

1,6-Methano[10]annulene as prospective organometallic ligand from the annulene family A DFT study of transition metal π-complexes and their inter-ring haptotropic rearrangements

I.P. Gloriozov, N.S. Zhulyaev, F. Gam, J.-Y. Saillard, Y.F. Oprunenko

▶ **To cite this version:**

I.P. Gloriozov, N.S. Zhulyaev, F. Gam, J.-Y. Saillard, Y.F. Oprunenko. 1,6-Methano[10]annulene as prospective organometallic ligand from the annulene family A DFT study of transition metal π-complexes and their inter-ring haptotropic rearrangements. Journal of Organometallic Chemistry, 2018, 867, pp.306-311. 10.1016/j.jorganchem.2017.11.023 . hal-01809148

HAL Id: hal-01809148

https://univ-rennes.hal.science/hal-01809148

Submitted on 14 Jun 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

ACCEPTED MANUSCRIPT

1,6-Methano[10]annulene as Prospective Organometallic Ligand from the Annulene Family: a DFT Study of Transition Metal π-Complexes and their Inter-Ring Haptotropic Rearrangements

I.P. Gloriozov [a], N.S. Zhulyaev [a], F. Gam[b], J.-Y. Saillard [b], and Yu. F. Oprunenko [a]**

[a] Chemistry Department, M.V. Lomonosov Moscow State University,

Vorob'evy Gory, 119899, Moscow, Russia

Fax: + 7 (495) 932 8846. Tel.: +1 (495) 939 2677;

E_mail: oprunenko@org.chem.msu.ru; oprunenko@mail.ru

http://fhmas.ru/ru/personal_oprunenko.htm

[b] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS, Universite de Rennes 1, 35042 Rennes cedex, France

Tel.: +33 223236728

E-mail: jean-yves.saillard@univ-rennes1.fr

http://www.scienceschimiques.univ-rennes1.fr/equipes/cti/

J. Organomet. Chem. Special Issue: "Organometallic Chemistry in Russia".

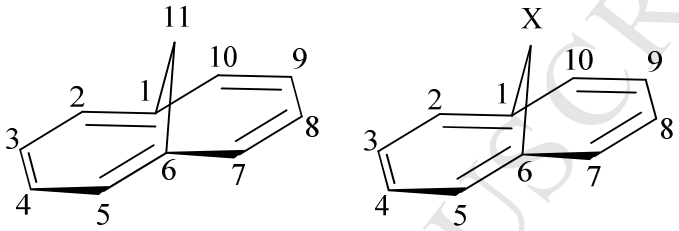
This article is dedicated to Prof. Irina P. Beletskaya in recognition of her merits in the field of the chemistry of organoelement compounds.

Abstract: The structural peculiarities (C1-C6 distances, bending of the ligand, conformation of organometallic group relative to the ligand, etc.), the isomerism and the mechanisms of inter-ring haptotropic rearrangements (IRHR) in $Cr(CO)_3$ and CoCp complexes of 1,6-methano[10]annulene were investigated by DFT. An activation barrier of 28.0 kcal/mol, lower than that corresponding to naphthalene, was computed for the η^6, η^6-IRHR in the mononuclear chromium complex. In the case of the mononuclear cobalt species, activations barrier of 33.8 and 31.3 kcal/mol were computed for the η^4, η^4-IRHR in the *trans* and *cis* isomers, respectively.

Keywords: DFT, transition metal complexes, polyaromatic hydrocarbons, annulenes, inter-ring haptotropic rearrangements IRHR.

Introduction

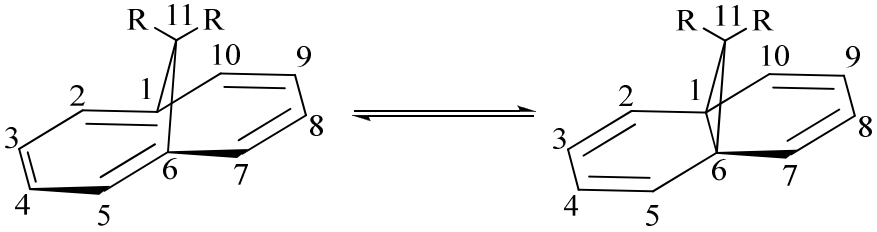
Recently, considerable progress has been made in the chemistry of annulene, including with respect to synthetic procedures [1]. In particular, many investigations were devoted to 1,6-methano[10]annulene **1**, first prepared by Vogel in 1964 as a simplest example of bridged [10]annulenes [2]. Substantial development was further observed in synthetic methodology for a number of other derivatives closely related to **1** with substituents at any of the C1-to-C10 carbon atoms, as well as with different X groups at the head of the bridge (Scheme 1) [3].



X=CH_2, CR_2, $C(CN)_2$, O, NH, SiH_2, $SiMe_2$, PH, S

Scheme 1

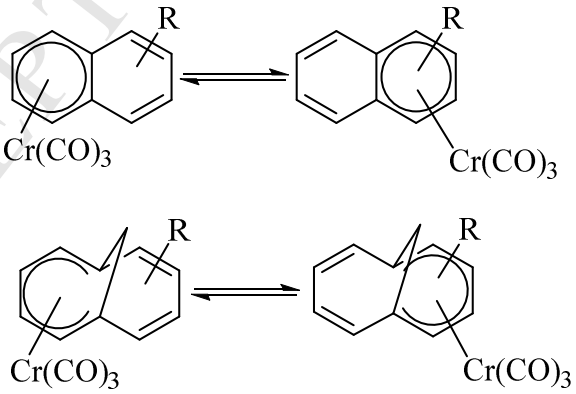
Such structures usually exhibit aromatic character with delocalized bonding. In some cases a temperature dependence of chemical shifts δ(C1-C6), both in liquid and in solid state NMR, was found and interpreted in terms of a fast tautomerism between the two forms displayed in Scheme 2 [4]. The existence of such a fast equilibrium between valent isomers in solution is widely dependent on the nature of the substituent R at C11. In this regard, a recent detailed theoretical investigation by Cremer and coworkers carried out at various levels of theory (including CASPT2) concluded to the existence of a single energy minimum, namely **1** (the aromatic structure, left side of Scheme 2), the tricyclic system (right side of Scheme 2) corresponding to a simple shoulder on the potential energy surface (PES) connecting the two structures [5]. In the case of R = Me, the same authors found an extremely flat PES, on which only one well is likely to be present, and to which a very large C1-C6 amplitude vibration is associated.



Scheme 2

It should be also noted that some substituted derivatives of **1** exist in solution mainly as tricyclic valent isomers with a well-distinguished C1-C6 bond, as for example for R = CN (**1-CN**), which was proven by spectroscopic and structural characterization. Indeed, the X-ray molecular structure of **1-CN** exhibits a C1-C6 distance of 1.542 Å, a value clearly featuring a single bond in the solid state [6-8].

Bicyclo[4.4.l]undecapenta-1,3,5,7,9-ene **1** (according to IUPAC nomenclature) occupies an intermediate position between cyclopolyolefines and aromatic hydrocarbons. The structure of **1** and relative compounds were characterized by a variety of experimental, e.g. X-ray [9] and theoretical methods [5-8, 10] and could be treated as an iso-π-electronic analogue of naphthalene, a common 10-π-electron polycyclic organometallic ligand. Being relatively cheap (≈ 300 $/g), **1**, together with its derivatives, constitute an interesting and prospective family of ligands for the preparation of a number of new transition-metal organometallic π-complexes, with different hapticities from η^1 to η^6, for the investigation of their chemical and catalytic activity as well as their dynamic behavior.



Scheme 3

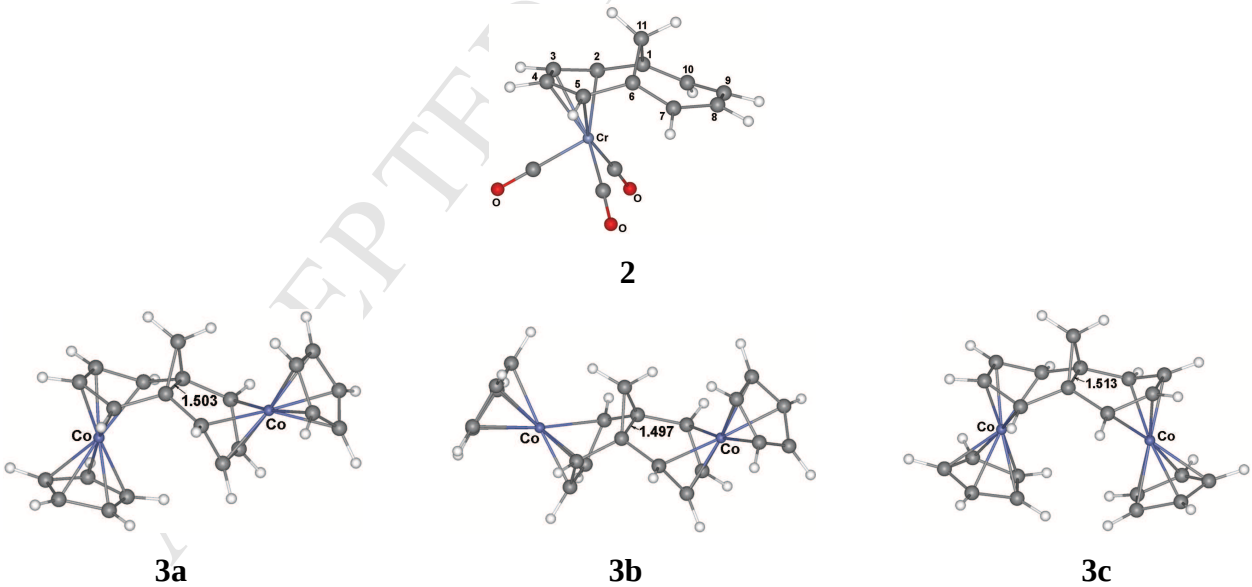
One of the possible dynamic processes which could exist in such complexes is inter-ring haptotropic rearrangements (IRHR) when an ML_n organometallic metal fragment migrates from a six-member ring in **1** to the other one. Such η^6,η^6-IRHR have been thoroughly investigated for

ACCEPTED MANUSCRIPT

complexes of different metals with substituted naphthalenes and some other polyaromatic hydrocarbons (PAH), both theoretically and experimentally [11]. In particular, such rearrangements have been extensively investigated in the case of chromium tricarbonyl complexes in various solvents. They proceed via a non-dissociative and intramolecular mechanism (Scheme 3, top) [12].

It should be noted that, though to a lesser extent, $\eta^n \rightleftharpoons \eta^n$-IRHR (n=2, 4) were also investigated both experimentally and theoretically for transition metals possessing hapticity lower than 6 ($\eta^2 \rightleftharpoons \eta^2$-IRHR for Ni, Rh, Ru, Pd and Os, and $\eta^4 \rightleftharpoons \eta^4$-IRHR for Ir), mainly for complexes of PAH. [13, 14] In the case of $\eta^2 \rightleftharpoons \eta^2$-IRHR (Ni, Rh, Ru, Pd and Os), the reaction proceeds quite rapidly and could be followed by means of DNMR. [13].

So far, only three π-complexes of **1** have been isolated: one mono-η^6-chromium [15] and two η^4-bis-cobalt [16]. The 18-electron diamagnetic complex (tricarbonyl((1,2,3,4,5,6-η)-l,6-methano[10]annulene)chromium) **2** was characterized by NMR [17] and X-ray crystallography [18] and has been the subject of a qualitative theoretical investigation [19]. The total evidence available proves that a delocalized system of π-bonds exists in **2**: The Cl-C6 bond is absent, and therefore **2** may be regarded as a η^6-π-complex, with the metal bonded in a similar manner as in its hexahapto cycloheptatriene relative. It is also strongly related to η^6-naphthalene tricarbonylchromium (Fig. 1).



2 **3a** **3b** **3c**

Fig. 1. Molecular structures of **2**, **3a** and **3b**, as characterized in the solid state, [**15, 16**] and the hypothetical isomer **3c** (DFT calculations, this work).

On the other hand, The X-ray structures of the bis-cobalt complexes of **1**, viz. **3a** and **3b** (Fig. 1), exhibit the expected η^4-coordination of the CpCo moieties which allow the metals

ACCEPTED MANUSCRIPT

reaching the 18-electron configuration. [16] The Cl-C6 distances of 1.512Å and 1.499Å in **3a** and **3b**, respectively, are characteristic of a single bond, and consequently of a "norcaradiene"-type tricyclic structure. The related mono-η^4-π-complexes of Co are unknown. These hypothetical species, (cyclopentadienyl(l,6-methano[10]annulene)cobalt) **4a,b,b'** (see below), appears probably in a first step during the synthesis of complexes **3a** and **3b**. Our DFT calculations (see below) confirm the stability of **4** and indicate that in one of its three low-energy isomers the Cl-C6 bond is surprisingly absent, contrarily to its bis-cobalt relatives **3a** and **3b**. Until now, no experimental or theoretical data are available on degenerate η^6,η^6-IRHR in **2** and diatropic η^4,η^4-simultaneous IRHR of two cobalt groups in **3a** and **3b** or of the single cobalt group in the corresponding elusive mono-π-complexe **4**.

In this paper, we investigate the possible η^6,η^6-IRHR in **2** theoretically by means of DFT (Scheme 3, bottom), in order to elucidate the reaction mechanisms and to estimate their activation barriers $\Delta G^{\#}$. The so far unknown mono-η^4-π-complexes of Co (**4**) are similarly investigated. We hope that this will encourage organometallic chemist to synthesize new transition metal complexes with different hapticities of a number of already available but neglected annulene family (Scheme 1), to find synthetic methods for their labeling, to provide corresponding kinetic measurements and thus systematically investigate both thermally [20] and optically [21] induced η^n, η^n-IRHR (n = 2, 4, 6) in such complexes.

2. Computational details

The geometries of molecules, transition states and intermediates were fully optimized by means of DFT calculations which were performed with the PRIRODA04 program written by D.N. Laikov [22], on the MBC100k cluster at the Joint Supercomputer Center (JSCC) (Moscow, Russia). The PBE functional [23] and the full electron basis sets L1 were used, where L1 stands for double set size. The number of contracted and primitive functions used in L1 is respectively {2,1}/{6,2} for H; {6,4,3,1}/{10,9,7,4} for C; {4,3,1}/{14,11,3} for P; {6,5,3,1}/{19,15,11,5} for Cr and Co. [24]. Stationary points on the potential energy surface (PES) were identified by analyzing Hessians. Corrections for zero-point energies were calculated in the harmonic approximation. The thermodynamic Gibbs function (free energy, G) at 298.15 K was calculated using the approximation of restricted rotator and harmonic oscillator. Reaction paths were found by the intrinsic reaction coordinate (IRC) method. The representations of the Kohn-Sham orbitals were made using the ADFGUI graphical interface [25] on results obtained from single-point calculations with the ADF package [26] on the PRIRODA04-optimized structures, employing the PBE functional, and using the standard TZ2P basis set.

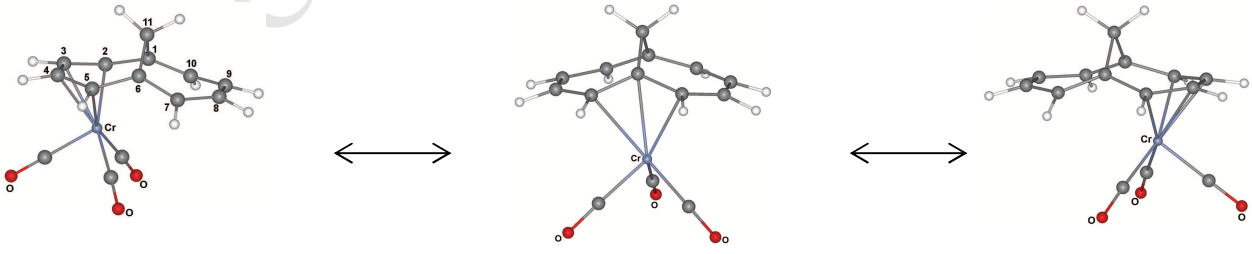
ACCEPTED MANUSCRIPT

1. Results and discussion

The geometries of the ligands **1** and **1-CN** were first optimized for comparison with the corresponding X-ray data from the literature, in order to test our calculation accuracy for this class of compounds. Selected bond distances and angles given in Table S1 show that our results are in a very good agreement with experiment. In particular, the deviation of **1** from planarity is well reproduced. The optimized C1-C6 distances are 2.271Å and 1.577Å for **1** and **1-CN**, respectively. The corresponding X-ray values are 2.235 Å and 1.542 Å, respectively.

The geometry of the chromium tricarbonyl complex **2** was also fully optimized. It is also in good agreement with its X-ray structure [18] (Table S1). In particular, the C-C bond alternation in the coordinated six-member rings which is characteristic for such complexes [9] is well reproduced. The Cr to C1 and C6 bond distances are a bit longer than the four other Cr-C bonds, as also observed in chromium tricarbonyl complexes of naphthalene [27] and anthracene [28], but it is clear that **2** has an η^6-structure.

On a subsequent stage we investigated the mechanism of the thermally induced η^6, η^6-IRHR in **2** (Fig. 2). The reaction proceeds without any intermediates via a single η^3-transition state: **2→TS2→2**. The **TS2** transition state, in which Cr, lying in a peripheral position, is bonded to C5, C6 and C7, is very similar to that found in η^6-(naphthalene)$Cr(CO)_3$. The computed activation barrier, $\Delta G^{\#}$ = 28.0 kcal/mol, evidences an easier shifting of the chromium tricarbonyl group along the ligand from one six-membered ring to the other than in related small PAH ($\Delta G^{\#} \geq$ 30 kcal/mol), including the strongly related complexes of substituted naphthalene. [11] This difference originates from the absence of a C1-C6 bond in the formally 14-electron species **2TS**, which provides it more structural flexibility, and therefore minimizes the electron deficiency. This is illustrated by the moderate difference between the frontier MO diagrams of **2** and **2TS** (Fig. 3).



ΔG=0 ΔG=28.0 (ωi=85.5i) ΔG=0

Fig 2. The stationary points along the η^6,η^6-IRHR in **2**. Free energies are given in kcal/mol and imaginary vibrational frequencies in cm^{-1}.

ACCEPTED MANUSCRIPT

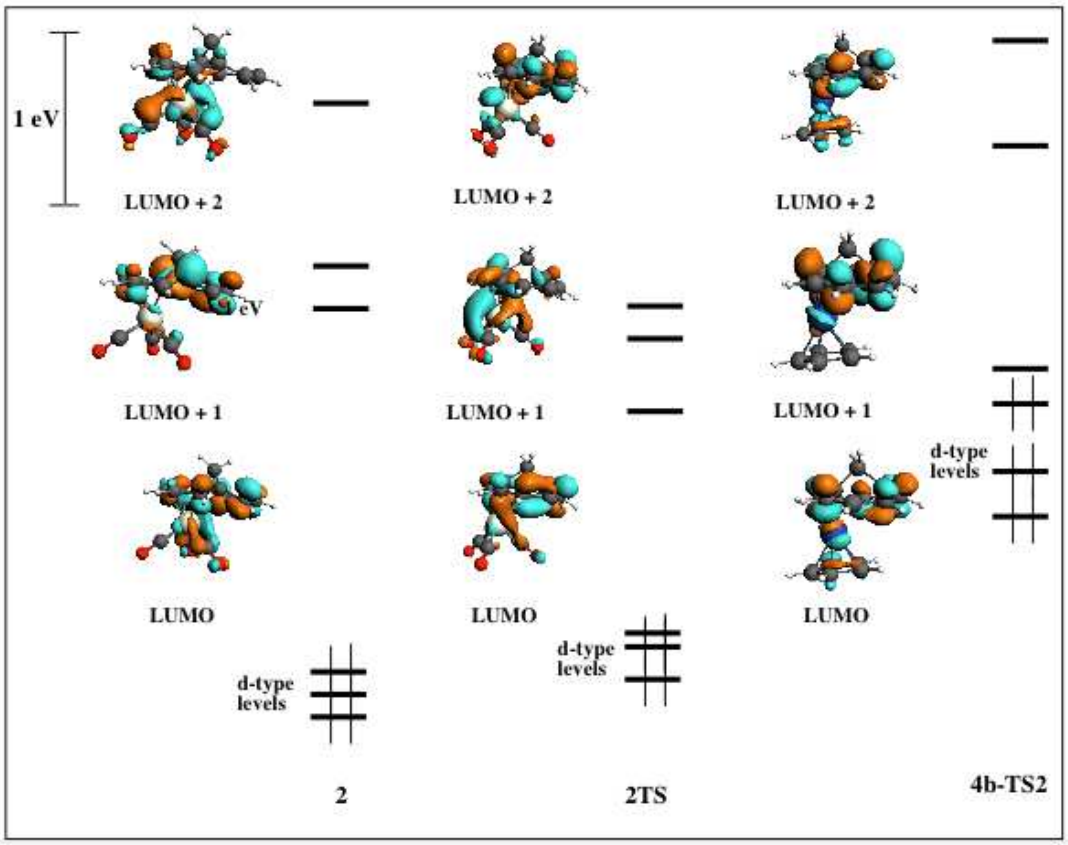


Fig. 3. Kohn-Sham frontier orbital diagrams of **2**, **2TS** and **4b-TS2.**

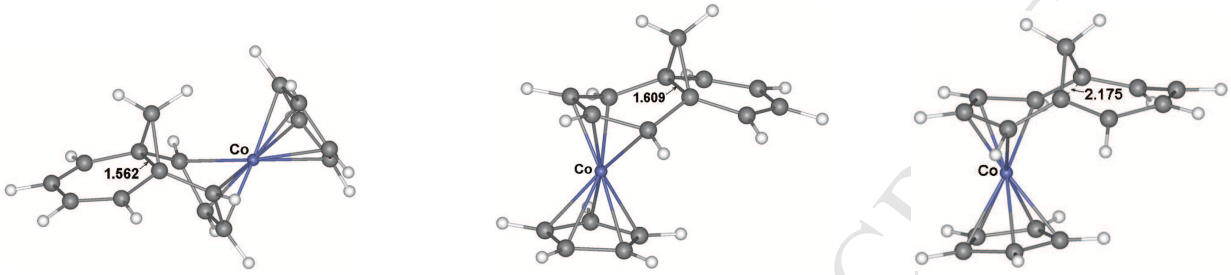
This difference makes transition metal complexes of **1** and their derivatives prospective candidates for the search of dynamic phenomena in such complexes, including thermally and optically induced IRHR.

The cobalt dinuclear isomers **3a** and **3b** were also investigated by DFT. Their optimized geometries agree very well with the experimental X-ray structures (see Fig. 1 and Table S2). The computed C1-C6 distance is 1.497Å and 1.503Å in **3a** and **3b**, respectively. The less sterically hindered *trans* complex **3a** is higher in energy than its *cis* counterpart **3a** by ΔG = 3.7 kcal/mol. This may be due to considerable folding of the ligand. We also find a third isomer **3c** (not experimentally reported, so far) with a *cis*-arrangement of the CoCp groups, both being *trans* to the CH_2 bridge (Fig. 1). This elusive complex, in which C1-C6 = 1.513Å, lies higher in energy than **3b** by ΔG=4.9 kcal/mol. This could explain why it was not found in the isomer synthetic mixture. [16]

Whereas the dinuclear cobalt species **3** are obviously unlikely to afford IRHR, this is not the case for their synthetically unknown mononuclear relatives **4**. Three low-energy isomers of **4** were found in which Co is η^4 coordinated (**4a-c**, see Fig. 3 and Table S2). It is noteworthy that for both **4a** and **4b** (*cis* and *trans* localization of Co with respect to the CH_2 bridge, respectively), a C1-C6 bond was found (1.562Å, and 1.609Å, respectively). **4a** is computed to be slightly more

ACCEPTED MANUSCRIPT

stable than its less sterically hindered isomer **4b** by ΔG =2.1 kcal/mol. Surprisingly, the third isomer **4b'** is structurally very similar to the *trans* isomer **4b**, except that it has no C1-C6 bond (corresponding distance: 2.175 Å). It is the lowest energy isomer, but lying below **4a** by only ΔG=0.1 kcal/mol, a negligible value. Moreover, the **4b** and **4b'** isomers are computed to be in equilibrium through a very low transition state lying at 2.1 kcal/mol (free energy) (Fig. 4) above **4b**. These results are in light with those obtained by Cramer on the free ligand **1**. [5]



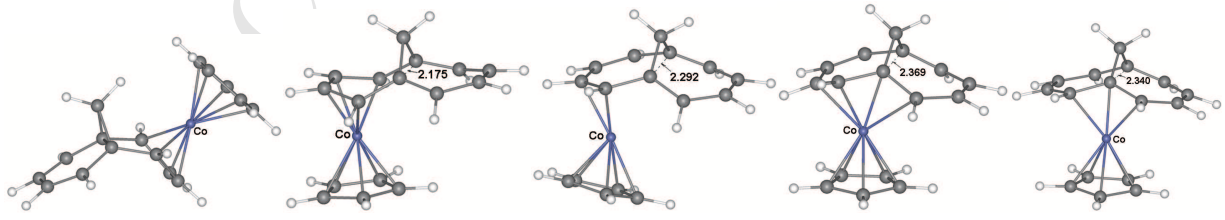
4a ΔG = 0 kcal/mol

4b ΔG =2.1 kcal/mol

4b' ΔG = - 0.1 kcal/mol

Fig 4. The three computed isomers of the mononuclear cobalt species.

In a following step, we investigate possible η^4,η^4-IRHR processes in the hypothetical *trans*-complexes **4b** and **4b'**, which are less sterically hindered than their *cis* isomer **4a** for allowing an easy rearrangement. It turns out that the low-energy pathway of **4b** was found to require first its easy isomerization into **4b'**. Therefore, both **4b** and **4b'** afford the same η^4,η^4-IRHR process. This IRHR is more complex than in the corresponding chromium complex **2**: The stationary states on the PES follow the sequence **4b´→4b´-TS1→4b´-IM→4b´-TS2→4b´-IM´→4b´-TS1´→4b´**, via three transition states (mirror symmetry) **4b´-TS1**, **4b´-TS1´**and **4b´-TS2** (two η^2-state and one η^3-states) and two mirror-symmetrical η^4-intermediate **4b´-IM** and **4b´-IM´** (Fig. 5).



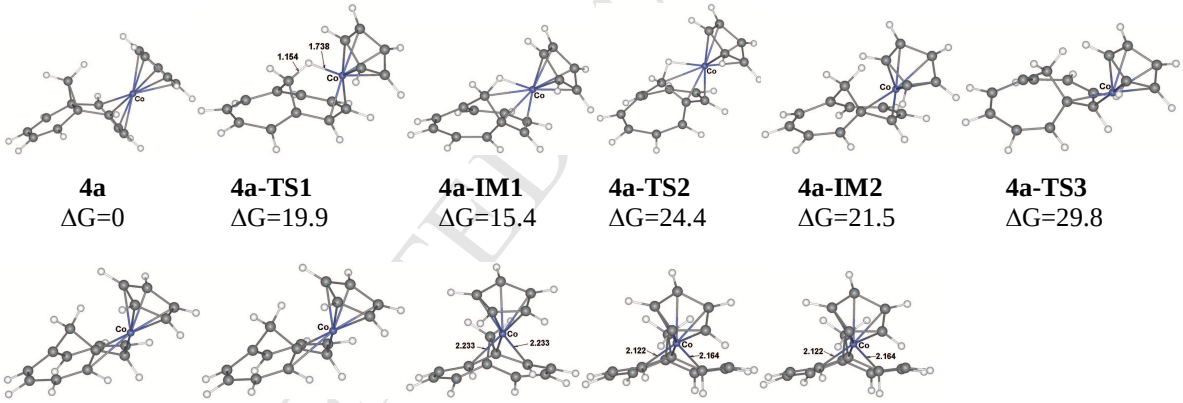
ΔG=0 **4a** ΔG=2.1 **4b´** ΔG=23.9 **4b´-TS1** ω_i= 118.0i ΔG=9.7 **4b´-IM** ΔG=31.3 **4b´-TS2** ω_i=398.2i

Fig 5. The stationary points along the η^4,η^4-IRHR in **4b'**. Free energies are given in kcal/mol and imaginary vibrational frequencies in cm^{-1}.

ACCEPTED MANUSCRIPT

The η^4,η^4-IRHR ($\Delta G^{\neq}$=31.3 kcal/mol, **4b´-TS2** ω_i=398.2i cm^{-1}) proceeds with a higher barrier than the corresponding η^6,η^6-IRHR for **2** ($\Delta G^{\neq}$=28.0 kcal/mol). Consistently, the **4b'-TS2** intermediate has a much lower HOMO-LUMO gap (Fig. 3), thus is less stabilized than its related **2TS** system. The reason is likely due to the less diffuse character of the cobalt orbitals which allows less extra stabilization in the transition states.

Complex **4a** being much more hindered than **4b´**, its η^4,η^4-IRHR proceeds also along the side edge of the annulene ligand, though in a much complex way than in **4b´**, with nine stationary states on the *first half* of the mechanism (Fig. 5, Table 2) before reaching transition state **4a-TS5** which has the maximal activation barrier ($\Delta G^{\neq}$=33.8 kcal/mol). Surprisingly, three of them exhibit an hydrogen *bridge* (*e.g.* **4a-IM1**). The next mirror images **4a-IM4** and **4a-IM4´** and the other seven symmetric stationary states (**4a-TS4´**, **4a-IM3´**, **4a-TS3´**, **4a-IM2´**, **4a-TS2´**, **4a-IM1´**, **4a-TS1´** and **4a**) from the second half of mechanism on the PES are connected through the above mentioned largest barrier of the whole process ($\Delta G^{\neq}$=33.8 kcal/mol). This barrier is considerably higher than the corresponding barrier for the less hindered η^4,η^4-IRHR in **4b´** ($\Delta G^{\neq}$=31.3 kcal/mol) (Fig. 6; some symmetric structures are omitted for the sake of shortness and simplicity).



4a ΔG=0 | **4a-TS1** ΔG=19.9 | **4a-IM1** ΔG=15.4 | **4a-TS2** ΔG=24.4 | **4a-IM2** ΔG=21.5 | **4a-TS3** ΔG=29.8

4a-IM3 ΔG=26.9 | **4a-TS4** ΔG=30.4 | **4a-IM4** ΔG=29.5 | **4a-TS5** ΔG=33.8 | **4a-IM4** → **4a**

Fig 6. The stationary points along the first half of the η^4,η^4-IRHR mechanism in **4a**. The second half (starting at **4a-IM4´**) is its mirror-image. Free energies are given in kcal/mol.

Conclusions

Transition-metal complexes of annulenes have considerable diversity in their structure, ligand flexibility, bonds, conformations and hapticities. In particular, DFT predicts that it is possible to stabilize one of the π-delocalized or "norcaradiene" ligand isomers by choosing the

ACCEPTED MANUSCRIPT

proper ML_n fragment(s) to graft to. Our calculations predict peculiar dynamical activity to such complexes, in particular with respect to IRHR.

Acknowledgments

YFO and IPG are grateful to Alexander von Humboldt Foundation (Alexander von Humboldt Stiftung, Bonn, Germany) for purchasing work station and other computer equipment on which DFT calculation were partially done. F.G. thanks the Région Bretagne for a PhD studentship (ARED NANOCLU).

ACCEPTED MANUSCRIPT

References

1. E.L. Spitler, Charles, A. Johnson II, M.M. Haley, Chem. Rev. 106 (2006) 5344-5386.
2. E. Vogel, H. D. Roth, Angew. Chem., Int. Ed. Engl. 3 (1964) 228-229.
3. W. Kitching, H.A. Olszowy, I. Shott, W. Adcock, D.P. Cox, J. Organomet. Chem. 310 (1986) 269-284.
4. H.C. Dorn, C.S. Yannoni, H.-H. Limbach, E. Vogel, J. Phys. Chem. 98 (1994) 11628-11629.
5. A. Humason, W. Zou, D. Cremer, J. Phys. Chem. A, 119 (2015) 1666−1682.
6. E. Vogel, Chimia 22 (1968) 121-125; R.C. Haddon, V.R. Haddon, L.M. Jackman, 16/2 (1971) Nuclear magnetic resonance spectroscopy of annulenes. In: NMR Spectroscopy of Annulenes. Fortschritte der Chemischen Forschung, Springer, Berlin, Heidelberg 103-220.
7. E. Vogel, T. Scholl, J. Lex, G. Hohlneicher, Angew. Chem. Int. Ed. Engl. 21 (1982), 869-870.
8. D. Cremer, B. Dick, Angew. Chem. Inr. Ed. Engl. 21 (1982) 865-866.
9. R. Bianchi, T. Pilati, M. Simonetta, Acta Cryst. B, 36 (1980) 3146-3148.
10. G.F. Caramori, K.T. de Oliveira, S.E. Galembeck, P. Bultinck, M.G. Constantino, J. Org. Chem. 72 (2007) 76-85.
11. a) Y.F. Oprunenko, Russ. Chem. Rev. 69 (2000) 683-704;
    b) Y.F. Oprunenko, I.P. Gloriozov, J. Organomet. Chem. 694 (2009) 1195-1211.
12. Y.F. Oprunenko, S. Malyugina, P. Nesterenko, D. Mityuk, O.J. Malyshev, J. Organomet. Chem. 597 (2000) 42-47.
13. a) R. Benn, R. Mynott, I. Topalović, F. Scott, Organometallics 8 (1989) 2299-2305;
    b) R.H. Crabtree, C.P. Parnell, Organometallics, 3 (1984), 1727-1731.
14. a) Y.F. Oprunenko, I.P. Gloriozov, Russ. Chem. Bull. 60, (2011) 213-222;
    b) Y.F. Oprunenko, I.P. Gloriozov, Russ. Chem. Bull. 59, (2010) 2061-2067. c) Y.F. Oprunenko, I.P. Gloriozov, Russ. J. Phys. Chem. A, 86 (2012) 979-986.
15. a) E.O. Fischer. H. Rühle, E. Vogel. W. Grimme, Angew. Chem. Int. Ed. Eng1. 5 (1966) 518-519; b) Y.F. Oprunenko, M.D. Reshetova, S.G. Malyugina, Y.A. Ustynyuk, N.A. Ustynyuk, A.S. Batsanov, Y.T. Struchkov, Organometallics, 13, (1994) 2284-2290.
16. P. Mues, R. Benn, C. Krüger, Y.H. Tsay, E. Vogel, G. Wilke, Angew. Chem. Int. Ed. Eng. 21 (1982), 868-868; X-ray data stored: Fachinformationszentrum Energie Physik Mathematik, D-7541 Eggenstein-Leopoldshafen (CSD 50 247).

ACCEPTED MANUSCRIPT

17. H. Günther, R. Wenzl, W. Grimme, J. Amer. Chem. Soc. 91 (1969) 3808-3812.
18. P.E. Baikie, O. S. Mills, Chem. Comm. 19 (1966) 683-684.
19. T.A. Albright, R. Hoffmann, P. Hofmann, Chem. Ber. 111 (1978) 1591-1602.
20. Y.F. Oprunenko, S.G. Malugina, Y.A. Ustynyuk, N.A. Ustynyuk, D.N. Kravtsov, J. Organomet. Chem. 338 (1988) 357-368.
21. a) G. Zhu, J.M. Tanski, D.G. Churchill, K.E. Janak, G. Parkin, J. Amer. Chem. Soc. 124 (2002) 13658-13659. b) G. Zhu, K.E. Janak, J.S. Figueroa, G. Parkin, J. Am. Chem. Soc, 128 (2006) 5452-5461
22. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 77 (1996) 3865−3868.
23. Dyall, K. G., J. Chem. Phys. 1994, 100, 2118−2127.
24. a) D.N. Laikov, Chem. Phys. Lett., 2005, 416, 116−120; (b) D.N. Laikov, Chem. Phys. Lett. 1997, 281, 151−156; (c) D.N. Laikov, Yu.A. Ustynyuk, Russ. Chem. Bull., Int. Ed., 2005, 54,820−826.
25. GUI 2013, SCM, Amsterdam, The Netherlands, http://www.scm.com.
26. a) G. te Velde, F.M. Bickelhaupt, S.J.A. van Gisbergen, C. Fonseca Guerra, E.J. Baerends, J.G. Snijders, T. Ziegler, *J. of Comput. Chem.,* 22 (2001) 931-967. b) C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, *Theo. Chem. Acc*. 99 (1998) 391-403. c) ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com
27. V. Kunz, W. Nowacki, Helv. Chim. Acta 50 (1967) 1052–1056.
28. F. Hanic, O.S. Mills, J. Organomet. Chem. 11 (1968) 151–158.
29. M. Sodeoka, M., M. Shibasaki, 7 (1993) 643-658.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

First DFT study of the structure and dynamics of chromium and cobalt complexes of 1,6-methano[10]annulene.

First mechanistic approach (with activation energies) of inter-ring haptotropic rearrangements in such complexes.

ACCEPTED MANUSCRIPT