Response to "Comment on 'Topological Analysis of the Electron Density in the Carbonyl Complexes M(CO)$_8$ (M = Ca, Sr, Ba)'"

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ABSTRACT: The Comment by Holzmann et al. does not properly reflect the conclusions of the original article, as shown in the current response. New calculations on the title compounds, as well as on M(CO)$_2$ (M = Ca, Sr, Ba) complexes with both $D_{\infty h}$ and C_{2v} symmetry, included in the current response and based not only on the Quantum Theory of Atoms in Molecules but also on the Natural Bond Orbital approach, strengthen the arguments of the original article.

In a recent publication,[1] the bonding in alkaline-earth carbonyl complexes Ca(CO)$_8$ (**1**), Sr(CO)$_8$ (**2**), and Ba(CO)$_8$ (**3**) in their ground states (T, O_h), which had been previously synthesized and analyzed,[2,3] was theoretically studied using both the Quantum Theory of Atoms in Molecules (QTAIM) and the Electron Localization Function (ELF) approaches, among others, through the calculation of several tools related to bond order, bond strength, and covalent/electrostatic character of bonds. In a Comment to that publication,[4] Holzmann et al. claim to have refuted one of its main conclusions (i.e., the absence of any significant π back-donation) by focusing themselves on just one of the many properties calculated: namely, the delocalization indexes for nonbonding M···O interactions (M = Ca, Sr, Ba) calculated using the QTAIM methodology. However, in the author's opinion, this is far from being proved, as stated below.

First, not only topological descriptors based on real-space partitioning methods are used in ref 1 to study the bonding in **1**−**3**, as Holzmann et al. claim. Bond orders (Table 4 of ref 1) are calculated directly from MOs (without any topological partition of the electron density) and, as explained in the Results and Discussion section of ref 1, when only π MOs are used the M−C bond orders are negligible in these complexes: "*This behavior is observed in other functions too, like in LBO-π and WBO-π, giving values of 0.001 and 0.058, respectively, for the Ba−C π bond order (compare with 0.120 and 0.626 in Table 4 for the global bond order), with equivalent results for the other two complexes.*"[1] It is highly unlikely that for any kind of bonding interaction (except for a pure electrostatic interaction), even for the highly polar M−C covalent bonds present in **1**−**3**, no trace of any significant π bond order for the M−C bond is present if π back-donation existed.

Second, also in the Results and Discussion section of ref 1, ELF and ELF-π functions are analyzed, which are not based on the QTAIM approach used for the calculation of delocalization indexes but on a completely different partition of the molecular space (namely, on the conditional same-spin pair density), leading to the same conclusion: "*In addition, when only π molecular orbitals are taken into account to calculate ELF (a procedure which is commonly known as ELF-π), a featureless picture is obtained in the metal-ligand bonding regions of **1**−**3** (see Figure S5 in the Supporting Information).*"[1] Here again, it is highly unlikely that for any kind of bonding interaction (except for a pure electrostatic interaction), even for the highly polar M−C covalent bonds present in **1**−**3**, no trace of any significant ELF-π is present in the M−C bonding region if π back-donation existed.

Third, even within the QTAIM approach many of the properties calculated are not based on the electron density alone, as Holzmann et al. claim.[4] On the contrary, most of them are obtained from the molecular wave function itself, since they need the first- or second-order reduced density matrices, such as, for instance, the delocalization indexes. This is the reason behind the fact that these indexes, among other properties, cannot be obtained from the *experimental* electron density, when they are available from X-ray data.

Fourth, in a comparison of theoretical data, in order to obtain reliable results, it is essential to use equivalent model chemistries, and this is not the case with the data reported in Table 1 of ref 4. The criticism in ref 4 is mainly based on their reported data for the complexes Ca(CO)$_2$ (**1′**), Sr(CO)$_2$ (**2′**), and Ba(CO)$_2$ (**3′**) in $D_{\infty h}$ symmetry, which are calculated using "the same M−CO distance as in M(CO)$_8$".[4] By performing a frequency calculation with that geometry, at the M06-D3/def2-TZVPP level used in ref 4 for their calculations, the number of imaginary frequencies found are respectively 4, 5, and 4 for the triplet states, which are the ground states (see below), with similar results for the singlet states. When the M06-2X-D3/def2-TZVPP level (used in refs 1 and 2) is utilized instead, the situation is not much better, as the number of imaginary frequencies found are respectively 2, 2, and 5, again for the triplet states, with similarly inconsistent results for the singlet states. Although it is true that Holzmann et al. used optimized geometries in order to calculate *frequencies*, they still

used the nonoptimized frozen geometries to calculate the *delocalization indexes*, thus leading to unreliable results. A proper geometry optimization (at both the M06-D3/def2-TZVPP and B3P86-D3/QZVP levels, see Table S1 in the Supporting Information) led to minima (no imaginary frequencies) in the three compounds **1′−3′** in their triplet states with $D_{\infty h}$ symmetry. When these results are followed by an electronic structure calculation using all-electron basis sets equivalent to those used in ref 1 (M06-D3/6-311++G-(3df,3pd),DKH3-QZP), the results included in Table 1 are

Table 1. Delocalization Indexes for M−C Bonding and M⋯O Nonbonding Interactions, and CO Stretching Frequency Shifts[a] **(Relative to Free CO), $\nu(CO) - \nu_0(CO)$ (in cm^{-1}) for Complexes 1′−3′ ($D_{\infty h}$) and 1″−3″ (C_{2v})**

complex	$\delta(M{-}C)$	$\delta(M{\cdots}O)$	$\Delta\nu$
$Ca(CO)_2$ ($D_{\infty h}$)	0.555	0.101	−225
$Sr(CO)_2$ ($D_{\infty h}$)	0.572	0.102	−230
$Ba(CO)_2$ ($D_{\infty h}$)	0.650	0.121	−220
$Ca(CO)_2$ (C_{2v})	0.519	0.101	−176
$Sr(CO)_2$ (C_{2v})	0.520	0.103	−182
$Ba(CO)_2$ (C_{2v})	0.676	0.144	−198

[a]The calculated values refer to the harmonic antisymmetric stretching frequencies, scaled by a correction factor of 0.9567, obtained from the quotient of the calculated value for free CO (2240 cm^{-1}) and its experimental value: $\nu_0(CO)$ = 2143 cm^{-1} (taken from ref 7).

found, which show $\delta(M{\cdots}O)$ values not only between 3 and 4 times higher than those calculated by Holzmann et al. but also between 4 and 5 times higher than those obtained for complexes **1−3** (see Table 3 in ref 1). In addition, $\delta(M{-}C)$ values for **1′−3′** (Table 1) are 3 times higher than those of **1−3** (see Table 2 in ref 1) and follow the correct tendency (increasing from **1′** to **3′**), which is not the case for the data reported by Holzmann et al. Moreover, if the following approximate relationship between the δ^{AB} delocalization index and the exchange-correlation term of the A−B interaction energy is used[5]

$$V_{xc}^{AB} \approx -\frac{\delta^{AB}}{2R}$$

(with R being the interatomic distance in au), then the values in Table 2 are found (compare with Table 7 in ref 1), which

Table 2. Approximate Exchange-Correlation Term Contribution, V_{xc}^{AB} (in kcal mol^{-1}), to the Bonding Interaction Energy for Complexes 1′−3′

interaction	$Ca(CO)_2$	$Sr(CO)_2$	$Ba(CO)_2$
M−C	−39.427	−37.811	−39.550
M⋯O	−4.798	−4.618	−5.178

show a relevant covalent contribution to the M−CO bonding of M⋯O interactions in **1′−3′**. To sum up, in complexes **1′−3′** the $\delta(M{\cdots}O)$ values obtained in the current study are consistent with a non-negligible π back-donation which could account for the calculated red shifts in these compounds, which is not the case for complexes **1−3**. Nevertheless, experimental results could well show a bent geometry with a C_{2v} symmetry instead of the $D_{\infty h}$ symmetry proposed by Holzmann et al., and hence they could have strong $C_{CO}{\cdots}C_{CO}$ interactions just as in complexes **1−3**. As a matter of fact, the

global minimum for the $M(CO)_2$ species (M = Ca, Sr, Ba) found by using both M06-D3/def2-TZVPP and B3P86-D3/QZVP levels of calculation is not given by the above linear complexes **1′−3′** but for the bent compounds **1″−3″** instead (see Figures S1−S3 and Table S1 in the Supporting Information), where bond critical points are found between C atoms, which are clear signs of some kind of noncovalent interaction between CO groups. $\delta(M{-}C)$ and $\delta(M{\cdots}O)$ delocalization indexes for **1″−3″** are included in Table 1, showing values very similar to those obtained for complexes **1′−3′**, but $\delta(C_{CO}{\cdots}C_{CO})$ values obtained for the bent C_{2v} complexes, which are 0.407, 0.392, and 0.352, respectively, show that $C_{CO}{\cdots}C_{CO}$ interactions are likely to be responsible for the red shifts predicted for these compounds, just as for complexes **1−3**.

Finally, in order to rationalize the mechanism of the $C_{CO}{\cdots}C_{CO}$ interactions observed in both complexes **1−3** and **1″−3″**, a Natural Bond Order (NBO) analysis has been performed,[6] leading to the existence of a significant charge transfer between the occupied π orbitals of each CO group and the empty π orbitals of their adjacent CO groups (see Figure 1). While no donation is detected from the metal d_π orbitals to π^* CO orbitals, the $\pi(CO) \to \pi^*(CO)$ charge transfer is estimated to be around 0.2e for each CO ligand.
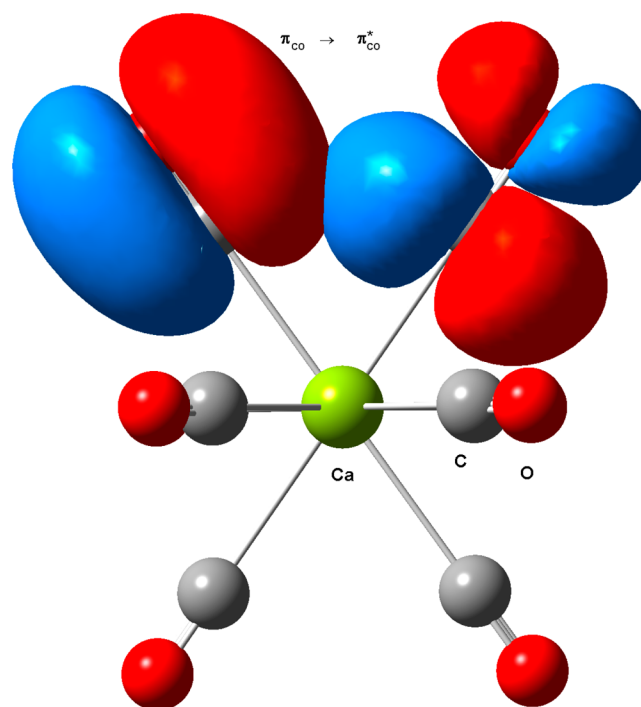

Figure 1. NBO representation of the overlap between a π orbital of a CO group and an empty π orbital of an adjacent CO group in complex **1** (isosurface value 0.022 au).

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■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00523.

Atomic coordinates of optimized structures at the M06-D3/def2-TZVPP and B3P86-D3/QZVP levels of complexes **1′−3′** and **1″−3″** (XYZ)

Representations of the molecular graphs for complexes **1″−3″** (PDF)

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Complete contact information is available at:

https://pubs.acs.org/10.1021/acs.organomet.0c00523

Notes

The author declares no competing financial interest.

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