

Foliacenes: Ab Initio Modeling of Metallocomplexes Exhibiting a Unique Form of 16-Electron, Metal-Induced Aromaticity

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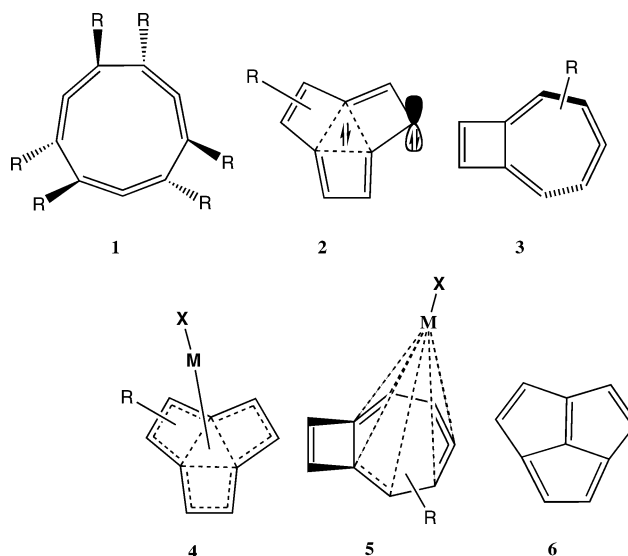
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Abstract: Ab initio calculations predict that the cyclic trefoilenes **2** can be stabilized by formation of a complex **4** with early transition metals. The metal atom within the complex is nested within the carbon ring and is considerably closer to the ring centroid than in traditional metallocene complexes. Stabilization is explained by a unique form of 16-electron delocalization involving the metal atom, for which we suggest the name “foliate aromaticity”. The aromaticity of various polyfoliate systems such as **9** suggests this 16-electron motif is more robust than Clar-like aromatic 6π -sextets. The open hemisphere of the metal in such foliacene complexes is predicted to coordinate a variety of ligands.

Introduction

Many diverse molecules containing some measure of stabilization arising from cyclical or spherical electron delocalization have been identified and described by the collective term “aromatic”.² We have recently reported³ on systems which might exhibit a specific form of aromaticity deriving from the cyclic conjugation of π electrons associated with an odd phase shift in the wave function, and termed “Möbius-aromatic” by Heilbronner.⁴ Molecule **1**, suggested as a possible example of a 12 π Möbius-aromatic,² is particularly intriguing given its isomeric relationship to **2**. The latter was first proposed by Alder, Clark, and Petts⁵ as an exemplar of another unusual, so-called trefoil aromatic mode originally hypothesized by Fukunaga, Simmons, Wendoloski, and Gordon.⁶ Thus, the trefoilene **2** contains 12 electrons deriving from the carbon p-orbitals, which partition into a 10 π Hückel aromatic system (8 deriving from the double bonds in the valence structure shown, and 2 from a p_π carbene), with the 2 remaining electrons held in a more novel three-center, two-electron bond responsible for the in-plane trefoil aromaticity.⁷ MNDO semiempirical calculations⁵ had indicated that unlike **1**, and despite its formally two-fold aromatic character, **2** was not a minimum on the potential surface, distorting instead to the bicyclic isomer **3**. With this demonstration of the instability of the trefoil isomer, theoretical interest in **2** understandably waned, and no further reports of its chemistry appeared.

Our interest was however kindled by noting that aromatic metallocene ligands exhibit a limited diversity of structural



forms, dominated of course by the 6π cyclopentadienyl anion (Cp) and benzene, with a much smaller known chemistry of 10 π ligands derived from the cyclooctatetraenyl (COT) dianion. It struck us that **2** in particular might be capable of donating either 2, 10, or 12 electrons toward a metal in forming a metallocycle or a metallocene complex (or some combination of both). Simple electron counting led us to concentrate on metal complexes of titanium and various titanium carbonyls, which would satisfy the 18-electron valence-shell rule. This choice was encouraged by existence of the known 18-electron species $\text{Cp}_2\text{Ti}(\text{CO})_2$,⁸ and the 17-electron $(\text{COT})\text{TiCp}$,⁹ which we used as reference compounds to test the accuracy of our calculations. We here pose the question: Can formation of a metallocycle

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Table 1. Computed Relative Free Energies (kcal mol⁻¹)^a

ring	2 (R = H) ^b	2 (R = F) ^c	3 (R = H) ^d	3 (R = F) ^d
C ₉ R ₆ ^e	+56.3	+82.5	-21.8	-35.5
C ₉ R ₆ ^f	+55.1	+82.8	-22.5	-34.9
foliacene M,X	4 (R = H) ^d	4 (R = F) ^d	5 (R = H) ^d	5 (R = F) ^d
Ti, ^{-e}	-56.7	-105.3	-73.9	-91.2
Ti,CO ^e	-66.6	-118.3 ^g	-93.3	-110.3
Ti,(CO) ₂ ^e	-64.6	-119.9	-114.5	-131.8
Ti,(CO) ₃ ^e	-59.8	-115.4	-121.1	-132.3
Zr, ^{-f}	-102.7	-155.1	-131.0	-145.7
Zr,CO ^f	-106.8	-162.4	-145.7	-159.0
Zr,(CO) ₂ ^f	-106.0	-165.1	-161.9	-173.7

^a ΔG_{298} values are relative to zero-value, standard states for these components: metal atoms (triplet state), CO, and the ring in conformation **1** (R = H, F). ΔG values for metal carbonyls are as follow: MCO, Ti 68.0, Zr 0.7; M(CO)₂, Ti 15.3, Zr -37.5; M(CO)₃, Ti 21.8. Values may be used analogously to those in standard tables of free energies of formation, e.g., **3** (R = F) + Ti → **5** (M = Ti, R = F, X = 0), $\Delta G = -91.2 - (-35.5 + 0) = -55.7$. ^b Nonminimum conformation (three imaginary frequencies). ^c Nonminimum conformation (five imaginary frequencies) ^d Conformational minimum. ^e KMLYP/6-31G(d) computation. ^f KMLYP/DZVP computation. ^g Results for KMLYP/6-311G(3d,p) and KMLYP/DZVP computations are -120.4 and -117.3 kcal/mol, respectively.

stabilize **2**, and could it then function as a monocyclic equivalent for two Cp ligands?

Methods

Ab initio DTF calculations were performed using Gaussian 03,¹⁰ employing the KMLYP rehybridization¹¹ of the widely used B3LYP method. Previous calculations on 10 π monocyclic systems have established¹² a fine balance between ring strain and aromaticity mediated by electron correlation (aromaticity on the edge of chaos), and we found the KMLYP method to be the more reliable approach to modeling such systems. The 6-31G(d) and DZVP basis sets were used for titanium and zirconium metallocenes, respectively. Such KMLYP/6-31G(d) calculations correctly reproduced the geometry of the reference compounds to within 0.02 Å for bond lengths and 2° for bond angles compared to experimental values. The larger 6-311G(3d,p) and the DZVP basis sets gave results similar to those obtained with 6-31G(d) for titanium compounds. Bond localization employed the GAMESS program and MacMolPlt.¹³ Calculated free energies at 298 K are based on zero-point energy and thermal enthalpies and entropies derived from unscaled vibrational frequencies.

Energies and Geometries

Calculated singlet free energies at 298 K indicate (Table 1) that the most stable stereoisomer of **1** (R = H, F) exists as a nonplanar nine-membered ring with D₃ symmetry, and that with

respect to this, the planar trefoilenes **2** are much higher energy stationary points (having three or more computed negative force constants), while **3** is -22 to -35 kcal mol⁻¹ more stable. When either **1** or **2** is optimized with the addition of MX [M = Ti, Zr; X = (CO)_n (n = 0–3)], the only minima located (no negative force constants) correspond to the metal complexes **4** (triplet states are about 60 kcal mol⁻¹ higher in energy). Minimum free energies are achieved at about X = (CO)_n, n = 1, corresponding to a metal with a filled valence shell. In contrast, the bicyclic system **3** forms stable metal carbonyl complexes **5** with maximum stability when n = 2–3, and which are similar or lower in free energies to **4**.

Free energy values indicate that the titanium bicyclic metallocene complex **5** is the isomer of greater stability compared to **4** for the R = H series, but in fluorinated metallocenes the trefoilene complex **4** is more stable than **5** for X = (CO)_n, n = 0, 1. Thus, our calculations predict that **2** is greatly stabilized by the formation of a transition metallocene. Replacing titanium with zirconium results in metallocenes that follow the same pattern of variation in the relative stabilities of **4/5**.

The ring in the optimized geometry of **4** (R = H, M = Ti, X = CO) has a symmetrical delocalized structure with C–C ring bond lengths of 1.425 and 1.376 Å and a noticeably concave shape that “wraps” the metal. This results in characteristics of both a metallocycle (with the metal occupying the ring centroid) and a metallocene (with the metal above the π cloud). We suggest the name “foliacene” (from the Greek word for nest) to describe this type of metallocene. With Ti–C lengths of 1.894 and 2.339 Å, the metal atom sits 1.067 Å above the ring centroid. In comparison, the crystal structures of (COT)TiCp and Cp₂Ti(CO)₂ show Ti–Cp and Ti–COT centroid distances of 2.029 and 1.441 Å, respectively. The foliate interaction between the metal and the ring leads to a lengthening of the Ti–CO distance to 2.253 Å compared to that in Cp₂Ti(CO)₂ of 2.029 Å. The geometry of the fluorinated foliacene **4** (R = F, M = Ti, X = CO) shows the metal at 1.028 Å above the ring centroid, and a Ti–CO distance of 2.318 Å. The isoelectronic vanadium(I) complex **4** (R = F, M = V⁺, X = CO), for which $\Delta G_f = -176.8$ kcal mol⁻¹, has the same geometry, but with the metal–ring centroid separation of 0.954 Å, and a V–CO distance of 2.220 Å. For both these complexes, greater stability is accompanied by the metal nesting closer to the ring centroid. **4** (R = F, M = Cr, X = O) reveals an even shorter metal–ring centroid distance of 0.87 Å. The calculated normal vibrational modes reflect the delocalized nature of these complexes; we illustrate one mode (Figure 1) that shows the symmetrical trefoilene–metal stretch to occur in the region 360–490 cm⁻¹.

The ligand in the bicyclic complex **5** (R = H, M = Ti, X = CO) is decidedly nonplanar, with the planar four-membered ring canted toward the metal at about an angle of 55° relative to the planar seven-membered ring. The metal atom is approximately located over the center of the seven-membered ring, with a ring centroid–metal distance of 1.425 Å. The Ti–CO distance is 2.118 Å.

Bonding and Aromaticity in Metallocenes 4

The molecular orbital energy diagram (Figure 2) explains the nature of the bonding in the foliacene complexes **4** (R = H, F, M = Ti, X = CO) In the planar trefoilene **2** (R = H), the HOMO/HOMO–1 and HOMO–3/–4 are two pairs of degen-

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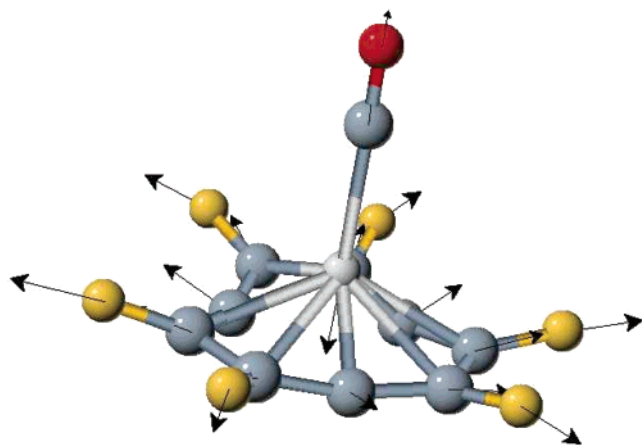


Figure 1. “Trampoline” mode corresponding to the symmetric trefoilene–metal stretch for **4** ($R = F$, $M = V^+$, $X = CO$), $\nu_{\max} = 489 \text{ cm}^{-1}$. Further examples are collected in the Supporting Information.

erate π orbitals, which together with a non-degenerate π orbital, HOMO–5, constitute a 10π aromatic pattern. HOMO–2 is the three-center orbital formed by the overlap of in-plane σ lobes from the middle quaternary carbon atoms. The degenerate LUMO and LUMO+1 comprise the other two orbitals of this three-center trefoil MO system as previously described.^{4,5} For **2** ($R = F$) the σ -trefoil bonding orbital, HOMO–4, is stabilized below the doubly degenerate π MOs, consistent with the usual interpretation that fluorine substitution for hydrogen stabilizes a ring σ -system relative to the π -system. In the metal complexes **4** ($R = H, F$), the ligand LUMO and LUMO+1 orbitals serve to accept four electrons from the Ti 3d shell. The top degenerate π pair in turn stabilizes by back-donation into the vacant metal d-orbitals; the remaining three π orbitals show significant interaction with the metal 4s and 4p AOs. The resulting complex is the first example (to our knowledge) of a novel, 16-electron aromatic system in which 10 electrons occupy orbitals derived from the ring π -MOs and 6 electrons occupy orbitals derived from the ring σ -MOs. Thus, the seemingly anti-aromatic electron count of 16 is compatible with conventional

Table 2. Changes upon Complexation for Various Ligands in **4** ($R = F$)

substitution	ΔH_{298}^a	ΔG_{298}^a	$r_{M-X}/\text{\AA}$	$\Delta\nu/\text{cm}^{-1b}$	$\Delta r/\text{\AA}^c$
Ti, CO ^d	–21.2	–13.0	2.318	58	–0.008
Zr, CO ^d	–14.7	–7.3	2.585	66	–0.002
Ti, H ₂ ^e	–5.7	+0.2	2.181	–194	0.010
Ti, N ₂ ^d	–14.9	–7.1	2.279	1	0.022
Ti, HCCH ^e	–25.5	–18.0	2.489	–42	0.009
Ti, H ₂ CCH ₂ ^e	–25.6	–17.8	2.544	–63	0.017
Zr, H ₂ CCH ₂ ^e	–18.7	–11.0	2.767	–41	0.011
Ti, H ₃ CCH ₃ ^e	–13.3	–3.5	2.528	–22	0.006
Ti, C ₃ H ₆ ^f	–23.1	–13.6	2.501	–1	0.049 ^g /–0.008 ^h

^a Energies in kcal mol^{–1} for the reaction **4** ($M, -$) + X → **4** (M, X).
^b Change in ligand stretching frequency: $\nu_{X(\text{complex})} - \nu_{X(\text{free})}$ (C–C stretch for C₃H₆).
^c Change in ligand bond length upon complexation.
^d Ligand axis approximately perpendicular to the ring.
^e Ligand axis approximately parallel to the ring.
^f Cyclopropane plane approximately perpendicular to the ring.
^g C–C bond nearest Ti.
^h Two other C–C bonds of ring.

aromaticity models by division into one class of 10 electrons and a second class of 6 electrons, each class following the $4n + 2$ rule. We suggest the name “foliate aromaticity” for this 16-electron, metal-induced aromatic system.

The energy diagrams for both complexes show the MO for the additional electron pair that constitutes the M–CO bond, which resides in HOMO–13, –17 for $R = H, F$, respectively. This electron pair completes the 18-electron valence shell for the metal.

Molecular orbitals for other foliacene complexes **4**, reported in Tables 1 and 2, retain the basic foliate MO pattern of one class of three and one class of five orbitals, showing variation only in the position of the MOs derived from the ring σ -trefoil orbitals relative to the position of those derived from the ring π set. The fact that fluorine substitution results in a significant lowering of the energy of the σ -trefoil MOs explains the stabilization of **4** ($R = F$) relative to **5**. The MO diagram of the isoelectronic vanadium(I) complex **4** ($R = F, M = V^+, X = CO$) is nearly identical to that of **4** ($R = F, M = Ti, X = CO$), except for an overall lowering by about 5 eV in the position of the MOs. We note the recent, analogous discussion of σ -trefoil,

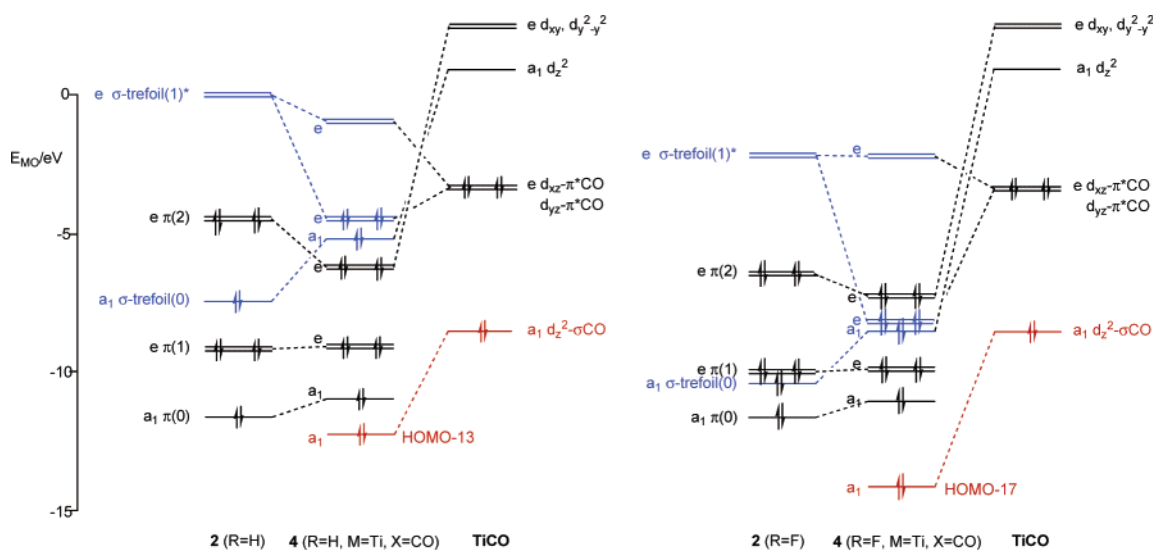


Figure 2. Molecular orbital energy level diagram for **4** ($R = H, F$, $M = Ti$, $X = CO$). The three MOs of the foliacene originating from the three-center, σ -trefoil MOs of the trefoilene ring are in blue, and the five MOs originating from the π MOs of the ring are in black. The lower a_1 and e components of this latter set of π MOs interact with the metal s/p AOs rather than the d AOs. The electron pair (in red) in HOMO–13, –17 ($R = H, F$) of the foliacene is essentially the σ lone pair on the CO ligand. The series of MOs between this latter MO and HOMO–7 are not shown and comprise the C–C σ system of the ring, having no interaction with the metal orbitals.

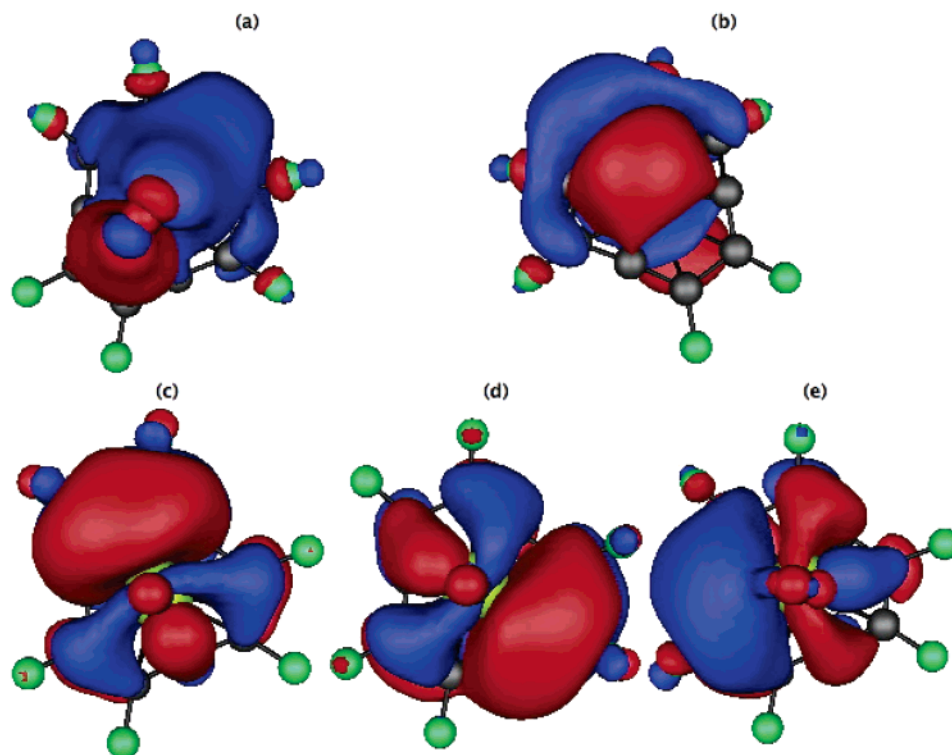


Figure 3. Orbitals localized using the Edmiston–Ruedenberg procedure for **4** (R = F, M = Ti, X = CO), illustrating (a) top (metal side) and (b) bottom views of one of the three equivalent orbitals deriving from the σ -“trefoil” and (c–e) the three π -derived localized functions.

three-center MOs to account for solid-state, interlayer interactions in $[\text{Ag}_2\text{Sn}_3]$,^{6–14} used to explain the band-gap in this material.

Localized molecular orbital calculations using the Ruedenberg procedure¹⁵ on **4** (R = F, M = Ti, X = CO) show that there are two types of ring–metal localized molecular orbitals. The three identical components of the first type (Figure 3a,b) involve bonding interactions between the Ti (predominantly d AOs, but with some s and p contributions) and three adjacent ring carbons (in-plane p orbitals). These are the local orbital equivalents to the three MOs derived from the ring σ -trefoil system. The five components of the second type (Figure 3c–e) involve the bonding interaction between the Ti and all the ring carbons (out-of-plane p orbitals), which are the equivalents to the five MOs derived from the ring π orbitals. These calculations further support our division of the 16-electron, foliate-aromatic system into two classes of 6 and 10 electrons, respectively.

The overall picture that emerges from this bonding scheme is that the metal center is an embedded component of both the 6-electron and the 10-electron aromaticity. The concept of enhanced aromaticity that varies in magnitude with the strength of the metal–ring interaction is borne out by more quantitative assessment using the NICS index¹⁶ (Figure 4). Probe centers

were located at various distances along the C_3 axis of symmetry from the ring centroid; specific values of these distances include the designation NICS(0) (for the centroid itself) and NICS(1) (for a distance of 1 Å from the centroid). The values for, e.g., benzene are NICS(1) \approx –11 ppm and NICS(0) \approx –9.7 ppm, the latter being the slightly less negative due to paratropic contributions from the C–C σ framework at the ring centroid. The values for **4** (Figure 4) reveal two characteristic differences from benzene. First, NICS(0) is far more negative than NICS(1), commensurate with major diatropic contributions from the σ -trefoil aromaticity. Second, NICS(1) also shows significantly greater negative values than for benzene, which supports the concept of these systems as both σ - and π -aromatic entities. This vividly contrasts with the reported anti-aromaticity¹⁸ of the transient 10π species acepentalene **6**, derived from **4** by replacing M = Ti (which has an accessible valence d-shell) by a carbon atom, M = C (which does not have such an accessible d-shell). We recognize that neither NICS(0) nor NICS(1) is an ideal measure¹⁷ of the aromaticity and magnetic properties of such molecules, but they serve here as useful semiquantitative indicators.

We also note here that the GIAO NMR calculations¹⁶ predict an aromatic ^1H shift (relative to TMS) of 7.1 ppm (**4**, R = H, M = Ti, X = CO) for the ring hydrogens, and values of 99 and 332 ppm for the two carbon environments. The latter (for the three quaternary carbons) may be highly characteristic for this type of complex.

Due to the nonplanar nature of the ligand in metal complexes **5**, the molecular orbital diagrams are difficult to interpret and are not illustrated here. We can only infer that, consistent with its structure, the bicyclic ligand donates fewer electrons to the metal, which accounts for the longer metal-to-ring-centroid

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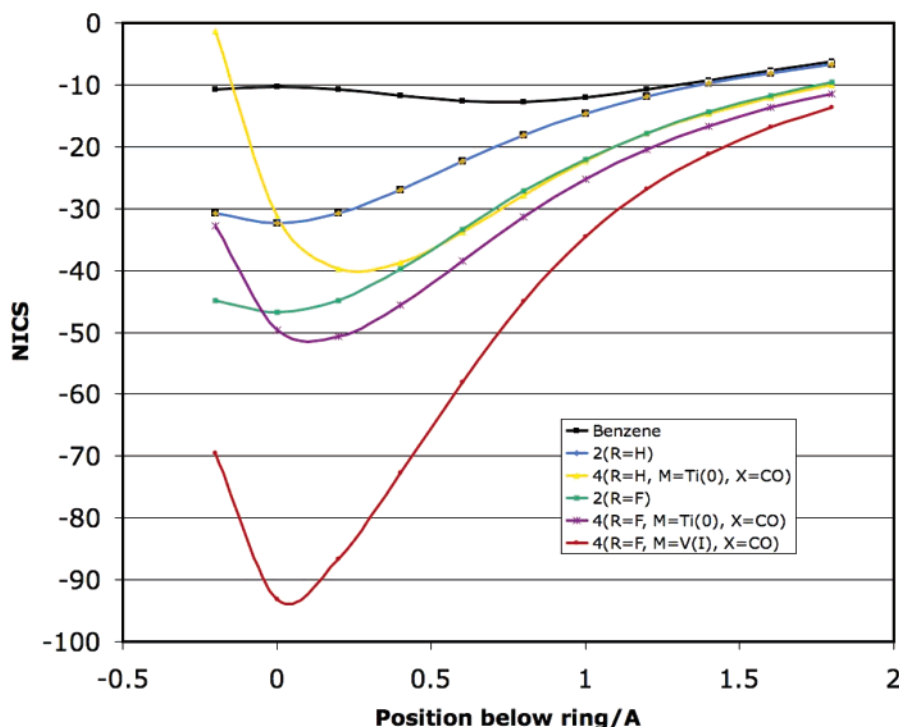
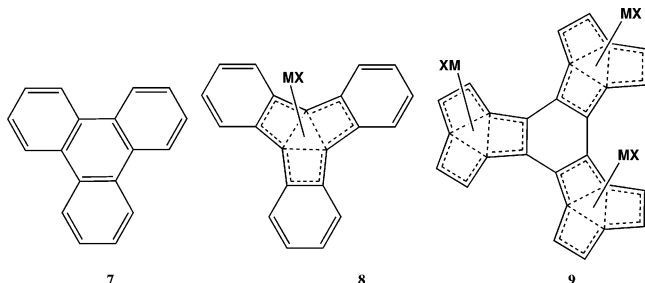


Figure 4. NICS plot for the planar trefoilene ring **2** and foliacenes **4** as a function of distance along the C_3 axis in the direction away from the metal atom. The ring centroid is at zero on this scale (about 1.1 Å below the metal atom for **4**).

distance and the shorter M–CO bond length, as well as the fact that the maximum stability in the series $X = (\text{CO})_n$ occurs at larger n than in **4**.

Aromaticity of the Foliolate Component

Modeling of structures **8** and **9** allows an interesting comparison between the aromaticity of the 16-electron foliate component and that of the benzene ring. The 6-electron sextet represents a robust aromatic motif with widespread occurrence, and its resistance toward disruption is exemplified by the Clar rule¹⁹ as applied to, e.g., polybenzenoid hydrocarbons (PBH).²⁰ The simplest Clar PBH is triphenylene **7**, for which estimates of the π -aromaticity using the NICS procedure indicate²⁰ the three outer rings to be conventionally aromatic (NICS(1) = –10.9 ppm), while the inner ring is somewhat less so (NICS(1) –6.1 ppm). When the foliate motif occupies the central ring, as in **8**, the NICS(1) for the foliate inner ring is computed as –24.3 ppm, while the benzo groups have NICS(1) values of –7.2 (syn to metal atom) and –8.4 ppm (anti to metal atom). Surrounding a foliate-aromatic unit with three benzo groups therefore does nothing to disrupt the aromaticity of the former, while attenuating slightly the latter.



One can probe this effect further via **9** ($M = \text{Ti}$), in which the relationship is inverted, with one benzene ring surrounded

by three foliate groups. The NICS(1) values for the 6-ring are +0.2 (syn to metal atom) and +3.7 ppm (anti to metal atom), while the foliate value is –20.0 ppm. Remarkably, the central benzene ring is now formally slightly anti-aromatic; its aromatic character has been entirely dismantled by the clearly more robust foliate unit.

Variation in the Metal Ligand X

In the foliacene complexes, the ligand–metal shared-electron system is effectively concentrated in a hemisphere about the metal, leaving an open hemisphere for the coordination of other ligands and suggesting the potential for unusual catalytic activity. Encouragingly, free energies are lowered (Table 2) when a variety of ligands are complexed to the metal, generally accompanied by a weakening of the ligand's internal covalent bonds. We note particularly the exothermic binding free energies of ligands such as ethane and cyclopropane as well as substantial values for the more conventional alkenes and alkynes.

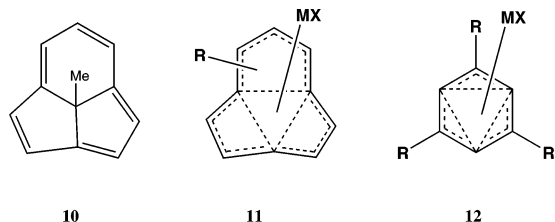
Variation in the Foliolate Ligand

The foliate component comprises 10 electrons deriving from a π -annulene periphery, two from the ligand σ framework and four contributed from the metal. Within these boundaries, alternative ligand ring structures can be designed. We illustrate this with two examples. Thus the central carbon in the known²¹ 10-annulene **10** could be replaced by a Ti–Cl group (**11**, $M = \text{Ti}$, $X = \text{Cl}$) to form a [3,2,2]trefoilene ligand, analogous to **2** in that one alkene double bond is replaced by an isoelectronic allyl cation (the charge then being balanced by the negative $X = \text{Cl}^-$ group). The orbital analysis indicates more mixing of the eight foliate MOs with the Ti–Cl bond, and decreased

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overlap of the expanded ring with the metal. This more complex conjugated system has somewhat attenuated aromatic properties (peripheral C–C lengths of 1.37–1.43 Å, $\nu_{\max} = 477/461 \text{ cm}^{-1}$, and NICS(1) = –13.5/–20.5 ppm for R = H, F, respectively) compared to **4**.



The ligand ring can instead be contracted by replacing, e.g., all three C=C fragments in **2** by an isoelectronic π -carbanion, this being equivalent to deprotonating benzene in the 1,3,5 positions. The resulting free ligand would have 6π and 6σ occupancy, but can be formalized to a [1,1,1]trefoilene by promoting four σ electrons to re-create a 10π system, prior to interaction with the metal to form the metallocomplex. The formal 3– charge must be balanced by the appropriate MX group, i.e., FeCl^{3+} , to give **12**. For, e.g., R = F this again reveals the characteristic (Figure 2) pattern of eight occupied orbitals (conjugated with the Fe–Cl bond), a nonalternating short ring bond length (1.392 Å), a ring \cdots MX stretch of $\nu_{\max} = 495 \text{ cm}^{-1}$, and a large NICS(1) of –36 ppm. A family of related compounds exhibiting 16-electron foliate aromaticity could potentially be constructed using this approach.

Another variation is to decrement the electrons on the ligand **12** by four, resulting formally in 6π and 2σ occupancy of the resulting (known²²) C_6R_3^+ species. When combined with R = F, M = Ti, X = Cp^- , this results in a neutral system with a filled 18-electron metal valence shell, but with a 12-electron foliate unit. Unlike the 16-electron unit, however, the predicted

structure of this system shows larger alternation of the C–C bond lengths (1.415–1.37 Å) and NICS(1) values of –6.9 and –10.5 ppm for the C_6F_3 and Cp rings, respectively. The latter is conventionally aromatic, but the former is much less so than the 16-electron foliate unit.

Conclusions

We conclude that the trefoil isomer **2** can be stabilized by metal complexation and subsequently enhanced by ligand fluorination, resulting in creation of a new type of 16-electron, metal-induced foliate-aromatic system. The relatively compact nature of the ligand in such foliacenes leaves a large and invitingly open hemisphere around the metal for further coordination and potential catalytic activity. A further degree of variability is introduced by the potential of the ligand to (reversibly) sequester two electrons into a ligand C–C σ bond (as in **5**), resulting in potentially chameleon-like properties for the system that vary in response to the nature of the ligands bound to the open hemisphere of the metal. The **4/5** balance is also potentially tunable via the ring substituents R. The foliate-aromatic system is predicted to persist with variation in the ligand ring size, and we speculate that it may be possible to create extended sheets or even ultimately spherical aromatic systems by fusing multiple foliacene units and benzene rings.

Supporting Information Available: 3D coordinates for all molecular geometries (CML [Chemical Markup Language] and Molfile), normal vibrational modes (XYZ), and molecular and localized orbitals (3DMF). This material is available free of charge via the Internet at <http://pubs.acs.org/>

JA046734J

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