

## Review

## Benzannulated homologues of cyclopentadienide as ligands in organometallic chemistry

F. Pammer<sup>a,\*</sup>, W.R. Thiel<sup>b</sup><sup>a</sup> Institut für Organische Chemie II und Neue Materialien, Universität Ulm, Albert Einstein Allee 11, 89081 Ulm, Germany<sup>b</sup> Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße 54, 67663 Kaiserslautern, Germany

## Contents

1. Introduction .....	15
2. Properties of benzannulated Cp <sup>-</sup> -anions .....	16
2.1. General considerations .....	16
2.2. Coordination chemistry of simple Cp-analogs .....	17
2.3. Aromatic stabilization of Cp-anions: NICS-studies .....	17
3. Ligands and transition metal complexes .....	19
3.1. Benz[e]- and benz[f]indenide .....	19
3.1.1. Ligand synthesis .....	19
3.1.2. Transition metal complexes .....	19
3.2. Bi- and trifunctional Cp-analogs .....	20
3.2.1. Dicyclopentahelicenes .....	20
3.2.2. Triindene and truxene .....	20
3.2.3. Dibenzopentalenes .....	20
3.2.4. Benz[cd]azulene .....	21
3.3. Benzofluorenes and related ligands .....	21
3.4. Dibenzofluorenes: Dibenzo[c,g]fluorenone .....	22
3.4.1. Ligand synthesis .....	22
3.4.2. Transition metal complexes .....	23
3.4.3. Electronic structure and reactivity of the c,g-Dbf anion and c,g-Dbf complexes .....	23
3.5. Tetrabenzofluorenone .....	25
3.5.1. Ligand synthesis .....	25
3.5.2. Transition metal complexes .....	25
3.6. Cyclopent[a]acenaphthylenide .....	25
3.6.1. Synthesis of cyclopent[a]acenaphthylene .....	25
3.6.2. Transition metal complexes .....	25
3.7. Cyclopenta[l]phenanthrene and Cyclopenta[c]phenanthrenes .....	26
3.7.1. Ligand synthesis .....	26
3.7.2. Transition metal complexes .....	26
3.8. 'Non-classic' ligand structures .....	27
3.9. Fullerene fragments: corannulene and sumanene .....	27
4. Conclusion .....	28
Acknowledgments .....	28
References .....	28

## ARTICLE INFO

## Article history:

Received 1 July 2013

Accepted 20 August 2013

Available online 7 September 2013

## ABSTRACT

Organometallic coordination chemistry is dominated by the pervasive cyclopentadienide (Cp<sup>-</sup>) ligand and its benzannulated derivatives indenide (Ind<sup>-</sup>) and fluorenone (Flu<sup>-</sup>). However, in the past decades a diverse coordination chemistry involving higher benzannulated homologues has developed. In this review, the synthesis and electronic structure of  $\pi$ -extended Cp-ligands will be discussed, as well as the

\* Corresponding author. Tel.: +49 7315022855.

E-mail addresses: [frank.pammer@uni-ulm.de](mailto:frank.pammer@uni-ulm.de), [fpammer@gmx.com](mailto:fpammer@gmx.com) (F. Pammer).

Keywords:  
NICS calculations  
Metallocenes  
Polycyclic aromatic hydrocarbons  
Helicenes  
 $\pi$ -Complexes

factors that affect complex stability. An overview of known transition metal complexes containing both 'classic' benzannulated Cp-ligands, and 'non-classic' ligands derived from polycyclic arenes will be given.

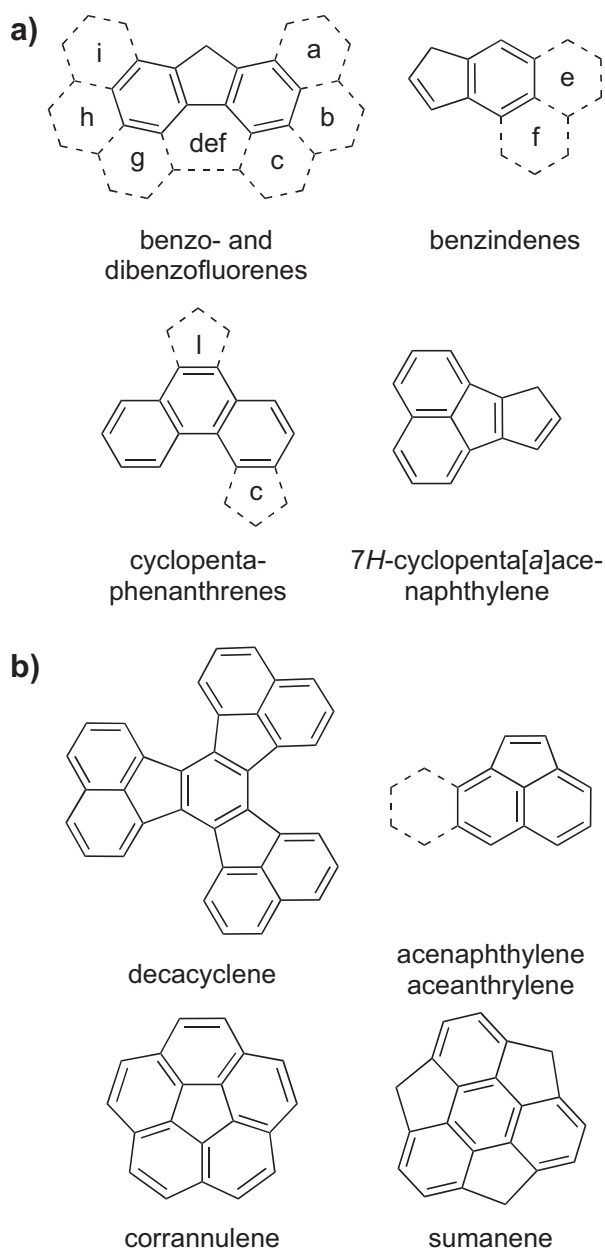
© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

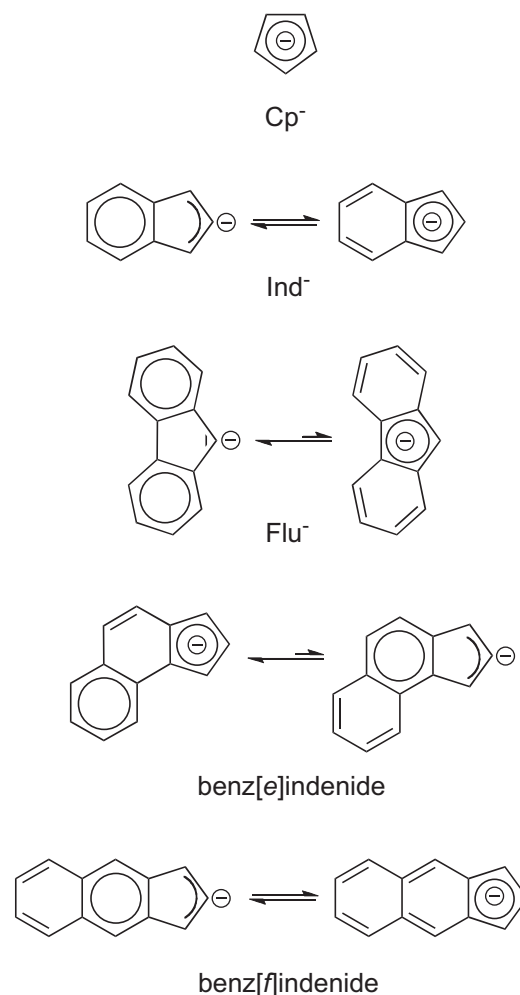
Benzannulation of aromatic compounds leads to extended  $\pi$ -systems which are of decisive importance for novel materials, finding application in organic electronics and photo physics. On the other hand, the cyclopentadienide anion ( $\text{Cp}^-$ ) is the ligand system that mainly stimulated the development of organometallic chemistry beginning with the discovery of ferrocene in the early 1950s

[1]. It is therefore not astonishing, that benzannulated cyclopentadienides have attracted the attention of chemists from the very beginning of organometallic chemistry. The most simple members of this series, indenide ( $\text{Ind}^-$ ) and fluorene ( $\text{Flu}^-$ ) have found to be introduced as ligands for (transition) metal complexes already in the late 1950s and early 1960s [1,2]. Their coordination chemistry as well as the application of the derived metal compounds e.g. in catalysis were covered by a series of review articles [3,4] and therefore shall not be matter of this review.

We here will focus on the organometallic chemistry of benzofluorenes, benzindenenes and related Cp-analog ligands (Chart 1a) as well as of selected non-classic anionic  $\pi$ -ligands (Chart 1b). The extended  $\pi$ -systems of these ligands give rise to interesting physical properties that were elucidated by means of experiment and theory. These properties and central aspects of ligand and complex synthesis will be outlined. To keep the scope of this manuscript manageable, the coordination chemistry of anionic fullerenes [5], carboranes [6], and uncharged  $\eta^6$ -arene complexes [7] have not been included.



**Chart 1.** Organometallic ligand structures covered in this survey. (a) 'Classic'  $\text{Cp}^-$  analogs. The letters correspond to benzo-rings annulated at the respective position according to the rules of nomenclature. (b) Examples for other ligand structures.



**Scheme 1.** Aromatic resonance structures of  $\text{Cp}^-$ -anions.

Download English Version:

<https://daneshyari.com/en/article/1300970>

Download Persian Version:

<https://daneshyari.com/article/1300970>

[Daneshyari.com](https://daneshyari.com)