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Response to Comment on “Observation of alkaline earth complexes $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$) that mimic transition metals”

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Landis *et al.* claim in their comment that Ca does not bind like a transition metal in $\text{Ca}(\text{CO})_8$. We reject their statement, which is based on a misconception of bonding models and misleading application and interpretation of quantum chemical methods for analyzing chemical bonds.

We welcome the comment by Landis *et al.* (1) on our recent report on the observation and bonding analysis of the heavy alkaline earth octacarbonyls $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) (2), because it gives us the opportunity to clarify the interpretation and description of the chemical bonds in the complexes in terms of bonding models, which in our viewpoint are misinterpreted by the authors.

The bonding model of concerted $M \leftarrow L$ σ -donation and $M \rightarrow L$ π -backdonation was introduced by Dewar in 1951 to explain the peculiar structure of Zeise's salt $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ (3). It was generalized by Chatt and Duncanson in a series of papers where they showed that this model is very useful for the description of chemical bonds in transition metal complexes (4). The Dewar-Chatt-Duncanson (DCD) model considers the orbital interactions between a metal fragment and a donor ligand prior to bonding, using the fragments in the respective electronic reference state. The DCD model has become the standard model for transition metal complexes (5).

The synergic σ -donation and π -backdonation interactions for carbonyl complexes $[\text{M}]-\text{CO}$ are shown schematically in Fig. 1. The relative contribution of the $[\text{M}] \leftarrow \text{CO}$ σ -donation and $[\text{M}] \rightarrow \text{CO}$ π -backdonation can vary with the nature of the metal fragment and the charge of the complex. The latter term is usually dominant and responsible for the observed red shift of the carbonyl stretching frequencies with respect to free CO in most carbonyl complexes, whereas CO adducts that feature a blue shift are termed nonclassical carbonyls (6).

The value of the DCD model for describing the bonds in carbonyl complexes has been demonstrated for the series of isoelectronic species $\text{TM}(\text{CO})_6^q$ ($\text{TM}^q = \text{Hf}^{2-}, \text{Ta}^-, \text{W}, \text{Re}^+, \text{Os}^{2+}, \text{Ir}^{3+}$), where the trend of the C-O stretching frequencies and

the nature and strength of the metal-CO interactions could be nicely explained with the help of various methods, including energy decomposition analysis (EDA) (7). Note that in the application of the DCD model, the carbonyl ligand is always considered as a neutral species, which serves as a σ -donor and π -acceptor fragment (5–8). The more electron-rich and electropositive the metal is, the stronger becomes the contribution of the $[\text{M}] \rightarrow \text{CO}$ π -backdonation.

Landis *et al.* challenge the classification of $\text{Ca}(\text{CO})_8$ as a transition metal carbonyl complex, because the actual charge distribution suggests an ionic formulation of $\text{Ca}^{2+}[(\text{CO})_8]^{2-}$ for the bonding situation. In support of their claim, they present EDA-NOCV (natural orbitals for chemical valence) calculations (see their table 1), which show that the orbital interactions ΔE_{orb} between the charged species Ca^{2+} and $[(\text{CO})_8]^{2-}$ are weaker than for the neutral species Ca and $(\text{CO})_8$. This indicates that the former choice of interacting fragments is better suited to describe the actual nature of the metal-CO bonding.

The two sets of EDA-NOCV results presented by Landis *et al.* nicely demonstrate the variability of the EDA-NOCV method, which provides information not only about the final bond but also about the changes during bond formation in $M(\text{CO})_8$. The calculations using neutral M and $(\text{CO})_8$ include the overall charge flow $M \rightarrow (\text{CO})_8$, which conforms to the DCD model using the fragments before bond formation takes place. The results show that the contribution of the $[\text{M}] \rightarrow \text{CO}$ π -backdonation is, as expected, much larger than that of the $[\text{M}] \leftarrow \text{CO}$ σ -donation because of the electropositive nature of the alkaline earth atoms. The calculations using doubly charged fragments instead of neutral atoms are obviously better suited to describe the final bonds for $M = \text{Ca}, \text{Sr}$ but

not for $M = \text{Ba}$. However, Landis *et al.* miss the even better description of the actual bonding situation, which takes place in terms of interactions between singly charged fragments M^+ and $[(\text{CO})_8]^-$. Table 1 shows the results of the EDA-NOCV calculations using the latter fragments, which give even lower ΔE_{orb} values for $M = \text{Ca}, \text{Ba}$ and a similar value for $M = \text{Sr}$ compared with the results using doubly charged fragments. Because the singly charged fragments are radical ions with one unpaired electron each with the same spin, there is now one-electron charge donation from the singly occupied orbitals of the fragments in either direction. The calculations suggest that the π -donation of the singly occupied π^* orbitals of the ligands into the $d(\pi)$ atomic orbital (AO) of the metal, $M \leftarrow (\text{CO})_8$, is much weaker than the donation of the singly occupied $d(\pi)$ AO of the metal into the vacant π^* orbital of CO, $M \rightarrow (\text{CO})_8$. The conclusion is that the large $M \rightarrow L$ π -backdonation, which is due to the electropositive alkaline earth atoms, induces a strong charge shift that eventually leads to very polar donor-acceptor bonds. This can straightforwardly be described with the DCD model, which always takes neutral CO as reference in carbonyl complexes. In a similar fashion, we argue that LiF has a polar electron-sharing bond but not a dative bond, although the best fragments for describing the interactions in the eventually formed bond are Li^+ and F^- , not neutral atoms.

The EDA-NOCV calculations suggest that the ionic fragments M^+ and $[(\text{CO})_8]^-$ are the best choice as reference for the eventually formed complexes $M(\text{CO})_8$. The use of the $^2D (n-1)d^1$ excited state of M^+ is also energetically feasible, because it is the first excited state of M^+ having rather low excitation energies from the $^2S (n)s^1$ ground state (9). But the DCD model is always used with respect to the neutral atom in the electronic reference state, even when the latter is very high in energy. For example, the DCD model for the bonding situation in $\text{Cr}(\text{CO})_6$ (8) uses for Cr the highly excited singlet state with $(n-1)d^6$ electron configuration, which is >101 kcal/mol above the heptet $(n)s^1(n-1)d^5$ ground state (10). It is a fictitious situation that is used for a bonding model, which is not related to the actual energy of the metal electronic state. Landis *et al.* mistake physical reality for a model when they dismiss the $3d^2$ configuration of Ca for the DCD model of $\text{Ca}(\text{CO})_8$. Furthermore, they consider the electronic structure after bond formation in $M(\text{CO})_8$ for the DCD model, which is a misconception of the model.

The discussion of the bonding situation in $M(\text{CO})_8$ by Landis *et al.* does not distinguish between a polar covalent bond and an ionic bond. Ionic bonds exist approximately only in ionic solids, where the overlap of atomic valence orbitals is negligibly small and where the combined Coulomb forces of the ions stabilize the charge-separated species. Polar covalent bonds are due to the interference of the wave functions between atoms, which have different electronegativities. This

usually leads to a larger electrostatic contribution to the bond but not to ionic bonding. Ionic bonds are due to electrostatic attraction, but electrostatic attraction does not necessarily indicate ionic bonding. The physical misinterpretation of polar covalent bonds as partly ionic bonds goes back to the work of Pauling, who explained the quantum theoretical nature of the chemical bond solely using valence bond theory. Valence bond theory has only terms for nonpolar covalent bonds and for ionic terms. The direct identification of the valence bond theory terms with the physical nature of the chemical bond is misleading.

Landis *et al.* mention the wealth of experimental knowledge about calcium chemistry since Liebig's work in 1834, saying that "its chemistry is dominated by the formation of 'saline' compounds with Ca^{2+} ions." But this refers to calcium compounds in the condensed phase and not to isolated molecules in the gas phase or in low-temperature matrices. CaO is an ionic compound only in the solid state with a cubic (Fm-3m) form, where each Ca^{2+} ion is surrounded by six O^{2-} ions. Diatomic CaO has a polar double bond, which dissociates into neutral atoms.

Landis *et al.* present NBO calculations of $\text{Ca}(\text{CO})_8$ that give an occupation of only $0.4e$ in the $3d$ AO of calcium. But the NBO method is inherently biased against the inclusion of d orbitals of main-group atoms in chemical bonds, because it considers only those AOs as genuine valence orbitals, which are occupied in the electronic ground state of the atom, whereas vacant AOs are considered as so-called Rydberg functions (11). Valence AOs and Rydberg AOs are treated differently in the algorithm of the natural bond orbital (NBO) method giving strong preference to the former orbitals. This leads to biased results concerning the relevance of the AOs for chemical bonding, which has been criticized in the past (5). For example, the NBO method treats the $(n)p$ AOs of transition metal atoms as Rydberg functions, which leads to a 12-electron valence space for transition metal compounds. It was suggested that the 18-electron rule should be replaced by a 12-electron rule (12), which was rejected by several authors (5, 7). A recent paper showed that NBO calculations lead to an obviously misleading interpretation of the bonding in a novel type of nickel complexes (13).

Landis *et al.* present calculations of $\text{Ca}(\text{CO})_8$ without d orbital on Ca, which lead to an increase of the Ca-CO distance by "just 0.4 \AA ." We do not agree with the authors that a bond lengthening of 0.4 \AA is a "modest" change in the geometry. On the contrary, we think that the shortening of the interatomic distance by 0.4 \AA caused by the inclusion of d orbitals suggests a significant change in the nature of the bond. Solid CaO has a Ca-O distance of 2.42 \AA , whereas diatomic CaO has a bond length of 1.821 \AA . The former value agrees with an ionic bond, whereas the latter data come from a polar covalent double bond. The shortening of the Ca-CO distance by

0.4 Å caused by the inclusion of the d orbitals reveals the great importance of the latter valence functions, in agreement with the EDA-NOCV results.

Finally, Landis *et al.* present the calculated enthalpies of formation for subsequent CO addition in $\text{Ca}(\text{CO})_n$ for the singlet and triplet states of $\text{Ca}(\text{CO})_n$. This is interesting information, but it is totally irrelevant for the question about the nature of the chemical bonds in the octacarbonyl complex $\text{Ca}(\text{CO})_8$.

The assignment of the atoms to different groups in the periodic system of the elements is made according to the atomic valence orbitals that are used in covalent bonds. Main-group atoms belong to the s/p block, transition metals to the s/p/d block, and lanthanides and actinides to the s/p/d/f block. The relevance of the individual AOs is in some cases not undisputed. But there is general agreement that the most important orbitals of the transition metals are the $(n-1)d$ orbitals, which serve only as polarization functions for main-group atoms even in so-called hypervalent molecules (14). The EDA-NOCV analysis of the metal-CO interactions in $\text{M}(\text{CO})_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) shows that the covalent (orbital) interactions are always dominated by the contribution of the d orbitals of the metal atoms, irrespective of the choice of the fragments. The use of the neutral fragments following the DCD model suggests that the polar covalent metal-CO bonds in $\text{M}(\text{CO})_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) are mainly due to the valence d orbitals. Calcium, strontium, and barium bind like transition metals in the octacarbonyls. Further evidence for this is provided by the recent observation of further earth alkaline compounds $\text{M}(\text{N}_2)_8$ (15), which mimic transition metals.

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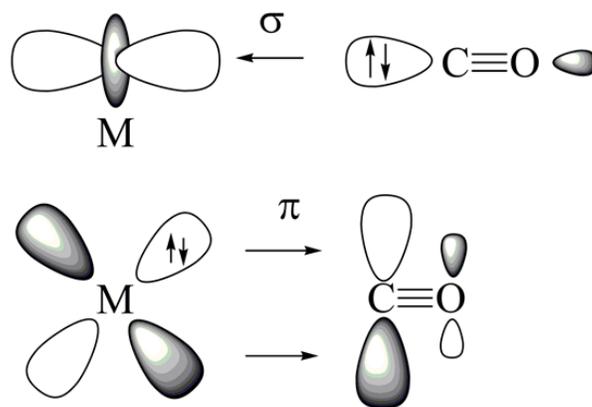


Fig. 1. Schematic representation of the Dewar-Chatt-Duncanson bonding model for transition metal–carbonyl complexes.

Table 1. EDA-NOCV results at the M06-2X/TZ2P level for $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) using M^+ [doublet, $(n)s^0(n-1)d^1$] and $[(\text{CO})_8]^-$ (doublet) as interacting fragments. Energy values are given in kcal/mol.

Energy terms	Orbital interaction	$\text{Ca}^+ + [(\text{CO})_8]^-$	$\text{Sr}^+ + [(\text{CO})_8]^-$	$\text{Ba}^+ + [(\text{CO})_8]^-$
ΔE_{int}		-262.3	-251.8	-223.2
$\Delta E_{\text{hybrid}}^*$		25.6	27.5	17.5
ΔE_{Paul}		46.0	51.2	49.1
$\Delta E_{\text{elstat}}^\dagger$		-172.8 (51.8%)	-170.7 (51.7%)	-169.3 (58.4%)
$\Delta E_{\text{orb}}^\dagger$		-161.1 (48.2%)	-159.7 (48.3%)	-120.5 (41.6%)
$\Delta E_{\text{orb}(1)}^\ddagger (e_g)$	$[\text{M}(d)]^+ \rightarrow [(\text{CO})_8]^- \pi\text{-backdonation}\S$	-75.3 (46.7%)	-80.5 (50.4%)	-46.3 (38.4%)
$\Delta E_{\text{orb}(2)}^\ddagger (e_g)$	$[\text{M}(d)]^+ \leftarrow [(\text{CO})_8]^- \pi\text{-donation}\S$	-10.6 (6.6%)	-10.1 (6.3%)	-12.0 (10.0%)
$\Delta E_{\text{orb}(3)}^\ddagger (t_{2g})$	$[\text{M}(d)]^+ \leftarrow [(\text{CO})_8]^- \sigma\text{-donation}$	-34.5 (21.4%)	-32.0 (20.0%)	-28.6 (23.7%)
$\Delta E_{\text{orb}(4)}^\ddagger (a_{1g})$	$[\text{M}(s)]^+ \leftarrow [(\text{CO})_8]^- \sigma\text{-donation}$	-5.7 (3.5%)	-5.2 (3.3%)	-4.2 (3.5%)
$\Delta E_{\text{orb}(5)}^\ddagger (t_{1u})$	$[\text{M}(p)]^+ \leftarrow [(\text{CO})_8]^- \sigma\text{-donation}$	-9.6 (6.0%)	-7.5 (4.7%)	-6.1 (5.1%)
$\Delta E_{\text{orb}(6)}^\ddagger (a_{2u})$	$(\text{CO})_8$ polarization	-2.6 (1.6%)	-2.8 (1.8%)	-3.6 (3.0%)
$\Delta E_{\text{orb}(\text{rest})}^\ddagger$		-22.8 (14.2%)	-21.6 (13.5%)	-19.7 (16.3%)

*Contribution of the metahybrid term in M06-2X. †The values within the parentheses show the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. ‡The values within the parentheses show the contribution to the total orbital interaction ΔE_{orb} . §One-electron donation.

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