

Review

Bonding in pentalene complexes and their recent applications

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ABSTRACT

Molecular orbital (MO) theory is used to describe the bonding in transition metal pentalene complexes in a variety of its coordination modes. The various MO models account for structural parameters and lead to simple rules for electron counting in pentalene complexes. Recent applications of pentalene complexes are also reviewed, in the areas of small molecule activation and catalysis and as molecular models for conducting organometallic polymers.

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Abbreviations: BH, bridgehead; COT, cyclooctatetrenyl, C₈H₈; COT⁺, C₈H₆(1,4-SiⁱPr₃)₂; Cp', generic abbreviation for a cyclopentadienyl ligand; Cp, C₅H₅; Cp⁺, C₅Me₅; Ct, ring centroid; CV, cyclic voltammetry; DFT, density functional theory; FA, fold angle; Flu, fluorenyl, C₁₃H₉; HA, hinge angle; HOMO, highest occupied molecular orbital; Ind, indenyl, C₉H₇; IVCT, inter-valence charge transfer; Ln, lanthanide metal; MAO, methylaluminoxane; MO, molecular orbital; MV, mixed-valence; NIR, near infra-red; NWT, non-wingtip; PE, Photoelectron; Pn', generic abbreviation for a pentalene ligand; Pn, C₈H₆; Pn⁺, C₈Me₆; Pn⁺, C₈H₄(1,4-SiⁱPr₃)₂; RHF, restricted Hartree-Fock; SOMO, singly occupied molecular orbital; TMEDA, N,N,N',N'-tetramethylethylenediamine; Tp^{Me2}, hydrotris(3**5-dimethylpyrazolyl)borate; VE, valence electron; WT, wingtip.

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1. Introduction

In the last 20 years the use of pentalene as a ligand in transition metal organometallic chemistry has become more frequent, largely due to improvements in the synthesis of suitable precursors. The broad areas in which pentalene complexes have found application range from small molecule activation and catalysis to molecular models for conducting polymers in materials chemistry. Previous articles have reviewed the syntheses and structures of pentalene complexes [1,2] and described bonding in reported and hypothetical complexes in the context of their electron numbers [3]. In this article we present bonding models for pentalene complexes in a variety of its coordination modes and review certain aspects of their chemical and physical properties.

2. Pentalene and its dianion

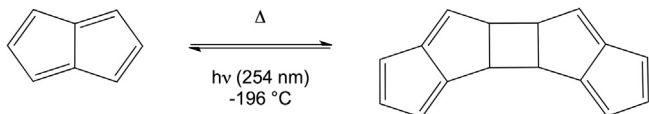
Early speculation suggested pentalene might possess aromatic character [4]. Prediction of its polyolefinic nature [5], subsequently confirmed by MO calculations, has been verified experimentally [6]. Pentalene, C_8H_6 , is an eight carbon molecule that can be considered as the double-ring fused relative of cyclopentadiene, or as cyclooctatetraene with a 1,5-transannular bond [7]. The neutral species is an 8π Hückel *anti*-aromatic hydrocarbon with a double-bond alternant C_{2h} structure, and the molecule has only been isolated in matrices at very low temperatures [6]. Neutral pentalene is unstable above $-196^\circ C$ and undergoes a rapid Diels-Alder reaction to the [2+2] dimer (Scheme 1) [8]. Introduction of bulky substituents inhibits dimerisation, such that hexaphenyl pentalene [9] and 1,3,5-tri-*t*-butyl pentalene have both been isolated at room temperature [10].

In contrast the dianionic form of pentalene, $[C_8H_6]^{2-}$, is a 10π aromatic species and is consequently thermally stable at room temperature. The pentalenyl dianion has been crystallographically characterised as a dilithiated dimethoxyethane (DME) adduct $[Li(DME)]_2Pn$ [8], and the carbocycle shows D_{2h} symmetry, with lithium ions in an η^5, η^5 -coordination mode on opposite faces of the planar pentalene ring.

The π symmetry MO of $[C_8H_6]^{2-}$ are represented in Fig. 1 together with those of $[C_8H_8]^{2-}$. The ten π electrons occupy up to π_5 , which is non-bonding. The orbitals principally involved in covalent bonding to metals are π_4 and π_5 , which lie close in energy. The closely related orbitals of the cyclooctatetraene dianion, $[C_8H_8]^{2-}$, are degenerate; the formation of the transannular bond in pentalene imparts bonding character to π_4 and lowers it in energy with respect to π_5 . In contrast π_3 is raised in energy compared to π_2 and becomes of suitable energy to mix with metal orbitals.

3. Coordination modes of pentalene complexes

In this review the Covalent Bond Classification (CBC) method is employed [12,13], wherein a complex is denoted by a formula ML_r-



Scheme 1. Dimerisation of neutral pentalene [8].

X_xZ_z . M indicates a central atom most commonly a metal. All ligands are treated as neutral, without charge, and L denotes a 2 electron donor ligand, X a one electron donor ligand and Z a zero electron donor ligand. When acting as a ligand with transition metals pentalene has a maximum of 8 bonding electrons and shows a variety of multihaptic bonding modes (Fig. 2). The π electron system of neutral pentalene is equivalent to three donor double bonds and two unpaired electrons hence it classifies as an L_3X_2 ligand when coordinated to a metal in an η^8 mode.

4. η^8 -mode of bonding

4.1. Structural studies of η^8 -pentalene complexes

The η^8 -mode, in which all eight carbons are involved in bonding to the metal (Fig. 2(a)), leads to a folding of the ligand about its C–C bridgehead bond towards the metal centre. This is commonly encountered in pentalene complexes with f- and early d-block elements, as the ‘umbrella’-like effect of the folded ligand aids the steric stabilisation of the metal centres [1]. This distortion from planarity is accompanied by a loss of aromaticity, and is quantified by the ‘fold angle’ (FA in Fig. 3), which is dependent on both steric and electronic factors.

In general, for complexes with a given ligand set the FA may be simply related inversely to the size of the central metal [1]. For example, $(\eta^8-Pn)MCp$ complexes show a marked increase in FA from $M = Ti$ (37.0°) to V (43.0°) in accordance with the decreasing ionic radii (0.670 vs 0.640 Å respectively for 6-coordinate M^{3+} ions) [14]. However comparing the series of group 4 permethylpentalene complexes $(\eta^8-Pn^*)MCpCl$ and $(\eta^8-Pn^*)MCp_2$ for $M = Ti, Zr, Hf$, [15] the titanium and hafnium species have near identical FAs, despite the considerably larger size of Hf^{4+} (0.71 Å) relative to Ti^{4+} (0.605 Å) [15]. O’Hare and co-workers attributed this to the more diffuse nature of the atomic orbitals for the 3rd row transition metal leading to better orbital overlap with Pn^* , which compensates for the loss in aromaticity as the ligand folds away from planarity [15]. Within a series of complexes bearing the same metal and pentalene ligand, the FAs increase as electron deficiency at the metal centre increases. For example, the mononuclear tantalum(V) complexes $(\eta^8-Pn^*)TaCl_xMe_{3-x}$ for $x = 0-3$, which show a small but discernable increase in FA as the number of electron withdrawing chloride ligands increases [16]. Furthermore, the electronic properties of the pentalene ligand itself have an effect on the FA, as first shown by comparison of the FAs for $(\eta^8-Pn)ZrCpCl$ (33.0°) [17] and $(\eta^8-Pn^*)ZrCpCl$ (30.7°) [15,18], which provides evidence for the enhanced donor ability of the permethylated ligand.

The group 4 bis(permethylpentalene) sandwich complexes $M(\eta^8-Pn^*)_2$ ($M = Zr, Hf$) have recently been synthesised and structurally characterised [19]. The average M–Ct (Ct = ring centroid) distances (2.149(7) Å Zr; 2.126(6) Å Hf) are greater than those for previously reported Pn^*Zr and Hf complexes [15,20], attributed to the greater steric demand of two Pn^* ligands preventing closer approach to the metal centre. The C–C distances and the FA about the carbon skeleton in $M(\eta^8-Pn^*)_2$ are in good agreement with those predicted for $M(\eta^8-Pn)_2$, despite the extra inductive effect of the methyl groups on Pn^* . However, the twist angle (θ in Fig. 3) between the Pn^* ligands ($41.6(5)^\circ$ Zr; $42.8(6)^\circ$ Hf) is less

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