

Simulating the Agostic Interaction in Electron-deficient (16-e) Group (VI) ML₆ Complexes: [M(CO)₅(C(Me)OMe)] (2+) (M = Cr, Mo, and W) as Models

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ABSTRACT

A large number of theoretical studies have focused on understanding the molecular features of the agostic interaction in various kinds of molecular environments. However, there is a lack of electronic structure information about the agostic interaction in electron-deficient group (VI) ML₆ organometallic complexes. In this simulation study, a unique case of an intramolecular stabilizing interaction has been discovered and evaluated. A geometric analysis revealed that beta-(C-H) and alpha-(C-C) can occupy the seventh and eighth coordination sites in the title Fischer carbene complexes as agostic interactions, which allows classifying the carbene as a η^3 ligand in these cases. This theory was supported by the relative energies of the conformers and an NBO analysis. Both C2-C1 (σ) and C2-H1 (σ) were found to interact with the antibonding orbital of M-C6 (σ^*), therefore these interactions are classified as $\sigma \rightarrow \sigma^*$. These two simultaneous interactions have significant impact on the carbene characteristics; the structure, the atomic charges, infrared stretching vibrations (C-H, C-C, and C-O), and the ¹H and the ¹³C-NMR chemical shifts. From a fundamental organic-organometallic chemistry point of view, this is a new addition to the orbital interaction theory and to group (VI) chemistry.

KEYWORDS

DFT, agostic interaction, NBO analysis, NPA charges, IR, GIAO-NMR.

1. Introduction

There are over a thousand articles and 40 reviews addressing the concept of the agostic interaction (SciFinder results, May 2010). This large number of publications attests the importance of this interaction in structure and activity of organometallic compounds. Brookhart and Green^{1,2} provided the first basic framework for the agostic interaction which is considered the cornerstone for understanding this concept. An agostic interaction is a stabilizing intramolecular interaction between an electronically unsaturated transition metal and a sigma bond that is located at an appropriate position with respect to the metal to achieve efficient overlap. The sigma bond is a source of an electron pair which might be a C-H, C-C, Si-H or a B-H bond. Therefore, the interaction is classified as 3-centre-2-electron bond. The sigma bond may be at the alpha-, beta-, or even gamma-position, therefore it is often named as an α -, β -, or γ -agostic interaction.

The earliest criteria used to decide whether an agostic interaction exist or not is the structure of the complex. The distance that separates the hydrogen atom and the metal is in the range of 1.8–2.3 Å, while the M-H-C angle is in the range 90–140°. With recent advances in the computational chemistry theoretical methods have become powerful tools in characterizing such interactions. Recently, Lein³ published a review presenting the computational efforts in this area.

The β -agostic interaction of a carbene ligand is known only in two examples. The first one is in the tungsten(II) complex, Tp(CO)₂W=C(Me)Ph⁺ (Tp is tridentate nitrogen chelate), characterized by Feng⁴ and the second is in the rhenium(III) complex, (PNP)Re(H)₂[=C(CH₂)₅] (PNP is tridentate 2P and 1N chelate), characterized by Ozerov.⁵ Both examples are

isoelectronic and electron deficient, the metal has 16-valence electrons and a coordination number of six (not including the agostic interaction).

Despite the large number of the theoretical studies, there are no electronic structure studies of electron-deficient (16-e) group (VI) ML₆ organometallic complex that include an agostic interaction. Thus, the effort of this work was devoted to investigate this remarkable phenomenon in the title complexes as models. Many interesting features will be presented and discussed. The optimized structures of the neutral and the cationic formulas are presented in Fig. 1.

2. Computational Details

All the calculations were performed using Gaussian 03 suite of programs.⁶ Recently, the hybrid functional B3LYP⁷ has been used to study various organometallic molecular systems and gave satisfactory results.^{8–11} Therefore, the structures in this study were optimized using the computational procedure B3LYP/6-31G(d)-SDD. The basis set 6-31G(d)¹² was assigned for carbon, hydrogen, and oxygen, while the basis set SDD¹³ (with the effective core potential of Hay and Wadt) was assigned for the group VI metals chromium, molybdenum, and tungsten. After performing the frequency calculations and observing that the number of the imaginary frequencies was equal to zero it became clear that each of the optimized structures is a true minimum on the potential energy surface. The intermolecular interactions were estimated based on a second-order perturbation (SOP) analysis. The atomic charges were calculated based on the natural population analysis (NPA) scheme. Both NPA and SOP were obtained by the standard natural bond orbitals (NBO) method.¹⁴ The data presented in Tables 3 and 4 are the stabiliza-

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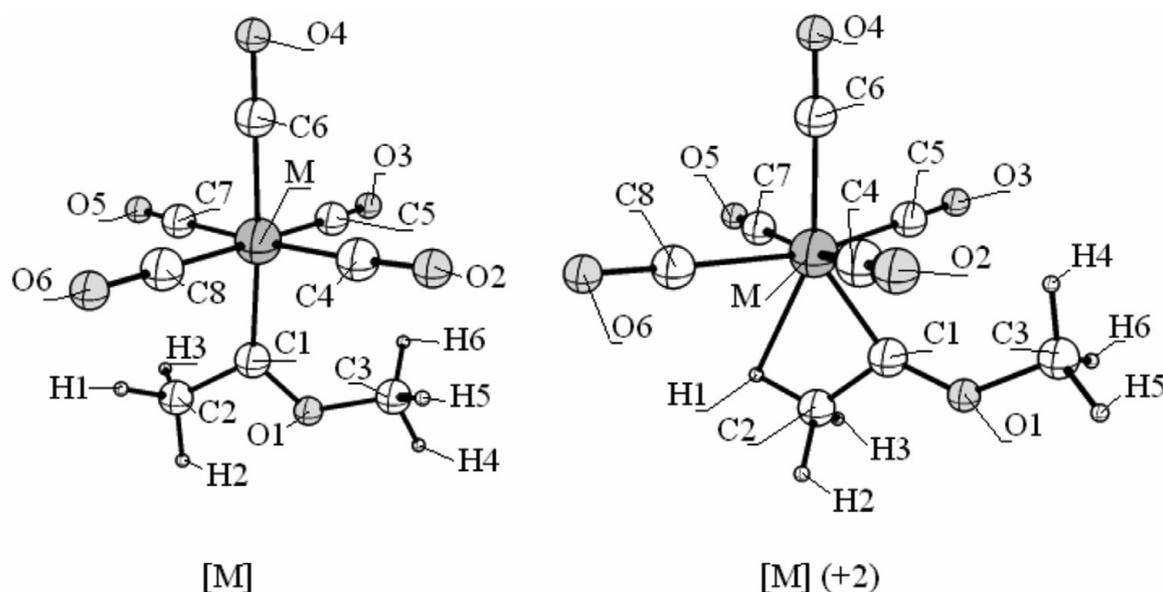


Figure 1 Structures of the chromium complexes in the neutral and the cationic states. The molybdenum and tungsten complexes have very similar structures.

tion energies associated with charge delocalization (intramolecular interactions) and appear in the NBO section of the output files as $E^{(2)}$ (kcal/mol). The NMR chemical shifts were calculated using the GIAO method¹⁵ and tetramethylsilane (TMS) was employed as reference. The graphics interphase ChemCraft¹⁶ was used to read the output files and to visualize the infrared vibrations.

3. Results and Discussion

3.1. Geometrical Parameters

Selected geometric parameters of the neutral and the cationic complexes are presented in Table 1. The most important structural feature is the H1-M distance (entry 1). The difference $\Delta H1-M (+2/0)$ (entry 2) is strong evidence that there is a new attractive interaction between H1 and the metal centre in the

three cationic structures. The observed values of H1-M are in the range of 2.314–2.422 Å which is at the upper end of the range that has been observed experimentally for agostic interactions (1.8–2.3 Å). A second important criterion is the observed change in the dihedral angle H1-C2-C1-M (entry 18). The range of its value in the neutral structures is 35–40 degrees, while in the cationic structures it is 0°. As can be seen from the optimized geometries (Fig. 1) and as noticed from the incredible decrease in the value of the C2-C1-M angle (entries 19 and 20) the carbene ligand converts from a monodentate ligand to a chelate. The proposed interaction between H1 and M led to an elongation in the C2-H1 bond (entries 3 and 4) while the changes in the C2-H2 and C2-H3 bonds are small and not significant. In addition, it is noted that the M-H1-C2 angle in the cationic structures is at the lower end of the experimentally observed range (90–140°) for an agostic interaction (entry 21 and 22).

Table 1 Selected geometrical parameters, bond lengths (Å) and angles (degrees) for the cationic and the neutral complexes.

Entry	Parameter	Cr(+2)	Cr(0)	Mo(+2)	Mo(0)	W(+2)	W(0)
1	H1-M	2.314	3.237	2.373	3.319	2.422	3.313
2	$\Delta H1-M(+2/0)$	0.923		0.946		0.891	
3	C2-H1	1.105	1.093	1.112	1.093	1.113	1.092
4	$\Delta C2-H1$	0.012		0.019		0.021	
5	C2-H2	1.098	1.095	1.098	1.096	1.098	1.096
6	C2-H3	1.098	1.099	1.098	1.100	1.098	1.100
7	C1-C2	1.507	1.515	1.509	1.513	1.511	1.514
8	$\Delta C1-C2$	0.008		0.004		0.003	
9	C1-O1	1.255	1.317	1.256	1.316	1.259	1.318
10	$\Delta C1-O1$	0.062		0.060		0.059	
11	O1-C3	1.487	1.441	1.485	1.441	1.483	1.440
12	$\Delta O1-C3$	0.046		0.044		0.043	
13	C3-H4	1.089	1.090	1.089	1.090	1.089	1.090
14	C3-H5	1.090	1.090	1.090	1.091	1.090	1.091
15	C3-H6	1.090	1.090	1.090	1.090	1.090	1.091
16	C1-M	1.934	2.059	2.059	2.202	2.074	2.204
17	$\Delta C1-M$	0.125		0.143		0.130	
18	H1-C2-C1-M	0.0	40.0	0.0	38	0.0	35.5
19	C2-C1-M	94.6	122.5	94.8	122.0	95.8	122.2
20	$\Delta C2C1M$	27.9		27.2		26.4	
21	M-H1-C2	88.8	75.4	91.7	77.8	91.2	78.4
22	$\Delta M-H1-C2$	13.4		13.9		12.8	

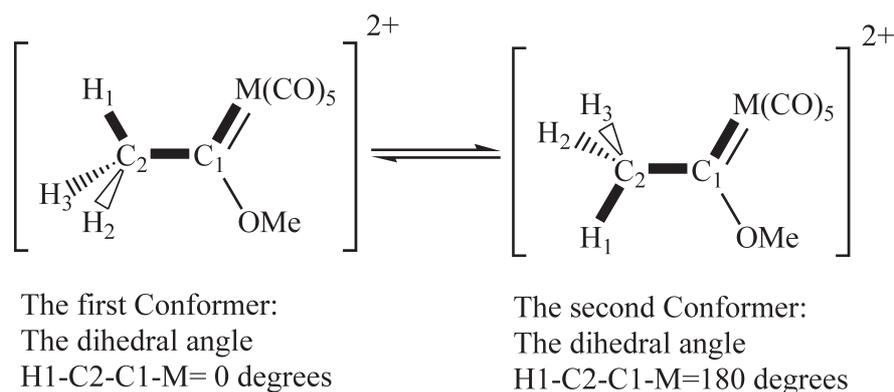


Figure 2 An illustration for the conformation process. The first conformer is the optimized $[M](+2)$ (Fig. 1) and the second conformer was generated by rotating the C2-C1 bond.

The carbene interaction with the $M(CO)_5$ moiety led to shorter C1-C2 bonds (entries 7 and 8) in the cationic structures. The metal in the cationic structures being electron deficient ($16e$) demands more electron density from the carbene and makes C1 more positive, which in turn induces more delocalization of the oxygen lone pair toward the empty p-orbital of C1. This would decrease the distance between C1 and O1. The values in entries 9 and 10 are consistent with this analysis and confirm that C1-O1 bond became shorter. In addition to this, the observed change in C1-M and $\Delta C1-M$ (entries 16 and 17) are consistent with this analysis. The difference among the three values of $\Delta C1-O1$ for the three metals is small and indicates that the $M(CO)_5$ moieties take similar amounts of charge from the carbene ligand.

Contrary to the observed decrease in the C1-O1 bond length, the distance between O1 and C3 increased in the cationic structures (entries 11 and 12), which suggests the existence of a repulsive interaction (steric strain) between the methyl group and the carbonyl ligands. In addition to this, the similarities in the C3-H (4, 5, 6) (entries 13, 14, 15) in the cationic and the neutral structures indicate that there is no attractive interaction between the $M(CO)_5$ moieties and any of the C3-H bonds.

3.2. Relative Energies of Conformers

In order to distinguish presence of a stabilizing interaction between C2-H1 and the metal in the cationic complexes the energies of two conformers were compared. The first cationic conformer is the optimized structure ($[M](+2)$) appearing in Fig. 1. In this conformer, the H1-C2-C1-M dihedral angle is 0° , while the second conformer was generated by rotating the C2-C1 in $[M](+2)$ and adjusting the dihedral angle to become equal to 180° (Fig. 2 and Table 2). This puts H1 at the furthest point from the metal and gives the largest energy difference. Complete conformational ($0^\circ \rightarrow 360^\circ$) analysis is not necessary here to support the idea that there is an attractive interaction be-

Table 2 Energies (Hartree) of the two conformers of the cationic complexes and the neutral complexes.

Structure	E (0°)	E (180°)	ΔE /(kcal/mol)
Cr(+2)	-846.118031	-846.106468	7.26
Mo(+2)	-827.399316	-827.386223	8.22
W(+2)	-826.296010	-826.282958	8.19
E			
Cr(0)	-846.826851		
Mo(0)	-828.097973		
W(0)	-826.997593		

tween C2-H1 and the metal. Indeed, the calculated values of ΔE indicate that there is a stabilizing interaction between the sigma bond of C2-H1 and the metal and that the strongest interaction exists in the molybdenum structure. However, the three values of ΔE are close to each other and, qualitatively, they appear equivalent.

3.3. The Second-order Perturbation (SOP) Analysis

An SOP analysis (Tables 3 and 4) provides a more detailed description of the intramolecular interactions. Careful inspection of the intramolecular interactions of the first conformers (the dihedral angle H1-C2-C1-M = zero degree) indicates that there are two important donations (bonding to antibonding) from the carbene (Table 3). The first is between the electron pair of the C2-H1 sigma bond (σ) and the antibonding orbital of M-C6 bond (σ^*). The energy values indicate that the strongest interaction is in the molybdenum structure as predicted by the relative stability of the conformers (Table 2). Unexpectedly, the second intramolecular interaction that has equivalent contribution exists between the same antibonding orbital and the electron pair of the C2-C1 sigma bond (σ). The first and the second

Table 3 Selected charge delocalization energies, the absolute differences ($|\Delta E = E(0^\circ) - E(180^\circ)|$), and their summation (ΔE_t) for the two conformers (H1-C2-C1-M = 0° and 180°) of the cationic complexes. All the values are in kcal/mol.

Structure	Conformer (0°)	Energy	Conformer (180°)	Energy	$ \Delta E $	ΔE_t
Cr(+2)	C2-H1 \rightarrow Cr-C6	14.72	C2-H3 \rightarrow Cr-C6	5.47	3.71	4.43
			C2-H2 \rightarrow Cr-C6	5.54		
Mo(+2)	C1-C2 \rightarrow Cr-C6	16.54	C1-C2 \rightarrow Cr-C6	15.82	0.72	6.31
	C2-H1 \rightarrow Mo-C6	16.45	C2-H3 \rightarrow Mo-C6	5.29		
			C2-H2 \rightarrow Mo-C6	5.26		
W(+2)	C1-C2 \rightarrow Mo-C6	16.06	C1-C2 \rightarrow Mo-C6	16.47	0.41	6.66
	C2-H1 \rightarrow W-C6	10.44	C2-H3 \rightarrow W-C6	2.04		
			C2-H2 \rightarrow W-C6	2.04		
	C1-C2 \rightarrow W-C6	11.99	C1-C2 \rightarrow W-C6	12.29		

Table 4 Selected charge delocalization energies (kcal/mol) of the neutral complexes.

Substrate	Interaction	Energy
Cr(0)	C2-C1 → Cr-C6	6.46
	C2-H1 → Cr-C6	0.21
	C2-H3 → Cr-C6	0.21
Mo(0)	C2-C1 → Mo-C6	5.43
	C2-H1 → Mo-C6	0.11
	C2-H3 → Mo-C6	0.31
W(0)	C2-C1 → W-C6	1.29
	C2-H1 → W-C6	0.00
	C2-H3 → W-C6	0.08

intramolecular interactions explain very well the observed geometric changes (Fig. 1). This analysis may allow describing the carbene as a tridentate ligand, one strong donation from C1 and two weak interactions from C2-C1 and C2-H1. In the second conformer (Fig. 2; the dihedral angle H1-C2-C1-M = 180 degree) the two sigma bonds C2-H2 and C2-H3 are in a position facing the metal, which allowed donation to the antibonding orbital of M-C6 (but smaller than that from C2-H1 in the first conformer). Donation from C1-C2 did not change significantly in the second conformer with only a small change in the energy value.

In order to confirm the nature of the above interactions, an NBO analysis was performed on the neutral structures and these data are presented in Table 4. The energy values indicate that these structures do not include any donation from C2-H (1, 2, 3) to any metal-related empty orbital. While in case of the C2-C1 bond, there is still some donation to the metal but of less significant value.

It is noticed that the energy difference, calculated based on the conformational stability (ΔE : Table 2) and the absolute energy difference of C2-H1→M-C6 versus C2-H3→M-C6 and C2-H2→M-C6 ($|\Delta E|$: Table 3) are different. The difference is larger in the first case, which is attributed to steric hindrance that is not predicted by the SOP analysis. The strain appears in the second conformer and exists between the two hydrogen atoms H2 and H3 and the carbonyl groups.

3.4. The NPA Atomic Charges

The atomic and group charges of the cationic and the neutral structures are presented in Table 5. Based on the SOP analysis (Table 5), both conformers of the three cationic structures include C2-H donation to the metal. However, the energy values (Table 3) indicated that the interaction between M-C6 (σ^*) with C2-H1 (σ) is stronger than C2-H2 (σ) and C2-H3 (σ) together (observe the $|\Delta E|$ values). This implies that the charge donated from the methyl group of C2 in the first conformer is more than that donated in the second conformer. These values are presented in the entries 1 and 2 of Table 5. The amount of the donated charge by C2-H1 in the three cationic structures can be calculated based on ΔCH_3 (C2, entry 2, Table 5) and $|\Delta E|$ (C2, Table 3). In case of chromium, if ΔCH_3 (0.033) corresponds to $|\Delta E| = 3.71$ kcal/mol then the energy value 14.72 kcal/mol (C2-H1→Cr-C6) would correspond to 0.131 of donated charge. Similarly, in the other two cationic structures the donated (C2-H1→M-C6) charges would be 0.112 (Mo), and 0.064 (W). The donated charge decreases with an increase in the distance of H1-M (Table 1, entry 1), which is consistent with general chemical intuition.

Entry 3 (Table 5) indicates that the net charge on the carbene carbon (C1) remains the same in the two conformers. All the values indicate that C1 is an electron-deficient centre. The charge of the methoxy group (entries 4) is also a positive value. This is attributed to the donation from O2 to the carbene carbon. The values of ΔOCH_3 (entry 5) indicate that there is an increase in the donation from the methoxy group to the carbene carbon after changing the dihedral angle to 180°. This is expected and compensates for the charge that was donated from C2-H1 when the dihedral angle was equal to 0°.

The highest compensation is seen in the tungsten structure (entry 5: 0.027). This is normal and consistent with the total energy lost as a result of the conformation process as can be seen from the values of ΔEt (the sum of the $|\Delta E|$ values) in Table 3.

The negative charge of the metal decreased as a result of the conformation process (entries 6), which is more evidence of the charge delocalization from C2-H1 to the metal. On the other hand, the total charge on the $M(CO)_5$ moiety is positive but less than (+2). This indicates that part of the positive charge is

Table 5 Selected NPA charges for the two conformers (H1-C2-C1-M = 0° and 180°) of the cationic structures and also for the neutral complexes.

Entry	Atom	Cationic structures					
		Cr(0°)	Cr(180°)	Mo(0°)	Mo(180°)	W(0°)	W(180°)
1	CH3	0.183	0.150	0.194	0.154	0.192	0.153
2	ΔCH_3	0.033		0.040		0.039	
3	C1	0.558	0.555	0.539	0.540	0.484	0.484
4	OCH3	0.091	0.099	0.085	0.094	0.082	0.109
5	ΔOCH_3	0.008		0.009		0.027	
6	M	-0.600	-0.554	-0.548	-0.495	-0.357	-0.306
7	ΔM	0.046		0.053		0.051	
8	$M(CO)_5$	1.166	1.193	1.179	1.213	1.242	1.273
9	$\Delta M(CO)_5$	0.027		0.034		0.031	
10	MeCOMe	0.832	0.804	0.818	0.788	0.758	0.746
11	$\Delta MeCOMe$	0.028		0.030		0.012	
12	Total	1.998	1.997	1.997	2.001	2.000	2.019
		Neutral structures					
		[Cr]		[Mo]		[W]	
13	$M(CO)_5$	-0.316		-0.290		-0.250	
14	MeCOMe	0.316		0.290		0.248	
14	Total	0.000		0.000		0.002	

carried by the carbene skeleton, which is clear from the data presented in entry 10. The positive charge of the $M(CO)_5$ moiety increases (entry 9) and that of the MeCOMe moiety decreases as a result of the conformation process. This is consistent with the previous SOP data of the intramolecular interactions. Entries 12 and 14 of Table 5 present the values of the summed rounded charges. The values indicate that rounding the numbers creates some error but in all cases it may be neglected in such a qualitative treatment.

3.5. Infrared Stretching Vibrations

Table 6 presents selected infrared stretching vibrations for the different complexes. Only those for C1-C2 and C1-O1 bonds are presented because the cationic and the neutral structures have different vibrational modes for the rest of the structure. The small differences will not be analyzed to avoid over-discussing the data. Also, no correction was made to these data because they are analyzed qualitatively.

The values of the stretching frequencies of C1-C2 bond in the cationic structures are lower than those for the neutral structures. This is normal, when this bond donates electron density to an empty orbital located on the metal the bond order and consequently the force constant will decrease. On the other hand, the values of the C1-O1 bond increase in the cationic structure as a result of the enhanced donation from O1 to C1. The trend in these values is consistent with the observed bond length (Table 1, entry 9). The C1-O1 bond is the shortest and therefore the strongest in Cr (+2) while it is the longest and the weakest in the tungsten complex.

As in the case of C1-C2 and for the same reason, C2-H1 is weaker than C2-H2 and C2-H3 and stretches at separate frequency, which is considered more qualitative support for the notion that there is charge delocalization from C2-H1 toward the metal. On the other hand, the C3-H (4, 5, 6) bonds have one symmetric stretching among them which indicates that C3-H4 does not interact with the carbonyl groups. This conclusion is consistent with the bond lengths of C3-H (H4, 5, 6) (Table 1, entries 13, 14, 15), which are nearly equivalent. As could be seen, the calculated infrared stretching frequency of a C-H that is involved in an agostic interaction is weaker than that of a typical C-H bond. The observed changes are consistent with previous literature results.^{1,2,17,18}

3.6. Selected 1H and ^{13}C NMR Chemical Shifts

Table 7 presents selected chemical shifts for the two conformers of the three structures. The values in brackets belong to the neutral structures. The most intriguing values are those for H1 and C2. They are highly shielded with respect to the same atoms in the neutral structures. Qualitatively, this indicates that the

Table 6 Selected stretching vibrations (cm^{-1}) for the cationic structures. The abbreviations (sym.) and (asym.) refer to symmetric and asymmetric stretchings, respectively. The values in brackets are the stretching vibrations of the neutral complexes.

Vibration	Cr (+2)	Mo (+2)	W (+2)
C1-C2	957 (1050)	958 (1051)	952 (1055)
C1-O1	1634 (1315)	1632 (1319)	1626 (1315)
C2-H1	2998	2924	2922
C2-H2/3 sym.	3074	3068	3067
C2-H2/3 asym.	3124	3130	3130
C3-H4,5,6 sym	3107	3107	3106
C3-H5/6 asym.	3225	3224	3223
C3-H(4/5 and 6) asym.	3228	3228	3226

overlap between the sigma bonds of C2-H1 and C2-C1 with the antibonding orbital of M-C6 is efficient.

In each metal case, switching from the first to the second conformer causes significant increase in the chemical shift of H1. Consistent with this change, the chemical shifts of the hydrogen atoms H2 and H3 decrease as they become in an interaction position with the metal. However, chemical shifts of the two atoms in the second conformer (0.90 ppm) is higher than that of H1 in the first conformer which indicates that the interaction between H2 and H3 and the metal in the second conformer is weaker than that in the case of H1 in the first conformer. This conclusion is consistent with that reached by the SOP analysis.

Careful examination of the SOP results, confirms that there is no interaction between C3-H4 and the $M(CO)_5$ moiety which indicates that the observed difference between the chemical shifts of H4 versus H5 and H6 is only due to a through-space shielding. It is observed that the chemical shifts of H5 and H6 of the cationic structures are larger than those of the neutral structures, which may be explained as follows. The oxygen atom O1 donates more electron density to C1 in the cationic with respect to the neutral structures. This decreases the electron density on O1 which is compensated by dragging electron density from the sigma bond of O1-C3 making the methyl group of C3 more deshielded. This analysis connects directly to the chemical shifts of C3 which are higher in the cationic structures.

A large difference is observed in the chemical shifts of C1 between the cationic (relatively shielded) and the neutral states and it is thought that two factors participate in this effect. Firstly, shielding of C1 is caused by the lone pair of O1 as it moves closer to C1 in the cationic structures. Secondly, as the carbene carbon C1 moves closer to the metal and to the M-CO bonds in the cationic structures which also cause a shielding. The same trend is observed for C2. As in case of the H1, the interaction with the metal is the main reason for the observed significant shielding. As could be seen, the calculated NMR chemical shifts of carbon

Table 7 Selected 1H - and ^{13}C -NMR chemical shifts (ppm) for the two conformers (H1-C2-C1-M = 0° and 180°) of the cationic structures. The values in brackets are the chemical shifts of the neutral complexes.

Atom	Cr(0°)	Cr(180°)	Mo(0°)	Mo(180°)	W(0°)	W(180°)
H1	-0.70 (3.74)	3.59	0.71 (3.44)	3.89	1.17 (3.32)	3.98
H2	1.36 (2.14)	0.90	1.49 (2.06)	1.49	1.52 (2.07)	1.58
H3	1.36 (2.89)	0.90	1.49 (2.62)	1.49	1.52 (2.51)	1.58
H4	4.58 (4.69)	4.28	4.76 (4.59)	4.55	4.72 (4.52)	4.48
H5	6.31 (4.82)	6.27	6.15 (4.39)	6.15	6.09 (4.40)	6.03
H6	6.31 (4.82)	6.27	6.15 (4.39)	6.15	6.09 (4.35)	6.03
C1	274 (352)	275	267 (338)	268	264 (326)	266
C2	-34 (49)	-37	-28 (47)	-29	-27 (46)	-28
C3	79 (63)	79	78 (64)	79	78 (63)	78

and hydrogen involved in the agostic interaction are shifted upfield with respect to typical values which is consistent with the literature data.^{19–25}

4. Conclusion

In general, the computational procedure B3LYP/6-31G-SDD produced homogeneous sets of data for the conformation process, the geometries, the SOP analysis, the NPA charges, the infrared vibrations, and the NMR chemical shifts of electron-deficient group (IV) complexes. Analysis of the data revealed that the cationic structures include two unique cases of agostic interaction. The antibonding orbital of M-C6 can interact with the sigma bonds C2-H1 and C2-C1. This allows classifying the carbene ligand in this case as a tridentate ligand (η^3), with one strong donation and two weak interactions. To the best of our knowledge, this is the first theoretical evidence for this type of interaction.

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