for the increased rotation barrier. This is supported by the $C_{carbene}$−O NBO (Wiberg) bond order in the pentacarbonyl-[methoxymethyl]chromium(0)carbene complex (1.10 au) compared to a $C_{carbene}$−S NBO bond order (1.51 au) for the isostructural thiocarbene complex **15**.

Figure 5 represents the calculated reaction coordinate for the *syn*-**15** → *anti*-**15** and *syn*-**21** → *anti*-**21** isomerization processes. The computed activation energies are 18.8 kcal/mol for complex

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Table 3. Calculated Activation Energies (E_a,[a,b] in kcal/mol) and Reaction Energies ($\Delta E(syn-anti)$,[a,c] in kcal/mol) for the $syn \rightarrow anti$ Isomerization Process in Different Solvents
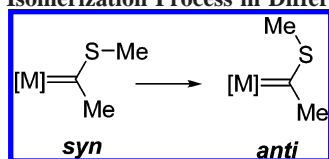
	E_a		$\Delta E(syn\text{-}anti)$	
ϵ (solvent)	M = Cr(CO)$_5$	M = W(CO)$_5$	M = Cr(CO)$_5$	M = W(CO)$_5$
1 (gas phase)	+18.80	+17.84	−1.68	−1.03
4.9 (CHCl$_3$)	+20.42	+19.57	−2.54	−1.79
5.621 (C$_6$H$_5$Cl)	+20.51	+19.67	−2.58	−1.83
20.7 (acetone)	+21.04	+20.30	−2.85	−2.07
32.63 (MeOH)	+21.10	+20.39	−2.89	−2.10

[a] All values have been calculated at the B3LYP/LANL2DZ&6-31+G*+ΔZPVE level. [b] E_a values computed as $E_a = E(TS) − E(syn)$. [c] $\Delta E(syn−anti)$ values computed as $\Delta E = E(syn) − E(anti)$.

Table 4. Relative Energies (ΔE,[a,b] kcal mol^{-1}) of syn and $anti$ Conformations of Free and Fischer-Type Thiocarbenes 9, 15, and 27−30 and M=C$_{carbene}$ Bond Lengths (in Å, in parentheses; first value corresponds to the syn-isomer and the second one to the $anti$-isomer)
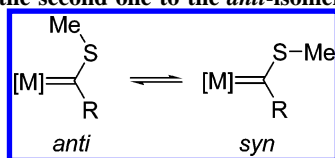
[M] = none		[M] = (CO)$_5$Cr	
9, R = Me	+1.44	**15**, R = Me	−1.68
			(2.053, 2.073)
27, R = Ph	+2.17	**29**, R = Ph	−2.77
			(2.051, 2.082)
28, R = C≡CH	+1.34	**30**, R = C≡CH	−3.19
			(2.054, 2.070)

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

15 and 17.8 kcal/mol for complex **21**.[18] These energies match the values experimentally determined by NMR.[16]

The effect of the solvent in the latter process was also computed by using the SCRF approach, under the Onsager−Kirkwood formalism, with sequential single-point calculations at the gas-phase-optimized geometries of the complexes depicted in Figure 5. The data compiled in Table 3 indicate that both the activation energies of the isomerization process and the $\Delta E(syn−anti)$ are larger in solution than in the gas phase. This is due to a movement from the more polar syn-isomer (**syn-15**, 6.22 D) to the less polar $anti$-isomer (**anti-15**, 4.31 D) through a less polar transition state (**TS-15**, 2.62 D). The more polar syn-isomer is the most stable complex in polar solvents, leading

to higher activation and reaction energies of the isomerization process, compared to that observed in vacuo.

Finally, the effect of the substituent attached to the carbene atom in the isomer preference was addressed. Three substituents were compared: Me, Ph, and the linear ethynyl moiety. Substitution at the carbon has no effect on the preferred conformation of free or metalla-thiocarbenes. The preference for the $anti$-isomer was maintained for free thiocarbenes, while the syn disposition was observed in chromium-carbenes. Moreover, the conformational preference of ethynyl-substituted alkoxychromium(0)carbene complexes (which existed in the syn disposition opposite other alkoxycarbene complexes) previously reported by us, was also found in the ethynylchromium(0)-complex **30**. The reason for this behavior is found in the linear structure of the triple bond. In this case, and according to our model,[3] the decrease in the steric interaction between the linear triple bond and the S-methyl group stabilizes further the syn-isomer, leading to a higher $syn−anti$ energy difference.

Conclusions

Excellent correlations between DFT computational energies for free alkoxy- and thio-substituted carbenes and experimental steric data (Taft parameters) have been obtained. These results clearly show that the steric volume determines the conformation of free carbenes **1−14**, at the expense of the electronic interaction. Alkoxy derivatives are more sensitive to steric effects than thiocarbenes due to the shorter C$_{carbene}$−O bond distances compared to the longer C$_{carbene}$−S bonds. This strong steric dependence of the conformation with the steric hindrance is not applicable to metal-complexed carbenes. Thio-substituted carbene complexes exist exclusively as syn-isomers due to a combination of an interaction of the sulfur lone pair with two CO ligands and the steric repulsion with the "CO-wall". In contrast, the stereoelectronic interaction of the alkyl substituent and the CO prevails against the steric repulsion in alkoxy Fischer carbene complexes, leading to $anti$-isomers. The stronger C$_{carbene}$−S bond compared to the C$_{carbene}$−O bond is responsible for the increased $syn−anti$ rotation barrier observed for the alkylthio-substituted metal carbene complexes. The differences in polarity between syn- and $anti$-isomers of alkylthio-substituted metal carbene complexes also explain the increment of the isomerization barrier with the polarity of the solvent. The substituent attached to the carbene carbon has no effect on the conformation of these compounds.

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.

(18) Interestingly, the dihedral angle Me−C(Cr)−X−Me moves from an initial value of −0.1° in the **syn-15** isomer to −100.3° in the transition structure **TS-15**, while the staggered conformation of the carbene moiety and the cis-CO ligands is maintained in the transition state. The final dihedral for the **anti-15** isomer is −178.0°, which is again in a staggered conformation. Therefore, the staggered disposition of the carbene is maintained during the $syn \rightarrow anti$ isomerization process that occurs by rotation across the C(M)−S−Me without affecting the M=C bond and therefore the coordination sphere of the transition metal.

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