Mechanism of the Generation of Ketenimine−M(CO)$_n$ Complexes (M = Cr, W, Fe) from Fischer Carbenes and Isocyanides

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The mechanism of the thermal formation of ketenimine complexes through the reaction of group 6 (chromium and tungsten) and 8 (iron) Fischer carbenes and isocyanides has been studied computationally within the density functional theory framework. The computational data have been compared to the reported experimental results. It is found that the insertion of the N≡C bond of the isocyanide into the M=C bond of the Fischer carbene complexes, which leads to *N*-metalated-ketenimine complexes, occurs via metallacyclopropanimine species, rather than the proposed ylide complexes, followed by isomerization and 1,2-metallotropic rearrangement. We also studied the 6π-electrocyclization process of dienyl−ketenimine complexes, which leads to *o*-alkoxy aniline compounds. In terms of the synchronicity, activation energy, and aromaticity, the effect of the metal in this electrocyclization transformation is almost negligible.

Introduction

Fischer carbene complexes have proved themselves to be irreplaceable building blocks for organic and organometallic synthesis because they enable nonconventional, high-yielding transformations under mild conditions.[1] In spite of the considerable diversity of reactions performed with these complexes, proper selection of substrates and careful adjustment of the reaction conditions have allowed, in most cases, the totally selective preparation of valuable compounds.

Ketene-like complexes are readily available from Fischer carbene complexes both thermally[2] and photochemically.[3] Recently, we reported a detailed experimental−computational study of the mechanism of photocarbonylation from group 6 carbene complexes[4a] leading to coordinated ketenes and their ulterior reaction with imines to produce 2-azetidinones.[4b] The irradiation of alkoxychromium(0) carbene complexes, either in the LF band followed by relaxation to the MLCT band or directly in the MLCT band, results in the excitation of these complexes to the S_1 state, which readily decays to T_1 by intersystem crossing (ISC), thus leading to coordinatively unsaturated chromacyclopropanone T_1 structures with a biradical character. The evolution of the metallacyclopropanone species occurs by a decay (spin inversion) to the S_0 hypersurface by coordination of a molecule of the solvent, leading to ketene-derived products in the presence of ketenophiles or reverting to the starting carbene complex in their absence. Interestingly, the structure of the reactive S_0 species corresponds to an acylchromate rather than a metallacyclopropanone.

In contrast to the above photocarbonylation reaction, and other thermal processes occurring through intermediate vinyl ketene complexes, which involve the participation of a CO ligand to generate the ketene species, Fischer carbene complexes **1** react thermally with isonitriles **2** to produce metal-complexed ketenimines **3**. The evolution of ketenimines **3** is substrate and reagent dependent, leading to different products. The metal carbene/isonitrile stoichiometry also plays a role in the nature of the reaction products.[2] The mechanism for the formation of complexes **3** has been proposed to occur by a 1,2-insertion of the N≡C bond into the M=C bond, via ylide complexes **4** and/or (with charge neutralization) via metallacyclopropanes **5**. Intermediates **4** and **5** are in turn formed by nucleophilic attack of the isocyanide carbon atom to the electrophilic carbene carbon (Scheme 1). This proposal was based on the observation that alkoxychromium(0) carbene complexes having carbene and isocyanide ligands in a *cis* arrangement are stable under the reaction conditions.[2,5] This fact ruled out a hypothetical reaction pathway in which the isocyanide first coordinates to the metal atom and further evolves to intermediates **4** and **5**.

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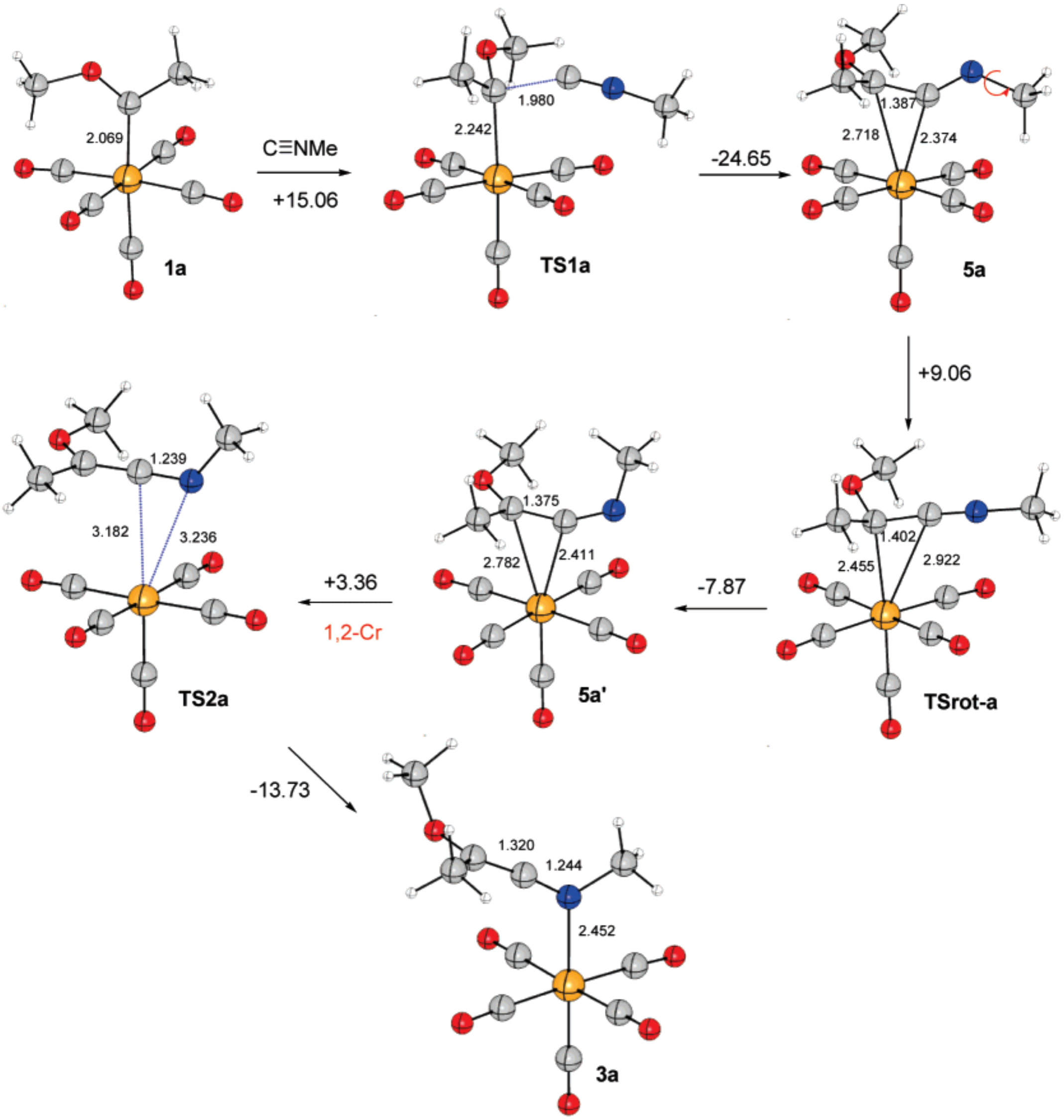
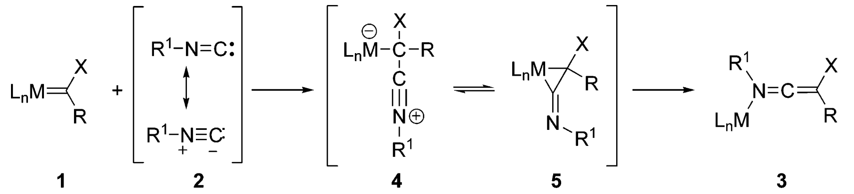


Figure 1. Stationary points found in the reaction between Fischer carbene complex **1a** and methylisocyanide to yield ketenimine **3a**. All structures correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) geometries. Bond distances and energies are given in Å and kcal/mol, respectively. Numbers over the arrows correspond to the relative energies between the corresponding structures. Zero-point vibrational energy corrections have been included (kcal/mol). Unless otherwise stated, white, gray, red, blue, and orange colors denote hydrogen, carbon, oxygen, nitrogen, and chromium atoms, respectively.

Scheme 1



X = O-alkyl, S-alkyl, N=CR$_2$, PR$_3$
R,R^1 = alkyl, aryl, alkenyl, alkynyl
M = Cr, Mo, W, Mn, Fe, Os, Th, U
L = CO, PR$_3$, η^5-CH$_3$C$_5$H$_4$, η^5-C$_5$H$_5$

The stability and thence the possibility of isolation of species **4** and **5** and/or **3** is metal dependent. Thus, the species **3** has been characterized crystallographically for chromium,[6] while metallacyclopropanimine **5** has been isolated for iron.[7] Moreover, the coexistence of a mixture of species **3**−**5** in solution has been reported for manganese on the basis of NMR data.[8] Therefore, with these experimental data in hand the apparently simple scenario sketched in Scheme 1 becomes much more complicated.

One of the key reactions of this class of compounds is the reaction of chromium(0) dienyl−ketenimine complexes **6** to

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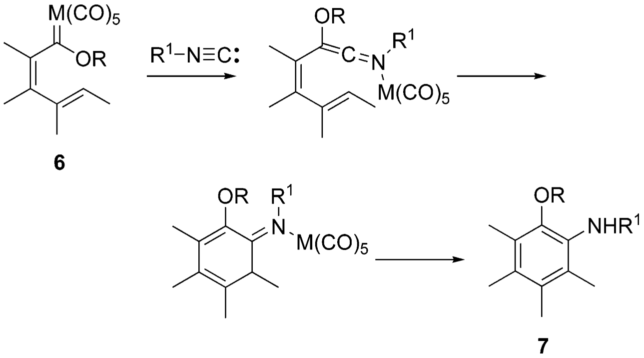
Scheme 2



produce *o*-alkoxyanilines **7** via a 6π electrocyclization process (Scheme 2).[9] This reaction has been successfully applied to the preparation of analogues of indolocarbazole natural products,[10] to the total synthesis of calphostins,[11] and more recently to the synthesis of highly functionalized indazoles[12a] and *o*-quinodimethide precusors.[12b]

We report in this paper the systematic study of the potential energy surface for the formation of coordinated metallaketenimines derived from Cr, W, and Fe Fischer carbene complexes, the comparison between their corresponding structures, and also the reactivity of these complexes with protic nucleophiles. To complete this study, we will compute the reaction of a model reaction for the transformation of complexes **6** to *o*-methoxy-*N*-methylaniline. This reaction will be compared with the organic (metal-free) dienyl−ketinimine in terms of activation energy, aromaticity of the transition state, and synchronicity. The role of the metal in these processes will be thus established.

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 03 suite of programs.[13] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[14] and the standard 6-31+G* basis set[15] for hydrogen, carbon, oxygen, and nitrogen and the Hay−Wadt small-core effective core potential (ECP) including a double-ξ valence basis set[16] for the metal atoms (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[17] and 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.[18] Nucleus independent chemical shifts (NICS) were evaluated by using the gauge-invariant atomic orbital[19] (GIAO) approach, at the GIAO-B3LYP/LANL2DZ&6-31+G* level.

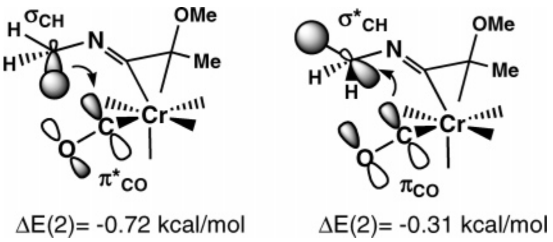


Figure 2. Two-electron interactions and associated second-order perturbational energies between an alkyl group and a CO ligand in intermediate **5a**.

The synchronicity[20,21] of the reactions was quantified by using a previously described approach.[22] For a given concerted reaction, "synchronicity" is defined as[23]

$$S_y = 1 - \frac{\sum_{i=1}^{n} \frac{|\delta B_i - \delta B_{\mathrm{AV}}|}{\delta B_{\mathrm{AV}}}}{2n - 2}$$

where n is the number of bonds directly involved in the reaction (in this case, $n = 5$) and δB_i stands for the relative variation of agiven bond index B_i at the transition state (TS), according to the following formula:

$$\delta B_i = \frac{B_i^{\mathrm{TS}} - B_i^{\mathrm{R}}}{B_i^{\mathrm{P}} - B_i^{\mathrm{R}}}$$

where the superscripts R and P refer to the reactants and the product, respectively. The average value of δB_i, denoted as δB_{AV}, is therefore

$$\delta B_{\mathrm{AV}} = n^{-1} \sum_{i=1}^{n} \delta B_i$$

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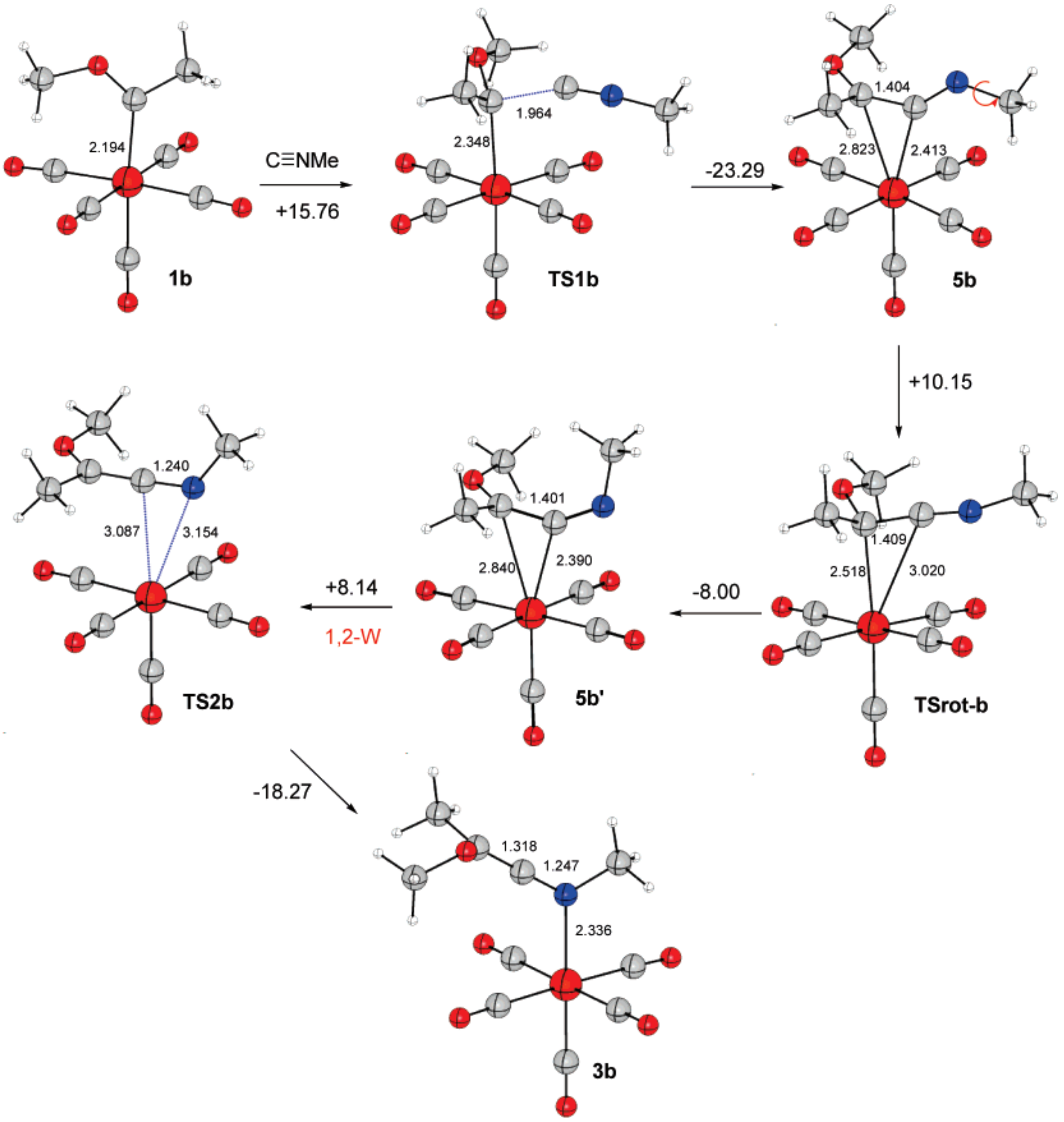

Figure 3. Stationary points found in the reaction between Fischer carbene complex **1b** and methylisocyanide to yield ketenimine **3b**. All structures correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) geometries. Bond distances and energies are given in Å and kcal/mol, respectively. Orange color denotes tungsten atoms. See Figure 1 caption for additional details.

The Wiberg bond indices[24] B_i were computed using the natural bond orbital (NBO) method.[25]

Results and Discussion

DFT calculations (B3LYP/LANL2DZ&6-31+G*) were carried out starting with the *anti*-form of the pentacarbonyl(methoxymethyl)chromium(0) carbene complex **1a**, the most stable conformation in the gas phase and in the solid state.[26] We located the saddle point **TS1a**, which corresponds to the proposed addition of the methyl isocyanide to the electrophilic carbene carbon of the chromium complex **1a**. The intrinsic reaction coordinate (IRC) study from **TS1a** led to the chromacyclopropanimine **5a** (Figure 1). The activation energy of this transformation is 15.1 kcal/mol, while the reaction energy is −9.6 kcal/mol. Therefore, the addition of isocyanides to alkoxychromium(0)carbene complexes is exothermic and occurs directly to the carbene carbon. This finding is consistent with the available experimental results.[2,5] All efforts to locate ylides related to **4** (see Scheme 1) at the gas phase and even in the condensed phase using the polarizable continuum method (with chloroform as solvent) meet with no success. Complex **5a** isomerizes to intermediate **5a′**, which lies only 1.2 kcal/mol above **5a**, through the transition state **TSrot-a**, associated with the rotation about the C−NMe bond.

The energy difference between complexes **5a** and **5a′** may be ascribed to a two-electron stabilizing interaction between the N-Me group hydrogen atoms and the CO ligand *cis* to the carbene moiety. Thus, the NBO analysis on **5a** shows that the two-electron donation from the σ_{CH} orbital of the N-Me group to the π^*_{CO} orbital of the CO ligand (−0.72 kcal/mol) coupled to the feedback-donation of the π_{CO} orbital to the σ^*_{CH} orbital

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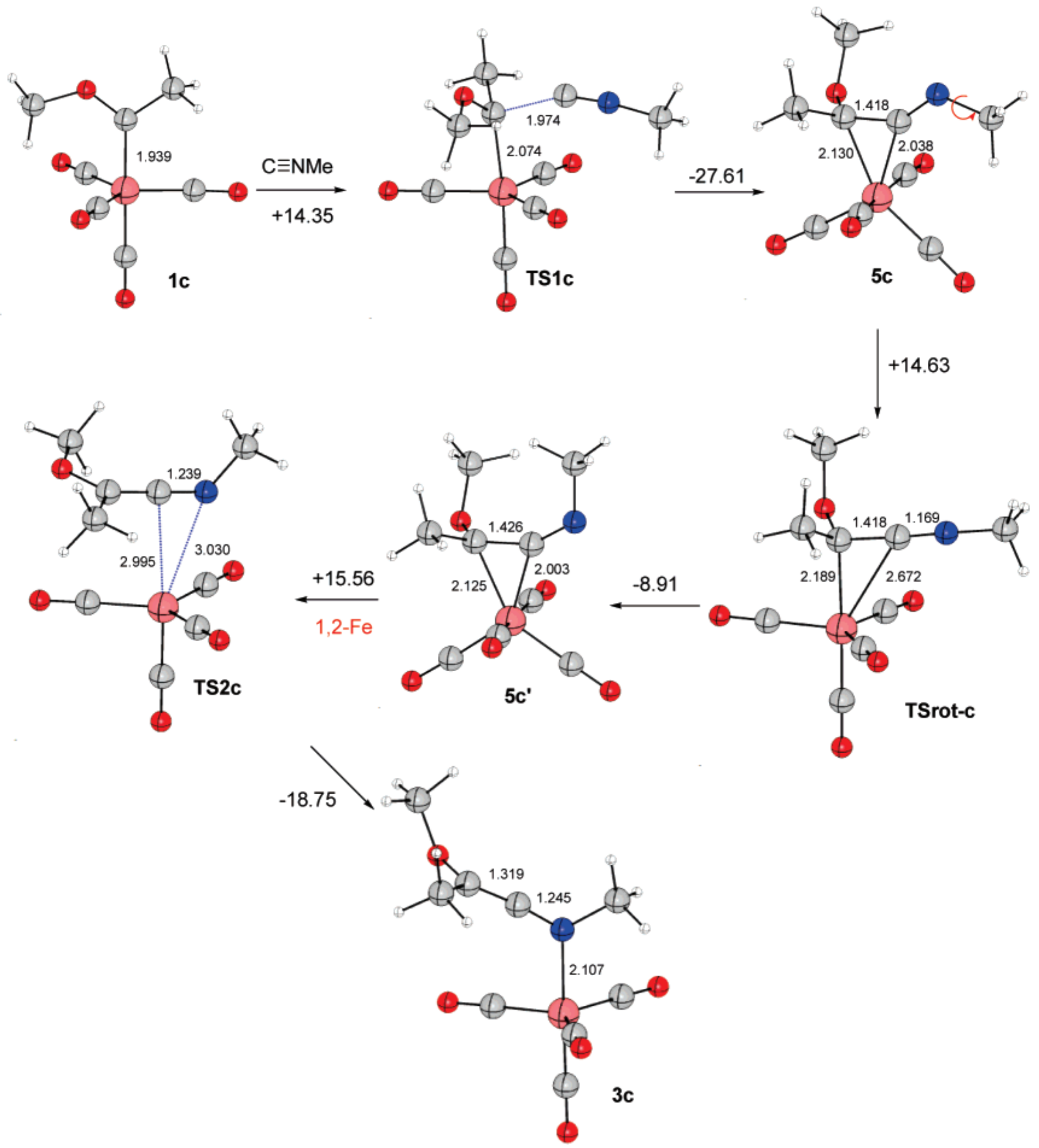

Figure 4. Stationary points found in the reaction between Fischer carbene complex **1c** and methylisocyanide to yield ketenimine **3c**. All structures correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) geometries. Bond distances and energies are given in Å and kcal/mol, respectively. Pink color denotes iron atoms. See Figure 1 caption for additional details.

(-0.31 kcal/mol) results in a significant stabilizing contribution in the **5a** isomer that is not present in **5a′** (Figure 2).[27]

Intermediate **5a′** leads to chromiun(0)ketenemine **3** via the transition state **TS2a**. As readily seen in Figure 1, the latter saddle point is associated with the 1,2-migration of the chromium from the carbon atom to the nitrogen atom. This kind of metallotropic process is often encountered in the chemistry of Fischer carbene complexes. In fact, such migrations have been reported by us in the addition of simple nucleophiles to α,*β*-unsaturated carbene complexes,[28] in the stepwise photodyotropic rearrangements of aminocarbene complexes,[29] and interestingly, in the reaction of the photochemically produced ketene-like species with imines to form *β*-lactams.[4b]

The above results show that the insertion of the isocyanide into the M═C bond of the chromium(0) Fischer carbene complexes to produce ketenimine complexes **3** occurs via the metallacyclopropanimine **5**, rather than the ylide complex **4** (see Scheme 1), followed by a 1,2-metallotropic rearrangement. The global process from **1a** and methylisocyanide to produce **3a** is highly exothermic ($E_r = -18.8$ kcal/mol). Therefore, it is not surprising that complexes **3** are the isolated products in the reaction of chromium(0) Fischer carbene complexes and isocyanides at the expense of complexes **5**.

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(27) A similar two-electron stabilizing interaction was found to be responsible for higher stability of the *anti*-alkoxymetal(0) carbene complexes with respect to their *syn*-isomers. See ref 26.

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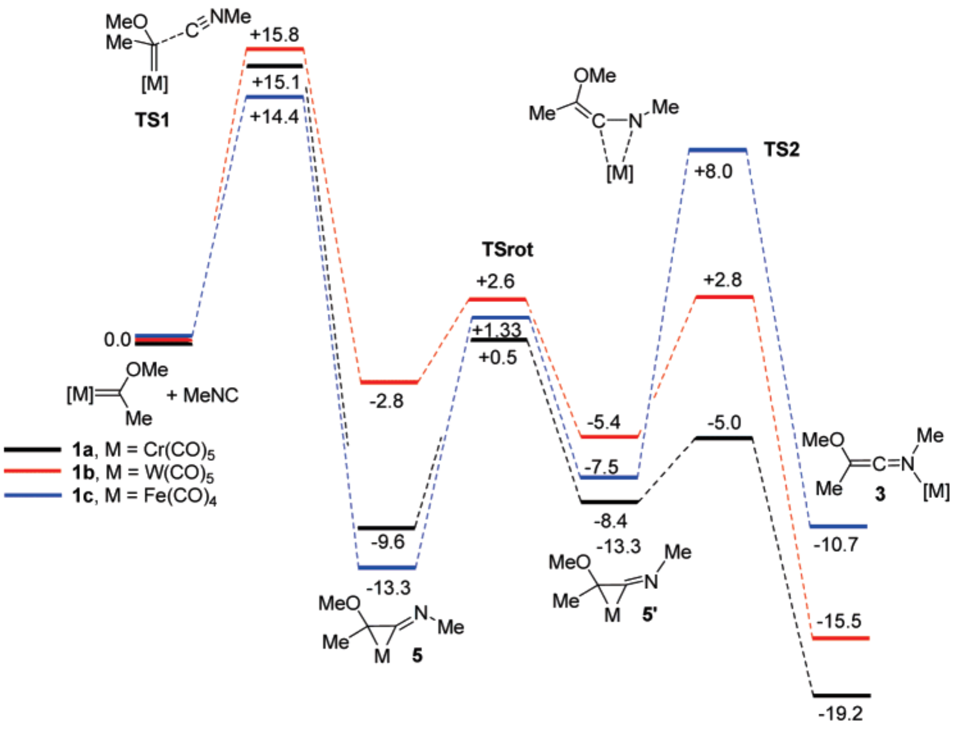


Figure 5. Reaction profiles found for the **1a**,**c** → **5a**,**c** → **3a**,**c** transformations.

Table 1. Selected Bond Distances (r(X−Y), in Å), Angles (in deg), and Bond Orders (B(X−Y), in au, in parentheses) for Complexes 1a,b and Intermediates 3a,b and 5a,b

	1a	1b	3a	3b	5a	5b
r(M−C$_{carb}$)	2.069	2.194			2.718 (0.15)	2.823 (0.17)
r(M−C═**N**)					2.374 (0.22)	2.412 (0.30))
r(C$_{carb}$−C(═**N**))			1.318 (1.78)	1.318 (1.79)	1.387 (1.37)	1.404 (1.32)
r(C═**N**)			1.244 (1.89)	1.247 (1.85)	1.256 (1.96)	1.265 (1.91)
C−M−C(═N)					30.7	29.8

Figure 3 shows the reaction pathway from *anti*-pentacarbonyl(methoxymethyl)tungsten(0) carbene complex **1b** and methyl isocyanide to produce the ketinimine complex **3b**. The results are analogous to those obtained for the isostructural chromium carbene complex **3a**. Again, the transformation involves the formation of the corresponding tungstenacyclopropanimine **5b** through **TS1b**, isomerization to **5b′** via the respective **TSrot-b**, and 1,2-tungsten migration from carbon to nitrogen to form the ketenimine **3b** in a highly exothermic process ($E_r = -15.5$ kcal/mol). The only outstanding difference between Cr and W is the higher activation barrier from **5b′** to **3b** ($E_a = 8.1$ kcal/mol) compared to the activation energy from **5a′** to **3a** ($E_a = 3.4$ kcal/mol). This is very likely due to the stronger W−C bonds in **5b′** compared to the corresponding Cr−C bonds. In fact, both metal−carbon NBO bond orders are higher in **5b′** (W−C(former isonitrile) = 0.29 au and W−C(former carbene) = 0.16 au) than in **5a′** (Cr−C(former isonitrile) = 0.18 au and Cr−C(former carbene) = 0.12 au).

The reaction of iron Fischer carbene complex **1c** and methylisocyanide was computed next. The most stable form of the iron trigonal-bipyramid carbene complex **1c** in the gas phase is the *anti*-form as well, where the methyl group of the methoxy substituent is directed toward the metal fragment.[26] Analogously to Cr and W carbenes, the reaction begins with the nucleophilic attack of the methylisocianyde to the electrophilic carbene-carbon atom of **1c**, leading to the ironcyclopropanimine **5c** via transition state **TS1c**, with comparable activation energy (E_a = 14.4 kcal/mol for Fe, 15.1 kcal/mol for Cr, and 15.8 kcal/mol for W). Following the general reactivity pattern, the species **5c** isomerizes to **5c′**, through the respective **TSrot-c**. To complete the reaction, the 1,2-Fe migration should occur to produce the iron−ketenemine **3c** (Figure 4). On the contrary, the square-pyramidal species **5c** is the global minimum on the energy potential surface (in fact, **5c** lies 2.5 kcal/mol below the ketenimine **3c**). Moreover, the energy of activation for the 1,2-Fe migration is now 15.6 kcal/mol, which renders this process unfavorable compared to the corresponding chromium or tungsten metallotropic processes ($E_a = 3.4$ kcal/mol for Cr and $E_a = 8.1$ kcal/mol for W; see Figure 5). According to these results, the isolable compound in this case should be metallacyclopropanimines **5** and not metal-coordinated ketenimines **3**. This is in full agreement with the isolation and crystallographic characterization of Fe−cyclopropanimines but not Fe−ketenimines.[7]

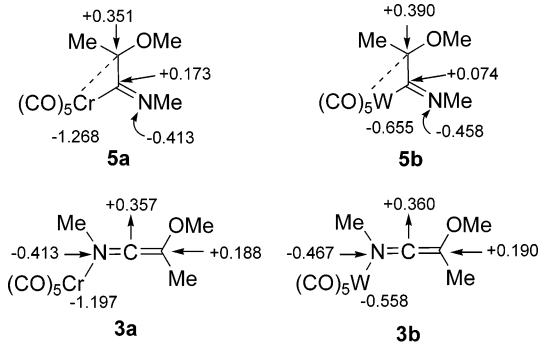


Figure 6. NBO charges for species **3a**,**b** and **5a**,**b**.

The structures of the species **3** and **5** deserve further analysis. Table 1 compiles the essential geometric features of these species. Metallacyclopropanimines **5** have elongated M−C$_{carbene}$ bonds compared to those in the starting carbene complexes **1** ($\Delta r \approx 0.63$ Å). The new bond formed between the metal and

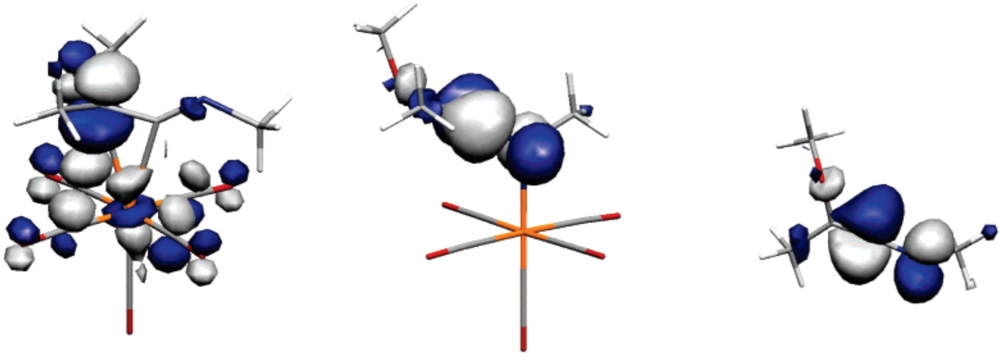
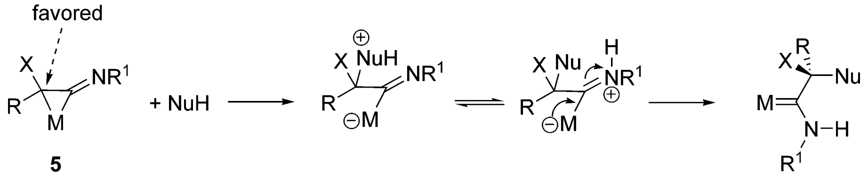


Figure 7. LUMO of species **5a**, **3a**, and the corresponding organic ketenimine.

Scheme 3



NuH = R'OH, R'SH, R'$_2$NH
M = Cr(CO)$_5$, Mo(CO)$_5$, W(CO)$_5$
Mn(CO)$_2$(Cp), Fe(CO)$_4$

the carbon atom of the methyl isocyanide is much shorter ($r \approx 2.4$ Å) than the M−C$_{\text{carbene}}$ bond ($r \approx 2.7-2.8$ Å), which means a stronger bond between the metal and this carbon compared to the metal former carbene−carbon bond. Furthermore, the length of the new C−C bond is approximately 1.4 Å (NBO bond order ca. 1.35 au), while the NBO bond order of the C=N bond is ca. 2.0 au, which makes the latter bond a true double C=N bond. Therefore, the structure of the metallocyclopropanimine **5** corresponds to a ketene species coordinated to the metal with a highly polarized Cr−C (former carbene) bond. In fact, the NBO analysis carried out on **5** (Figure 6) gives a high negative charge value for the metal atom (−1.268 au for **5a** and −0.655 au for **5b**) and also a high positive charge value for the carbene C atom (+0.350 for **5a** and +0.390 au for **5b**). Therefore, the species **5** are better described as iminoacylmetalates than as metallacyclopropanimines.[30] Regarding the species **3**, the data gathered in Table 1 confirm that these species are true ketenimines coordinated to the metal through the nitrogen atom, a fact already established by X-ray studies. In fact, we found that NBO bond orders for the C=C and C=N bonds in compounds **3** are close to 2.0 au.

To complete this discussion, a higher positive charge of species **3** is found on the central carbon atom. Therefore, it is very likely that the addition of protic nucleophiles occurs on species **5**, where the higher positive charge is on the terminal carbon atom, rather than in species **3** (Scheme 3). We want to restate that metal-free ketenimines add protic nucleophiles to the central carbon atom. Therefore, it becomes clear that species **3** are very similar to classical organic ketenimines. This simple NBO charge analysis may justify the "reactivity umpolung" found in ketenimine ligands by the metal residue, which permits addition of protic nucleophiles to the terminal carbon atom of the ketenimine ligand instead of to the central atom.[2]

Inspection of the LUMOs of the different species leads to a similar conclusion. As readily seen in Figure 7, the LUMO of complex **5a** is centered on the terminal carbon atom, while the LUMO+1 is centered on the central carbon atom in complex **3a**.[31] Interestingly, the LUMO of the corresponding metal-free ketenimine is similar to the LUMO of **3a**. Therefore, if metal-coordinated ketenimines are the reactive compounds toward NuH, identical products to those obtained with metal-free ketenimines will be expected.

The effect of the metal moiety in the 6π electrocyclization process of chromium(0) dienyl−ketenimine complex **6a**, which leads to complex **7a**, was finally addressed. As readily seen in Figure 8, this transformation is concerted and occurs through the six-membered transition state **TS6a**. It is also noteworthy that this process is found to be close to perfect synchronicity (S_y = 0.93). The aromaticity of the transition state[32] was computed using the nucleus-independent chemical shifts (NICSs).[33] Given the unsymmetrical character of our cyclic systems, we needed to define the inner points of these systems unambiguously. We proposed[34] that the (3,+1) ring critical point of the electron density, as defined by Bader,[34] is an unambiguous choice for the calculation of the NICSs, since only at this point is the electron density a minimum with respect to motion on the ring's plane and a maximum with respect to motion perpendicular to the plane defined by the ring. The position of the ring critical point of **TS6a** and the NICS value at this point is also indicated in Figure 8. **TS6a** exhibits a negative NICS value (NICS = −8.84 ppm), which should be attributed to strong diamagnetic shielding due to the aromaticity provoked by the involvement of 6π electrons in the transformation. We also studied the same process involving the corresponding metal-free ketenimine **6b**. As expected, we found that the electrocy-

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[30] Interestingly, a similar structure was found for the ketene-like complexes obtained by irradiation of carbene complex **1a**. See ref 4a. However, the acylchromate character of the ketene-like complexes obtained photochemically is lower than in compounds **5**.

[31] The LUMO of complex **3a** is centered on the metal fragment.

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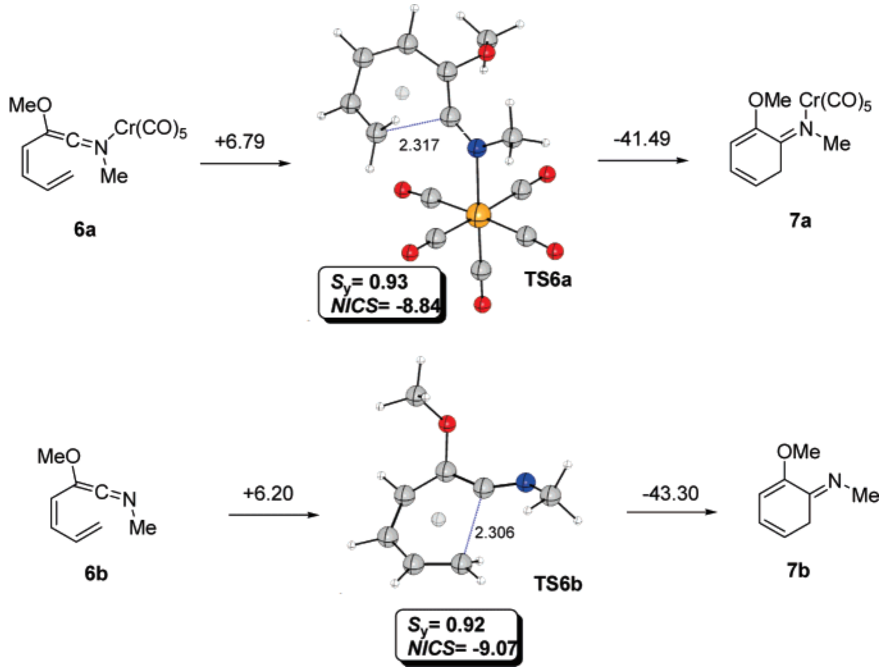

Figure 8. Chief geometric features of transition structures associated with the formation of compounds **7a**,**b** in the electrocyclization process of ketenimines **6a**,**b**. Bond distances are given in Å and energies in kcal/mol. The dummy atoms denote the ring point of electron density.

clization is concerted and very synchronous (S_y = 0.92) and occurs via the aromatic (NICS = −9.03 ppm) six-membered transition state **TS6b**. Interestingly, the C−C bond lengths in the latter transition state (r = 2.306 Å) and in the respective metal−**TS6a** (r = 2.317 Å) are also quite similar. Therefore, we can conclude that the metal moiety has no significant effect on the conversion of the ketenimine complexes, which are formed from the reaction between Fischer carbene complexes and isocyanides, to *o*-alkoxyanilines. This result is in nice agreement with the above-mentioned finding that the structure of ketenimines **3** is rather similar to the structure of metal-free organic ketenimines.

Conclusions

From the computational study reported in this paper the following conclusions can be drawn: (i) The insertion of the N≡C bond of the isocyanide into the M═C bond of the Fischer carbene complexes to produce *N*-metalated-ketenimine complexes occurs via metallacyclopropanimine species **5**, rather than the previously accepted intermediates, namely, ylide complexes **4**, followed by isomerization and 1,2-metallotropic rearrangement. (ii) While group 6 Fischer carbene complexes lead to ketenimines **3** in their reaction with isocyanides, it is very likely that iron−carbene complexes lead to metallacyclopropanimine **5**, in view of the considerably higher activation energy required for the 1,2-metallotropic process. (iii) The metal moiety has no significant effect on the conversion of the ketenimine complexes **3** to *o*-alkoxyanilines, as readily seen from the comparison between the activation energy, aromaticity, and synchronicity of the latter process and the transformation involving metal-free ketenimines. This result is in nice agreement with the finding that the structure of ketenimines **3** is rather similar to the structure of organic ketenimines.

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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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