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Alkylindium(I) vs Carbon Monoxide Bridges in Binuclear Iron Carbonyl Complexes: A Theoretical Study

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Summary: Polynuclear iron carbonyl complexes have been prepared only recently, in which bridging carbonyl ligands were replaced by isolobal monoalkylindium groups. A theoretical analysis of the compounds $(CO)_3Fe-(\mu-CO)_{3-x}(\mu-InCH_3)_xFe(CO)_3$ ($x = 0, 1, 2, 3$) shows the specific influence of a stepwise substitution of CO by RIn(I) fragments on their electronic, structural, and bonding properties. This influence is determined by the order of the σ donor $[RIn(I) \gg CO(bridge)]$ and π acceptor $[RIn(I) < CO(bridge) \ll CO(terminal)]$ capabilities of these ligands.

Introduction

A few ligands such as isonitriles, nitrogen monoxide, or methylenes form bi- and multinuclear transition metal carbonyl analogues by acting as bridges between two metal atoms.¹ Recently, a similar behavior has been observed also for organo-fragments of group III elements in the monovalent oxidation state. For example it has been shown that groups such as RAl(I) ($R = Cp^*$ or alkyl),² RGa(I) ($R = Cp^*$, alkyl, or $C(SiMe_3)_3$),³ and, in particular, RIn(I) ($R = C(SiMe_3)_3$)⁴ are able to lie across two metal atoms with or without a direct M–M bond. Similarly to CO, the ligands in question have a σ lone pair and two acceptor p_π orbitals, only one of which is effectively used in bridge bonding. Dialkyl fragments of group IV elements, with only one acceptor p_π orbital,

have corresponding donor–acceptor properties. Binuclear iron carbonyls with bridging methylenes (CH_2^5 and CF_2^6) as well as $SiMe_2$ and $GeMe_2$ groups⁷ have been prepared. Interestingly, while an increasing number of methylene substituents causes a decrease of the Fe–Fe distance,^{5,6} a pronounced elongation is experimentally observed on adding more RIn(I) fragments.⁴

In agreement with the high electropositivity of indium, simple qualitative MO considerations suggest that the axial lone pair of $InC(SiMe_3)_3$ is diffuse and high lying in energy (stronger σ donor than CO). Also, the degenerate set of indium-centered p_π orbitals lies definitely higher in energy than the CO π^* levels (weaker π acceptor than CO). With the differences pointed out, the concept of *isolobal analogy* can be still applied to CO and RIn(I) ligands as it has been proposed in the description of the mononuclear compound $Ni[InC(SiMe_3)_3]_4^8$ and its gallium analogue.⁹ These perfectly tetrahedral complexes, which seem to descend directly from $Ni(CO)_4$, have been investigated with quantum-chemical methods. According to the latter, there is a noninsignificant π back-donation from nickel into the p_π orbitals of Ga or In.⁹ A similar donor–acceptor behavior was pointed out by Fischer, Frenking, et al. for the strictly related fragment $Cp^*Al(I)$ when involved in the formation of mononuclear iron carbonyls.¹⁰

Corresponding theoretical studies have shown that BR ($R = F, NH_2, NMe_2$) ligands in mono- and binuclear complexes have slightly better σ donor and π acceptor capabilities than CO.¹¹

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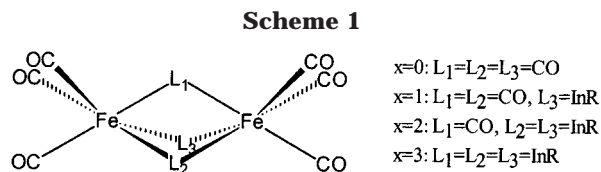


Table 1. Selected Structural Parameters (pm, deg) for $(CO)_3Fe(\mu-CO)_{3-x}(\mu-InCH_3)_xFe(CO)_3$ ($x = 0, 1, 2, 3$)^{a,b}

	$x = 0$	$x = 1$	$x = 2$	$x = 3$
Fe–Fe	252.6 (252.3)	263.6	280.6 (275.9)	309.7 (299.2)
Fe–In		256.3	255.2 (258.1)	255.3 (258.2)
Fe–C _{br}	200.8 (201.6)	200.3	200.9 (198.6)	
In–C		213.8	214.0 (217.7)	214.3 (221)
C _{br} –O _{br}	117.0 (117.6)	117.3	117.5 (117.3)	
Fe–C _{term}	181.6 (183.8)	179.3	177.5 (179.3)	175.8 (174)
C _{term} –O _{term}	114.7 (115.6)	115.3	115.7 (114.3)	116.4 (117)
Fe–In–Fe		61.9	66.7 (64.6)	74.7 (70.8)
Fe–C _{br} –Fe	79.0 (77.6)	82.3	88.6 (88.0)	

^a Averaged values for $x = 1$ and $x = 2$. ^b Experimental values (in parentheses) from ref 14 ($x = 0$) and (with $InC(SiMe_3)_3$) from ref 4c ($x = 2$) and ref 4d ($x = 3$).

It has been remarked that the molecular structures of bi- and trinuclear iron carbonyls are determined by a subtle balance between metal–bridge bonding, metal–metal bonding, and intermetallic repulsion.^{12,13} In this paper, we present a quantum-chemical study of the effects associated with the systematic replacement of the CO bridges by RIn(I) groups in the parent $Fe_2(CO)_9$ dimer. The model complexes $(CO)_3Fe(\mu-CO)_{3-x}(\mu-InR)_xFe(CO)_3$ with $x = 0, 1, 2, 3$ are illustrated in Scheme 1. The fragment $InC(SiMe_3)_3$, which was employed in the experimental investigations, was replaced by the $InCH_3$ group in order to reduce the computational effort. We hoped to get a detailed insight into the alteration of the electronic, structural, and bonding properties caused by the stepwise replacement of CO by RIn(I) ligands. Therefore, a triply bridged structure corresponding to that of $Fe_2(CO)_9$ was considered in all cases, although for $x = 1$ an experimental structure was found in which all carbonyl groups were in a terminal position and the Fe–Fe bond was bridged by one RIn(I) group only.^{4c}

Results and Discussion

Selected structural parameters resulting from the optimizations are presented in Table 1. Experimental values obtained from X-ray diffraction are given in brackets, and the agreement appears generally good. Most evident is the systematic increase of both the experimental and the computed Fe–Fe distances on going from $x = 0$ to $x = 3$. Since the metal–bridge distances remain nearly constant, the angles at the bridges open up. Conversely, the bonds between the metal atoms and the terminal carbonyls are strengthened at both the experimental and the computational

levels. Moreover, while the C–O separations in the terminal ligands increase (with the exception of the experimental value in the $x = 2$ system), no significant change occurs in the bridges.

The overall agreement between calculated and experimental structures led us to study the electronic reasons for the structural peculiarities of the compounds. In Table 2, selected values from a natural bond order (NBO) population analysis¹⁵ are reported. By looking at the systematic change of the metal populations, the stronger donor character of RIn(I) vs CO is confirmed. The larger the number of InR bridges, the more electron rich the iron centers. For each individual bridging ligand, InR as well as CO, the total electron population increases; hence the donor ability decreases by the subsequent addition of InR ligands, this being due to the competitive effects between the three bridging ligands.

Also in Table 2, the total populations of the bridges are separated into a σ and a π part (given in brackets). Into the π part, only the contributions of the p_π orbitals perpendicular to the plane spanned by the three bridging ligands are included. In the case of CO, these are C and O atomic orbitals which form the π and π^* molecular orbitals, while for $InCH_3$ it is a single formally empty p_π orbital localized at the indium atom. The contributions of the p_π orbitals lying *in* the plane spanned by the bridging ligands, which are not involved in any σ or π type interactions with metal orbitals, are included into the σ part of the NBO populations. The σ and π contributions of the bridge populations confirm that RIn(I) is indeed a much stronger σ donor and a slightly weaker π acceptor than CO.

The possible symmetry combinations of the three π acceptor orbitals of the bridging ligands (a_2'' and e'' for the D_{3h} , $x = 0$, system or the corresponding representations for the other systems) find their appropriate partners among the filled metal orbitals of the same symmetries. The interaction of a_2'' type, involving z^2 metal orbitals, is weak, as it is in the parent carbonyl system ($x = 0$), but it was considered formally important to track back the origin of the direct metal–metal bond¹³ (see below).

In terms of perturbation theory, the important interactions of the e'' type (Scheme 2), which represent the highest occupied complex MOs, are penalized by the larger energy gap between the indium-centered p_π orbitals and the metal orbitals. Figure 1 compares the resulting energetics of the e'' levels (or their split components in lower symmetry) for the whole series from $x = 0$ to $x = 3$. The levels are significantly destabilized for $x = 3$ compared to $x = 0$. Because of the decreasing back-donation, the corresponding complex MOs are more centered at the iron atoms. Consequently, their implicit d_π – d_π antibonding character causes greater four-electron repulsions. This can be highlighted by comparative MOOP diagrams (molecular orbital overlap population) obtainable at the EHMO level with the

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Table 2. NBO Population Values for $(\text{CO})_3\text{Fe}(\mu\text{-CO})_{3-x}(\mu\text{-InCH}_3)_x\text{Fe}(\text{CO})_3$ ($x = 0, 1, 2, 3$)^{a-c}

	x = 0	x = 1	x = 2	x = 3
Fe	16.577	16.633	16.696	16.773
InCH ₃		11.222 (10.925/0.297)	11.258 (10.969/0.289)	11.321 (11.035/0.286)
CO _{br}	13.985 (11.532/2.453)	14.043 (11.562/2.481)	14.088 (11.603/2.485)	
Σbridges	41.955 (34.596/7.359)	39.308 (34.049/5.259)	36.604 (33.541/3.063)	33.963 (33.105/0.858)
ΔΣbridges	-0.045 (-1.404/1.359)	-0.692 (-1.951/1.259)	-1.397 (-2.460/1.063)	-2.037 (-2.895/0.858)
CO _{term}	13.815	13.880/13.916	14.041/13.981	14.081
ΔCO _{term}	-0.185	-0.120/-0.084	0.041/-0.019	0.081

^a Averaged values for $x = 1$ and $x = 2$. ^b σ and π components (see text) in parentheses. ^c The standard populations of the free fragments are Fe: 16.000, InCH₃: 12.000 (12.000/0.000), CO: 14.000 (12.000/2.000).

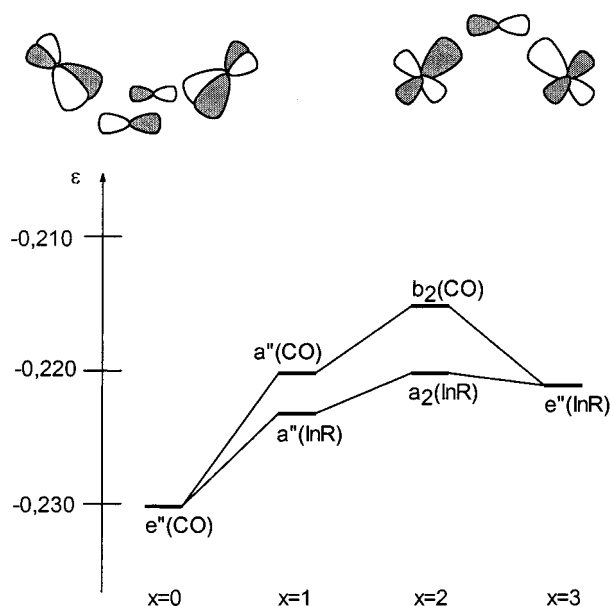
Scheme 2

Figure 1. Energetic position (au) of the two highest occupied molecular orbitals for $(\text{CO})_3\text{Fe}(\mu\text{-CO})_{3-x}(\mu\text{-InCH}_3)_x\text{Fe}(\text{CO})_3$ ($x = 0, 1, 2, 3$).

graphic package CACAO.¹⁶ Given the same Fe–Fe separation of 270 pm, the repulsion appears ca. 30% more effective in the complex with three InR bridges than in the parent $\text{Fe}_2(\text{CO})_9$ system; hence it should be one of the major causes for the stretching of the Fe–Fe distance. We remark that this trend is inverted with three CH_2 (or CF_2) bridges, which are better π acceptors than the CO ligands.

Greater interelectronic repulsion between the metals is also consistent with the strong σ donor character of the RIn(I) bridges and the accumulation of negative charge at the iron atoms.

The strong σ donation from the InR bridges to the metal centers, which is only slightly diminished by a π acceptor effect, has a remarkable influence on the coordination of the terminal ligands. A significant part of the excess electronic density is transferred from the iron centers to the terminal carbonyls. These ligands act as relatively strong π acceptors, as it can be seen from the accepted electronic density (Table 2) and from the terminal bond lengths (Table 1). The calculated and the experimental Fe–CO bond lengths steadily decrease from $x = 0$ to $x = 3$, indicating increasing bond strengths. Correspondingly, the calculated C–O bond lengths increase, indicating decreasing bond strengths,

and the experimental values show, at least for the cases $x = 0$ and $x = 3$, the same trend.

It can be concluded from the present analysis that the complex molecular structure of the systems under study is determined by the σ donor order $\text{RIn(I)} \gg \text{CO}$ (bridge) and the π acceptor order $\text{RIn(I)} < \text{CO}$ (terminal) $\ll \text{CO}$ (terminal).

Concerning the aged question of a direct M–M bond in compounds of this type, the MO picture is formally similar to that of the parent $\text{Fe}_2(\text{CO})_9$ system. It was proposed for the latter¹³ that sufficient back-donation from the filled σ^* combination of z^2 orbitals into the appropriate combination of CO π^* orbitals, transforms eventually a four-electron repulsion between metal lone pairs (z^2 -based) into a bonding attraction. In the extreme situation with three RIn(I) bridges, the long Fe–Fe separation, >300 pm, is practically inconsistent with a sufficient overlap between the contracted iron z^2 orbitals. Hence, the idea of a direct bonding must be dismissed despite its chemically intuitive prediction (34 valence electrons).

Perhaps these systems should not be regarded as simple coordination compounds with bridging and terminal ligands, but actual clusters with the indium and iron metal atoms forming the skeleton of a trigonal-bipyramid. A similar viewpoint has been adopted in the description of triple-decker compounds of the type $\text{L}_3\text{M}(\mu\text{-P}_3)\text{ML}_3$, which also have 34 electrons and where an M–M bond is physically unattainable unless it pierces the equatorial P_3 unit.¹⁷ In the present systems, the absence of equatorial In–In bonds is due to the impossibility of populating the bonding combinations of high lying p_π orbitals orthogonal to the Fe–Fe axis. Still a major cementing force for the bipyramid is the overall delocalized bonding combination of *in-pointing* σ hybrids of both iron and indium atoms. Further attention needs to be devoted to mixed clusters of main and transition metal elements also to restate properly the electron-counting rules¹⁸ in cases where the very different electronegativity of the elements is significant.

Computational Details

Density functional theory (DFT) optimizations applying the B3LYP functionals¹⁹ were performed using the Gaussian98 package.²⁰ Effective core potentials with 10- and 46-electron

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cores in connection with $8s5p5d\{341|311|41\}$ and $3s3p\{21|21\}$ valence basis sets were employed for Fe and In, respectively.²¹ For the other atoms, the standard 6-31G* basis set was used.

The optimizations were carried out keeping certain symmetries for the structures. For $x = 0$, this is clearly the D_{3h} symmetry, but for $x = 1$, $x = 2$, and $x = 3$ we used C_s , C_{2v} , and C_{3h} symmetry, respectively, as a consequence of a certain symmetric orientation of the CH_3 substituents. Frequency calculations for the optimized structures present, for the cases

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$x = 2$ and $x = 3$, some small imaginary frequencies. They are related to certain rotations of the CH_3 groups, but preserve the triply bridged structures. This points to some slight distortions of the chosen symmetries. The imaginary frequency, which results for the case $x = 1$, is somewhat larger (93i). A C_1 optimization leads to a singly bridged structure in agreement with the experiment.^{4c} The triply bridged structure for $x = 1$ could be discussed as a transition state or even a metastable species. In this paper, we have considered only triply bridged structures for the sake of making systematic and direct comparisons within the series from $x = 0$ to $x = 3$.

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