

Aromaticity of Tri- and Tetranuclear Metal–Carbonyl Clusters Based on Magnetic Criteria

Clémence Corminboeuf,* Paul von Ragué Schleyer, and R. Bruce King^[a]

Abstract: Recently, the σ -aromaticity model proposed for cyclopropane by Dewar was employed to account for the stability of Group 8 trinuclear metal–carbonyl compounds $[M_3(CO)_{12}]$ ($M = Fe, Ru, Os$). This paper further examines this hypothesis and provides the first quantitative evidence for the σ -aromatic/antiaromatic nature of the $[M_3(CO)_{12}]/[M_4(CO)_{16}]$ species based

on structural and nucleus-independent chemical-shift analysis. In addition, the extent of electron delocalization in tet-

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rahedral $[M_4(CO)_{14}]$ and butterfly $[M_4(CO)_{15}]$ is analyzed and compared to prototype cycloalkanes. While remarkable analogies exist between metal–carbonyls and cycloalkanes, transition metals provide additional overlap possibilities that affect both the ring strain and the magnetic properties of metal–carbonyl rings and cages.

Introduction

Trinuclear metal–carbonyl clusters have been known since the isolation of $[Fe_3(CO)_{12}]$ (**1**) by Dewar and Jones approximately a century ago (Figure 1).^[1] However, the trinuclear nature of **1** was only realized by Hieber and Becker^[2,3] in 1930 after cryoscopic molecular weight determinations in $[Fe(CO)_5]$. The correct triangular C_{2v} structure of **1** with two bridging CO groups was established definitively by X-ray diffraction only in 1966 after considerable controversy^[4] and difficulties with disorder problems.^[5,6] The ruthenium and osmium analogues $[M_3(CO)_{12}]$ ($M = Ru, Os$), unlike $Fe_3(CO)_{12}$, have structures with exclusively terminal CO groups and have more robust metal–metal bonds in their M_3 triangles.^[7–10]

These triangular metal–carbonyl complexes may be regarded as analogues of cyclopropane in which the three CH_2 groups are replaced by isolobal and isoelectronic $M(CO)_4$ groups ($M = Fe, Ru, Os$). In this connection, the σ -aromaticity model used for cyclopropane and related triangular molecules^[11] was recently applied to these trinuclear metal–car-

bonyl complexes to account for their stability^[12] as well as to saturated inorganic rings.^[13] This model replaces the three two-center two-electron (2c-2e) bonds along the edges of the triangle in the localized bonding model by one 3c-2e radial bond in the center of the triangle with Hückel topology and one 3c-4e peripheral bond with Möbius topology. Note that both the localized $3 \times (2c-2e)$ bond model and the σ -aromatic $(3c-2e) + (4c-2e)$ model use three orbitals and six electrons for the triangle skeletal bonding so that these models are indistinguishable from simple electron and orbital counting.

The saturated tetranuclear metal–carbonyl clusters $[M_4(CO)_{16}]$ ($M = Fe, Ru, Os$), which are similar metal–carbonyl analogues of cyclobutane, are found to be much less stable than their trinuclear relatives.^[14] Thus $[Fe_4(CO)_{16}]$ (**2**) and $[Ru_4(CO)_{16}]$ (**6**) are still unknown (Figure 1). The corresponding osmium derivative $[Os_4(CO)_{16}]$ (**10**) was reported and structurally characterized by Pomeroy et al. in 1987.^[14] However, **10** was found to be relatively unstable and decomposed readily in solution under nitrogen at room temperature to give the much more stable $[Os_3(CO)_{12}]$ (**9**). The X-ray structure of **10** reveals a cyclobutane-like Os_4 core with C_{2v} symmetry and long Os–Os bonds (up to 3.0 Å). In view of the σ -antiaromatic behavior of cyclobutane,^[15] it is reasonable to assume similar destabilization in the metal–carbonyl analogues, such as **10**.

Two other, much more stable, tetranuclear osmium–carbonyl analogues have been synthesized, namely $[Os_4(CO)_{15}]$ (**12**) with a planar Os_4 butterfly-like structure consisting of

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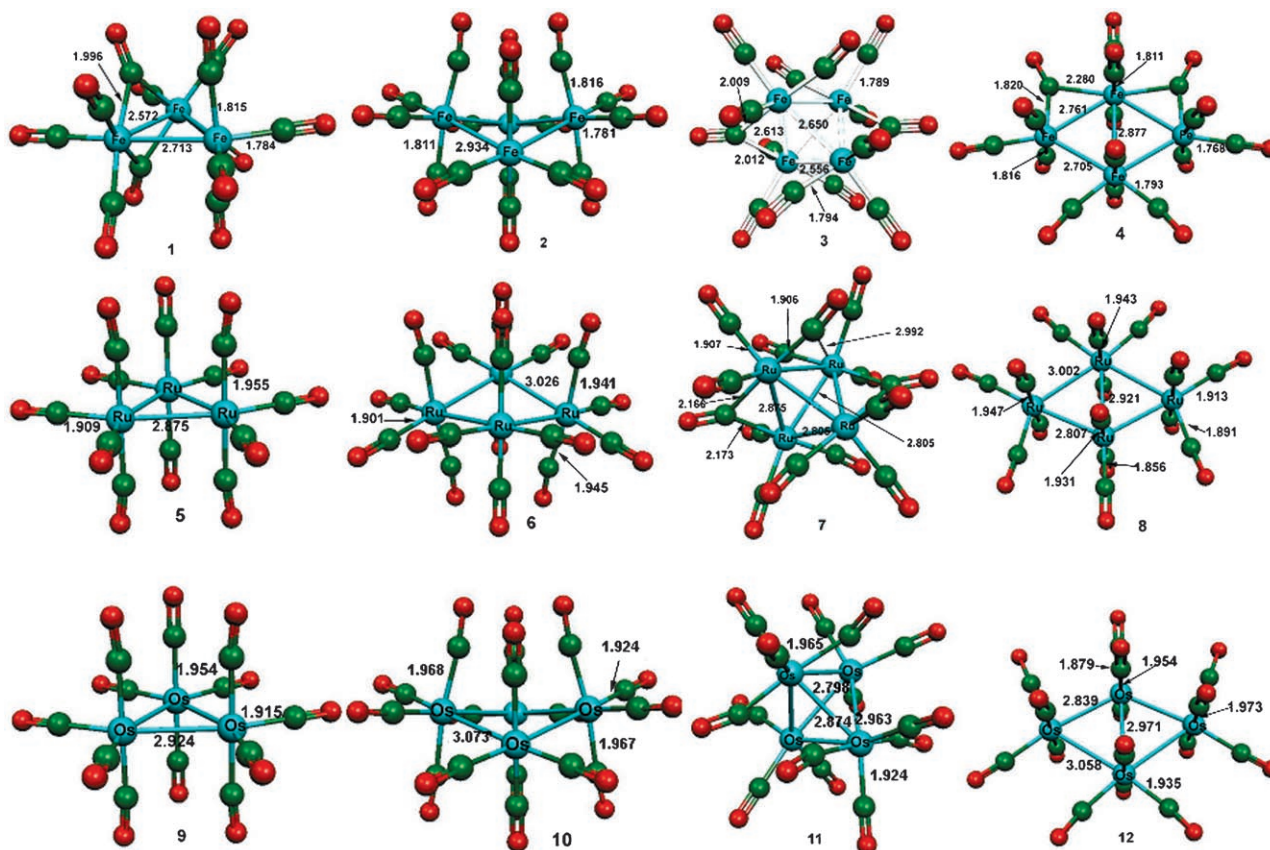


Figure 1. Optimized geometries for compounds 1–12. Illustrative bond lengths are given in Angstroms.

two triangles sharing an edge^[16] and $[\text{Os}_4(\text{CO})_{14}]$ (**11**) with a tetrahedral Os_4 structure^[17] (Figure 1). The latter structure is of particular interest because of its potential spherical σ -delocalization similar to that found in the “super-aromatic” tetrahedrane, which exhibits a large diatropic C–C(σ) effect.^[15]

The present study focuses on the structures and nucleus-independent chemical-shift (NICS) analysis^[18] of Group 8 metal–carbonyl clusters $[\text{M}_n(\text{CO})_m]$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$, $n=3$, $m=12$ and $n=4$, $m=14, 15, 16$) with the aim of obtaining more evidence for their hypothetical σ -(anti)aromatic character thereby accounting for differences in their thermal stabilities. Additional comparisons with prototype cycloalkanes provide striking insights into the aromatic nature of these compounds.

Computational Methods

The geometries of the trinuclear iron–carbonyl clusters $[\text{Fe}_3(\text{CO})_{12}]$ were taken from previous work^[19] on unsaturated $[\text{Fe}_3(\text{CO})_n]$ derivatives performed at the BP86^[20] level using double- ζ plus polarization GTO basis sets. A similar level, BP86 with the double- ζ plus polarization basis sets,^[21] implemented in the Turbomole package,^[22] was employed for optimizing the tetranuclear iron carbonyls ($[\text{Fe}_4(\text{CO})_n]$, $n=14, 15, 16$) using the Gaussian 03 program.^[23] To account for the scalar relativistic effects, the quasirelativistic energy-adjusted small-core pseudopotentials of the Stuttgart group^[24] were employed for the osmium and ruthenium atoms

in the analogous triangular, square and tetrahedral carbonyls $[\text{M}_3(\text{CO})_{12}]$ D_{3h} , $[\text{M}_4(\text{CO})_n]$ ($\text{M}=\text{Ru}, \text{Os}$). Note that the spin-orbit coupling relativistic effects were not considered in this study. The valence electrons were described by the def2-TZVPP valence basis sets^[25] of the Turbomole package,^[22] $(7s6p5d1f)/[5s3p3d1f]$ and $(7s6p5d1f)/[6s3p3d1f]$ for the ruthenium and osmium atoms, respectively, using both the PW91^[26] and BP86^[20] exchange correlation functionals. The PW91 geometries were closer to the experimentally characterized structures^[14,16,17] and thus kept for the computation of magnetic properties. Computations of the vibrational frequencies indicate that the investigated structures are all minima.^[27]

Nucleus-independent chemical shifts^[18] (NICS), NICS(1),^[28] and NICS_{zz}^[29] were computed at the PW91 level by using the GIAO formalism^[30] as implemented in the Gaussian 03 program.^[23] The NICS_{zz}^[29] index, which is more closely related to the current density, reflects the magnetic response of a molecule toward a magnetic field applied perpendicular to the plane (the z direction is used by convention). The NICS indexes were rather insensitive to the theoretical level. However, for consistency the pseudopotential approximation was used for the three transition-metal atoms in conjunction with triple- ζ valence basis sets.^[31] While the use of pseudopotentials does not allow for an accurate description of the chemical shielding at these “pseudoatom” positions, reliable NICS values can be provided.^[32] The NBO 5.0 program^[33] was used for the computation of the individual canonical molecular orbitals contribution to NICS (CMO-NICS).^[34]

Results and Discussion

Triangular $[\text{M}_3(\text{CO})_{12}]$ and quadrilateral $[\text{M}_4(\text{CO})_{16}]$: Our study of the Group 8 trinuclear metal–carbonyl clusters is

limited to only those experimentally characterized. Thus $[\text{Fe}_3(\text{CO})_{12}]$ has a C_{2v} structure with two bridging groups,^[5] in contrast to the D_{3h} symmetry of the ruthenium- and osmium-carbonyl clusters with only terminal CO groups.^[35] The stability of $[\text{M}_3(\text{CO})_{12}]$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) clusters is generally explained in terms of σ -aromaticity,^[12] which has long been invoked in the description of the electronic structure of cyclopropane,^[11,36,37] strong evidence^[11g] exists for this phenomenon.^[15,38–43] The concept was rationalized, for instance, in terms of the ellipticity of the density at its critical points.^[40] Akin to the cyclic circulation of π -electrons, the in-plane delocalization of σ -electrons in cyclopropane is also associated with a large magnetic chemical shielding at the center of the molecular plane resulting in upfield ^1H NMR chemical shifts, a large diamagnetic susceptibility, and a strong diamagnetic ring current.^[15,41–43] Such a typical effect on the magnetic properties of cycloalkanes is indicated by the axial component of the NICS tensor (NICS_{zz}).^[29] The NICS indexes ($\text{NICS}(0)$, $\text{NICS}(1)$, NICS_{zz}) for cyclopropane, $[\text{Fe}_3(\text{CO})_{12}]$ (**1**), $[\text{Ru}_3(\text{CO})_{12}]$ (**5**), and $[\text{Os}_3(\text{CO})_{12}]$ (**9**) are given in Table 1. The $\text{NICS}(0)$ values for both the cycloalkane and the trinuclear metal clusters are all large and negative (≈ -40 ppm). As typical of in-plane aromatic systems,^[44] NICS dies off dramatically when moving above the ring for cyclopropane ($\text{NICS}(1)^{[15]} = -8.7$ ppm) and more slowly for the $[\text{M}_3(\text{CO})_{12}]$ species ($\text{NICS}(1) \approx -20$ ppm).

Significant variations are obtained when considering the more physically relevant NICS_{zz} criterion. Although all values are clearly negative, the NICS_{zz} of $[\text{Fe}_3(\text{CO})_{12}]$ (**1**) is 20 ppm more negative than those of its heavier congeners (**5** and **9**), thereby suggesting a larger in-plane delocalization in the iron compound. The very similar $\text{NICS}(1)_{zz}$ values of all three compounds (**1**, **5** and **9**) reflect the rapid decay of the in-plane σ diamagnetic shielding above the transition-metal rings. Note that this seemingly irregular behavior does not arise from the presence of the bridging carbonyl groups as similar results are

Table 1. GIAO-NICS indexes in ppm for **1–12** and their hydrocarbon analogues at the PW91 level. Def2-TZVPP valence basis sets were used for H, C, O, Fe, Ru, and Os. Negative (positive) NICS values in interior positions of rings or cages indicate the circulation of induced diatropic (paratropic) ring currents.

	NICS(0)	NICS(1)	NICS _{zz} (0)	NICS _{zz} (1)
C_3H_6 D_{3h}	-43.8	-8.7	-31.9	-24.3
C_4H_8 D_{2d}	-0.1	-0.3	+55.1	+4.2
C_4H_4 T_d	-47.5/(-49.7) ^[a]	-	-	-
C_4H_6 C_{2v}	-39.7 ^[b] /(-48.3) ^[a]	-9.9 ^[c]	-31.5 ^[b] /(-36.8) ^[a]	-18.5 ^[c]
C_4H_6 D_{2h}	+10.8/(-3.2) ^[a]	+3.0	+64.0/(+34.4) ^[a]	+13.0
$[\text{Fe}_3(\text{CO})_{12}]$ C_{2v} (1)	-37.1	-18.5	-48.4	-23.6
$[\text{Fe}_3(\text{CO})_{12}]$ D_{3h}	-38.7	-20.9	-47.7	-15.5
$[\text{Ru}_3(\text{CO})_{12}]$ D_{3h} (5)	-36.0	-21.7	-21.4	-15.4
$[\text{Os}_3(\text{CO})_{12}]$ D_{3h} (9)	-36.6	-20.7	-20.4	-17.4
$[\text{Fe}_4(\text{CO})_{16}]$ C_{2v} (2)	-23.5	-17.8	-13.2	-4.6
$[\text{Ru}_4(\text{CO})_{16}]$ C_{2v} (6)	-20.9	-12.9	+0.6	+1.0
$[\text{Os}_4(\text{CO})_{16}]$ C_{2v} (10)	-19.1	-11.8	+5.0	+2.2
$[\text{Fe}_4(\text{CO})_{14}]$ C_2 (3)	-33.9/(-34.8) ^[d]	-	-	-
$[\text{Ru}_4(\text{CO})_{14}]$ C_2 (7)	-22.4/(-25.8) ^[d]	-	-	-
$[\text{Os}_4(\text{CO})_{14}]$ C_2 (11)	-28.9/(-32.3) ^[d]	-	-	-
$[\text{Fe}_4(\text{CO})_{15}]$ C_{2v} (4)	-38.9/(-34.9) ^[a]	-17.5	-63.0	-14.9
$[\text{Ru}_4(\text{CO})_{15}]$ C_{2v} (8)	-39.9/(-31.6) ^[a]	-19.7	-24.4	-6.8
$[\text{Os}_4(\text{CO})_{15}]$ C_{2v} (12)	-42.5/(-32.8) ^[a]	-21.0	-25.0	-12.7

[a] NICS and/or NICS_{zz} values at the center of the triangular face are given in parenthesis. [b] NICS values at the center of mass. [c] NICS and NICS_{zz} values 1 Å above the center of mass. [d] NICS values at the center of the $\text{M}_2\text{M}'$ triangular face are given in parenthesis ($\text{M}=\text{M}(\text{CO})_3$ and $\text{M}'=\text{M}'(\text{CO})_4$). Note that the NICS values at the center of the M_2M triangular face have similar magnitude (within 1 ppm).

obtained for the D_{3h} $[\text{Fe}_3(\text{CO})_{12}]$ structure with only terminal carbonyl groups (see Table 1).

The diatropic enhancement observed in $[\text{Fe}_3(\text{CO})_{12}]$ (**1**) is better understood by considering the contributions of the individual canonical molecular orbitals to NICS (CMO-NICS). This analysis provides crucial and suitable^[45] information regarding the magnetic nature of these systems by focussing solely on orbitals involved in the σ -aromaticity model^[12] (i.e., the three-center two-electron (3c-2e) radial orbital with Hückel topology and the 3c-4e peripheral bond with Möbius topology, see Figure 2a and b). Interestingly, the contribution of these orbitals is paratropic or weakly diatropic at the center of the three-membered rings (3-MRs) (Figure 3). However, the same set of orbitals gives rise to a large shielding zone slightly away from the center of the cyclopropane (Figure 3a) and iron rings (Figure 3b), demonstrating the importance of probing the magnetic shielding at

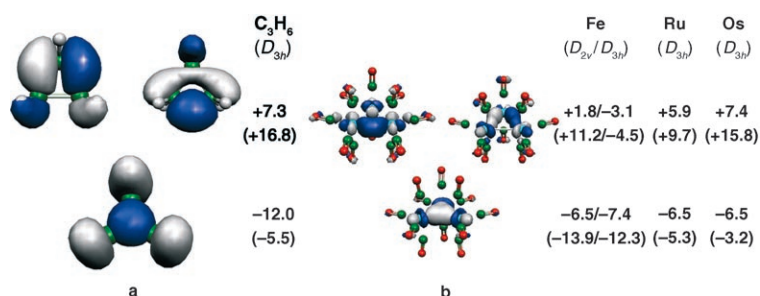


Figure 2. Isotropic NICS (NICS_{zz} given in parenthesis) contributions at the ring center for the three Walsh orbitals (the 3c-2e radial orbital with Hückel topology and the 3c-4e peripheral orbitals with Möbius topology) in a) cyclopropane and b) C_{2v}/D_{3h} $[\text{Fe}_3(\text{CO})_{12}]$, D_{3h} $[\text{Ru}_3(\text{CO})_{12}]$, and D_{3h} $[\text{Os}_3(\text{CO})_{12}]$. Values are in ppm and the NICS contributions are summed for the set of degenerate MOs.

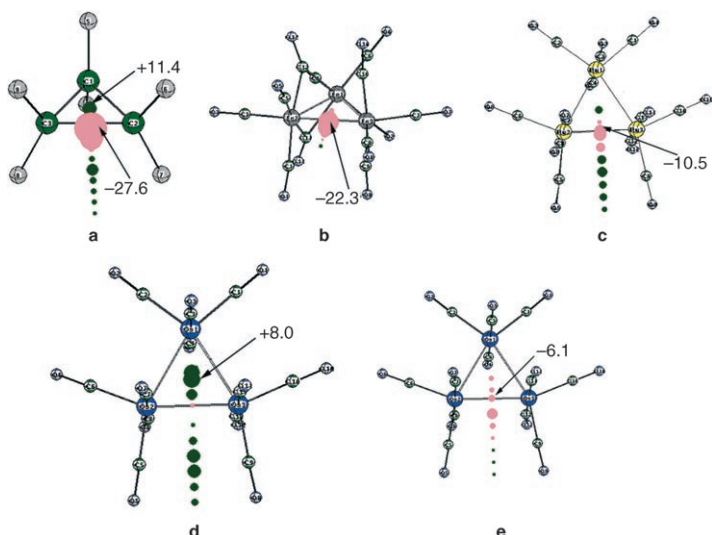


Figure 3. Grid of NICS_{zz} contribution coming from the three Walsh molecular orbitals displayed in Figure 2 for a) D_{3h} cyclopropane, b) C_{2v} $[\text{Fe}_3(\text{CO})_{12}]$, c) D_{3h} $[\text{Ru}_3(\text{CO})_{12}]$, and d) D_{3h} $[\text{Os}_3(\text{CO})_{12}]$. The distinct contribution of the 3c-2e radial orbital with Hückel topology is represented in (e) for D_{3h} $[\text{Os}_3(\text{CO})_{12}]$. Values are in ppm. Light (dark) dots represent negative (positive) NICS_{zz} values and the dot size is in line with the NICS magnitude.

various positions. While the shielding effect is much weaker in D_{3h} $[\text{Ru}_3(\text{CO})_{12}]$ (Figure 3c), the diatropicity of the three-center two-electron radial orbital of D_{3h} $[\text{Os}_3(\text{CO})_{12}]$ is compensated by the paratropic effect of the degenerate set MOs with Möbius topology (Figure 3d,e). In other words, the overall diatropic character of $[\text{Os}_4(\text{CO})_{16}]$ (> -20 ppm) and to some extent that of $[\text{Ru}_3(\text{CO})_{12}]$ cannot be explained solely by the σ contribution of the Walsh orbitals according to NICS.

Geometry optimizations of all three M_4 skeletons in $[\text{M}_4(\text{CO})_{16}]$ ($M = \text{Fe}$ (**2**), Ru (**6**), Os (**10**)) lead to the expected distorted C_{2v} symmetry akin to D_{2d} cyclobutane. The relatively long metal–metal bonds in **2**, **6** and **10** suggest weakness. The structure of $[\text{Fe}_4(\text{CO})_{16}]$ is similar to that of its heavier congeners favoring terminal carbonyl groups in contrast to $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Fe}_4(\text{CO})_m]$ ($m = 15, 14$) (vide infra) (see Figure 1). While $[\text{Fe}_4(\text{CO})_{16}]$ (**2**) and $[\text{Ru}_4(\text{CO})_{16}]$ (**6**) are not known experimentally, the σ -aromaticity model is generally used to explain the much larger thermal stabilities of trinuclear osmium carbonyl clusters $[\text{Os}_3(\text{CO})_{12}]$ (**9**) relative to the tetranuclear species C_{2v} $[\text{Os}_4(\text{CO})_{16}]$ (**10**).^[16]

The chemical shifts of the hydrogen atoms attached to a cyclobutane ring appear at slightly lower field than other typical saturated hydrocarbons in opposition to the archetypal σ -aromatic cyclopropane molecule.^[38,46] Dewar first argued that cyclobutane should be considered as σ -antiaromatic, but predicted a quite small antiaromatic energy.^[11e] The σ -antiaromaticity hypothesis was then followed by others.^[15,43,47] Thus Schleyer et al.^[15] used Walsh orbital contributions to NICS to demonstrate that the carbon framework in cyclobutane is responsible for the paratropic character of the 4-MR cycloalkane, which contrasts sharply with

the diatropicity of cyclopropane (Table 1). Comparisons of NICS between trinuclear and tetranuclear metal–carbonyl clusters reveal similar, but smaller, contrasts in their magnetic behavior (Table 1). The isotropic NICS of the C_{2v} $[\text{M}_4(\text{CO})_{16}]$ ($M = \text{Fe}, \text{Ru}, \text{Os}$) clusters are about one third less negative than those of their trinuclear congeners. Likewise, the NICS_{zz} of $[\text{Fe}_4(\text{CO})_{16}]$ is relatively small (> 15), whereas those of $[\text{Ru}_4(\text{CO})_{16}]$ and $[\text{Os}_4(\text{CO})_{16}]$ are even slightly paratropic (see Table 1). Nevertheless, such arguments are not sufficient for the identification of $[\text{M}_4(\text{CO})_{16}]$ species as σ -antiaromatic. While the paratropic current (e.g., NICS_{zz}) of typical in-plane antiaromatic systems, such as cyclobutane, is generally reduced above the molecular framework (see Table 1), the $\text{NICS}_{zz}(0)$ and $\text{NICS}_{zz}(1)$ values of $[\text{Fe}_4(\text{CO})_{16}]$ (**2**) appears less diatropic rather than less paratropic at 1 Å and nearly no variation is observed for the ruthenium and osmium carbonyl compounds.

Such differences between cyclobutane and transition-metal 4-MRs can be analyzed in detail using CMO-NICS. The highest set of σ -type degenerate occupied molecular orbitals (i.e., Walsh type orbitals, see Figure 4) is dramatically

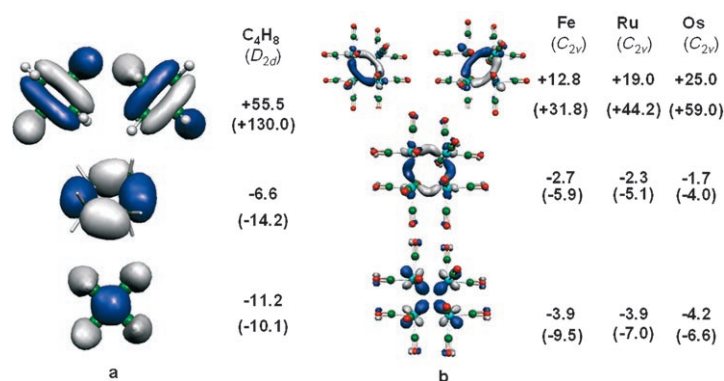
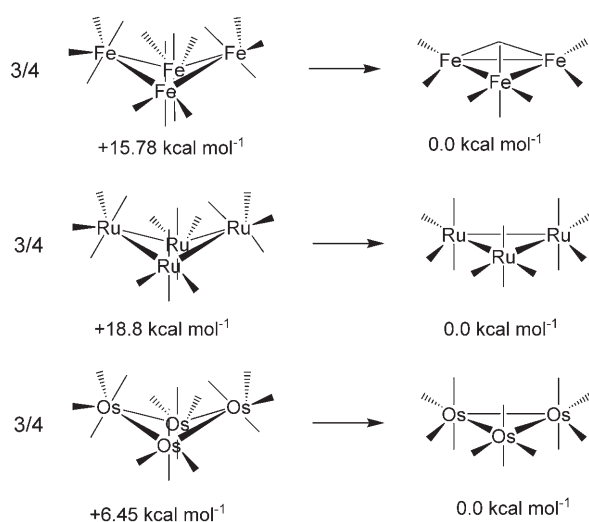


Figure 4. Isotropic NICS (NICS_{zz} are given in parenthesis for the Walsh molecular orbitals of a) the D_{2d} isomer of C_4H_8 and b) C_{2v} $[\text{M}_4(\text{CO})_{16}]$ ($M = \text{Fe}, \text{Ru}, \text{Os}$). Values are in ppm. The NICS contributions are summed for the degenerate set of MOs.

paratropic in D_{2d} cyclobutane ($\text{HOMO-NICS}_{zz} = +130.0$) and appreciably paratropic in the corresponding carbonyl derivatives $[\text{M}_4(\text{CO})_{16}]$ ($\text{HOMO-NICS}_{zz} = +31.8, +44.5$ and $+59.0$ for $M = \text{Fe}$ (**2**), Ru (**6**), and Os (**10**), respectively). Predictably, these paratropic contributions die off away from the ring center. As large paratropic HOMOs are generally indicative of antiaromaticity,^[48] the conclusion can be drawn that the $[\text{M}_4(\text{CO})_{16}]$ species exhibits some paratropic ring currents although less than their cycloalkane counterparts.

Although there is no direct and clearly convincing link between energetic instability and magnetic antiaromaticity, reaction energies (see reference [31] for details) provide further evidence for the destabilization of the paratropic tetranuclear species over diatropic trinuclear compounds (Scheme 1).



Scheme 1.

Tetrahedral $[M_4(CO)_{14}]$: The experimental^[17] and theoretical structures of $[Os_4(CO)_{14}]$ (**11**) both show an irregular tetrahedral framework of metal atoms with a twofold axis, two semibridging carbonyl groups, four different Os–Os bond lengths and thereby two triangular face types. In view of the polarized character of the Os–Os bonds, the cage is best described by two $\{Os(CO)_4\}^+$ and two $\{Os(CO)_3\}^-$ units, with each osmium atom having the favored 18-electron configuration. Our computations indicate that the tetrahedral framework is also conserved for the iron analogue **3**, although two symmetrical carbonyl bridges are formed in addition to the semibridging carbonyls (Figure 1). Unexpectedly, the C_2 ruthenium species **7** also has symmetrical bridging carbonyl groups.

In 1986, Gauss and Cremer^[37] first described tetrahedrane and other cages formed by three-membered ring (3-MR) subunits as σ -aromatic by using the notion of “volume delocalization”. The diatropic nature of 3-MR-containing hydrocarbon and inorganic cages was then investigated in detail by Schleyer et al.^[13,15] Based on a NICS analysis, they identified tetrahedrane as being “super σ -aromatic” and T_d As_4 ^[13] as highly aromatic. Also Hirsch et al.^[49] consider isoelectronic tetrahedral species such as P_4 to exhibit spherical aromaticity. Although the bonding in the tetrahedral framework of $[M_4(CO)_{14}]$ ($M=Fe, Ru, Os$) differs considerably from that of T_d C_4H_4 or P_4 , electron delocalization is anticipated inside as well as on the 3-MR faces of the transition-metal cage. NICS indeed reveals a significant diatropic character (at least -20 ppm) inside the three transition-metal cages, and an even stronger effect at the center of their 3-MR faces (at least -25 ppm). Once again, the presence of bridging carbonyl groups does not significantly influence the extent of electron delocalization inside the cages or at the 3-MR faces. However, even though the $[M_4(CO)_{14}]$ ($M=Fe, Ru, Os$) species are clearly diatropic, the polarized metal–metal bonds seemingly affect the diamagnetic current. Thus no particular diatropic enhancement, that is, no “super-aro-

maticity,^{[15]”} is perceived at the center of the transition-metal cages in contrast to their hydrocarbon analogue.^[15]

The “butterfly” $[M_4(CO)_{15}]$: In 1959 Wiberg and Ciula^[50] successfully synthesized bicyclo[1.1.0]butane (C_4H_6) despite previous predictions that this ring system would have too much strain to be isolable as a stable compound. Subsequently, Haller and Srinivasan^[51] interpreted infrared and Raman data on bicyclo[1.1.0]butane that implied C_{2v} symmetry with essentially equilateral triangular rings sharing a common edge. Several years later, Cox et al.,^[52] provided a complete set of structural parameters from the microwave spectra of the four isotopic species of bicyclo[1.1.0]butane. The two rings in bicyclo[1.1.0]butane were found to not be coplanar but to have a puckered angle of 58° .

Bicyclo[1.1.0]butane is an interesting hydrocarbon exhibiting several unusual properties, such as high acidity for deprotonation as well as a remarkably large dipole moment of 0.7 D.^[53] Perhaps the most intriguing property of the bicyclo[1.1.0]butane skeleton is the negative sign of its carbon–carbon spin coupling $J(C,C)$ between bridgehead carbons.^[54] This reflects the unique nature of the bridgehead–bridgehead carbon–carbon bond indicating almost pure p character.^[55] Because of the low s character of the central carbon–carbon bond, geminal delocalization was suggested to be bonding and thereby responsible for the ring strain relaxation.^[56]

In contrast to the butterfly C_{2v} geometry of bicyclo[1.1.0]butane, the X-ray structure of $[Os_4(CO)_{15}]$ (**12** in Figure 1) reveals an unexpected planar skeleton (“flat butterfly”) with adjacent short (2.775 Å) and long (2.998 Å) metal–metal bonds. This unusual arrangement is rationalized in terms of three-center, two-electron metal–metal bonds, which suggest the presence of electron delocalization^[57] in addition to reduced ring strain. Our computed $[Os_4(CO)_{15}]$ geometry displays the same features as the experimentally determined geometry but with longer bond lengths (Figure 1). The metal frameworks of $[Ru_4(CO)_{15}]$ (**8**) and $[Fe_4(CO)_{15}]$ (**4**) are also computed to be planar. However, the iron compound, as expected, favors a structure with two bridging carbonyl groups rather than all terminal carbonyls.

The diatropicity of these planar C_{2v} $[M_4(CO)_{15}]$ skeletons differs sharply from the paratropicity of bicyclo[1.1.0]butane when constrained to D_{2h} planar geometry (NICS_{zz} = $+64$ ppm, Table 1). The dramatic paratropic character of D_{2h} bicyclo[1.1.0]butane is essentially dominated by the two Walsh orbitals with one nodal plane (CMO-NICS_{zz} = $+50.0$ and $+68.6$ ppm, respectively, see Supporting Information). To a lesser extent, the π system also is paratropic (NICS_{zz} = $+14.3$ ppm). The distortion into C_{2v} symmetry changes the overall character of bicyclo[1.1.0]butane radically from paratropic to diatropic at the center of the equilateral triangular rings (NICS_{zz} = -36.8 , see Table 1) and between the bridgehead carbons (NICS_{zz} = -52.6 ppm, not in Table 1). The diatropic NICS_{zz} values at the ring center and at the equilateral triangular rings of the planar C_{2v} $[M_4(CO)_{15}]$ clusters also suggest a considerable ring current,

which falls off at 1 Å above the transition metal rings. Unexpectedly, the NICS values of the $[M_4(CO)_{15}]$ species are even more diatropic (NICS = −38.9 to 42.5 ppm) than those of their trinuclear and tetrahedral metal–carbonyl congeners $\{[M_3(CO)_{12}]$ and $[M_4(CO)_{14}]$: M = Fe (**1**, **2**), Ru (**5**, **6**), and Os (**9**, **10**)}. Once again, the NICS values of the iron species are considerably more negative (NICS_{zz} = −63 ppm) than those of its heavier congeners.

One may wonder, why do the structural and magnetic properties of these planar C_{2v} $[M_4(CO)_{15}]$ skeletons differ so considerably from those of D_{2h} bicyclo[1.1.0]butane? Transition metals, unlike second row elements, use d as well as s and p orbitals for their chemical bonding, thereby providing additional orbital overlap possibilities. Whereas all of the carbon–carbon bonds in C_4H_6 share two electrons and are clearly single bonds, resonance structures with multiple metal–metal bonding contribute to the framework of the tetranuclear metal–carbonyls $[M_4(CO)_{15}]$.^[57c] Clearly, the hybridization of the ring atoms also affects the structural, electronic and magnetic properties of strained 3- or 4-MRs.^[13] The increased “d character” when substituting second-period atoms by third-period transition-metal elements is most likely responsible for the release of ring strain leading to planar $[M_4(CO)_{15}]$ butterflies.

Conclusion

The present study provides striking insights into the magnetic criteria for aromaticity in the Group 8 metal–carbonyl clusters $[M_n(CO)_m]$ (M = Fe, Ru, Os, $n = 3$, $m = 12$; $n = 4$, $m = 14, 15, 16$). While significant structural differences exist within the Group 8 column of the periodic table, the magnetic properties within this family of clusters show a modest dependence on the transition metal present. Typically, C_{2v} $[Fe_3(CO)_{12}]$ exhibits the same type of diatropic behavior as D_{3h} cyclopropane, arising essentially from one 3c–2e radial Hückel orbital and the 3c–4e peripheral Möbius orbitals. While the former radial orbitals remain diatropic in both D_{3h} $[Ru_3(CO)_{12}]$ (**5**) and $[Os_3(CO)_{12}]$ (**9**), the degenerate set of peripheral MOs contribute positively to the NICS of **9**. The paramagnetic current that characterizes cyclobutane also affects the transition-metal frameworks of C_{2v} $[M_4(CO)_{16}]$, but to a lesser extent. In sharp contrast, the $[M_4(CO)_{14}]$ C_2 cages are clearly diatropic, although they cannot be labeled like tetrahedrane (C_4H_4 , T_d) as “superaromatic”. The analogy with the prototype cycloalkanes reaches its limit when considering the planar butterfly C_{2v} $[M_4(CO)_{15}]$ structures, which are largely diatropic in contrast to the geometrically constrained planar D_{2h} bicyclo[1.1.0]butane.

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