Structure and Neutral Homoaromaticity of Metallacyclopentene, -pentadiene, -pentyne, and -pentatriene: A Density Functional Study

Eluvathingal D. Jemmis,*,† Ashwini Kumar Phukan,† Haijun Jiao,*,‡ and Uwe Rosenthal‡

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, and
Leibniz-Institut für Organische Katalyse an der Universität Rostock e. V.,
Buchbinderstrasse 5-6, 18055 Rostock, Germany

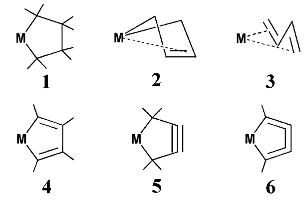
Received September 8, 2003

Density functional calculations were carried out on a series of metallacycles (**1**−**6**) to analyze the bonding and specifically to find the presence of any metal−π interaction in them. While there is no interaction between the metal and the middle carbon atoms in metallacyclopentane (**1**) and metallacyclopentadiene (**4**), strong metal−π interaction is found in the other metallacycles. The metallacyclopentene (**2**) and metallacyclopentyne (**5**) are found to be neutral bishomoaromatic, while the metallacyclopentatriene (**6**) is neutral in-plane aromatic. The calculated nucleus-independent chemical shift values and other bonding parameters support the strong cyclic delocalization of electrons in **2**, **5**, and **6**. A comparison of the calculated hydrogenation energies of the parent hydrocarbons and the metallacycles indicates that the metal fragment nearly eliminates the strain energy.

Introduction

In the realm of transition metal organometallic chemistry, the in situ generated metallocenes, biscyclopentadienyl titanium (Cp_2Ti) and biscyclopentadienyl zirconium (Cp_2Zr) with d^2 valence electron count, play a key role.[1] In their many different forms, these metallocenes are extensively used as catalysts in olefin polymerization, which is an important research area in catalytic chemistry.[2] Their importance arises from the extraordinary control that they have over the properties of the resulting polyolefins such as stereoregularity and stereoselectivity. Cp_2Ti and Cp_2Zr are also used in the synthesis of several precursors for the study of organometallic chemical vapor deposition of ceramic thin films.[3] They play an important role in the stoichiometric C−C coupling and cleavage reactions of unsaturated molecules such as alkynes, olefins, acetylides, and vinylides.[4] A variety of metallacycles, both saturated and unsaturated, results from such reactions, and some of these are represented in Scheme 1 in the order of increasing number of formal π bonds.[5−10] The five-membered metallacycles occupy a special place in the chemistry of transition metal organometallics, as they are involved in important reactions such as the synthesis of carbocyclic and heterocyclic compounds and their unusual ability to stabilize highly reactive organic entities.[4] We concentrate here on the electronic structure of some of them (**1**−**6**).

Scheme 1. Representative Metallacycles (1−6)



---

* Corresponding author. E-mail: edjsc@uohyd.ernet.in and hjiao@ifok.uni-rostock.de.

† University of Hyderabad.

‡ Leibniz-Institut für Organische Katalyse an der Universität Rostock e. V.

[1] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[2] (a) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (c) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (d) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (e) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

[3] (a) Choukroun, R.; Donnadieu, B.; Zhao, J.-S.; Cassoux, P.; Lepetit, C.; Silvi, B. *Organometallics* **2000**, *19*, 1901. (b) Choukroun, R.; Cassoux, P. *Acc. Chem. Res.* **1999**, *32*, 494. (c) Danjoy, C.; Zhao, J. S.; Donnadieu, B.; Legros, J.-P.; Valade, L.; Choukroun, R.; Zwick, A.; Cassoux, P. *Chem. Eur. J.* **1998**, *4*, 1100.

[4] (a) *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Ed.; Wiley-VCH: Weinheim, 1998; Vols. 1 and 2. (b) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835. (c) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (d) Ohff, A.; Pulst, S.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (e) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (f) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (g) Miura, K.; Funatsu, M.; Saito, H.; Ito, H.; Hosomi, A. *Tetrahedron Lett.* **1996**, *37*, 9059. (h) Rosenthal, U.; Burlakov, V. V. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim **2002**, 355. (i) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884.

[5] (a) Takahashi, T.; Fischer, R.; Xi, Z.; Nakajima, K. *Chem. Lett.* **1996**, 357. (b) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444.

[6] (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Chem. Lett.* **1981**, *226*, 519. (b) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (c) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

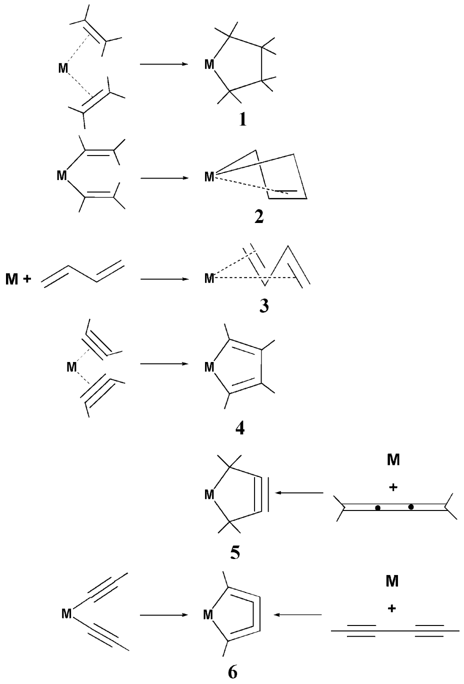
[7] Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344.

[8] (a) Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67. (b) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

[9] (a) Suzuki, N.; Nishiura, M.; Wakatsuki, Y. *Science* **2002**, *295*, 660. (b) Lam, K. C.; Lin, Z. *Organometallics* **2003**, *22*, 3466.

10.1021/om034161y CCC: $25.00
Publication on Web 10/28/2003

Scheme 2. Experimental Approaches toward 1−6



The experimental approaches toward the realization of **1**−**6** are given in Scheme 2. The saturated metallacyclopentane (**1**) can be isolated after the treatment of *tert*-butyl-substituted zirconocene dichloride with ethylene in the presence of *n*-butyllithium[5] or after the treatment of zirconocene bis(trimethylsilyl)acetylene with ethylene.[12a] Complex **2**, usually obtained by the 1:1 reaction of zirconocene dichloride with enediylmagnesium in THF,[6] can be prepared also from dialkenyl complexes,[11a] and **3** by the photocatalysis of diphenyl zirconocene in the presence of a conjugated diene.[7] The metallacyclopentadiene (**4**) can be formed by the photolysis of dimethyl zirconocene or titanocene in the presence of diphenyl acetylene[8] and substitution of bis(trimethylsilyl)acetylene in titanocene and zirconocene complexes by 2 equiv of acetylenes.[4d,h,i] The recently reported metallacyclopentyne **5** is prepared by the reaction of zirconocene dichloride with 2 equiv of *n*-butyllithium or *n*-butyl Grignard reagent and (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene.[9a] Metallacyclocumulene **6** can be prepared by the treatment of titanocene and zirconocene bis(trimethylsilyl)acetylene with 1,3-butadiynes or by the photocatalytic rearrangement of permethylzirconocene bisacetylides.[10] The formation of **2** and **6** through the direct coupling of two vinylides or two acetylides is favored thermodynamically, and the reverse C−C cleavage reactions were observed only under drastic conditions.[11] In contrast, the olefin and alkyne coupling products **1** and **4** often were found to be less stable, and the reverse C−C cleavage and retro-cycloaddition can occur even under very mild conditions.[4a,e,h,i,12a,c] For example, zirconacyclopentane very easily undergoes β−β' carbon−carbon bond cleavage via a suggested zirconocene bisolefin complex $Cp_2Zr(CH_2{=}CH_2)_2$ as intermediate.[13]

While the complexes **1**−**4** are well known in metallocene chemistry, the more exotic examples **5** and **6** were characterized only recently; the organic counterparts of **5** and **6** have been elusive so far.[9,14] On the basis of single-crystal X-ray structural data and IR spectra on 1-zirconacyclopent-3-yne (**5**) with $Si(CH_3)_3$ or $C(CH_3)_3$ as substituents, it was concluded that there is no considerable interaction between the metal center and the C≡C triple bond.[9a] This is in contrast with the metallacyclocumulene complex **6**, where there is substantial interaction between the metal and the middle C=C bond. The titanium counterpart of **5** is unknown so far.

There are few theoretical studies about the structure and bonding of these metallacycles.[15−17] An earlier study of a zirconocene−butadiene complex based on extended Hückel method predicts strong interaction of the metal with the terminal carbon atoms for the cis isomer while strong metal−middle carbon interaction for the trans isomer.[15] Another ab initio MO theoretical study on titanacyclopentadiene using a small basis set shows strong interaction between the metal center and the terminal carbon atoms while ruling out any significant interaction with the middle carbon atoms.[16] A recent density functional theory study on the *cis*- and *trans*-butadiene complexes of zirconocene concludes the same.[17] While preparing this article, we came across an article by Lin and co-workers that discusses the structure and stability of the recently synthesized zirconacyclopentyne complex **5**.[9b] On the basis of DFT calculations, the authors concluded that **5** is a resonance hybrid between a metallacyclopentyne form and a cumulene complex Lewis structure. Their study shows effective interaction between the metal atom and the central C=C bond of the cumulene ligand. We present here a systematic comparison of the structure and aromaticity of **1**−**6**. The bonding parameters of various experimentally known five-membered metallacycles are given in Table 1 for comparison. Due to the unavailability of d electrons in the formal Ti(IV) or Zr(IV) center, the traditional Dewar−Chatt−Duncanson model[18] of π-donation and metal back-donation is not readily applicable here. Our

---

(10) (a) Pellny, P.-M.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2000,** *122*, 6317. (b) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999,** *121*, 8313. (c) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112. (d) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605. (e) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 967.

(11) (a) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686. (b) Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952.

(12) (a) Mansel, S.; Thomas, D.; Lefeber, C.; Heller, D.; Kempe, R.; Baumann, W.; Rosenthal, U. *Organometallics* **1997**, *16*, 2886. (b) Mashima, K.; Takaya, H. *Organometallics* **1985**, *4*, 1464. (c) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1995**, *501*, 179.

(13) (a) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852. (b) Takahashi, T.; Suzuki, N.; Hasegawa, M.; Nitto, Y.; Aoyagi, K.; Saburi, M. *Chem. Lett.* **1992,** 331. (c) Suzuki, N.; Aoyagi, K.; Kotora, M.; Hasegawa, M.; Nitto, Y.; Saburi, M.; Takahashi, T. *J. Organomet. Chem.* **1994**, *473*, 117. (d) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591.

(14) March, J. In *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; p 158.

(15) (a) Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*, 145. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

(16) Knight, E. T.; Myers, L. K.; Thompson, M. E. *Organometallics* **1992**, *11*, 3691.

(17) Green, J. C.; Green, M. L. H.; Taylor, G. C.; Saunders, J. *J. Chem. Soc., Dalton Trans.* **2000**, 317.

(18) (a) Dewar, M. J. S.; *Bull. Soc. Chim. Fr.* **1951**, C71−C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

Table 1. Bond Parameters of Different Experimentally Known Metallacycles of Ti and Zr with the Generic Ligand C_5H_5 or Its Derivatives

M−C1	M−C2	C1−C2	C2−C2′	ref
1Zr/$(C_5R_5)_2ZrC_4R_8$				
2.307	3.065	1.547	1.502	5
2.346	3.010	1.551	1.332	15a
2.305	3.0	1.556	1.494	26a
2Zr/*cis*-$(C_5R_5)_2ZrC_4R_6$				
2.300	2.597	1.451	1.398	7
2.293	2.709	1.469	1.392	27
2.313	2.461	1.436	1.370	19
2.296	2.557	1.450	1.394	19
3Zr/*trans*-$(C_5R_5)_2ZrC_4R_6$				
2.509	2.391	1.435	1.467	29
2.453	2.352	1.402	1.393	30
4Zr/$(C_5R_5)_2ZrC_4R_4$				
2.265	3.05	1.359	1.499	8a
2.265	3.01	1.351	1.503	31a
2.264	2.945	1.362	1.512	31b
2.245	2.861	1.358	1.481	31b
2.271	3.015	1.358	1.488	31c
2.245	2.951	1.351	1.518	31d
5Zr/$(C_5R_5)_2ZrC_4R_4$				
2.50	2.29	1.415	1.206	9
6Zr/$(C_5R_5)_2ZrC_4R_2$				
2.434	2.320	1.285	1.326	10a
2.423	2.305	1.292	1.336	10b
2.344	2.328	1.304	1.327	10b
1Ti/$(C_5R_5)_2TiC_4R_8$				
2.194	3.017	1.532	1.529	15b
2.209	2.950	1.526	1.532	26b
2.215	3.0	1.537	1.550	26b
4Ti/$(C_5R_5)_2TiC_4R_4$				
2.141	2.951	1.371	1.496	8b
2.160	2.946	1.362	1.493	31e
2.165	2.996	1.373	1.488	10e
2.177	2.872	1.353	1.490	15c
6Ti/$(C_5R_5)_2TiC_4R_2$				
2.252	2.210	1.244	1.338	10e

study based on geometric and magnetic properties shows strong metal−π interaction in these metallacycles. The nucleus-independent chemical shift (NICS) values of several complexes indicate that the delocalization of the π electrons to the Zr and Ti centers is substantial, leading to the description of neutral homoaromatic for **2**, **5**, and **6**. Homo- and bishomoaromaticity are usually observed in charged species,[19] but neutral homoaromatic systems are very rare.[20] To the best of our knowledge, these transition metal complexes studied here are the first examples of neutral homoaromaticity.

Computational Details

All the molecules (**1**−**6**) were fully optimized using the B3LYP density functional method.[21] This is based on Becke's three-parameter functional including Hartree−Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke together with the nonlocal correction for the correlation energy provided by Lee et al. We used the LANL2DZ basis set with the effective core potentials of Hay and Wadt and an additional set of polarization functions.[22] Frequency calculations were carried out at the same level to characterize the nature of the optimized structures. The nature of bonding was studied through NBO analysis.[23] To judge the extent of cyclic delocalization of electrons in **1**−**6**, NICS[24] calculations were carried out at the geometrical center point of the ring. This gives an insight into the possible interaction between the Ti and Zr centers and the C=C or C≡C bonds in the metallacycles. The Gaussian 98 suite of programs was used for all the calculations.[25] The contour plots were obtained by using the MOLDEN visualization program.[26] The computed total electronic energies and coordinates are given in the Supporting Information.

Results and Discussion

The theoretical bond parameters and natural bond orbital analysis of all the parent metallacycles (**1**−**6**) are given in Tables 2 and 3 and of the metallacyclopentyne complex **5** with CH_3 and SiH_3 as the substituents in Table 4. Contour plots of the MOs corresponding to the in-plane metal C2−C2′ interaction in **1**−**6** are given in Figure 1 to study the nature of bonding in these metallacycles.

1-Metallacyclopentanes (1). The calculated bond parameters for **1Zr** and **1Ti** are found to be comparable with the available experimental data (Tables 1 and 2). Optimization gives a twisted five-membered ring (C_2 symmetry) for both complexes, and this agrees well with the experimental findings.[12,27] An NBO and MO analysis shows a typical σ-bonding between M and C1, and no interaction between M and C2 is found (Table 3 and Figure 1). The M−C2 distance of 3.0 Å might serve as a reference for no bonding. Therefore, **1** can be considered as a η^2-σ,σ-complex, in agreement with the discussion in the literature.[1,9b] This M−C σ-bond length can be used as a standard for comparison to all the other M−C distances.

---

[19] For leading reviews of homoaromaticity, see: (a) Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185. (b) Williams, R. V. *Eur. J. Org. Chem.* **2001**, 227.

[20] Stahl, F.; Schleyer, P. v. R. Jiao, H.; Schaefer, H. F., III; Chen. K. S.; Allinger, N. L. *J. Org. Chem.* **2002**, *67*, 6599.

[21] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 2398. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[22] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Dunning, T. H., Jr.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; p 1. For polarization functions, see: Huzinaga, S.; Anzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

[23] (a) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Program 3.1*; Madison, WI, 1988. (b) Reed, A. E.; Weinhold, F.; Curtiss. L. A *Chem. Rev.* **1988**, *88*, 899.

[24] (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E.. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P.v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, G. V.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.

[25] Frisch, M. J. Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[26] Shaftenaar, G. *MOLDEN 3.6*; CAOS/CAMM Center Nijmegen: Toernooiveld, Nijmegen, The Netherlands, 1991.

[27] (a) Lee, L. W. M.; Piers, W. E.; Parvez, M.; Rettig, S. J.; Young, V. G. *Organometallics* **1999**, *18*, 3904. (b) Horáček, M.; Štěpnička, P.; Gyepes, R.; Císařová, I.; Tišlerová, I.; Zemánek, J.; Kubišta, J.; Mach, K. *Chem. Eur. J.* **2000**, *6*, 2397.

Table 2. Theoretical Bond Parameters for the Parent Metallacycles (1−6)[a]

	M−C1	M−C2	C1−C2	C2−C2′
1Zr	2.313 (0.542)	3.045 (0.066)	1.558 (0.997)	1.550 (1.008)
2Zr	2.439 (0.338)	2.536 (0.538)	1.455 (1.090)	1.399 (1.717)
3Zr	2.504 (0.510)	2.403 (0.351)	1.432 (1.154)	1.423 (1.539)
4Zr	2.260 (0.613)	2.955 (0.110)	1.367 (1.855)	1.488 (1.055)
5Zr	2.440 (0.502)	2.330 (0.353)	1.424 (1.098)	1.259 (2.579)
6Zr	2.345 (0.625)	2.351 (0.366)	1.310 (1.887)	1.335 (1.745)
1Ti	2.201 (0.779)	2.993 (0.053)	1.548 (0.999)	1.542 (1.008)
2Ti	2.227 (0.771)	2.447 (0.420)	1.443 (1.112)	1.397 (1.687)
3Ti	2.435 (0.520)	2.297 (0.323)	1.413 (1.415)	1.431 (1.229)
4Ti	2.126 (0.823)	2.902 (0.078)	1.364 (1.843)	1.474 (1.075)
5Ti	2.341 (0.633)	2.201 (0.401)	1.406 (1.139)	1.259 (2.516)
6Ti	2.212 (0.710)	2.227 (0.419)	1.297 (1.929)	1.337 (1.698)

[a] The NLMO bond order is given within parentheses.

1-Metallacyclopentenes (2). Both the structures **2Zr** and **2Ti** were optimized as C_1 symmetry energy minima, although they are only slightly distorted from C_s symmetry. Due to the large interaction between the C=C double bond and the metal center, the five-membered ring is pocked rather than planar. The computed structural parameters for **2Zr** agree well with the available X-ray data for structures bearing methyl[7] or phenyl[28] substituents. In addition, the formal C=C double bond in **2Zr** of 1.399 Å is longer than that in the parent cyclopentene (1.335 Å), but close to the benzene value (1.400 Å) at the same level. The Zr−C2 distance of 2.536 Å in **2Zr** is longer than in **5Zr** (2.330 Å), but shorter than in **1Zr** (3.045 Å), as given in Table 2. Although no experimental data are known for **2Ti**, the same trend of structural changes is found for **2Ti**, as compared with **5Ti** and **1Ti**, and this indicates a strong Ti and C=C interaction in **2Ti**.

An NBO analysis in Table 3 shows a C=C double bond that interacts strongly with the metal center, and this results in a three-center and two-electron (3c−2e) bonding. Figure 1 shows the concentration of contour in the plane defined by the metal and the two middle carbon atoms of the metallacyclic ring in **2**. In **2Zr**, Zr contributes 9.5%, and Ti contributes somewhat more (12.0%) in **2Ti**. In these 3c−2e bondings, both carbon and metal are pure p or d orbital, and the calculated bond orders for M−C2 and C=C are 0.538 and 1.717 for **2Zr** and 0.420 and 1.687 for **2Ti**, respectively (Table 3). Therefore, **2** can be described as an η^2-$\sigma,\sigma + \eta^2$-π complex. In addition to the pocked conformation, we have also computed the structure with a planar five-membered ring for **2Zr**. This planar structure (C_{2v}) is found to have an imaginary vibrational frequency (−89i cm^{-1}) and therefore a transition state on the potential

Table 3. Hybridization and Orbital Occupancy (%) of the Parent Metallacycles (1−6)

	M−C1/σ	C1−C2/σ	C1−C2/π	C2−C2′/σ	C2−C2′/π
1Zr	sd$^{8.3}$ (Zr, 24.3%) sp$^{3.0}$ (C1, 73.6%)	sp$^{2.7}$ (C1, 48.5%) sp$^{2.8}$ (C2, 49.6%)		sp$^{2.8}$ (C2+C2′, 99.2%)	
2Zr	sd$^{15.2}$ (Zr, 25.0%) sp$^{5.2}$ (C1, 66.1%) p (C2+C2′,7.3%)	sp$^{2.6}$ (C1, 48.0%) sp$^{2.0}$ (C2, 50.1%)		sp$^{2.1}$ (C2+C2′, 98.8%)	d (Zr, 9.5%) p (C2+C2′, 85.8%)
3Zr	sd$^{21.8}$ (Zr, 26.3%) sp$^{6.3}$ (C1, 59.6%) p (C2+C2′, 12.0%)	sp$^{2.5}$ (C1, 47.7%) sp$^{2.0}$ (C2, 50.9%)		sp$^{2.1}$ (C2+C2′, 98.4%)	d (Zr, 12.2%) p (C2+C2′, 81.4%) sp$^{11.6}$ (C1+C1′, 4.2%)
4Zr	sd$^{7.0}$ (Zr, 24.4%) sp$^{2.0}$ (C1, 73.3%)	sp$^{1.9}$ (C1, 48.3%) sp$^{1.8}$ (C2, 50.3%)	d (Zr, 2.2%) p (C1, 45.0%) p (C2, 48.5%)	sp$^{2.1}$ (C2+C2′, 98.8%)	
5Zr	sd$^{16.9}$ (Zr, 23.9%) sp$^{4.4}$ (C1, 64.5%) p (C2+C2′, 10.0%)	sp$^{3.0}$ (C1, 46.4%) sp$^{1.1}$ (C2, 51.7%)		sp$^{1.3}$ (C2+C2′, 98.8%)	d (Zr, 4.0%) p (C2 + C2′, 92.4%) d (Zr, 9.2%) p (C2 + C2′, 87.0%)
6Zr	sd$^{12.5}$ (Zr, 23.6%) sp$^{2.2}$ (C1, 64.9%) p (C2+C2′, 10.4%)	sp$^{2.3}$ (C1, 46.4%) sp$^{1.0}$ (C2, 52.0%)	d (Zr, 3.4%) p (C1, 42.6%) p (C2, 48.4%)	sp$^{1.4}$ (C2+C2′, 98.6%)	d (Zr, 9.6%) p (C2 + C2′, 85.6%)
1Ti	sd$^{15.0}$ (Ti, 36.5%) sp$^{3.4}$ (C1, 61.2%)	sp$^{2.6}$ (C1, 48.5%) sp$^{2.8}$ (C2, 49.7%)		sp$^{2.8}$ (C2+C2′, 99.2%)	
2Ti	d (Ti, 33.5%) sp$^{5.9}$ (C1, 56.4%) p (C2+C2′, 6.6%)	sp$^{2.5}$ (C1, 47.9%) sp$^{2.0}$ (C2, 50.1%)		sp$^{2.1}$ (C2+C2′, 98.8%)	d (Ti, 12.0%) p (C2 + C2′, 80.8%) sp$^{11.4}$ (C1+C1′, 4.8%)
3Ti	d (Ti, 38.0%) sp$^{8.6}$ (C1, 49.3%) p (C2 + C2′, 8.1%)	d (Ti, 37.7%) p (C1, 38.6%) p (C1+C1′, 12.0%) p (C2, 9.3%)		sp$^{2.7}$ (C2, 47.9%) sp$^{2.2}$ (C2′, 51.1%)	sd$^{10.6}$ (Ti, 11.7%) sp$^{8.6}$ (C1, 45.4%) p (C2, 38.2%)
4Ti	sd$^{14.6}$ (Ti, 36.2%) sp$^{2.2}$ (C1, 61.2%)	sp$^{1.8}$ (C1, 48.3%) sp$^{1.9}$ (C2, 50.2%)	d (Ti, 1.5%) p (C1, 44.5%) p (C2, 49.1%)	sp$^{2.2}$ (C2+C2′, 98.8%)	
5Ti	d (Ti, 33.7%) sp$^{5.4}$ (C1, 54.9%) p (C2+C2′, 10.0%)	sp$^{2.9}$ (C1, 46.6%) sp$^{1.2}$ (C2, 51.6%)		sp$^{1.3}$ (C2+C2′, 99.0%)	d (Ti, 5.1%) p (C2+C2′, 91.4%) d (Ti, 12.8%) p (C2+C2′, 80.4%) sp$^{5.9}$ (C1+C1′, 4.6%)
6Ti	d (Ti, 33.7%) sp$^{2.4}$ (C1, 54.5%) p (C2+C2′, 10.5%)	sp$^{2.2}$ (C1, 46.4%) sp$^{1.0}$ (C2, 52.0%)	d (Ti, 2.9%) p (C1, 42.8%) p (C2, 48.2%)	sp$^{1.4}$ (C2+C2′, 98.8%)	d (Ti, 13.2%) p (C2+C2′, 79.0%) sp$^{4.5}$ (C1+C1′, 4.8%)

Table 4. Computed Bond Parameters and NLMO Bond Orders (in *italics*) for the Parent as Well as Substituted 1-Zirconacyclopent-3-yne (5Zr) and 1-Titanacyclopent-3-yne (5Ti)

ligand (R)	M−C1	M−C2	C1−C2	C2−C2′	C1−C2−C2′
5Zr	2.440	2.330	1.424	1.259	151.2
(R = H)	*0.502*	*0.353*	*1.098*	*2.579*	
5Zr-*cis*	2.482	2.336	1.422	1.261	152.9
(R = CH_3)	*0.499*	*0.355*	*1.095*	*2.573*	
5Zr-*trans*	2.483	2.337	1.421	1.261	152.0
(R = CH_3)	*0.498*	*0.358*	*1.103*	*2.570*	
5Zr-*cis*	2.501	2.333	1.418	1.259	153.9
(R = SiH_3)	*0.461*	*0.365*	*1.122*	*2.565*	
5Zr-*trans*	2.503	2.333	1.417	1.259	154.0
(R = SiH_3)	*0.458*	*0.366*	*1.127*	*2.567*	
5Ti	2.341	2.201	1.406	1.259	150.9
(R = H)	*0.633*	*0.401*	*1.139*	*2.516*	
5Ti-*cis*	2.435	2.220	1.399	1.259	154.6
(R = CH_3)	*0.578*	*0.626*	*1.143*	*2.515*	
5Ti-*trans*	2.421	2.215	1.400	1.261	154.2
(R = CH_3)	0.627	0.404	1.144	2.508	
5Ti-*cis*	2.454	2.216	1.397	1.258	155.8
(R = SiH_3)	*0.564*	*0.565*	*1.164*	*2.505*	
5Ti-*trans*	2.447	2.213	1.398	1.259	155.5
(R = SiH_3)	*0.587*	*0.563*	*1.169*	*2.503*	

energy surface. Following the imaginary mode leads to the pocked C_1 structure. The computed barrier ($\Delta G^{\ddagger}$, 298 K) for the ring pocking is 9.0 kcal/mol, and this is close to the estimated 12.8 kcal/mol at 268 K on the basis of dynamic ^{13}C NMR measurements.[28]

Complexes with *s-trans-η*^{4}-Butadiene (3). It is found experimentally that **2Zr** equilibrates with its *s-trans-η*^{4} isomer (**3Zr**) with a ratio of 45 (**2Zr**) to 55 (**3Zr**) at 298 K in C_6D_6.[29] This ratio indicates that both isomers are very close in energy. At the same level of theory, the computed difference in free energy between **2Zr** and **3Zr** is only 0.2 kcal/mol at 298 K, and this agrees well with the experiment and gives also the error limit of theory to be less than 0.5 kcal/mol.

The optimized structural parameters for **3Zr** agree at least with one set of the X-ray data for the 1,4-diphenyl-*trans*-butadiene,[30] since there are two independent molecules in the unit cell. It is shown both theoretically and experimentally that the Zr−C2 distance in **3Zr** is shorter than the Zr−C1,[31] and this is in contrast to those in **2Zr**, in which the Zr−C1 bond is shorter than the Zr−C2 distance. In comparison with free *trans*-butadiene (1.341 and 1.458 Å), the C−C bond lengths in **3Zr** are nearly equal (1.432 and 1.423 Å), and therefore it is hard to ascribe **3Zr** simply as an η^4-complex.

In contrast to **3Zr**, the corresponding **3Ti** complex is not known experimentally and no direct comparison is possible. The energy difference between **2Ti** and **3Ti** is much larger than that between **2Zr** and **3Zr**. At the same level of theory, **3Ti** is 5.6 kcal/mol more stable than **2Ti**, and the difference in free energy at 298 K is 4.6 kcal/mol. The absence of either of them points to some inherent unfavorability of Ti in these geometries. This may be related to the smaller size of Ti in relation to Zr. For example, on reaction with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$, $Cp^*{}_2Ti$ forms the three-membered titanacyclopropene (η^2-complex) $Cp^*{}_2Ti(\eta^2\text{-}1,2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$, while $Cp^*{}_2Zr$ produces the five-membered zirconacyclocumulene (η^4-complex) $Cp^*{}_2Zr(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$.[10b]

NBO analysis supports a bonding description that is similar to that of **2Zr**, i.e., a strong Zr−C1 σ bond and a 3c−2e bonding between the Zr center and the middle C═C double bond (Table 3). Compared to **2Zr**, the Zr−C interactions in **3Zr** involve contribution from the terminal carbon atoms also. Therefore, one can conclude critically that the bonding in the formal η^4-*s-trans*-butadiene **3Zr** can be described as an η^2-σ,σ + η^2-π-complex between Zr and *trans*-1,4-but-2-enediyl.

Metallacyclopentadienes (4). For **4Zr**, both the computed and experimental[8,32] structural parameters (Tables 1 and 2) reveal the delocalized bonding pattern as in the case of cyclopentadiene (1.349 and 1.479 Å). Both C−C bond lengths (1.367 and 1.488 Å) and NBO analysis (Table 3) show double-bond character between C1 and C2, while conjugated single bond between C2 and C2′. Zr contributes only slightly (2.2%) to the C1−C2 double bond. A contour plot of **4** shows σ bonding between the metal and the terminal carbon atoms, while no bonding interaction is found with the middle carbon atoms (Figure 1). Therefore, bonding in complex **4** can be described as η^2-σ,σ. The same is found for the Ti analogue (**4Ti**). The computed and X-ray bond parameters show that M−C1 bond is of σ character and the C4 unit has typical butadiene characteristics, as evidenced by our NBO analysis and in tune with earlier theoretical studies.[16]

1-Zirconacyclopent-3-ynes (5Zr). Recently, Suzuki and co-workers reported the synthesis of a zirconacyclopentyne complex (**5**) with a trimethylsilyl or *tert*-butyl group as the substituent. The X-ray structure of **5** shows an unusually short C−C middle bond (1.206 Å), prompting them to call it a metallacyclopentyne. The Zr−C2 and Zr−C3 bonds (2.289 Å) are shorter than Zr−C1 and Zr−C4 bonds (2.500 and 2.504 Å). The cis and trans conformations of **5Zr** with R = CH_3 or SiH_3 as the substituents were optimized under the C_s and C_2 symmetry constraints, respectively, and they were found to be minima on the potential energy surface. The trans isomers are found to be only slightly more stable than the cis one, and the difference in free energy ($\Delta G°$) is only 0.2 kcal/mol for R = SiH_3 or CH_3. This agrees well with the experimental findings. At room temperature, for example, equilibrium cis/trans ratios of 36/64 and 12/88 are found for R = $SiMe_3$ and *tert*-CMe_3, indicating that the trans isomers are slightly more populated than the cis one.

Table 4 lists a set of computed bond parameters for the parent and substituted **5Zr**. The bond parameters around the five-membered ring do not depend considerably on conformations (cis/trans) and substituents (R = SiH_3 or CH_3), and the only significant change is found

---

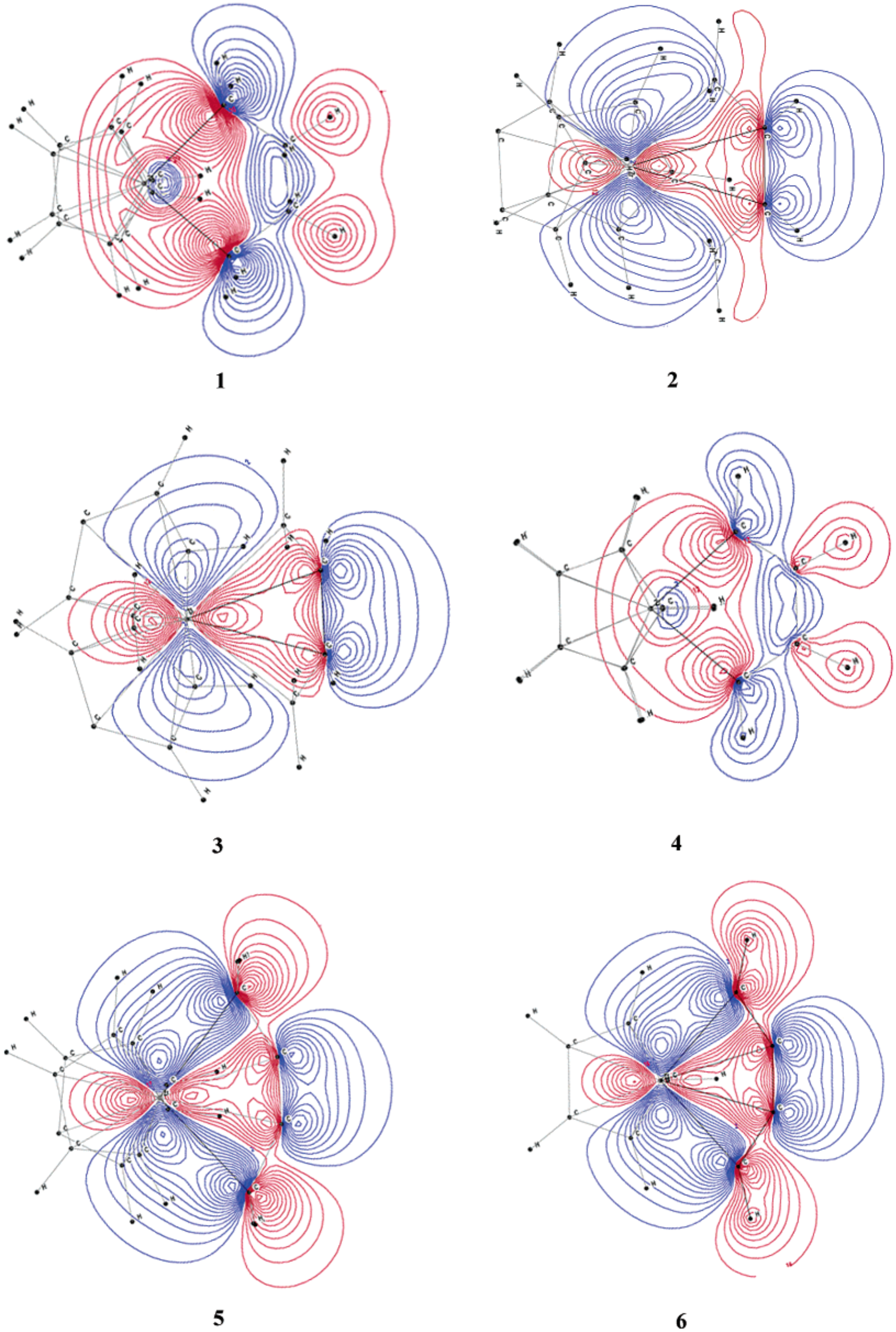
(28) Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311.

(29) Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300.

(30) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191.

(31) Dahlmann, M.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 4459.

(32) (a) Jones, S. B.; Petersen, J. L. *Organometallics* **1985**, *4*, 966. (b) Erker, G.; Zwettler, R.; Krüger, C.; Kryspin, I. H.; Gleiter, R. *Organometallics* **1990**, *9*, 524. (c) Kempe, R.; Spannenberg, A.; Peulecke, N.; Rosenthal, U. *Z. Kristallogr.* **1998**, *213*, 789. (d) Westerhausen, M.; Digeser, M. H.; Gückel, C.; Nöth, H.; Knizek, J.; Ponikwar, W. *Organometallics* **1999**, *18*, 2491. (e) Peulecke, N.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 419.

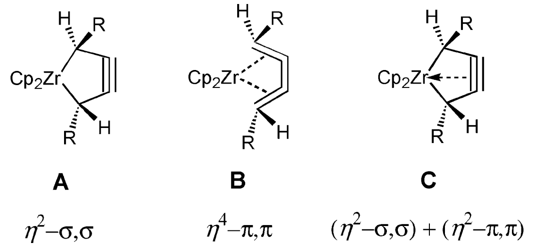


1 2 3 4 5 6

Figure 1. Contour plots of the MOs corresponding to the interaction of the metal and C2−C2′ for structures **1**−**6**.

for the Zr−C1 distance with R = H. Our calculations show that theory agrees reasonably well with the experiment, except for the formal C2−C2′ triple bond, which is calculated to be longer (1.259 Å) than that found experimentally (1.206 Å) by Suzuki and co-workers.[9a] In addition, the computed stretch frequencies of the triple bonds of 2018 (R = SiH_3) and 2010 cm^{-1} (R = CH_3) also agree with the experimental values of 2014 (R = $SiMe_3$) and 2011 cm^{-1} (R = $C(CH_3)_3$), respectively. The shortening of the C≡C bond led Suzuki and co-workers to conclude that Zr does not interact considerably with the triple bond and **5Zr** prefers the η^2-σ,σ- (**A**) rather than the η^2-π,π bonding (**B**), as shown in Scheme 3. However, the agreement of all other calculated geometric parameters with experiment makes us feel that the calculated C2−C2′ bond length is closer to reality. This led us to conclude the following. While there may be a small contribution from structures corresponding to **A** and **B**, major contribution to the actual structure must come from **C**. A more refined

Scheme 3. Possible Resonance Structures (A−C) for 5



diffraction experiment may lead to a longer C2−C2′ distance.[33] Since there is no substantial difference between the substituted and free molecule in bond parameters, our further computation and discussion will be on the basis of the parent systems.

In addition to the results discussed above, we have also analyzed the interaction between the Zr center and the triple bond. As shown in Table 2, all Zr−C2 bonds are shorter than Zr−C1. In comparison with 2-butyne (1.473 and 1.219 Å), which is calculated at the same level of theory, the C1−C2 distance in **5Zr** of 1.424 Å is shorter, while the C2−C2′ triple bond of 1.259 Å is longer. Since the ligand in **5Zr** is bent rather than linear, we have also computed bent 2-butyne with the same CCC angle of 151.2°, as found in **5Zr**. The computed C−C triple bond length in bent 2-butyne of 1.226 Å is somewhat longer than in free 2-butyne, but still much shorter than in **5Zr**. Therefore, the elongation of the C−C triple bond in **5Zr** is mainly due to the interaction with metal rather than bending.

The strong interaction between the Zr center and the triple bond is also indicated by the calculated bond order (Table 4), both with and without substitutents. Taking the plane of the five-membered ring as reference, there are two possible Zr−π interactions: the in-plane and the out-of-plane. As shown in Table 3, only σ bonds are found for Zr−C1 and C1−C2, but two types of three-center, two-electron interactions (3c−2e) are found between Zr and the triple bond. Detailed analysis shows that the in-plane interaction is stronger than the out-of-plane one, as indicated by the contribution from the Zr center. A contour plot of **5** also shows strong cyclic delocalization of electrons in the ring (Figure 1). On this basis, one can conclude that the bonding in **5Zr** is η^2-$\sigma,\sigma + (\eta^2$-$\pi,\pi)$ and structure **C** should be the reasonable resonance description. In addition, the calculated C1−C2 and C2−C2′ also do not support the cumulenic resonance form (**B**). For example, the C1−C2 (1.422 Å) and C2−C2′ (1.259 Å) bonds in **5Zr** are much longer and much shorter than the corresponding cumulated C=C bonds in *cis*-RHC=C=C=CRH (R = H (1.330 vs 1.281 Å), CH_3 (1.332 vs 1.281 Å), and SiH_3 (1.333 vs 1.282 Å), respectively). On the other hand, a cumulenic C=C double bond in interaction with a metal center should be much longer than in its free form, as indicated by a central C−C bond length of 1.399 Å in **2Zr**, and this is not the case in **5Zr**. Therefore, our analysis is in contrast with the work by Lin,[9b] where they have emphasized the importance of resonance structures **A** and **B**.

Such coexisting in-plane and out-of-plane cyclic delocalized systems were considered as double aromatic, as found in 3,5-dehydrophenyl cation and cyclo[6]-carbon.[34] Therefore, **5Zr** can be double aromatic, indeed neutral bishomoaromatic. This is in contrast with the conclusion arrived at by Suzuki et al. based on bond lengths alone.[9a]

1-Titanacyclopent-3-ynes (5Ti). In contrast to **5Zr**, the corresponding **5Ti** is yet to be synthesized. However, similar bonding types between **5Ti** and **5Zr** are found. For example, as given in Table 4, the C2−C2′ triple bond in **5Ti** is also elongated and has nearly the same bond order as in **5Zr**. In addition, population analysis also shows that Ti interacts strongly with the triple bond and forms the in-plane and out-of-plane 3c−2e interaction (Table 3). Therefore, **5Ti** with an η^2-$\sigma,\sigma + (\eta^2$-$\pi,\pi)$ bonding as **5Zr** should also be bishomoaromatic. It is found that Ti (+0.295) is less positively charged in **5Ti** than Zr in **5Zr** (+1.282).

To aid experimental investigations, we have also computed the substituted **5Ti** with R = CH_3 and SiH_3. The trans isomers are C_2 symmetrical, while the cis isomers have C_1 symmetry. The C_s symmetrical cis isomers with one imaginary frequency for the rotation of C_5H_5 rings are less than 0.2 kcal/mol higher in energy for both R = CH_3 and SiH_3. Therefore, the C_s structures are used for analysis. The calculated bond parameters are summarized in Table 4. As in the case of **5Zr**, the trans isomer is more favored energetically than the cis one, and the calculated free energy difference at 298 K is 1.5 kcal/mol for R = SiH_3 and 1.3 kcal/mol for R = CH_3, respectively. Therefore, one might expect a less pronounced equilibrium between them (cis/trans = 7/93 for R = SiH_3 and 10/90 for R = CH_3). The calculated stretch frequencies of the formal triple bonds in **5Ti** (2047 cm^{-1}, R = SiH_3) are slightly higher than those found in **5Zr**.

Metallacyclopentatrienes (6). For both **6Zr** and **6Ti**, the computed bond parameters are comparable to those found experimentally (Tables 1 and 2).[10] The metal atom and the four carbon atoms of the metallacyclocumulene ring are coplanar. The bonding properties have been analyzed, and a strong interaction between the metal and the in-plane π bond is found.[35] The computed bond indexes and populations (Tables 2 and 3) reveal the cumulenic nature in **6Zr**. The additional in-plane interaction is also a 3c−2e bonding in which Zr contributes 9.6%, comparable with those in **2Zr** and **5Zr**. The contour plot of **6** shows significant delocalization of electrons in the ring similar to that in **5** (Figure 1). In agreement with X-ray results, a similar structural pattern is found for **6Ti**. The similarity in the bonding pattern of **5** and **6** was reported earlier[35a] and subsequently reinforced by the work of Lin and coworkers.[9b]

Ring Strain in 1−6. The ring strains in the metallacycles were calculated by successive hydrogenation

---

(33) This difference is due to the unsatisfactory quality of the reported crystal structure. For example, the C−C distances of the cyclopentadienyl rings in the *trans*-1,4-ditrimethylsilyl-substituted **5Zr** and the *trans*-1,4-di-*tert*-butyl-substituted **5Zr** are in the ranges 1.36−1.43 and 1.33−1.40 Å, respectively. In addition, the central C−C bond length of the *trans*-1,4-di-*tert*-butyl-substituted **5Zr** is 1.41(2) Å. See the Supporting Information of ref 9a.

(34) Schleyer, P.v. R.; Jiao, H.; Glukhovtsev, M. N.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 7429.

(35) (a) Jemmis, E. D.; Phukan, A. K.; Giju, K. T. *Organometallics* **2002**, *21*, 2254. (b) Jemmis, E. D.; Phukan, A. K.; Rosenthal, U. *J. Organomet. Chem.* **2001**, *635*, 204.

Table 5. Successive Hydrogenation Energies (kcal/mol)[a]

M	2 → 1	4 → 2	5 → 2	6 → 4
CH_2	25.8	23.1	106.3	123.4
Cp_2Ti	19.8	20.1	20.7	38.5
Cp_2Zr	13.1	30.4	24.7	31.5

[a] At B3LYP/LANL2DZP + ZPE (B3LYP/LANL2DZP).

energies from the unsaturated metallacyclopentatriene (**6**) to the saturated metallacyclopentane (**1**). As given in Table 5, the two C═C double bonds in cyclopentadiene (**4CH$_2$**) do not differ much from that in cyclopentene (**2CH$_2$**), since the hydrogenation energies are close (23.1 and 25.8 kcal/mol, and the experimental values are 24.0 and 26.4 kcal/mol,[36] respectively). The same is also found for **4Ti** and **2Ti** (20.1 and 19.8 kcal/mol), but their hydrogenation energies are smaller than those of **4CH$_2$** and **2CH$_2$**. In contrast, the hydrogenation energy of **4Zr** of 30.4 kcal/mol is larger than that (13.1 kcal/mol) of **2Zr**. It is interesting to note that the hydrogenation energy of **2Ti** is larger that that of **2Zr**, but that of **4Ti** is smaller than that of **4Zr**.

As expected, the C−C triple bond in cyclopentyne (**5CH$_2$**) and the C−C cumulenic bond in cyclopentatriene (**6CH$_2$**) have huge hydrogenation energies (106.3 and 123.4 kcal/mol), which are more than four and five times the value of cyclopentadiene. Such large differences indicate the enhanced strain in both **5CH$_2$** and **6CH$_2$**, and it is not very surprising why they are still elusive.

In contrast to the parent hydrocarbons, the hydrogenation energy of **5Ti** is very close to those of **2Ti** and **4Ti**, while that of **6Ti** is about double those of **2Ti**, **4Ti**, and **5Ti**, respectively. Because both **4Ti** and **6Ti** are known in the experimental literature, the currently elusive **5Ti** should be the target for experimental realization. The small hydrogenation energies for both **5Zr** and **6Zr**, which are close to that of **4Zr**, indicate that these molecules are not strained, as pointed out by Lin and co-workers.[9b] These reduced hydrogenation energies can be ascribed to the very strong stabilization interaction between the metal center and the ligands, as indicated by the NBO analysis, and the aromatic stabilization as discussed below.

NICS Characterization. NICS calculations (Table 6) give a fair idea about cyclic delocalization of electrons or aromaticity[24] as well as possible interactions between the metal and the C═C bond in these metallacycles. As expected, the saturated metallacyclopentanes (**1**) are nonaromatic. This is also indicated by the calculated NICS values at the ring center, NICS(0), and 1 Å above the ring center, NICS(1). Similarly, metallacyclopentadienes **4Zr** and **4Ti** with small NICS(1) values of −1.5 and −2.8 are also not aromatic, which is in agreement with their geometric parameters.

In contrast, a very strong metal−π interaction is found in both **2Zr** and **2Ti**, as indicated by their large NICS(0) and NICS(1) values. These are due to the 3c−2e bonding. The NICS(1) values for the concave (−18.1 vs −21.7) side and convex (−11.9 vs −10.6) side are larger than or close to the benzene value. Thus, one might conclude that they are neutral bishomoaromatic, as compared to the parent 4-cyclopentenyl cation.[37] As given in Table 6, cyclocumulene complexes **6Zr** and **6Ti** have nearly the same NICS(0) values (−34.4 and −36.2) as cyclopentene derivatives **2Zr** (−32.0) and **2Ti** (−33.2). This is due to the fact that they have an in-plane 3c−2e interaction, as indicated in the population analysis (Table 3). Therefore, complex **6** can be considered to be in-plane aromatic.

Table 6. Calculated NICS(x) Values for Five-Membered Metallacycles[a]

	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)
1Zr	−5.8	−5.1	−3.5	−1.2
2Zr	−32.0	−18.2[b]	−11.9[b]	−8.7[b]
		(−31.6)[c]	(−18.1)[c]	(−12.0)[c]
4Zr	+0.3	−0.7	−1.5	−1.8
5Zr	−49.4	−37.2	−19.8	−11.5
6Zr	−34.4	−26.3	−15.0	−9.6
1Ti	−8.3	−6.6	−3.4	−1.0
2Ti	−33.2	−16.8[b]	−10.6[b]	−7.9[b]
		(−35.0)[c]	(−21.7)[c]	(−16.3)[c]
4Ti	−3.2	−3.4	−2.8	−2.0
5Ti	−53.3	−40.2	−21.3	−12.5
6Ti	−36.2	−28.3	−16.7	−11.4

[a] Calculated at the center (0) and above the ring center (0.5−1.5 Å). [b] At the convex side. [c] At the concave side.

From the population analysis in Table 3, we found two 3c−2e interactions in the metallacyclopentyne complexes (**5Zr** and **5Ti**), the in-plane and the out-of-plane types. Therefore, it is expected that the NICS values at the ring centers in **5Zr** and **5Ti** should be more negative than those in **2** and **6**. Indeed, we found more negative NICS(0) values for **5Zr** (−49.4) and **5Ti** (−53.3), and one might conclude that they are neutral bishomoaromatic.

Conclusions

A comparison of the structure and bonding of the metallacycles **1**−**6** shows that there is considerable metal−π interactions in **2**, **5**, and **6**. Our analysis of geometric and magnetic properties (NICS) shows the presence of strong delocalization in these systems including that of the metallacyclopentyne (**5**), which is contrary to previous conclusions.[9] The metallacyclopentene (**2**) and metallacyclopentyne (**5**) are found to be neutral bishomoaromatic, while the metallacyclocumulene (**6**) is in-plane aromatic. A comparison of the hydrogenation energies of the parent carbocycles and metallacycles shows that the strain present in cyclopentynes and cyclopentatrienes is practically removed when the CH_2 group is replaced by a Cp_2M fragment (M = Ti, Zr).

Acknowledgment. This work was supported by the Council of Scientific and Industrial research (CSIR) and Department of Science and Technology, New Delhi, India. A.K.P. thanks CSIR for a Senior Research Fellowship.

Supporting Information Available: Total electronic energies and Cartesian coordinates are given. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034161Y

---

(36) *CRC Handbook of Chemsitry and Physics*, 80th ed.; Lide, D. R., Editor in Chief; CRC Press: Boca Raton, FL, 1999−2000.

(37) Winstein, S.; Sonnenberg, J. de Vries, L. *J. Am. Chem. Soc.* **1959**, *81*, 6532.