## COMMUNICATION

# On the incidence of non-covalent intramolecular interligand interactions on the conformation of carbene complexes: a case study†

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**The prevalence of a counterintuitive carbene conformation in a series of piano-stool Mn(ɪ) alkylalkoxycarbene complexes was rationalized by means of DFT calculations and high-resolution XRD analysis in terms of stabilizing non-covalent C–H⋯C≡O interligand interactions.**

Seminal MO calculations by Hoffmann *et al.*[1] have predicted that carbene ligands in piano-stool complexes of the type Cp-$(CO)_2M = C(R^1)R^2$ should adopt the so-called vertical coordination mode (**A** or **B**, Fig. 1), rather than the horizontal one (**C**, Fig. 1),[2] so as to maximize the overlap between the frontier orbitals of the metal fragment and of the carbene ligand. This situation is actually found in the solid-state structure of all Mn(ɪ) piano-stool *alkoxycarbene* complexes reported so far[3–5] except one.[6] Early theoretical (SCF)[7] and structural "normal resolution" XRD[3b] studies of the $Cp(CO)_2Mn≡C(OR)Ph$ (R = Me or Et) complexes have, however, revealed some discrepancies between the predicted and observed rotamers.
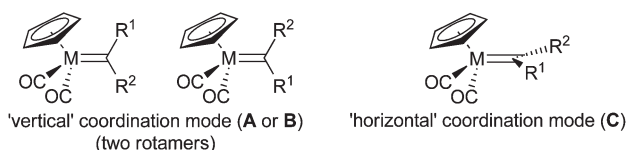


**Fig. 1** Vertical *vs.* horizontal coordination mode of carbene ligand in piano-stool complexes $Cp(CO)_2M = C(R^1)R^2$.

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In this context and in line with our previous investigations on the recurrent incidence of non-covalent interligand interactions on the conformation of carbene ligands in their complexes,[8] we were prompted to reinvestigate the structure of Mn(ɪ) alkylalkoxycarbene complexes by means of DFT calculations and high-resolution XRD analysis.

Initial DFT calculations using the dispersion-corrected M06L functional (M06L/def2-TZVPP level)† on the model complex $Cp(CO)_2Mn=C(OMe)Me$ revealed five possible minima on the potential energy surface: **1-A**$_{anti}$, **1-A**$_{syn}$, and **1-B**$_{syn}$ where the carbene ligand adopts a vertical coordination mode, **1-C**$_{anti}$ where it sits in a horizontal coordination mode, and one minimum, we shall call eclipsed, **1-D**$_{anti}$, very close in energy to **1-C**$_{anti}$, in which the carbene moiety plane and one CO ligand appear to be coplanar (Fig. 2). Gratifyingly, the most stable conformer was found to be a vertical one, in agreement with the above-mentioned seminal studies,[1] and appeared to be the one in which the methoxy group is proximal to the carbonyl ligands and points toward them in an *anti* conformation, **1-A**$_{anti}$.[9] Such an orientation might be considered as counterintuitive for steric reasons as it brings two hydrogen atoms of the methoxy substituent in the vicinity of the carbonyl ligands, *i.e.* the computed H1$_{OMe}$⋯C1$_{CO}$ and H2$_{OMe}$⋯C2$_{CO}$ distances being relatively short (2.423 Å and 2.542 Å, respectively), far below the sum of the VdW radii of the corresponding atoms (2.9 Å). Yet, our calculations suggest that this conformation is the result of attractive interactions. Indeed, application of the second-order perturbation theory (SOPT) of the Natural Bond Orbital (NBO)† method revealed the occurrence of stabilizing two-electron delocalizations from both σ-(C–H$_{OMe}$) molecular orbitals (MO) of the methoxy group into the π*-(C≡O) MO of the closest carbonyl ligand, coupled with a reverse donation from the π-(C≡O) to the vacant σ*-(C–H$_{OMe}$) (Fig. 3). The computed associated SOPT energies (ΔE$^{(2)}$ of −0.95, −0.82, and −0.68 kcal mol$^{-1}$ for the σ(C–H1) → π*-(C1≡O), σ(C–H2) → π*-(C2≡O), and π-(C1≡O) → σ*(C–H1) delocalizations, respectively)[10] indicate that these interactions are weak yet significant and in part responsible for the *anti* conformational preference.

**1-A**$_{anti}$
{cnt-Mn=C-O(Me)} = -173.5°
{Mn=C-O-Me} = 5.2°
$E_{rel}$ = 0.0

**1-A**$_{syn}$
{cnt-Mn=C-O(Me)} = -178.7°
{Mn=C-O-Me} = -179.8°
$E_{rel}$ = 2.7

**1-B**$_{syn}$
{cnt-Mn=C-O(Me)} = 0.0°
{Mn=C-O-Me} = 180.0°
$E_{rel}$ = 1.1

**1-C**$_{anti}$
{cnt-Mn=C-O(Me)} = -92.1°
{Mn=C-O-Me} = -4.4°
$E_{rel}$ = 2.3

**1-D**$_{anti}$
{cnt-Mn=C-O(Me)} = 60.1°
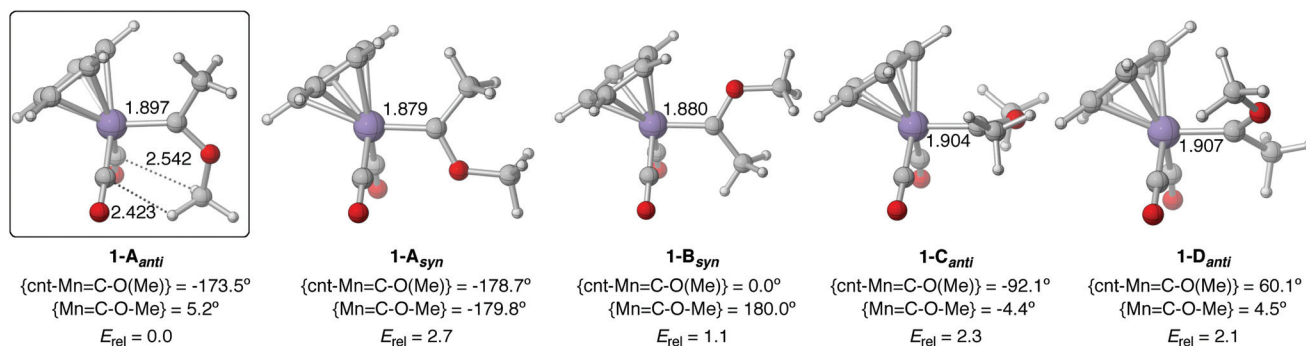{Mn=C-O-Me} = 4.5°
$E_{rel}$ = 2.1

**Fig. 2** M06L/def2-TZVPP optimized geometries for the possible conformers of complex **1** (bond lengths in Å and relative energies ($E_{rel}$) in kcal mol$^{-1}$).
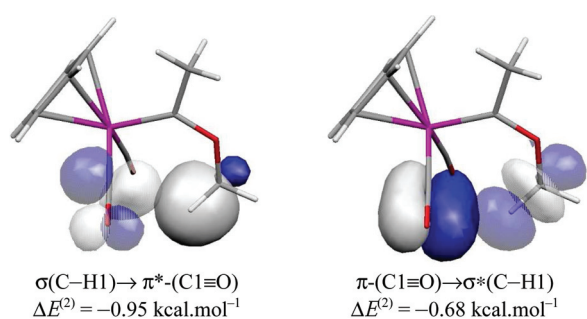


$\sigma(C-H1) \rightarrow \pi^*-(C1\equiv O)$
$\Delta E^{(2)} = -0.95$ kcal.mol$^{-1}$

$\pi-(C1\equiv O) \rightarrow \sigma^*(C-H1)$
$\Delta E^{(2)} = -0.68$ kcal.mol$^{-1}$

**Fig. 3** NBO-molecular orbitals responsible for the C–H···C≡O stabilization stabilizing interactions in conformer **1-A**$_{anti}$.



**Fig. 4** Perspective view (left; 50% probability level) and experimental molecular graph (right; blue lines are bp's, red sphere are bcp's, yellow cubes are rcp's, and purple diamonds are ccp's) for complex **2**.

Remarkably, a literature search revealed that nine[3] over a total of eleven[3,5,6] piano-stool Mn(I) alkoxycarbene complexes possessing methyl or methylene hydrogen atoms disposed to develop a similar interaction exhibit an **A**$_{anti}$ conformation, whereas those lacking such hydrogen atoms invariably display a **B**$_{syn}$ conformation.[4] This suggests that the possibility of building C–H···C≡O interligand interactions may play a key role regarding the conformation of the former complexes in the solid-state.

Being aware by experience that the archetypal Mn(I) alkoxycarbene complex MeCp(CO)$_2$Mn=C(OEt)Me (**2**), displaying an **A**$_{anti}$ conformation, could be obtained as high quality single crystals, and considering that the DFT calculations did predict in **2** the occurrence of similar stabilizing C–H···CO interligand interactions,[11] we seized the opportunity to visualize them experimentally by examining the topology of the electron density (ED) distribution $\rho(r)$ established by high-resolution XRD in the framework of Bader's "Atoms In Molecules" (AIM) theory.[12]

An accurate high-resolution XRD data set was thus collected on **2** at 100 K up to sin $\theta/\lambda < 1.1$ Å$^{-1}$ (MoK$_\alpha$).[†,‡] The experimental ED distribution $\rho(r)$ was derived from the XRD data using the MoPro multipolar refinement suite,[13] whereas its subsequent topological analysis was achieved using VMoPro[13] and WinXPro.[14] For the sake of comparison, the topological analysis of the theoretical ED based on the DFT gas-phase optimized geometry of **2** was also carried out using AIMAll.[15]
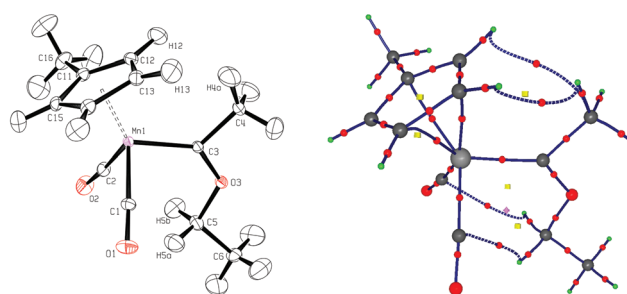
**Table 1** Values of the experimental and theoretical[a] (italic) orthodox parameters[b] at the intramolecular interligand bond critical points

| Contact | d | $\rho(r)$ | $\nabla^2\rho(r)$ | G | V | $E_{int}$ |
|---|---|---|---|---|---|---|
| H5a···C1 | 2.41 | 0.08 | 0.97 | 0.06 | −0.05 | 2.1 |
| | *2.422* | *0.08* | *0.95* | *0.06* | *−0.05* | *2.2* |
| H5b···C2 | 2.53 | 0.09 | 1.07 | 0.07 | −0.05 | 2.5 |
| | *2.515* | *0.08* | *0.99* | *0.06* | *−0.05* | *2.2* |

[a] ED computation (M06L/def2-TZVPP) based on the gas-phase optimized geometry (M06L/def2-TZVPP). [b] $d$ (Å), $\rho(r)$ (e Å$^{-3}$), $\nabla^2\rho(r)$ (e Å$^{-5}$), G (hartree Å$^{-3}$), V (hartree Å$^{-3}$), and $E_{int}$ (kcal mol$^{-1}$) are the interatomic distance, the ED, the Laplacian of the ED, kinetic, potential, electron energy densities, and interaction energy, respectively.

The carbene ligand in **2** effectively exhibits the expected **A**$_{anti}$ conformation ({cnt–Mn1–C3–O3} = 172.4°; Mn1–C3–O3–C5 = −3.4°), which, as in the model complex **1**, brings the methylene hydrogen atoms of the ethoxy substituent in the vicinity of the carbonyl ligands (Fig. 4 (left)). Noticeably, the multipolar refinement leads to short and dissymmetrical H5a···C1 and H5b···C2 distances, which are well reproduced in the gas-phase DFT optimized structure (Table 1), thus suggesting that crystal packing has little influence, if any, on the position of the CH$_2$ group relative to the CO ligands.

The molecular graph resulting from the topological analysis of the experimental ED in **2** (Fig. 4 (right)) reveals that all intraligand and metal-to-ligand bond critical points (bcp's) and

bond paths (bp's) that can be anticipated on the basis of chemical intuition are present,[†] except for the ($\eta^5$-MeCp)Mn unit, which displays a [3, 3, 1 + 1] topology – using Farrugia's terminology[16] – instead of the expected [5, 5, 1 + 1] one.[17] Remarkably, the molecular graph also reveals two pairs of extra *intramolecular interligand bcp*'s located approximately at mid distance between H5a and C1, and H5b and C2, and between H4a, and H12 and H13. The topological analysis shows that these bcp's are associated with H5a⋯C1, H5b⋯C2, H4a⋯H13, and C4⋯H12 bp's. This brings experimental support to the occurrence of stabilizing interactions between the corresponding atom pairs or triad, and in particular, between the methylene hydrogen atoms and the proximal carbonyl carbon atoms, in agreement with the results of the DFT/NBO approach. The orthodox parameters associated with the interligand bcp's are gathered in Table 1. The relatively low values of $\rho(r)$, and positive values of the Laplacian $\nabla^2\rho(r)$ and the electron energy density $H(\rho)$ at the bcp's, denote weak interactions of the closed-shell type.[18] Their interaction energies, $E_{int}$, were thus estimated using the Espinosa, Molins and Lecomte correlation scheme based on the semi-quantitative relationship between $E_{int}$ and the value of the potential energy density $V(\rho)$ at the bcp's.[19,20] The $E_{int}$ was found to be 2.1 kcal·mol$^{-1}$ and 2.5 kcal·mol$^{-1}$, for the CH$_2$/CO interactions, respectively (Table 1), and roughly half of those values, 1.2 kcal·mol$^{-1}$ and 1.1 kcal·mol$^{-1}$, for MeCp/Me ones.[†] The topological analysis of the experimental ED also revealed several intermolecular bcp's associated with H⋯O, and H⋯H bcp's whose associated interaction energies range from 0.2 to 1.0 kcal·mol$^{-1}$.[†] Naturally, these intermolecular interactions not only participate in the cohesion of the crystal, but they also necessarily act to some extent on the conformation of the molecules constitutive of the crystal cell, in a delicate balance with the intramolecular interactions. Yet, among all the weak interactions detected, the intramolecular ones between the methylene group and the carbonyl ligands clearly remain the strongest ones, which reinforces the idea that they do play a determining structuring role.

Farrugia *et al.* have recently demonstrated that bcp's and bp's associated with very weak interaction may actually be the result of artefacts inherent to the Hansen–Coppens multipole model,[21] which is used to determine the experimental ED distribution. In this respect, it is worth noting that the theoretical molecular graph for **2** globally matches the experimental one[†] (in spite of two notable differences[22]) providing evidence for the existence of two bcp's between H5a and C1, and H5b and C2, respectively, while the topological parameters at these points are in excellent agreement with the experimental ones (Table 1).

In conclusion, the case study presented here supports growing evidence that, beyond the observation of molecular structures obtained from normal resolution XRD, a conjunction of matching high-resolution XRD (experimental) analyses and DFT (theoretical) calculations is very helpful to rationalize the occurrence of weak interactions,[23] including intramolecular interligand interactions,[8] having possible effects on the conformation of organometallic complexes bearing flexible ligands like carbenes.

## Acknowledgements

## Notes and references

‡Crystal data for **2**: C$_{12}$H$_{15}$MnO$_3$, $M$ = 262.175; monoclinic, $P2_1/c$, $a$ = 11.1515(1) Å, $b$ = 7.8616(1) Å, $c$ = 14.1583(2) Å, $\beta$ = 109.389(7)°, $V$ = 1170.84(6) Å$^3$, $T$ = 100(1) K, $Z$ = 4, $F_{000}$ = 544; $D_c$ = 1.486 g cm$^{-3}$; $\mu$ = 1.114 mm$^{-1}$. 168 793 Bragg reflections were used up to sin $\theta/\lambda$ = 1.1 Å$^{-1}$. Final multipolar refinement of 488 parameters against 11 120 observed reflections ($I > 3\sigma(I)$) converged to $R$ = 0.0130 and $R_w$ = 0.0176, GOF = 1.13. CCDC 907309.

1 B. E. R. Schilling, R. Hoffmann and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.

2 K. G. Caulton, *Coord. Chem. Rev.*, 1981, **38**, 1.

3 (*a*) S. Fontana, U. Schubert and E. O. Fischer, *J. Organomet. Chem.*, 1978, **146**, 39; (*b*) U. Schubert, *Organometallics*, 1982, **1**, 1085; (*c*) C. S. Yi, G. L. Geoffroy, C. A. White and R. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 3806; (*d*) Y. Yong, C. Jiabi, W. Xiaoying, W. Qiangjin and L. Qiutan, *J. Organomet. Chem.*, 1996, **516**, 81; (*e*) C. Mongin, N. Lugan and R. Mathieu, *Organometallics*, 1997, **16**, 3873; (*f*) R. Streubel, M. Hobbold, J. Jeske and P. G. Jones, *J. Organomet. Chem.*, 2000, **595**, 12; (*g*) A. Rabier, N. Lugan and R. Mathieu, *J. Organomet. Chem.*, 2001, **617–618**, 681.

4 (*a*) C. Mongin, K. Gruet, N. Lugan and R. Mathieu, *Tetrahedron Lett.*, 2000, **41**, 7341; (*b*) E. O. Fischer, J. Chen and U. Schubert, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1982, **37**, 1284; (*c*) D. A. Valyaev, M. G. Peterleitner, L. I. Leont'eva, L. N. Novikova, O. V. Semeikin, V. N. Khrustalev, M. Yu. Antipin, N. A. Ustynyuk, B. W. Skelton and A. H. White, *Organometallics*, 2003, **22**, 5491.

5 H. Fischer, K. Weissenbach, C. Karl and A. Geyer, *Eur. J. Inorg. Chem.*, 1998, 339.

6 For the only exception of a horizontal conformation mode see: M. Landman, W. Barnard, P. H. Van Rooyen and D. C. Liles, *J. Mol. Struct.*, 2012, **1021**, 76.

7 N. M. Kostić and R. F. Fenske, *J. Am. Chem. Soc.*, 1982, **104**, 3879.

8 (*a*) D. A. Valyaev, R. Brousses, N. Lugan, I. Fernández and M. A. Sierra, *Chem.–Eur. J.*, 2011, **17**, 6602; (*b*) I. Fernández, N. Lugan and G. Lavigne, *Organometallics*, 2012, **31**, 1155.

9  (a) I. Fernández, F. P. Cossío, A. Arrieta, B. Lecea, M. J. Mancheño and M. A. Sierra, *Organometallics*, 2004, **23**, 1065; (b) D. M. Andrada, M. E. Zoloff Michoff, I. Fernández, A. M. Granados and M. A. Sierra, *Organometallics*, 2007, **26**, 5854.

10  The corresponding $\pi$-(C2≡O) → $\sigma^*$(C–H2) delocalization was not evidenced by the SOPT of the NBO method ($\Delta E^{(2)} < -0.5$ kcal mol$^{-1}$).

11  Computed associated SOPT energies $\Delta E^{(2)}$ of $-0.95$, $-0.87$, and $-0.71$ kcal mol$^{-1}$ for the $\sigma$(C–H5a) → $\pi^*$(C1≡O), $\sigma$(C–H5b) → $\pi^*$(C2≡O), and $\pi$(C1≡O) → $\sigma^*$(C–H5a) delocalizations.

12  R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990.

13  C. Jelsch, B. Guillot, A. Lagoutte and C. Lecomte, *J. Appl. Crystallogr.*, 2004, **38**, 38.

14  A. Stash and V. J. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371.

15  T. A. Keith, AIMAll, aim.tkgristmill.com, 2012.

16  L. Farrugia, C. Evans, D. Lentz and M. Roemert, *J. Am. Chem. Soc.*, 2009, **131**, 1251.

17  (a) The topology of $\pi$-carbocyclic/transition metal complexes arrangement has been studied in detail and is out of the focus of the present communication. See ref. 16 and references therein, and ref. 17b;   (b) A. O. Borissova, M. Y. Antipin and K. A. Lyssenko, *J. Phys. Chem. A*, 2009, **113**, 10845.

18  U. Koch and P. L. A. Popelier, *J. Phys. Chem.*, 1995, **99**, 9747.

19  (a) E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170; (b) E. Espinosa, I. Alkorta, I. Rozas, J. Elguero and E. Molins, *Chem. Phys. Lett.*, 2001, **336**, 457.

20  (a) $E_{int} = -313.754$ V, where $E_{int}$ is the interaction energy (in kcal mol$^{-1}$); (b) Yu. V. Nelyubina, M. Yu Antipin and K. A. Lyssenko, *Russ. Chem. Rev.*, 2010, **79**, 167.

21  L. J. Farrugia and H. M. Senn, *J. Phys. Chem. A*, 2012, **116**, 738.

22  First, the ($\eta^5$-MeCp)Mn unit here shows the expected [5, 5, 1 + 1] topology and second, no bcp's could be evidenced in the median Me/MeCp region, probably in correlation with the slightly different orientation of the methyl group in the gas-phase-optimized molecule (Table 1).

23  (a) P. M. Dominiak, E. Espinosa and J. G. Ángyán, Intermolecular interaction energies from experimental charge density studies, in *Modern Charge-Density Analysis*, ed. C. Gatti and P. Macchi, 2012, Springer, London, pp. 387–433; (b) For a recent perspective review see: K. A. Lyssenko, *Mendeleev Commun.*, 2012, **22**, 1 and references therein.