

Organometallic pentalene complexes*

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Abstract: There has been a recent renaissance in the organometallic chemistry of pentalene, following the discovery of the first complexes incorporating pentalene η^8 -ligated to a single metal center. This short review outlines recent work in the author's laboratory on the preparation of silylated pentalene ligands and the subsequent synthesis of novel, monometallic, and bimetallic pentalene sandwich and half-sandwich complexes of the f- and d-block elements.

INTRODUCTION

Of the two, dianionic 10π -electron aromatic 8-membered ring systems, the cyclooctatetraene ligand has historically played the most important role in early transition-metal and f-element organometallic chemistry—particularly for the actinides [1]. The second, the pentalene dianion (Fig. 1a), received comparatively little attention until recently. Early work in this area described binuclear, transition-metal systems that contain the planar pentalene dianion, e.g., $[M_2(\eta^5, \eta^5-C_8H_6)_2]$ ($M = Co, Ni$) [2] $[(\eta^3-C_3H_5)Ni(\eta^5, \eta^5-C_8H_6)Ni(\eta^3-C_3H_5)]$ [3], and $[(\eta^5-C_5Me_5)M(\eta^5, \eta^5-C_8H_6)M(\eta^5-C_5Me_5)]$ ($M = Fe, Co, Ni$) [4], in which the two metal fragments bind to the adjacent 5-membered rings of the pentalene ligand in a *trans* disposition (Fig. 1b). Binding of two transition-metal fragments on the same face of the pentalene ligand was also reported in 1975 by Stone *et al.*, e.g., $[\{Ru(MMe_3)(CO)_2\}_2(\eta^5, \eta^5-C_8H_6)]$ ($M = Si, Ge$), $[Ru_3(CO)_8(\eta^5, \eta^5-C_8H_6)]$, and $[Ru_3(CO)_8(\eta^5, \eta^5-C_8H_4\{SiMe_3-1,4\}_2)]$ [5], but results in folding of the pentalene about the bridgehead C–C bond by *ca.* 10° (Fig. 1c).

Binding to a *single* metal center in an η^8 mode requires a much more extreme distortion in the pentalene ligand than the 10° folding seen in $[Ru_3(CO)_8(\eta^5, \eta^5-C_8H_6)]$ (Fig. 1c); in the d-block elements, size and 16/18-electron rule considerations indicate that this is most likely to be achieved with an early metal. In 1997 we described the synthesis of $[Ta(\eta^8-C_8H_4\{SiMe_3-1,4\}_2)Cl_3]$, formed by protonolysis of $[Ta(\eta^8-C_8H_6\{SiMe_3-1,4\}_2)Me_3]$ with $[R_3NH]Cl$, which represented the first example of such ligation for a pentalene ligand (Fig. 2a), and in which the fold angle is 33° [6]. Shortly thereafter,

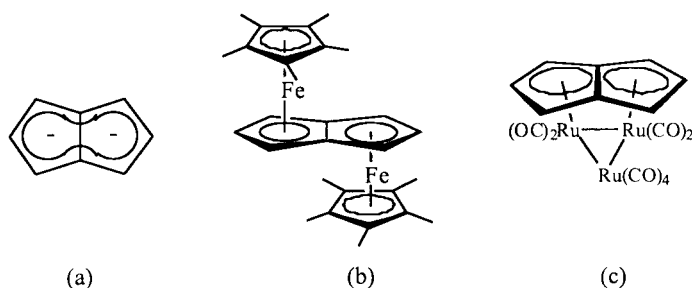


Fig. 1

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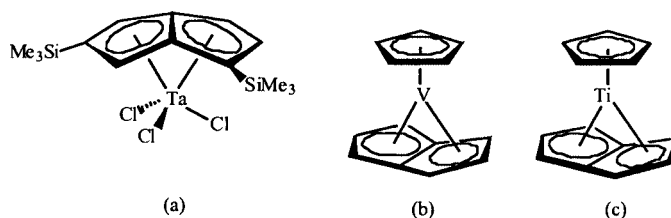


Fig. 2

Jonas reported several η^8 , unsubstituted pentalene complexes, e.g., of V [7] (Fig. 2b) and Ti [8] (Fig. 2c), with pentalene fold angles of 43 and 37° respectively; the fold angle can thus be seen to be simply related inversely to the size of the central metal.

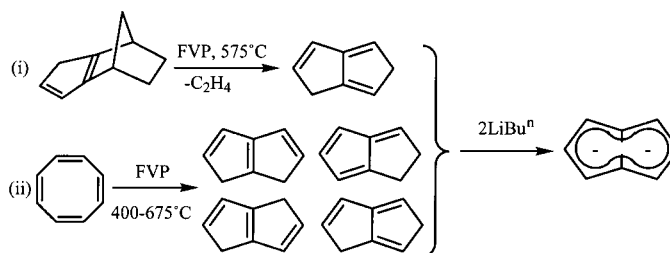
SILYLATED PENTALENE LIGANDS

The formation of $[\text{Ta}(\eta^8\text{-C}_8\text{H}_6\{\text{SiMe}_3\text{-1,4}\})_2\text{Me}_3]$ proceeds in modest yield, and by a mechanism which, at present, is not fully understood; accordingly, it seemed appropriate to develop a rational synthesis of bis(trialkylsilyl)pentalene ligands.

Synthesis

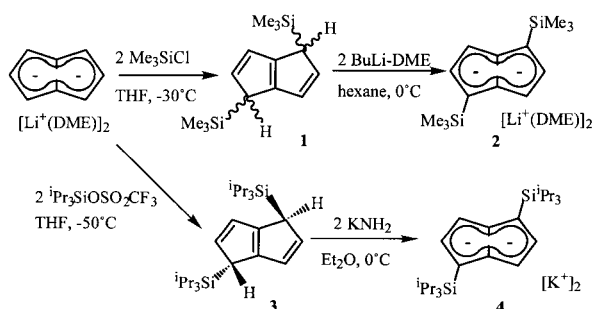
By analogy with the synthesis of the bis(trimethylsilyl)cyclooctatetraene dianion, via reaction of the cyclooctatetraene (COT) dianion with chlorotrimethylsilane and subsequent deprotonation of the resultant 1,4-bis(trimethylsilyl)cyclooctatriene [9], the starting point for the synthesis of trialkylsilyl pentalene derivatives was the pentalene dianion. The synthesis of the latter has been effected by a number of routes (Scheme 1): (i) the original method of Katz via the flash vacuum pyrolysis (FVP) of iso-dihydrodicyclopentadiene and subsequent deprotonation of the resultant 1,3-dihydropentalene with $n\text{BuLi}$ in tetrahydrofuran (THF) [10]; (ii) FVP of cyclooctatetraene under a variety of conditions to yield a mixture of isomeric dihydropentalenes [11] and their collective deprotonation with $n\text{BuLi}$ -DME to afford crystallographically characterized $[\text{C}_8\text{H}_6][\text{Li}(\text{DME})]_2$ [12]; (iii) a non-FVP, multistep synthesis based on ring expansion of cycloheptatriene has also been described [13]. We chose to employ route (ii); previously reported temperatures for this pyrolysis vary from 400–675 °C, with optimum conversion at 550–600 °C to give dihydropentalenes in up to 90% (nonisolated) yield [11]. In our hands, and under carefully optimized conditions (N_2 flow rate $1.5 \text{ cm}^3 \text{ min}^{-1}$, operating pressure 1.0 mbar, COT introduction rate $0.5 \text{ cm}^3 \text{ h}^{-1}$, pyrolysis temperature 615 °C) a typical isolated yield of $[\text{C}_8\text{H}_6][\text{Li}(\text{DME})]_2$ was 87% (based on COT), and on a scale of some 25 gm.

Treatment of $[\text{C}_8\text{H}_6][\text{Li}(\text{DME})]_2$ in THF with 2 equiv of chlorotrimethylsilane affords the pale yellow, thermally sensitive bis(trimethylsilyl)dihydropentalene $\text{C}_8\text{H}_6(\text{SiMe}_3\text{-1,4})_2$, **1**, as a mixture of racemic and meso isomers (Scheme 2).



Scheme 1

1 may be deprotonated with $^n\text{BuLi}$ -DME to give the dilithium bis(trimethylsilyl)pentalenide $[\text{C}_8\text{H}_4(\text{SiMe}_3\text{-}1,4)_2][\text{Li}(\text{DME})_2]_2$, **2** (Scheme 2). We were also interested in the synthesis of a bulkier variant of **2**, as a potential ligand in f-element chemistry: thus $[\text{C}_8\text{H}_6][\text{Li}(\text{DME})_2]_2$ was treated with tri(isopropyl)silyl triflate at *ca* -50°C in THF to afford $\text{C}_8\text{H}_6(\text{Si}^i\text{Pr}_3\text{-}1,4)_2$, **3** (Scheme 2). Only the *trans* (meso) isomer of **3** is formed, which we ascribe to the steric influence of the $-\text{Si}^i\text{Pr}_3$ groups during attack on $[\text{C}_8\text{H}_6][\text{Li}(\text{DME})_2]_2$; the former also confer a fair degree of thermal stability on **3**. It was felt desirable to prepare the dipotassium salt of the bis(triisopropylsilyl)pentalene dianion, again for reasons associated with the intended use of the latter in f-element chemistry where employment of lithium transfer reagents often results in salt incorporation and formation of “ate” complexes. Hence **3** was deprotonated with potassium amide in ether to give an essentially quantitative yield of base-free $[\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,4)_2]\text{K}_2$, **4** (Scheme 2).



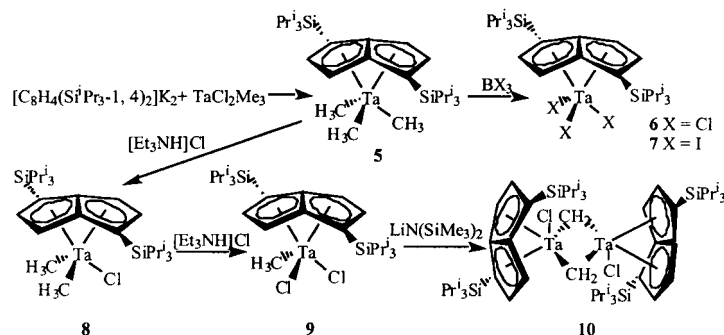
Scheme 2

Stereochemical features

The 1,4-bis(silylated) pentalene dianions have C_2 -symmetry and are facially enantiotopic; these features have important consequences for their derived metal complexes. For example, a sandwich compound incorporating two such ligands would be expected to exist in four diastereomeric forms (meso and racemic isomers of the staggered and of the eclipsed sandwich structures) although, in practice only two are observed since steric interactions between the silyl substituents preclude the other two (*vide infra*).

TRANSITION-METAL COMPLEXES OF SILYLATED PENTALENE LIGANDS

Half-sandwich compounds of tantalum



Scheme 3

The availability of $[\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,4)_2]\text{K}_2$ as a transfer reagent has enabled the rational synthesis of a range of mono(pentalene) complexes of Ta(V), summarized in Scheme 3 [14]. Comparison of the X-

ray structures of the series of halide, mixed halide/alkyl and trialkyl complexes **5**, **7**, **8**, and **9** reveals a trend in the pentalene fold angles, $9 > 7 > 8 > 5$, while the bridgehead carbon to metal distances remain essentially constant. Thus, the “wingtip” carbons on the pentalene ligand bend down towards the metal center as a direct function of the electronegativity of the other ligands bound to tantalum; this we ascribe to the resultant alleviation of electron deficiency at tantalum. Deprotonation of the dichloromethyl complex **9** with lithium bis(trimethylsilylamide) affords the novel bridging carbene complex **10** as, remarkably, the only observed diastereoisomer.

Bimetallic sandwich compounds

Bimetallic pentalene sandwich compounds were originally proposed by Katz in 1972 (Fig. 3, **11**), but not structurally authenticated [2]. However, using the $C_8H_4(Si^iPr_3-1,4)_2$ ligand, we have been able to prepare a series of such compounds which can be structurally characterized and are hydrocarbon soluble. Thus, treatment of $[Mo_2(OAc)_4]$ with $[C_8H_4(Si^iPr_3-1,4)_2]K_2$ gives **12** [15]; $[Rh_2(OAc)_4]$ and $[Pd(COD)Cl_2]$ react similarly to give **13** and **14** respectively (Fig. 3) [16].

The bonding in the molybdenum complex **12** has been examined by photoelectron spectroscopy and density functional theory (DFT) methods and shown to be very covalent, resembling that in simple metallocenes [17]. A bond order of 2 in this d^4-d^4 dimer is indicated, with the remaining 4 d electrons being localized in two, largely metal based orbitals **13** and **14**, which are also diamagnetic, have bond orders of 1 and 0 respectively.

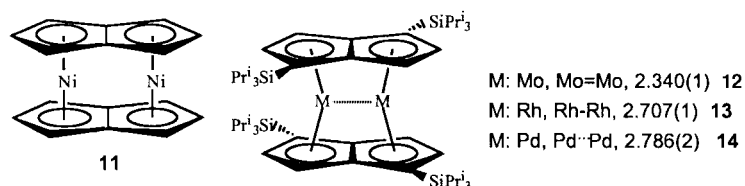


Fig. 3

F-ELEMENT COMPLEXES OF SILYLATED PENTALENE LIGANDS

Sandwich complexes

The reaction between $ThCl_4$ or UCl_4 and two equivalents of $[C_8H_4(Si^iPr_3-1,4)_2]K_2$ affords the novel actinide sandwich complexes **15** and **16**, respectively (Fig. 4) [18]. The latter exist in distinct, non interconvertible staggered (meso form) and semi-eclipsed (chiral form) isomers; the other two possible diastereoisomers (the chiral form of the staggered isomer and the meso form of the eclipsed isomer) are precluded on steric grounds, as discussed earlier. Photoelectron spectroscopy and DFT studies show the bonding in these compounds to be qualitatively similar to that in the cyclooctatetraene analogs, with the most important contribution arising from δ -symmetry interactions between metal 6d/5f orbitals and the

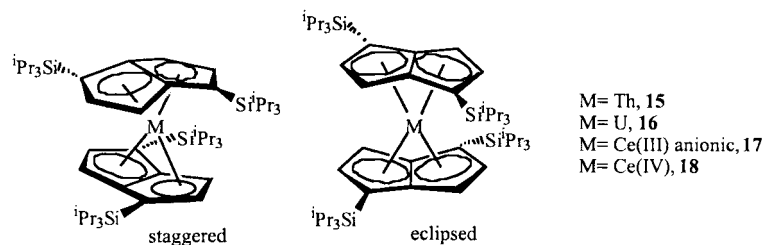


Fig. 4

pentalene rings [19]. A similar reaction between CeCl_3 and $[\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,4)_2]\text{K}_2$ affords the anionic lanthanide(III) complex $[\text{Ce}\{\eta^8\text{-C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,4)_2\}]\text{K}$ **17**, which displays similar structural features to **15** and **16**. Oxidation of **17** with $\text{Ag}[\text{BPh}_4]$ yields the intense blue neutral sandwich complex **18**—the Ce(IV) analog of the actinide complexes; there is currently some debate about the true oxidation state in Ce(IV) organometallics, particularly in the case of cerocene $[\text{Ce}(\eta^8\text{-C}_8\text{H}_8)_2]$ [20]. Magnetic studies and DFT calculations suggest that **18** is best regarded as a Ce(IV) compound [21].

Half-sandwich complexes

Equilibration of the actinide sandwich compounds **15** or **16** with a further equivalent of the metal tetrahalide affords the half-sandwich derivatives $[\text{M}(\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,4)_2)\text{Cl}_2]$, $\text{M} = \text{Th}, \text{U}$, which should prove versatile precursors for the synthesis of other derivatives [21]. The X-ray structure of the thorium compound reveals an interesting tetrameric structure (Fig. 5, **19**), in which the four thorium atoms are co-planar and the pentalene ligands are all related by C_2 symmetry axes. The synthesis of half-sandwich lanthanide(III) complexes has proved more challenging: however the use of the lanthanide triiodide as the starting material has enabled the synthesis of the crystallographically characterized dimeric, iodide-bridged yttrium complex **20** [21]. Finally, mono(pentalene) lanthanide(II) complexes are also accessible from the lanthanide diiodides as exemplified by the crystallographically characterized Yb(II) compound **21**.

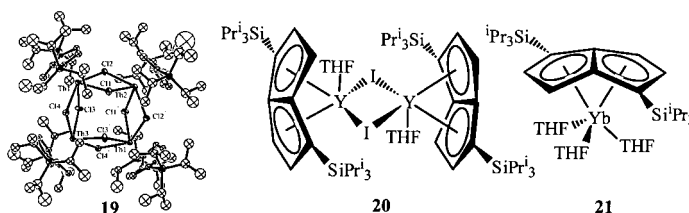


Fig. 5

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