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Review

The organometallic chemistry of pentalene

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Contents

Abstract

Carbocyclic, aromatic ligands have always played a central role in the growth of organometallic chemistry. In this review, we present work from our own laboratories and those of others on the development of the coordination chemistry of the eight-membered, bicyclic pentalene ring system, and its application to the synthesis of new types of organometallic compounds throughout the periodic table.

Keywords: Pentalene; Sandwich compounds; Organometallic; Molecular wires; Transition metals; f-Elements

1. Introduction

The role of carbocyclic ligands in the development of novel organometallic complexes has been substantial, most notably utilising the cyclopentadienyl, arene, cyclooctatetraenyl and their related ring systems [1]. Although the use of such ligands has been comprehensively researched, the organometallic chemistry of the pentalene dianion $[C_8H_6]^{2-}$ has not been as extensively explored—mainly due to difficulties associated with the synthesis of the ligand.

Since our last short review of the topic [2], interest in pentalene as a ligand has grown to an extent that we may present here a full review, covering over 40 years of research since the ring system was first isolated. This account will cover a brief description of the attempts to stabilise and isolate the neutral organic species C_8H_6, its possible electronic configurations, syntheses

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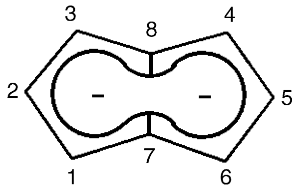


Fig. 1. Pentalenyl numbering scheme.

of the unsubstituted and substituted dianion and a full review of transition metal pentalene complexes, organised by periodic group (groups IV–X inclusively). Further sub-sections will deal with attempts to obtain pentalene-bridged polymetallic materials, and the chemistry of f-element and group III pentalene complexes. The review will cover material published to mid-2005.

1.1. Nomenclature

In this review, we use the term ‘pentalene’ to refer to any generic pentalene derivative, neutral or charged. Specific moieties referred to include ‘dihydropentalene’ [C_8H_8], ‘pentalenyl’ [C_8H_6]$^{2-}$, ‘hydropentalenyl’ [C_8H_7]$^-$ and ‘trihydropentalenyl’ [C_8H_9]$^-$. The carbon framework is denoted by the numbering system given in Fig. 1. Carbon atoms 7 and 8 are referred to as the ‘bridgehead’ carbons, 2 and 5 as the ‘wingtip’ carbons.

1.2. Synthetic and theoretical overview

Pentalene has been a molecule of significant interest for organic chemists for decades, due to both the synthetic challenges it has provided and the questions that have arisen over its aromaticity and structure. The unsubstituted molecule C_8H_6 is thermally unstable with respect to dimerisation (see Fig. 2), in a manner similar to cyclobutadiene, a fact that has forced chemists to seek derivatives stabilised by substituents. Le Goff isolated the first simple pentalene in 1962—hexaphenylpentalene, stabilised both sterically and electronically [3]; this was followed by the preparations of 1,3-bis(dimethylamino)pentalene [4] and of an aminopentalene carbonitrile [5], with electron-withdrawing substituents. These substituted pentalenes were found to be thermally stable at room temperature, unlike the first alkylated derivative 1-methylpentalene, reported in 1971 by Demayo and co-workers [6], which does not provide the sufficient steric protection to prevent dimerisation at ambient temperatures. This unstable molecule, partially characterised by means of UV and infrared spectroscopy and observed to give [2 + 2] dimers above −140 °C, pre-dated any successful preparations of the parent molecule.

In 1973, around the same time as the isolation of the sterically stabilised species 1,3,5-tri-*tert*-butylpentalene [7], Hafner et al. first detected unsubstituted pentalene indirectly by the characterisation of its dimerised products, photolysis of which gave UV spectra indicative of the monomer [8]. In 1997 further characterisation was obtained by Bally et al. using electronic and infrared spectroscopy; photolytic cleavage of the dimer in an Ar/N_2 matrix at approximately 20 K led to the parent molecule via a stepwise process [9]. Interestingly, another photochemical route to pentalene, from 5,6-diazaazulene, has been suggested and investigated theoretically [10], although currently there have been no attempts to pursue this route experimentally.

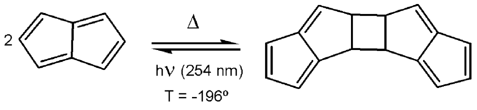


Fig. 2. Thermal dimerisation of pentalene (only one isomer illustrated).

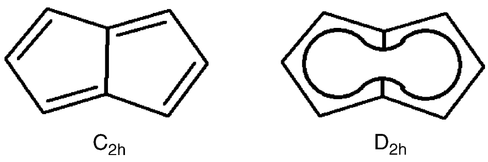


Fig. 3. Two ground state configurations considered theoretically for pentalene.

The existence of this reactive molecule has been considered from as early as 1922, when it was initially proposed as an aromatic system, giving pentalene a non-alternant, delocalised D_{2h} molecular symmetry [11]. Craig and Maccoll, in an attempt to justify its instability, used this assumption to generate inconsistent results between two applied methods for the ground state term (using valence-bond and molecular orbital treatments) [12]; a more complete study by Boer et al. also considered the possibility of a bond-alternant C_{2h} structure (Fig. 3) [13]. They concluded this to be the more likely structure, a consequence of the pseudo-Jahn–Teller effect—this was confirmed several years later using UV and IR data [9,14], and additionally with the X-ray structural characterisation of 1,3,5-tri-*tert*-butylpentalene, which was shown to be planar with localised double bonds [15]. This suggests pentalene to be best considered as a reactive 8π-Hückel *anti*-aromatic system, a view now supported by numerous studies [14,16,17]. Cyclooctatetraene, to which pentalene is often considered a bicyclic analogue, has a distorted tub-shaped geometry—this distortion from planarity prevents the π system from forming continuous overlap across the whole periphery, and assuming the *anti*-aromatic properties of an 8π cyclic system, and thus is observed to be a stable liquid at room temperature [18]. Calculations on the dianion and dication of pentalene indicate that these ions are best represented as delocalised 6π- and 10π-aromatic systems with D_{2h} symmetry [19], as expected from the extension of the Hückel ($4n + 2$) rule to these non-alternant systems.

Whilst the 8π *anti*-aromatic system was proving elusive to synthetic chemists, Katz and Rosenberg sought to prepare the aromatic pentalenyl dianion, with much greater success. In 1962 they reported dilithium pentalene as a thermally stable 10π species formed from double deprotonation of dihydropentalene with ^{n}BuLi in THF [20], mirroring the synthesis of LiCp from CpH. Further reports in the following two years substantiated these results and indicated the possibility of the mono lithium salt, as a 6π aromatic system delocalised around one half of the molecule, allowing the molecule to function, effectively, as a substituted Cp^- anion [21,22]. The parallels between the pentalenyl and the cyclopentadienyl ligand extend throughout much

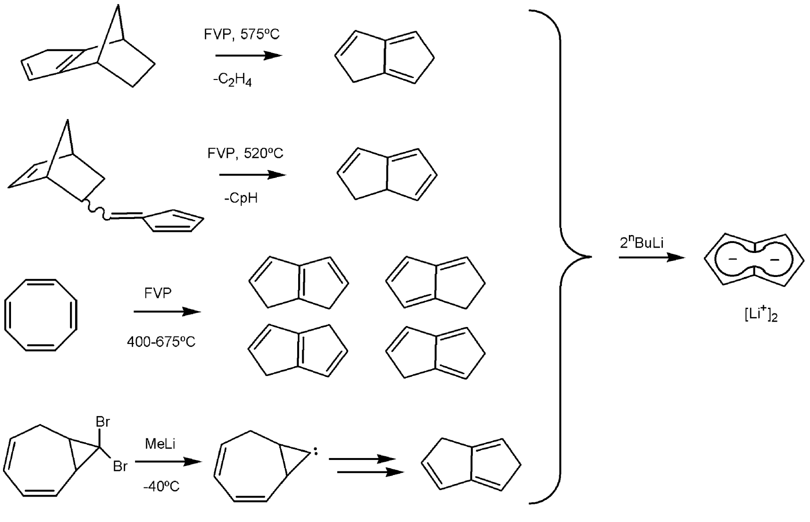


Fig. 4. Preparative routes to $C_8H_6[Li]_2$.

of the organometallic chemistry reviewed in this article—the pentalenyl dianion may be commonly considered to act as two fused Cp^- rings. This 10π-Hückel aromatic moiety is isoelectronic with naphthalene, and is related to the cyclopentadienyl anion as naphthalene is related to benzene. The dianion has been crystallographically characterised as a $C_8H_6[Li(DME)]_2$ adduct, and confirms the planar D_{2h} symmetry predicted; a preference for an *anti*-arrangement of lithium cations is observed [23]. Oxidation of this salt with $CuCl_2$ gives a diastereotopic mixture of neutral pentalene dimers [9]. Katz and co-workers demonstrated through their seminal work that pentalene may be stabilised by coordination to metal ions, as has been shown by others for unstable organic systems such as cyclobutadiene [24,25], trimethylenemethane [26] and heptafulvene [27], an approach which sparked research into this potentially rich field of organometallics.

2. Preparative routes to the pentalene dianion and derivatives

1,5-Dihydropentalene was prepared by Katz et al. from pyrolysis of isodicyclopentadiene at 575 °C (Fig. 4) [22]; it is found to be thermally unstable at room temperature, but may be stored under an inert atmosphere at −20 °C, with trace amounts of hydroquinone, without degradation. Jones and Schwab [28], and later Kochhan and co-workers [29], meanwhile showed that the flash vacuum pyrolysis (FVP) of cyclooctatetraene (COT) at 400–675 °C (proceeding with optimum conversion at 550–600 °C) [29] yields an isomeric mixture of dihydropentalenes, which may be collectively deprotonated with ^{n}BuLi–DME to afford $C_8H_6[Li(DME)]_2$. Further optimization of reaction conditions in our laboratory has allowed us to consistently produce $C_8H_6[Li(DME)]_2$ by this route in 87% yield (with respect to COT) on a 25 g scale [30]. Other pyrolytic routes reported include the cyclisation of 6-vinylfulvenes at 110 °C and of 5-cyclopentadienylidenemethyl-2-norbornene at 520 °C [31,32].

A non-pyrolytic route to $C_8H_6[Li]_2$ has been described, via a ring expansion of cycloheptatriene, in ca. 30% yield [33,34]; an improved synthesis following this route has afforded the salt as its DME adduct in up to 90% yield. The use of 7-alkyl substituted cycloheptatrienes gave the corresponding $C_8H_5^{(1\text{-}R)}[Li(DME)]_2$ (R = Me, Et and ^{i}Pr) species in moderate yields (ca. 40%) [35].

Mono- and dialkylated pentalenyl species may also be obtained by a preparation reported by Kaiser and Hafner [36]. The thermal cyclisation of 6-(2-aminovinyl)fulvenes gives 3-dialkylamino-1,2-dihydropentalenes, which may be lithiated with an alkyl- or aryl-lithium reagent, and hydrolysed to give the corresponding 1,3-R′,R″ 1,2-dihydropentalene (R′ = H, R″ = Me and Ph; R′ = Me, R″ = Me and Ph), as shown in Fig. 5. The latter may be deprotonated with ^{n}BuLi to give pentalenyl compounds for use in organometallic synthesis [37].

2.1. Main group derivatives

Thallium pentalene derivatives have been synthesised, and although rather toxic, are far less air-sensitive than the lithium analogues [38]. Thallium sulphate in aqueous KOH deprotonates dihydropentalenes to give $C_8H_7[Tl]$ [39], whilst thallium ethoxide will also react to give the mono-salt of methylated hydropentalenes $C_8H_6^{(1\text{-Me})}[Tl]$ [35]. The limited basicity of these reagents prevents the formation of the dianionic derivatives.

Stannylated compounds may be prepared from deprotonation of dihydropentalenes with either one or two equivalents

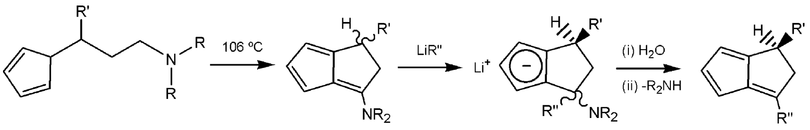


Fig. 5. Synthetic route to substituted dihydropentalenes (R′ = H, R″ = Me and Ph; R′ = Me, R″ = Me and Ph).

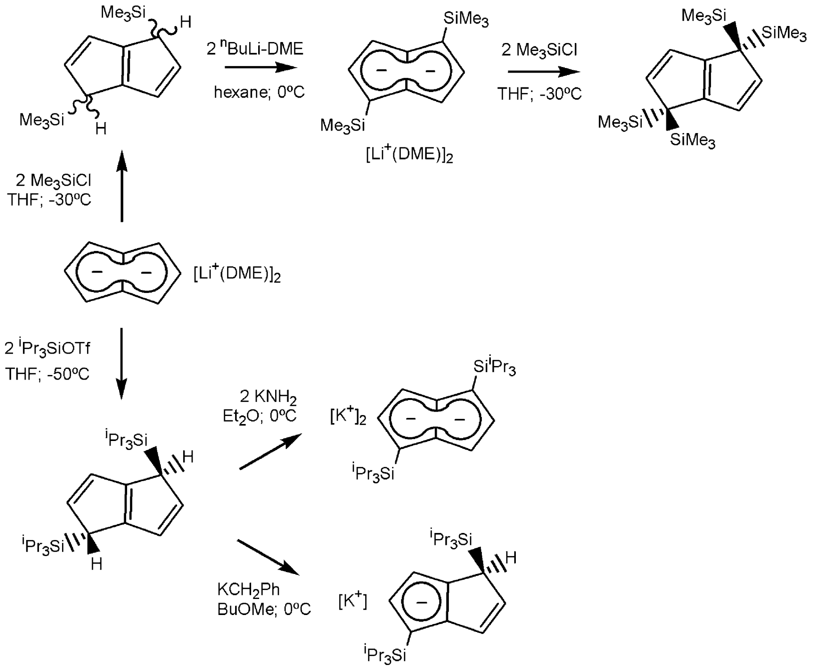


Fig. 6. Synthetic routes to silylated pentalenes.

of $Sn(NEt_2)Me_3$ [40,41]. In both cases the groups undergo rapid [1,5]-sigmatropic shifts around the ring as demonstrated by NMR spectroscopy, in a manner similar to that previously reported for similar tin(IV) compounds (e.g. the [1,2]-metallotropic shifts observed in cyclopentadienyl derivatives, $(C_5H_5)SnR_3$) [42].

Silylated derivatives of the pentalenyl dianion may be readily accessed from the reactions between $C_8H_6[Li]_2$ and silyl electrophiles [30], exclusively in 1,4-substitution analogous to the syntheses of similarly substituted COT products (see Fig. 6) [43]. These ligands were designed to provide a degree of steric bulk to the ligand to stabilise reactive metal centres, and in some cases, to confer an enhanced solubility of the resulting complexes—essential for characterisation and manipulation.

The trimethylsilyl derivatives were obtained by reaction of $C_8H_6[Li(DME)]_2$ with trichlorosilane; two equivalents in THF at −30 °C yielded $C_8H_6^{(1,4\text{-}SiMe_3)}$ as a thermally unstable semi-crystalline solid containing a mixture of racemic and meso isomers. Deprotonation with ^{n}BuLi–DME gave the corresponding dilithium salt $C_8H_6^{(1,4\text{-}SiMe_3)}[Li(DME)]_2$—further reaction of this with two equivalents Me_3SiCl gave a thermally stable tetra-substituted species $C_8H_4^{(1,1',4,4'\text{-}SiMe_3)}$ [30].

The bulkier triisopropyl pentalenes were similarly prepared, using triisopropyl triflate; the $Si^{i}Pr_3$ groups impart a degree of thermal stability and crystallinity to $C_8H_6^{(1,4\text{-}Si^{i}Pr_3)}$, in which they are found exclusively *anti* to each other [30]. This bulky ligand has particular application in the chemistry of the larger f-block metals, and as such it was necessary to obtain these derivatives as potassium salts—lithium and sodium counterions may create salts in metal halide metathesis that may be incorporated by these electropositive metals as "-ate" complexes. Treatment with two equivalents of potassium amide in diethyl ether, or with one equivalent of potassium benzyl in *tert*-butylmethyl ether, creates the di- and mono-potassium salts, respectively. Removal of solvent in vacuo at 60 °C leaves these compounds base-free.

2.2. Heterocyclic analogues

Given the subject of this review, it is worth noting the potential of the *N*-substituted heterocyclic system 4-azapentalenyl to be used as a *singly* anionic alternative to pentalene (Fig. 7). It is isoelectronic with $[C_8H_6]^{2-}$ and may well have significant application in the stabilisation of large, low valent metals. Although the anion has been known since Katz's syntheses of the lithium, sodium and potassium salts in 1967 [44], very little is known about their chemistry. Kissounko et al. reported the reactions of the unsubstituted and 1-methlyated lithium salts with chlorosilanes and trimethylchloride tin to obtain a range of stannlyated and silylated 3H-pyrrolizines [45(a)]. Gardiner and co-workers

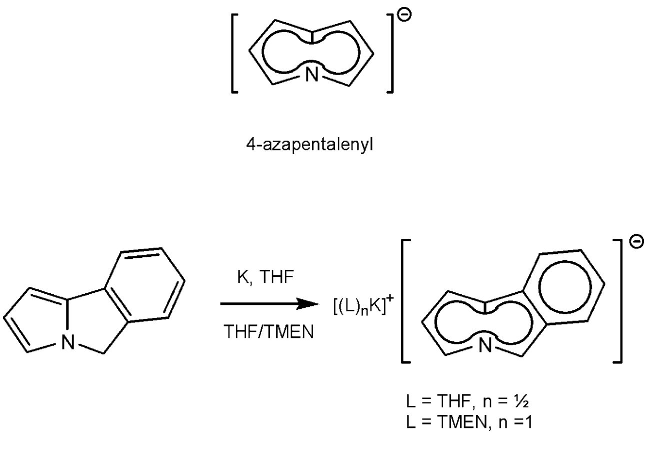


Fig. 7. 4-Azapentalenyl derivatives.

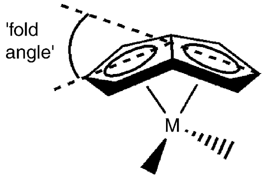


Fig. 8. The 'fold angle' for an η^8-bound pentalene ligand.

have recently obtained crystallographic data for a pair of solvated benzannulated derivatives (see Fig. 7) in which the anions are found to be almost planar in both cases. Further to this, DFT studies are reported which indicate the possibility of multi-hapto coordination to transition metals [45(b)].

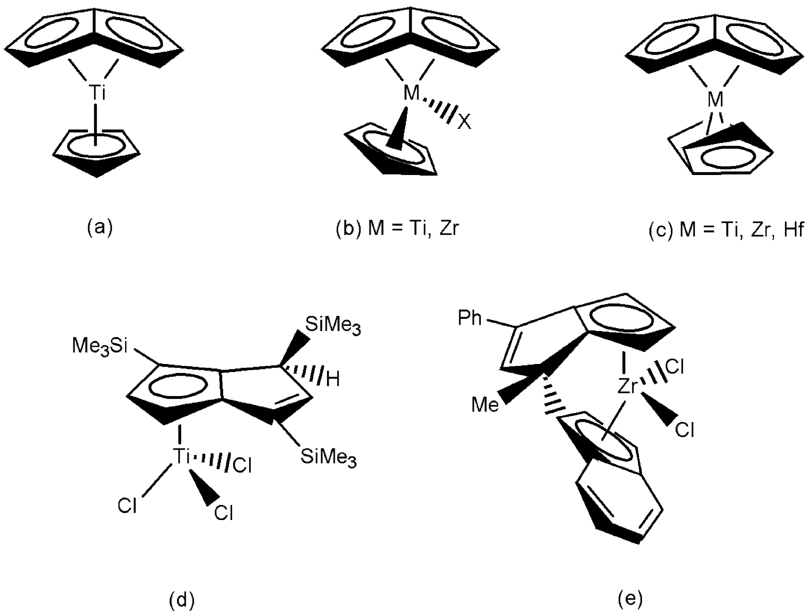
3. Transition metal complexes

3.1. Group IV complexes

Pentalene compounds of the early transition metals show a fascinating bonding mode in which the ligand folds along the bridgehead carbons to encompass a single metal centre, allowing all eight carbons to coordinate. The angle of this fold is shown to vary inversely with the size of the metal, and in all cases the bridgehead carbons are found to be located closest to the metal whilst the wingtip carbons are found furthest away (for the purposes of our review, we are defining the fold angle as the total angle by which the ligand is found to deviate from planarity, i.e. the angle between the wingtip carbons and the midpoint between the bridgehead carbons, as shown in Fig. 8). This distortion of the π-system causes a loss of aromaticity, as would be expected, and therefore only occurs in systems in which the bonding interactions are significantly increased by such coordination, giving an overall increase in stability. The fold angles for crystallographically characterised η^8-bound pentalene ligands in metal complexes are tabulated at the end of the review for reference (Table A.1, vide infra). Very recent work has shown that the bicyclic indenyl ligand $(C_9H_7)^-$ may also fold in a similar fashion to give a fully coordinated η^9-mode, and these fold angles are included for comparison [46].

Jonas et al. were the first to demonstrate this bonding mode of pentalene for complexes of the group IV metals [47]. Treatment of $Ti(Cp)Cl_2$ with dilithium pentalene or 2-methylpentalene formed $Ti(\eta^8\text{-}C_8H_5{}^{2\text{-}R})(Cp)$ (R = H and Me) shown in Fig. 9(a); reaction of this species with half an equivalent of either dichloro- or dibromoethane resulted in the facile oxidation of the Ti^{III} centre, affording the 18 electron species $Ti(\eta^8\text{-}C_8H_5{}^{2\text{-}R})(Cp)X$ (R = H and Me; X = Cl and Br). A Zr^{IV} homologue $Zr(\eta^8\text{-}C_8H_6)(Cp)Cl$ is prepared directly from $C_8H_6[Li]_2$ and $ZrCp_2Cl_2$ (Fig. 9(b)), in a reaction whereby a cyclopentadienyl ligand is substituted in preference for a chloride; presumably, bis(cyclopentadienyl)(pentalene) zirconium is too sterically saturated to be formed under these conditions. Structural analyses of the unsubstituted compounds have shown $Ti(C_8H_6)(Cp)Cl$ and $Zr(C_8H_6)(Cp)Cl$ to be isostructural with identical fold angles of 33°.

Homoleptic bis(pentalene) sandwich compounds are readily available by reaction of $Ti(\eta^8\text{-}C_8H_6)(Cp)X$ (X = Cl and Br) or $M(Cp)_2Cl_2$ (M = Zr and Hf) with one or two equivalents of $C_8H_6[Li]_2$, respectively—it is worth noting that zirconium and hafnium show an apparent preference for the pentalene ligand over two cyclopentadienyl ligands (Fig. 9(c)) [47]. The 2-methylpentalene analogues are prepared in an identical fashion, and show dynamic fluxionality between two conformers, as evidenced by ^1H NMR spectroscopy. Although structural data for these compounds have been lacking, Jonas has suggested a staggered D_{2d} geometry, in agreement with the ^{13}C NMR data for $M(C_8H_5{}^{2\text{-}Me})_2$ (M = Ti, Zr and Hf), PES data for the non-methylated analogues [48], and DFT ab initio calculations performed on $Ti(C_8H_6)_2$ [49].



(a) (b) M = Ti, Zr (c) M = Ti, Zr, Hf

(d) (e)

Fig. 9. (a–e) Some group IV pentalene complexes.

Initially, bis(pentalene)titanium(IV) was proposed as a diamagnetic “20e complex”, with the pentalene ligand considered as a 10π dianion; as such, these compounds would have been expected to be relatively unstable with two electrons in antibonding orbitals. A DFT study has shown that the ligands exhibit a bonding mode in which 1 of the 10 π-type orbitals does not overlap with any metal orbitals, forcing each ligand to act as a 9π-donor, and thus satisfying the 18 electron rule [49(a)]. Therefore, bis(pentalene)titanium represents a new example of a stable, neutral 18-electron sandwich complex (in a series including ferrocene and dibenzenechromium)—the bis(COT) analogue being found as a 16e asymmetric complex Ti(η^8-COT)(η^4-COT) [49(b)]. A theoretical paper has dealt with these differences using symmetry arguments and shows that the d_{z^2} orbital of the metal is of suitable symmetry to allow δ bonding in the D_{2h} bis(pentalene) complexes, but not in the D_{8h} bis(COT) sandwiches [49(c)]. Further calculations show that the dication $Ti(C_8H_6)_2{}^{2+}$ should be feasible as another 18e species – each pentalene would act as a typical 10π-donor in this case – although the oxidation state of the titanium centre in this proposed complex has not been made clear [49(a)].

Further derivatives have been synthesised for zirconium; Zr(η^8-C_8H_6)Cl_2(THF)$_2$ was obtained from an equimolar mixture of Zr(C_8H_6)$_2$ and $ZrCl_4$(THF)$_2$, and from this, further metathesis with allyllithium or indenyllithium gave Zr(η^8-C_8H_6)(η^3-allyl)$_2$ and Zr(C_8H_6)(indenyl)Cl, respectively [50].These compounds have application as Ziegler–Natta type catalysts; activities for Zr(C_8H_6)Cl_2, Zr(C_8H_6)(allyl)$_2$ and Zr(C_8H_6)(indenyl)Cl have been reported in a patent as 458 g, 6474 g and 31,531 g polyethylene/gram Zr/hr, respectively, under 2 bar of ethylene [51]. Given the widely demonstrated application of related group IV organometallics for olefin polymerisation, one would expect many of these pentalene compounds to be registered: indeed, other patents are available detailing also the synthesis and catalytic properties for similar trialkylsilyl substituted Ti^{IV} and Zr^{IV} analogues [52], and for the invention of a type of *ansa*-zirconocene derived from the fusion of dihydropentalenes with a ring system such as cyclopentadienyl or indenyl (Fig. 9(e)) [53].

A mixed-sandwich silylated COT/pentalene species Zr(η^8-$COT^{1,4\text{-}SiMe_3}$)(η^8-$C_8H_4{}^{1,4\text{-}SiMe_3}$) was isolated in 22% yield from the reaction between [Zr($COT^{1,4\text{-}SiMe_3}$)Cl_2]$_2$ and two equivalents of $C_8H_4{}^{(1,4\text{-}SiMe_3)}$[Li(DME)]$_2$ in toluene [54]. NMR studies indicate a similar product was obtained when using the analogous hafnium(IV) starting material.

One η^5-coordinated compound has been crystallographically characterised; Ti(η^5-$C_8H_4{}^{1,3,4\text{-}SiMe_3}$)$Cl_3$ was successfully isolated from the reaction between tetra-silylated $C_8H_4{}^{(1,1',4,4'\text{-}SiMe_3)}$ and $TiCl_4$, whereby the elimination of $SiMe_3Cl$ followed by a 1,2-silyl shift gives the product in reasonable yield (Fig. 9(d)) [55]. Additionally, the preparation of the bimetallic complex [Zr(allyl)$_3$]$_2$(μ-C_8H_6) has been reported, however with limited characterising data [56]; presumably the bridging pentalene ligand coordinates to the Zr^{IV} centres in an η^5- or η^3-manner, but this is speculative as no structural data have been published. It has been characterised by means of elemental analysis and is reported to decompose above −10 °C.

3.2. Group V complexes

In 1997, two independent groups simultaneously reported the first examples of η^8-pentalene complexes. Jonas et al. obtained a set of structurally characterised V^{III} mixed-sandwich species, V(η^8-$C_8H_5{}^{2\text{-}R}$)(Cp′) (R = H, Cp′ = Cp and Cp*; R = Me, Cp′ = Cp), from the reaction of $C_8H_5{}^{(2\text{-}R)}$[Li]$_2$ (R = Me and H) with V(Cp)(Cp′)X (X = Cl and Br; Cp′ = Cp and Cp*) [57]. These 18e diamagnetic complexes exhibit full η^8-coordination of the pentalene ligand, and the latter is found to be folded by 43° in V(C_8H_6)(Cp) (Figs. 10 and 12(a)).

Coincidentally, a half-sandwich tantalum(V) pentalene compound Ta(η^8-$C_8H_4{}^{1,5\text{-}SiMe_3}$)$Cl_3$ was obtained serendipitously in low yield in our laboratory from protonolysis of Ta($COT^{1,4\text{-}SiMe_3}$)Me_3 with three equivalents of [NH^{i}Pr$_2$Et]Cl in CH_2Cl_2, followed by sublimation at 140 °C/10^{-5} mbar (see Figs. 10 and 11) [58]. In this surprising reaction, a cyclooctatetraenyl ligand undergoes transannular dehydrogenation to give a pentalene ligand fully bound to a single tantalum(V) centre. The silyl groups remain attached to the ligand and are found exclusively in 1,5-substitution.

A rational synthesis for the trimethyl derivative has been investigated using the 1,4-triisopropyl silyl pentalene dianion [59]: Ta(η_8-$C_8H_4{}^{1,4\text{-}Si^iPr_3}$)$Me_3$ was obtained from the reaction of $C_8H_4{}^{(1,4\text{-}Si^iPr_3)}$[K]$_2$ directly with $TaCl_2Me_3$—this subsequently proceeds to form Ta(η^8-$C_8H_4{}^{1,4\text{-}Si^iPr_3}$)$Cl_3$ in high yield from reaction with excess BCl_3 (Fig. 11). Sequential protonolysis of Ta($C_8H_4{}^{1,4\text{-}Si^iPr_3}$)$Me_3$ with one or two equivalents of [NH^{i}Pr$_2$Et]Cl meanwhile affords Ta($C_8H_4{}^{1,4\text{-}Si^iPr_3}$)$Me_{3-x}Cl_x$ ($x = 1$ and 2); the bridged dimeric species [Ta($C_8H_4{}^{1,4\text{-}Si^iPr_3}$)Cl(μ-$CH_2$)]$_2$ has been obtained from the treatment of Ta($C_8H_4{}^{1,4\text{-}Si^iPr_3}$)$MeCl_2$ with LiN($SiMe_3$)$_2$ (Fig. 11). The X-ray structure analysis of this carbene bridged bimetallic shows a single diastereomer with triisopropyl silyl groups in an eclipsed arrangement. Examination of the structures for these Ta^V compounds reveals a consistent Ta–C (bridgehead) bond length for all species, but a variable Ta–C (wingtip) distance dependent on the electronegativity of the bound co-ligands. The pentalene ligand is observed to fold at the bridgehead towards the metal in order to ‘restore’ the electronic deficiency caused by electron-withdrawing substituents on the metal (see Table A.1).

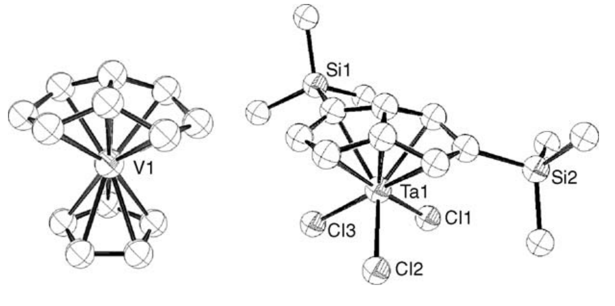


Fig. 10. ORTEP representations of V(η^8-C_8H_6)(Cp) and Ta(η^8-$C_8H_4{}^{1,5\text{-}SiMe_3}$)$Cl_3$.

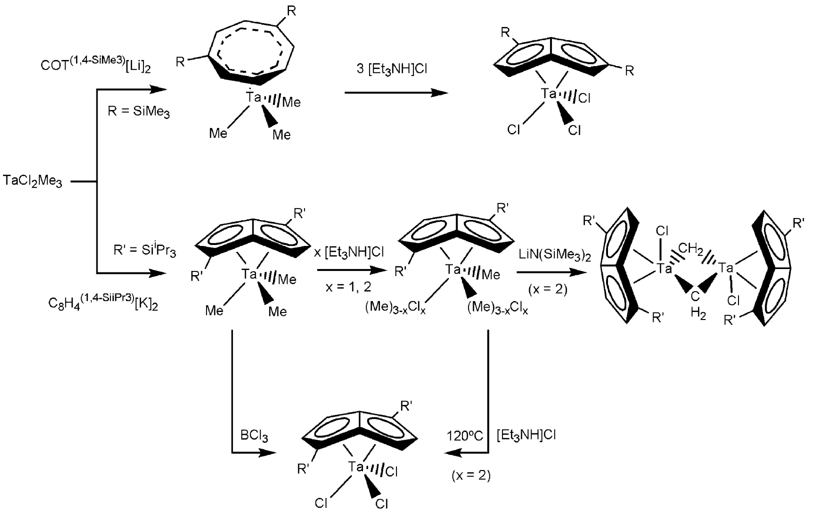


Fig. 11. Synthetic routes to tantalum(V) pentalene derivatives.

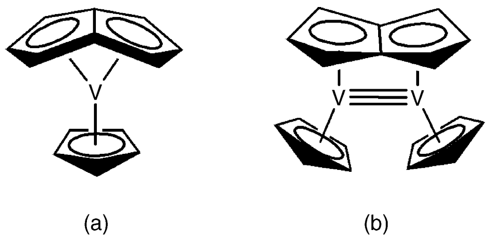
In a recent communication, O'Hare and co-workers isolated an interesting dinuclear V^{II} compound, formed from the reaction between $C_8H_6[Li(DME)]_2$ and $[V(Cp)Cl{\cdot}THF]_n$ (see Fig. 12(b)) [60,61], which exhibits a vanadium–vanadium triple bond much like that found in the isoelectronic $[V(Cp)]_2COT$ [62]. In $[V(Cp)]_2[\eta^5,\eta^5\text{-}C_8H_6]$ the ligand is folded slightly away (fold angle 13°) to hold the metal centres in close proximity as a *syn*-bimetallic. The two triple-bonded d^3 centres might be expected to give a diamagnetic 18 electron system; however, it was found to be weakly paramagnetic; magnetic measurements in both solution and solid-state show a singlet–triplet spin equilibrium due to anti-ferromagnetic coupling. The metal–metal bonding in the COT complex appears to be stronger; the V—V distance is found to be ca. 0.1 Å shorter than that in the pentalene analogue, presumably owing to a greater flexibility of the COT ligand, found to be folded at an angle of 56°. Solution-state studies show a decreased anti-ferromagnetic interaction in the COT compound [63], implying an increased HOMO–LUMO gap, consistent with a stronger V—V bond [60]. The pentalene compound is unstable in solution, and decomposes under a dinitrogen atmosphere to give the aforementioned V^{III} complex $V(C_8H_6)(Cp)$ and, presumably, an unknown vanadium species.

3.3. Group VI complexes

Characterised pentalene compounds of group VI metals are very scarce, but those known show new bonding modes for this ligand—and certainly indicate rich possibilities for future research.

O'Hare and co-workers isolated a highly unusual trimetallic chromium(II) species, in 2003, in which the ligand displays a unique η^5-,η^2-,η^2-bonding mode [61]. Reaction of $C_8H_6[Li(DME)]_2$ with $[Cr(Cp^*)Cl]_2$ affords not a simple bridged bimetallic, as might be expected, but the complex unit $[Cr(Cp^*)](\eta^5\text{-},\eta^2\text{-},\eta^2\text{-}C_8H_6)[Cr(Cp^*)]_2(\mu\text{-OMe})$ shown in Fig. 13. Structural determination has shown that the pentalene ligand binds $[CrCp^*]$ in a typical η^5-mode to one face, whilst $[Cr(Cp^*)]_2(\mu\text{-OMe})$ is bound in an η^2-,η^2-bonding mode similar to that shown by bimetallic allyl systems, in an *anti*-arrangement with respect to the $[CrCp^*]$ fragment. Solid-state magnetic susceptibility measurements (SQUID magnetometry) are consistent with a metal–metal bonded dimer showing anti-ferromagnetic coupling between the chromium(II) centres. The overall magnetism is consistent with the simple sum of that of a chromocene unit with this anti-ferromagnetically coupled Cr_2^{II} moiety. The bridging alkoxy group is found to be scavenged from the DME present in the starting material—an OEt bridged derivative was produced when DEE was used in its place, whilst no reaction was observed in its absence. This configuration gives 16e electron counts for all Cr^{II} centres, analogous to chromocene, and results in a chromium–chromium double bond.

A bridged bimetallic $[Cr(allyl)_2]_2(C_8H_6)$ has been characterised by means of elemental analysis but currently no further



(a) (b)

Fig. 12. (a and b) Representations of $V(C_8H_6)(Cp)$ and $[V(Cp)]_2$ $[\eta^5,\eta^5\text{-}C_8H_6]$.

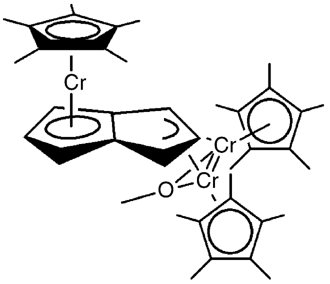


Fig. 13. A trinuclear chromium(II) pentalene complex.

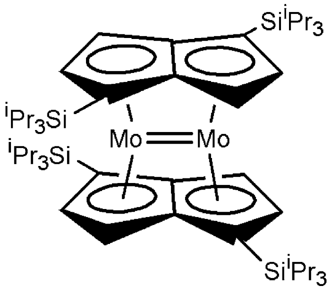


Fig. 14. A dimolybdenum bis(pentalene) sandwich complex.

data are available to substantiate the formulation of this compound; it is reported to decompose above −20 °C and is paramagnetic [56].

Katz and co-workers originally proposed planar sandwich compounds in the form of M_2bis(pentalene) dimers in 1972, with particular reference to two nickel(II) and cobalt(II) complexes (vide infra) [64,65]. These species have not been structurally verified; however, in 1998 X-ray diffraction of the molybdenum(II) derivative $Mo_2(\eta^5\text{-}, \eta^5\text{-}C_8H_4{}^{1,4\text{-}Si^iPr_3})_2$ confirmed the arrangement in this species, with two effectively planar pentalene rings found parallel to each other above and below the Mo_2 dimeric unit (Figs. 14 and 15) [66]. Synthesis of this compound was achieved in 22% yield by the reaction of $C_8H_4{}^{(1,4\text{-}Si^iPr_3)}[K]_2$ with $Mo_2(OAc)_4$ in a 2:1 ratio in THF, followed by quenching with oxygen-free water. This final step proved necessary to isolate a tractable product; NMR studies of the reaction mixture showed the presence of another isomer (conceivably the eclipsed stereoisomer or more likely an unusual Mo–Mo bridged “dumbell” shaped molecule with two η^8-,η^8-bound pentalene ligands capping either end of the dimer) and H_2O selectively decomposes this to allow successful crystallization of a single product.

The compound is rigorously diamagnetic, which suggests the presence of a double or quadruple bond between the metal centres, but the Mo–Mo bond distance was found to lie at an intermediary point between the typical values reported for the two former extremes. Density functional calculations have been performed on $Mo_2(C_8H_6)_2$ and indicate an Mo–Mo bond of order two [67]. This would lead to an electronically deficient system by standard electron counting (extension of the 18 electron rule) with a count of 28; however, the implicit effect on reactivity has not been observed, and $Mo_2(C_8H_4{}^{1,4\text{-}Si^iPr_3})_2$ is resistant to coordination with CO, PMe_3 or H_2O—this may be due to the sterically crowded environment around the metal centres.

3.4. Group VII complexes

In the complexes of the mid- to late-transition metals, there appears to be a strong tendency for the pentalene ligand to bind in an η^5-coordination mode (as opposed to η^8), with a consequent prevalence of bimetallic complexes.

In 1960 it was demonstrated that when $Mn_2(CO)_{10}$ is exposed to a high pressure of acetylene, the alkyne will undergo a cyclisation to give the hydropentalenyl Mn^I species $Mn(\eta^5\text{-}C_8H_7)(CO)_3$ (Fig. 16(a)) [68,69]. A rational synthesis for this compound has been achieved using $Mn(CO)_3(pyr)_2Br$ and $C_8H_7[Tl]$ [70]. The uncoordinated ring may be hydrogenated with H_2 to give an analogous trihydropentalenyl species with three $–CH_2–$ groups (Fig. 16(b)) [68]. A similar rhenium(I) carbonyl complex $Re(\eta^5\text{-}C_8H_9)(CO)_3$ containing the trihydropentalenyl ligand was obtained from the reaction of either 1,3- or 1,5-cyclooctadiene (COD) with decacarbonyldirhenium. The pentalene ligand is formed by transannular dehydrogenation of COD [71]. The hydropentalenyl analogue, $Re(\eta^5\text{-}$

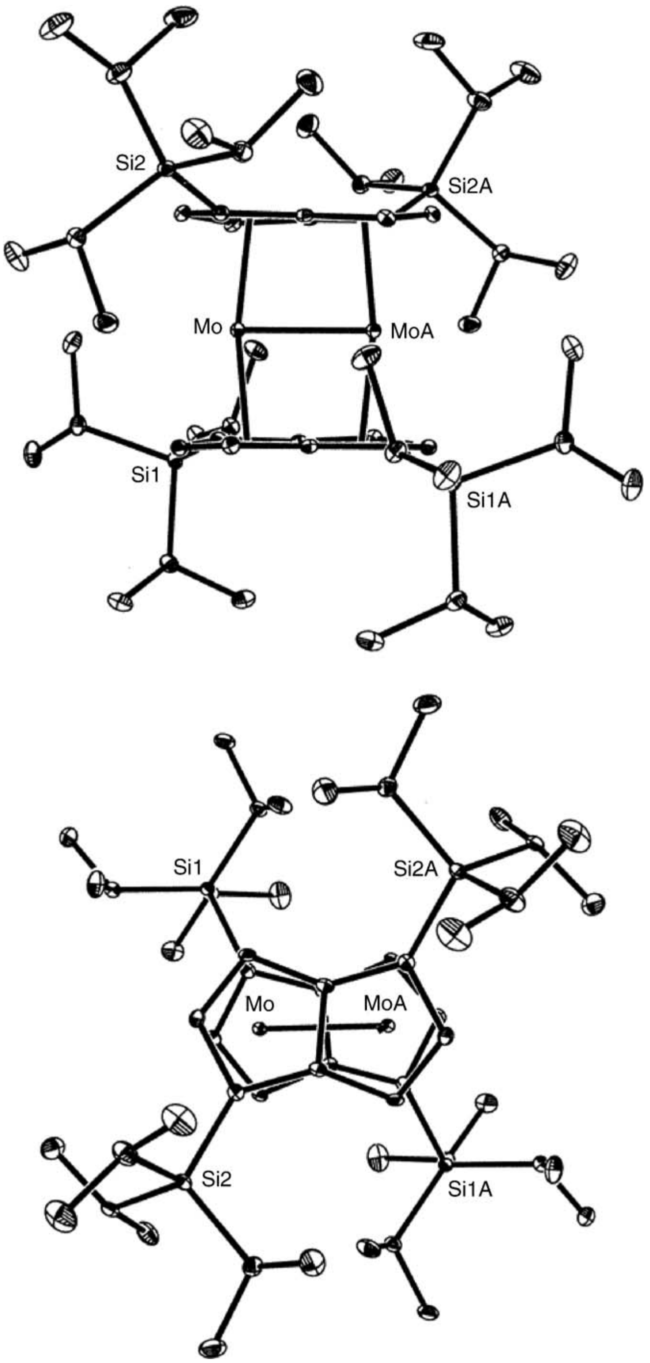


Fig. 15. Two orthogonal views of the molecular structure of $Mo_2(C_8H_4{}^{1,4\text{-}Si^iPr_3})_2$.

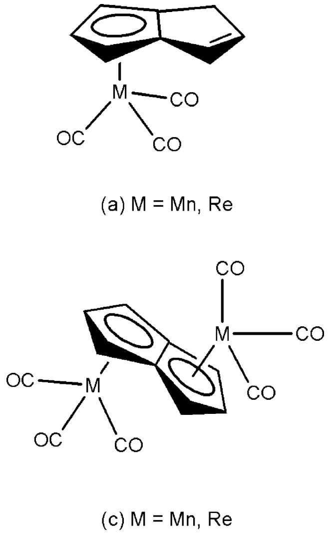

(a) M = Mn, Re (b) M = Mn, Re (c) M = Mn, Re (d)

Fig. 16. (a–d) Mono- and bimetallic complexes of group VII.

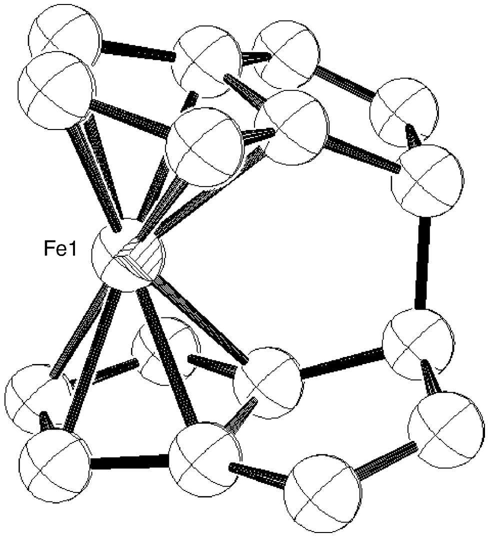


Fig. 17. Molecular structure of $Fe(C_8H_6)_2$.

$C_8H_7)(CO)_3$, was obtained in 60% yield from the reaction between $[Re(CO)_3(THF)Br]_2$ and two equivalents $C_8H_7[Tl]$. X-ray diffraction studies confirm the η^5-coordination mode [70].

Bimetallic complexes of group seven metal carbonyls are accessible from the reaction of $C_8H_6[Li(DME)]_2$ with two equivalents of $Mn(CO)_3(py)_2Br$ or one equivalent $[Re(CO)_3(THF)Br]_2$, affording $[Mn(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$ and $[Re(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$, respectively [72,73]. The Mn^I fragments are found exclusively *anti-* to each other (Fig. 16(c)), whereas the Re^I dimer exists as a mixture of *anti-* and *syn-*isomers (Fig. 16(c and d)); no metal–metal bond has been substantiated in the *syn*-isomer, and the ligand is folded slightly away from the metal axis. Cyclic voltammograms obtained for these rhenium(I) complexes display irreversible reductions. The manganese(I) bimetallic $[Mn(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$ is of special interest—it may be chemically and electrochemically reduced, the former giving both the dianion using KC_8, as a dipotassium salt, and the monoanion using $Fe(Cp)(C_6Me_6)$, stabilised with an $[Fe(Cp)(C_6Me_6)]^+$ counterion. The monoanion, formally a mixed-valence Mn^I/Mn^0 species, has been shown by UV, IR and NIR characterisation to be a highly delocalised system, vide infra.

3.5. Group VIII complexes

Historically, ferrocene has represented an archetype for organometallic chemists, and thus unsurprisingly this group contains the first example of a characterised pentalene metal complex obtained from pentalenyl starting materials. Katz and Rosenberg isolated the bis(hydropentalenyl) complex $Fe(\eta^5\text{-},\eta^5\text{-}C_8H_7)_2$ in 1963 from the reaction of two equivalents $C_8H_7[Li]$ with $FeCl_2$; a ferrocene-type environment was proposed for the iron(II) centre, with η^5-bonding modes akin to cyclopentadienyl (see Fig. 18(a)) [21]. Relatively recent crystallographic studies have confirmed this coordination environment, and show a 50/50 mixture of diastereomers with different relative positions of double bonds [74]. Further deprotonation of this species with ^{t}BuLi is possible to afford both $Fe(C_8H_7)(C_8H_6)[Li]$ and $Fe(C_8H_6)_2[Li]_2$ [21].

In an attempt to parallel results already achieved for nickel and cobalt, in which the M_2bis(pentalene) bimetallic sandwich compounds were synthesised from the reaction between equimolar quantities of $C_8H_6[Li]_2$ and MCl_2 (M = Co and Ni) [64,65], the corresponding reaction with $FeCl_2$ gave a monometallic product, $Fe(\eta^5\text{-}C_8H_6)_2$, shown in Fig. 18(b) [64]. The structure was confirmed by X-ray crystallography in 1973 and shows an unusual C–C bond bridging the two opposing, uncoordinated halves of the two pentalene ligands, distorting the ligands to give a bent ferrocene type structure (Fig. 17) [75]. A not dissimilar situation is seen in bis(azulene)iron, however, with a four, as opposed to two, carbon bridge between the bound π systems on opposite azulene rings; the distortion seen in the pentalene analogue is not observed in this case [76].

A dinuclear iron pentacarbonyl pentalene complex is obtained in substituted and unsubstituted forms from the reactions between 3-R′-1,2-dihydropentalene and an excess of $Fe(CO)_5$ (R′ = NMe_2 and Ph) [37,77], and also between an isomer of the neutral pentalene dimer and excess $Fe_2(CO)_9$ [78]. The structures of $[Fe_2(CO)_4(\mu\text{-}CO)](\eta^5\text{-},\eta^5\text{-}C_8H_5{}^{1\text{-}R'})$ (R′ = H, NMe_2 and Ph) have not been authenticated by X-ray methods but are proposed as *syn*-bimetallics with a bridging carbonyl group (Fig. 18(c)). It is worth noting that iron(0) carbonyls generally react with cyclic polyenes to give zerovalent complexes of the type $[Fe(CO)_3(\eta^4\text{-cyclic polyene})]$ [79]; dehydrogenation of cyclopentadiene with $Fe(CO)_5$ to give the dimer $[CpFe(CO)_2]_2$ requires elevated temperatures (140 °C) [80]. Presumably the greater ease of reduction of pentalene substrates reflects their inherent instability as neutral moieties.

Knox and Stone have shown, in a series of papers conveniently summarised in a 1974 review [81], the transannular dehydrogenation of unsubstituted, alkylated and silylated cyclooctatetraene substrates, giving coordinated pentalene derivatives, the transformation and subsequent coordination of which are effected by ruthenium carbonyls [82–86].

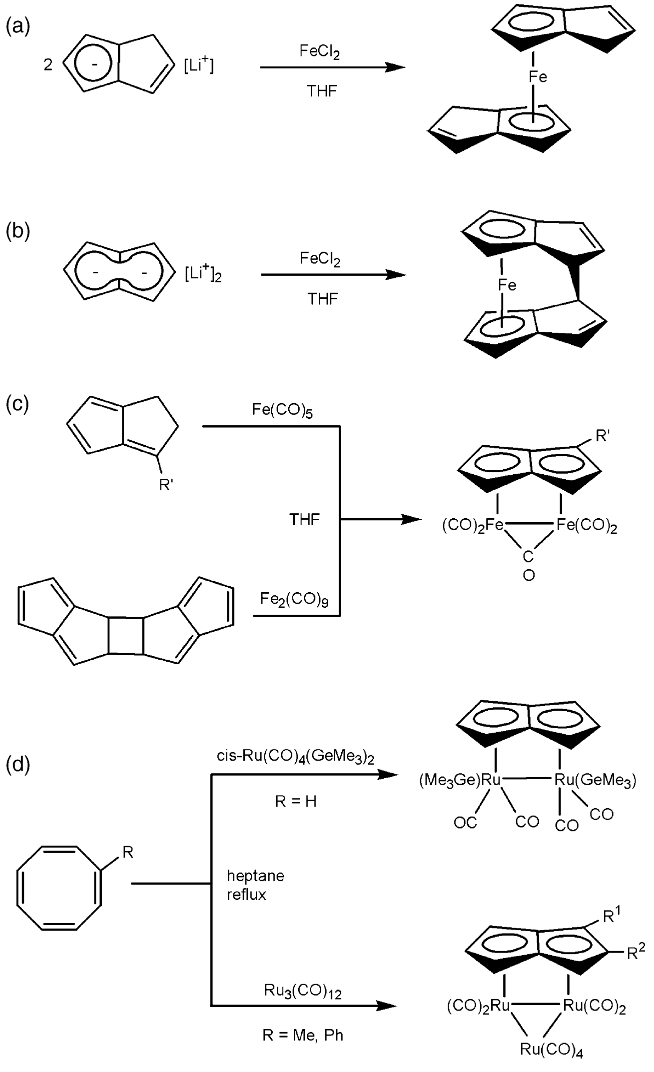


Fig. 18. (a–d) Syntheses of group VIII complexes.

This unusual ring closure of a cyclooctatetraene was first observed in the reaction between *cis*-Ru(CO)$_4$(GeMe$_3$)$_2$ and COT, under reflux in heptane, to yield a *syn*-bimetallic [Ru(CO)$_2$(GeMe$_3$)]$_2$(η^5-,η^5-C$_8$H$_6$) as shown in Fig. 18(d) [82]. Further studies revealed similar behaviour in a number of related ruthenium(II) systems; dodecacarbonyltriruthenium reacts similarly with unsubstituted and mono-substituted COT moieties to obtain the isomeric trimetallic species [Ru$_2$(CO)$_4$(μ-Ru(CO)$_4$)](η^5-, η^5-C$_8$H$_4{}^{1,2\text{-}R^1,R^2}$) (R^1 = R^2 = H; R^1 = Me/Ph, R^2 = H; R^1 = H, R^2 = Me/Ph; Fig. 18(d)), albeit in small yields. Reaction with the silylated cyclooctatrienes 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene or 3,5,8-tris(trimethylsilyl)cycloocta-1,3,6-triene leads to corresponding silylated, coordinated pentalene ligands in [Ru$_2$(CO)$_4$(μ-Ru(CO)$_4$)](η^5-, η^5-C$_8$H$_4{}^{1,5\text{-SiMe}_3}$) and [Ru$_2$(CO)$_4$(μ-Ru(CO)$_4$)](η^5-, η^5-C$_8$H$_4{}^{1,3,5\text{-SiMe}_3}$), respectively. Their work on these systems revealed some curious fluxional behaviour, observed by solution NMR studies, which was evident only in the unsubstituted species, the 2-substituted isomers (R^1 = H and R^2 = Me/Ph) and the symmetrically silylated compound, in which it has been suggested that the bridging ruthenium centre oscillates from one side of the near-planar pentalene ligand to the other, as illustrated in Fig. 19.

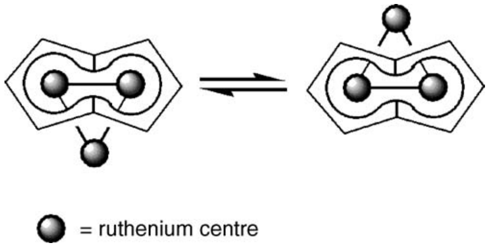


Fig. 19. "Pendulum"-type fluxional process observed in triruthenium complexes.

Manriquez et al. have isolated a number of iron(II) and ruthenium(II) bi- and trimetallic complexes; these are detailed later in the context of preparing extended pentalene polymetallic species (vide infra) [87–90]. The hydropentalenyl ruthenium(II) species Ru(η^5-C$_8$H$_7$)Cp* has been synthesised from the reaction between RuCp*Cl and C$_8$H$_7$[Li] [91].

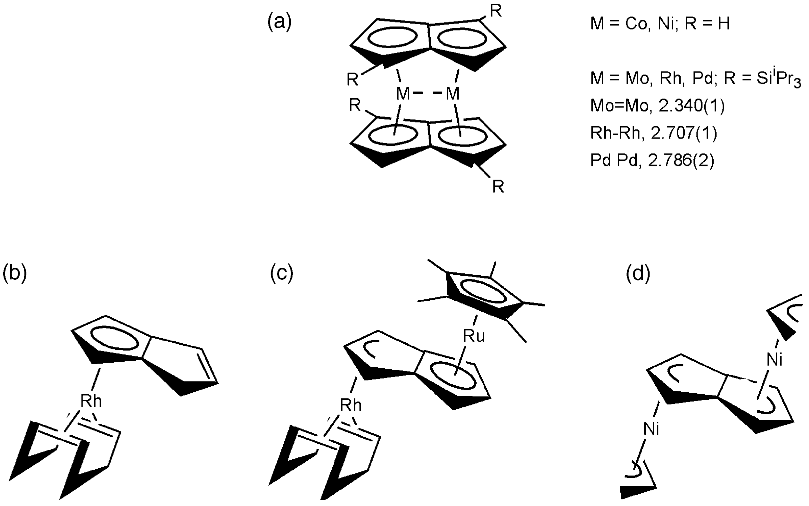
3.6. Group IX complexes

The M$_2$bis(pentalene) bimetallic sandwich compound Co$_2$(C$_8$H$_6$)$_2$ may be synthesised in low yield from the direct reaction of C$_8$H$_6$[Li]$_2$ with one equivalent CoCl$_2$ (see Fig. 20(a)) [64]. The ^{1}H NMR of this Co$^{\mathrm{II}}$ (d^7) species reveals unexpected diamagnetism; anti-ferromagnetic coupling of electronic density on adjacent nuclei, mediated by either a direct metal–metal bond or by overlap through the π system of the pentalene ligands, may explain this observation.

A similar silylated Rh$^{\mathrm{II}}$ compound Rh$_2$(η^5-, η^5-C$_8$H$_4{}^{1,4\text{-Si}^i\text{Pr}_3}$)$_2$ was isolated from the reaction between C$_8$H$_4{}^{(1,4\text{-Si}^i\text{Pr}_3)}$[K]$_2$ and Rh$_2$(OAc)$_4$. In this case single crystals were obtained, and structural data are consistent with a Rh–Rh single bond between the two metal centres [2,55].

Earlier work yielded Rh(C$_8$H$_7$)(η^4-COD) from the reaction of two equivalents of C$_8$H$_7$[Tl] with [Rh(1,5-COD)Cl]$_2$, which may be lithiated with ^{n}BuLi, and although η^5-ligation analogous to that in Rh(η^5-Cp)(η^4-COD) is assumed, crystallographic data are currently lacking (Fig. 20(b)) [39]. More recent work has shown that [Rh(1,5-COD)Cl]$_2$ may react with bulky terminal acetylenes RC≡CH in the presence of NEt$_3$ to give similar hydropentalenyl rhodium complexes Rh(η^5-C$_8$H$_3{}^{4R}$)(η^4-COD) (R = 1,3,3,5-^{t}Bu; 1,3,4,5-SiMe$_3$; 1,3,4,6-Rh(COD)(η^5-Me$_2$C$_5$H$_2$)) [92]. Crystallographic data have been obtained for these species and show η^5-coordination.

Other work has shown that the known ruthenium pentalene compound Ru(C$_8$H$_7$)Cp* (vide supra), once lithiated [93(a)], will react with [Rh(1,5-COD)Cl]$_2$ to afford the heterobimetallic [RuCp*](η^5-,η^3-C$_8$H$_6$)[Rh(η^4-COD)], in which each metallic fragment is found to be bound *anti*-, i.e. on opposing sides of the ligand (Fig. 20(c)) [93(b)]. The Rh(COD) fragment is bound to the pentalene system in an η^3-allyl fashion to give a 16e count for the unit, and further studies have shown that COD



M = Co, Ni; R = H

M = Mo, Rh, Pd; R = Si^iPr_3
Mo=Mo, 2.340(1)
Rh-Rh, 2.707(1)
Pd Pd, 2.786(2)

Fig. 20. (a–d) Monometallic and *syn*- and *anti*-bimetallic complexes of pentalene.

may be displaced by two molecules of CO without any degradation of the bimetallic structure [93(b)]. The allylic coordination parallels the ring slippage observed in a similar indenyl *anti*-bimetallic $[Cr(CO)_3](\eta^6\text{-},\eta^3\text{-}C_9H_7)[Rh(\eta^4\text{-COD})]$, in which the rhodium(I) COD unit is also bound in an η^3-fashion—a phenomenon which has been cited as the source of the higher reactivity of indenyl complexes over their Cp analogues and known as the 'indenyl effect' [94].

In addition to being an interesting example of a pentalene heterobimetallic, $[RuCp^*](\mu\text{-}C_8H_6)[Rh(COD)]$ is also found to be a highly active and selective catalyst for the dehydrogenative silylation of styrene [93(a)]. Activation presumably occurs at the Rh^I centre, given that rhodium organometallics have been previously noted for their high activities for this process [95,96].

3.7. Group X complexes

In work similar to that carried out for cobalt and rhodium, the M_2bis(pentalene) sandwich compounds $Ni_2(C_8H_6)_2$ and $Pd_2(\eta^5\text{-}, \eta^5\text{-}C_8H_4{}^{1,4\text{-}Si^iPr_3})_2$ were both obtained following the procedures outlined for their respective d^7 analogues (vide supra) using $NiCl_2$ (or $NiCp_2$) and $Pd(COD)Cl_2$ (Fig. 20(a)) [2,55,65]. The nickel(II) complex is diamagnetic, an effect ascribed to coupling mediated through ligand orbitals rather than metallic bonding [65,97]. The palladium(II) compound is similarly diamagnetic, although it is worth noting that electron pairing is not unusual for d^8 systems; the Pd–Pd distance of 2.786(2) Å found in the crystal structure does not reflect a direct bond [55]. The exact structural details of the Ni^{II} complex remain unclear; as a 36e organometallic bimetallic with, for example, electrons in ligand-based orbitals, electron pairing would be normally expected, without necessarily any interaction between metal centres. Burdett and Canadell have carried out extended Hückel type calculations for M_2bis(pentalene) complexes (M = Co and Ni) [97]; one possibility for bonding in the nickel complex is best described as involving two fused bis(allyl)nickel units—i.e. $\eta^3\text{-},\eta^3$-coordination.

Simple $\eta^5\text{-},\eta^5$-metallocenes for the second row transition metals Mo^{II}, Rh^{II} and Pd^{II} do not appear to be feasible with cyclopentadienyl derivatives. Nevertheless, crystallographic data obtained for $M_2(\eta^5\text{-}, \eta^5\text{-}C_8H_4{}^{1,4\text{-}Si^iPr_3})_2$ (M = Mo, Rh and Pd) show an $\eta^5\text{-},\eta^5$-metallocene-type environment for these metal centres. Metal–metal bonding may explain the stability of the molybdenum(II) and rhodium(II) structures; however, the palladium(II) complex appears to be unsupported in this way.

Reaction of dilithium pentalene with allylnickel(II) chloride affords a bridged allyl/pentalene bimetallic $[Ni(\eta^3\text{-allyl})]_2(\eta^3\text{-},\eta^3\text{-}C_8H_6)$ (see Fig. 20(d)) [56]. This compound, prepared by Miyake and Kanai in 1971, is notable for being the first transition metal pentalene compound studied by X-ray diffraction, and shows an *anti*-arrangement of allylnickel moieties across the bridging pentalene ligand. Coordination to the pentalene appears to be essentially allyl-like ($\eta^3\text{-},\eta^3\text{-}$), with significantly longer Ni–C (bridgehead) distances, represented in Fig. 21. This type of 'ring slippage' from an expected η^5- to an η^3-mode has been previously established with cyclopentadienyl and indenyl ligands, although the phenomenon is rare [94(b)]. As with the previous Ni^{II} and Pd^{II} compounds, this d^8 species was found to be diamagnetic.

One platinum hydropentalenyl complex is known; $Pt(\eta^5\text{-}C_8H_7)Me_3$ was obtained from thallium hydropentalenyl and trimethylplatinum iodide in 43% yield [39].

4. Pentalene bridged polymetallic complexes: towards extended 1D metal arrays

The delocalised π system of the pentalene dianion has a further consequence in organometallic chemistry, other than merely allowing effective ligation of the organic species to a metal. By overlap with metal orbitals of a suitable symmetry the planar ligand may delocalise excess electronic charge between bridged metals in polymetallic systems, thus allowing them to 'communicate' electronically. Manriquez et al. first cited this effect in the context of producing novel conducting materials, 'nanowires',

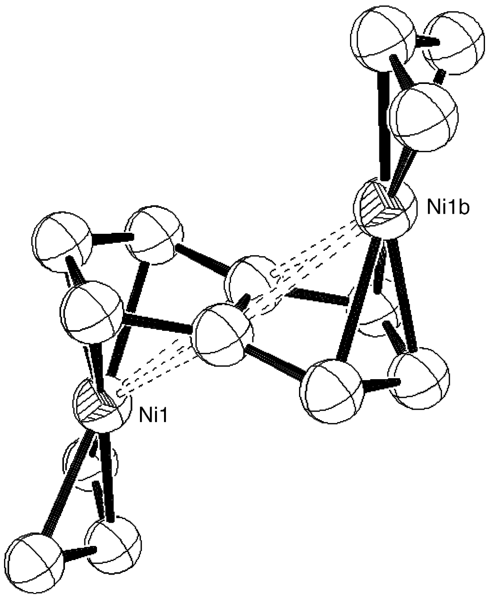


Fig. 21. Molecular structure of $[Ni(\eta^3\text{-allyl})]_2(\mu\text{-}C_8H_6)$.

which may demonstrate unusual, and potentially useful, electronic and/or magnetic effects [88,89,98].

Theoretical work by Burdett and Canadell into extended polymetallic sandwich compounds has predicted that a naphthalene-based metallic polymer $[M(\text{naphthalene})]_n$ would exhibit band gaps for iron and chromium [97]. Given that a staggered staircase-type arrangement has been predicted for $[M(\text{naphthalene})]_n$, it may be expected that a similar geometry would be found for $[M(\text{pentalene})]_n$, with η^5-coordination assumed (see Fig. 22(a)). The analogy between pentalenyl and naphthalene as homologous 10π Hückel aromatic systems has been previously highlighted; detailed analyses of the bonding modes in bimetallic compounds M_2bis(pentalene) and M_2bis(naphthalene) show similar metal–ligand interactions in both these systems [97].

Pentalene bridged *anti*-bimetallics $[MCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$ (Fig. 22(b)) were synthesised by Manriquez et al. from the reaction between $C_8H_6[Li]_2$ and $MCp^*(acac)$ (M = Fe, Co, Ni and Ru) [87,89]; hetero-bimetallic species $M(Cp^*)(\eta^5\text{-},\eta^5\text{-}C_8H_6)M'(Cp^*)$ (M = Fe, M′ = Ru and Co) were prepared from the corresponding reactions between $FeCp^*(C_8H_7)$ and $RuCp^*Cl$ or $CoCp^*(acac)$, employing ^{n}BuLi to lithiate intermediates [89].

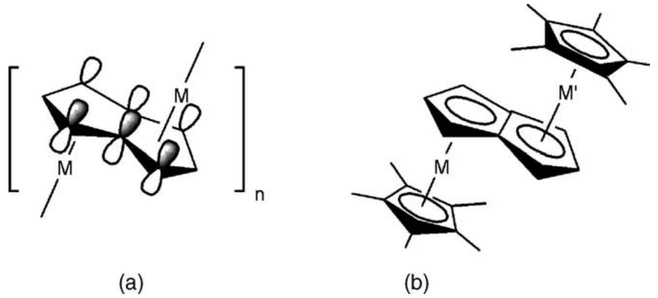


Fig. 22. (a) Theoretical pentalene 'nanowire'; ligand orbitals depicted of π_3 symmetry. (b) M = M′ = Fe, Co, Ni and Ru; M = Fe, M′ = Ru and Co.

Structural elucidation of $[Fe(Cp^*)]_2(\mu\text{-}C_8H_6)$ shows a distortion from ideal η^5-coordination of the pentalene ligand—the Fe–C (bridgehead) distances are significantly longer than other Fe–C (pentalene) distances and the C–C (bridgehead) shows elongation, consistent with a greater electron density around the periphery of the ligand [87]. The reasons for this, especially when one considers the classical stability of the ferrocene unit, remain unclear, but may be due to the symmetry of the pentalene π orbital contributions. The cobalt(II) and nickel(II) systems are diamagnetic, presumably as the unpaired electrons are coupled through the planar pentalene ring system, as seen in $[Ni(\eta^3\text{-allyl})]_2(\mu\text{-}C_8H_6)$ (vide supra). This delocalisation has been further evidenced by large potential separations between successive oxidations in the cyclic voltammograms obtained for these three compounds, apparently indicative of significant delocalisation within the intermediate cations [87,89]. These electrochemical results may be somewhat misleading however, as discussed below.

Chemical oxidation of these dimers with $[FeCp_2]BF_4$, and subsequently with HBF_4, gave a set of cationic and dicationic systems, respectively $\{[MCp^*](\eta^5\text{-},\eta^5\text{-}C_8H_6)[M'Cp^*]\}^{n+}$ (M = M′ = Fe, Co and Ni; $n = 1$ and 2) which have been studied by electronic and Mössbauer spectroscopy, cyclic voltammetry, EPR and SQUID magnetometry. These systems containing formally unpaired electrons demonstrate varying levels of ferro- and anti-ferromagnetic coupling, and show strong inter-valence charge transfer bands in the NIR spectrum with the mixed-valence species ($n = 1$; Fig. 23(a)) [89].

Similar investigations by O'Hare and co-workers into a formal Mn^I/Mn^0 mixed-valence system, $\{[Mn(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^-[\text{counterion}]^+$ (Fig. 23(b)) (vide supra) indicate that the level of delocalisation approaches that of a totally delocalised $Mn^{0.5}/Mn^{0.5}$ dimer (a class III Robin–Day species) [73]. Assuming this to be a class III species, the value for electronic coupling, $V = \nu_{max}/2 = 6400\,cm^{-1}$ ($V = H_{AB}$), appears to be the largest for any hydrocarbon bridged mixed-valence bimetallic in the literature [73], approaching the level of delocalisation found in some class III organic systems (see Table 1). It should be noted that there is an apparent discrepancy between these values and the electrochemical data reported for the 35e systems $\{[Mn(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^-[\text{counterion}]^+$ and $\{[CoCp^*](\eta^5\text{-},\eta^5\text{-}C_8H_6)[CoCp^*]\}^+[\text{counterion}]^-$ [70,73]. Electronic spectroscopy indicates the manganese complex to be more strongly delocalised (Table 1); however, data obtained using cyclic voltammetry show the cobalt complex to have a greater level of delocalisation (based on peak separations in the redox processes, $\Delta E_{1/2}$; see Table 2). It may be more appropriate in this case to disregard the electrochemical results, owing to the existence of complicating factors, such as solvent and counterion effects, inherent in the electrochemical technique. Indeed, Geiger and co-workers have previously shown that systematic variation of the solvent/electrolyte combination may alter the observed redox potential of bis(fulvalene)dinickel(II) (a Robin–Day class III bimetallic) from as much as $\Delta E_{1/2} = 212\,mV$ to $850\,mV$ ($K_c = 10^3\text{–}10^{14}$) [99].

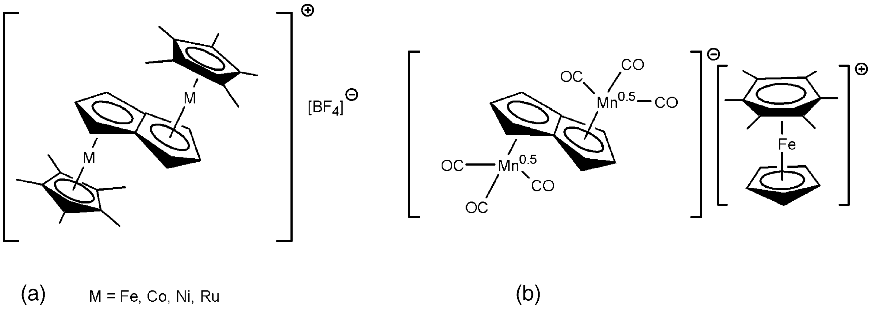
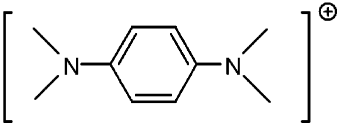
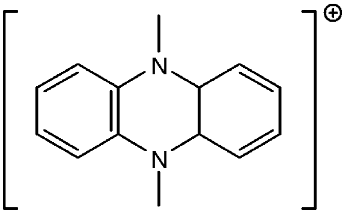


Fig. 23. (a and b) Mixed-valence pentalene bridged bimetallics.

Table 1
NIR data for selected organic and organometallic class III Robin–Day systems

	V (cm^{-1})	Reference
Class III organic species		
	8140	[100]
	6890	[100]
Class III bimetallic organometallic species		
$[Mn(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^-$	6400	[73]
$\{[Ru_3(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_6(CO)(DMAP)]_2(1,4\text{-pyrazine})\}^-$	6050	[101]
$\{[Re(Cp^*)(NO)(PPh_3)]_2(C{\equiv}CC{\equiv}C)\}^+$	5660	[102]
$[NiCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^+$	4970	[89]
$[CoCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^+$	4770	[89]
$[RuCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^+$	4100	[89]
$[FeCp*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)\}^+$	2270	[89]

Given the extremely strong coupling and delocalisation of charge between pentalene-bridged metals, further work has been undertaken towards synthesising higher chain oligomers. In an extension of Katz's original 1963 paper, Manriquez and co-workers exploited the opportunity provided by lithiation of the uncoordinated ring of a bound hydropentalenyl ligand, to extend the chain by further coordination of the resultant anion to other metal units (Fig. 24) [88]. Lithiation of bis(hydropentalenyl) iron(II) allows coordination of an $[MCp^*]^+$ unit by reaction with $MCp^*(acac)$ (M = Fe and Co), further lithiation of which and reaction with another equivalent of $FeCp^*(acac)$ yield a fully 'capped' trimetallic $\{[FeCp^*](\mu\text{-}C_8H_6)Fe(\mu\text{-}C_8H_6)[FeCp^*]\}$ [88].

Oxidation of the bimetallics $(MCp^*)(\mu\text{-}C_8H_6)Fe(C_8H_7)$ with one equivalent of $Cp_2^*FeBAr'_4$ gave $\{Cp^*M(\mu\text{-}C_8H_6)Fe(C_8H_7)\}^+$ (M = Fe and Co) stabilised by the bulky, fluorinated counterion $\{3,5(CF_3)_2C_6H_3)_4B\}^-$. Similar investigations to those carried out for earlier mixed-valence systems led to the conclusion that the Fe^{II}/Fe^{III} system is highly delocalised, whereas the heterobimetallic Fe^{II}/Co^{III} is better

Table 2
Electrochemical data for selected organometallic class III Robin–Day bimetallics

Complex	Solvent	Electrolyte	$\Delta E_{1/2}$ (mV)	K_c	Reference
$[FeCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$	THF	$[NBu_4]ClO_4$	850	3×10^{14}	[89]
$[CoCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$	THF	$[NBu_4]ClO_4$	710	1×10^{12}	[89]
$[NiCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$	THF	$[NBu_4]ClO_4$	650	1×10^{11}	[89]
$[Mn(CO)_3]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$	THF	$[NBu_4]PF_6$	410	9×10^{6}	[73]
$[RuCp^*]_2(\eta^5\text{-},\eta^5\text{-}C_8H_6)$	THF	$[NBu_4]ClO_4$	290	8×10^{4}	[89]
$Ni_2(\eta^5\text{-},\eta^5\text{-fulvalene})_2$	Various	Various	212–850	10^3–10^{14}	[99]

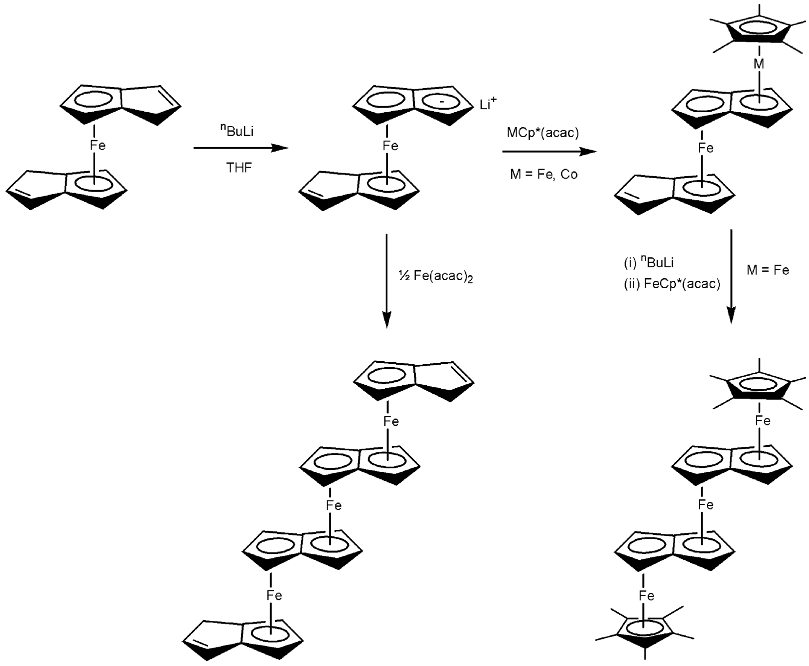


Fig. 24. Synthetic routes to bi- and trimetallic pentalene complexes.

considered as containing two localised units (i.e. a class I system), with the iron(II) centre identified by Mössbauer spectroscopy [90].

In a potentially iterative process towards an extended polymetallic, lithiated bis(hydropentalenyl) iron(II) was combined with one half equivalent $FeCl_2$ to produce a novel quadruple decker compound (Fig. 24) [88]. Unfortunately this species lacks a useful level of solubility in hydrocarbons (approximately 400 mg/l boiling toluene), hindering the production of higher chain oligomers, and impeding investigations into the delocalisation properties of any oxidised derivatives.

Subsequent investigations carried out using 1-methyl and 1,4-triisopropylsilyl pentalenes have shown that these substituents provide a significant level of solubility in hydrocarbon solvents to the triple- and quadruple-decker iron(II) complexes [55,70]. Unfortunately due to the asymmetry of the ligands these multidecker species may exist in several isomeric forms, and typically the mixtures of complexes were obtained as oils which were difficult to manipulate and purify, precluding any substantial characterisation.

It appears that the future for these materials lies in the successful synthesis of symmetric 2,5-di-, 1,3,4,6-tetra- or 1,2,3,4,5,6-hexa-substituted pentalenes (with, for example, alkyl or trialkylsilyl groups) which may react in the schemes described above to yield single isomers of soluble, isolable oligomeric or polymeric conducting compounds.

5. f-Element and group III complexes

Pentalene has continued to show its versatility as a ligand with the synthesis of full-, half- and mixed-sandwich compounds of the lanthanides and actinides; for the purposes of this review, the group III metals are discussed together with the lanthanides. Predominantly η^8-bonding to single metal centres is observed throughout—unsurprising given the large radii and the inapplicability of the 18 electron rule to f-elements. As previously discussed, the use of large substituents to stabilise and solubilise large metal centres, and of potassium counterions to prevent salt incorporation, has proved essential in obtaining these compounds.

The use of carbocyclic ligands in the organometallic chemistry of the f-block is well established, with pentamethylcyclopentadienyl and cyclooctatetraenyl in particular being of notable importance in this field [103–106]. The discovery of bis(COT) uranium(IV), more trivially known as uranocene, in 1968 proved to be a landmark in both synthetic and theoretical actinide chemistry, stimulating research into the organometallic chemistry of these heavy metals [104,107]. Notably, further research by Streitwesier and co-workers have produced thorocene $Th(COT)_2$ [108], cerocene $Ce(COT)_2$ [109,110] and a series of trivalent lanthanide sandwich and half-sandwich compounds $KLn(COT)_2$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd and Tb) and $[Ln(COT)(THF)_2(\mu\text{-}Cl)]_2$ (Ln = Ce, Pr, Nd and Sm) [111].

The pentalene analogues of uranocene and thorocene were unknown until 1997 when $M(\eta^8\text{-}C_8H_4{}^{1,4\text{-}Si^iPr_3})_2$ (M = Th and U) were prepared directly from reaction of two equivalents $C_8H_4{}^{(1,4\text{-}Si^iPr_3)}[K]_2$ with $ThCl_4$ or UCl_4 in THF [112,113]. Two isomers are found within the same crystal and reflect two non-interconvertible species of meso (≈S_4) and chiral (D_2) symmetries in which the faces of the ligand are bound on opposing sides, and can only be interconverted (in principle, not in practice) by complete disassociation of one ligand and re-association via the opposite enantiotopic face (Fig. 25). The bulky silyl groups are found in almost identical locations in both forms and dictate

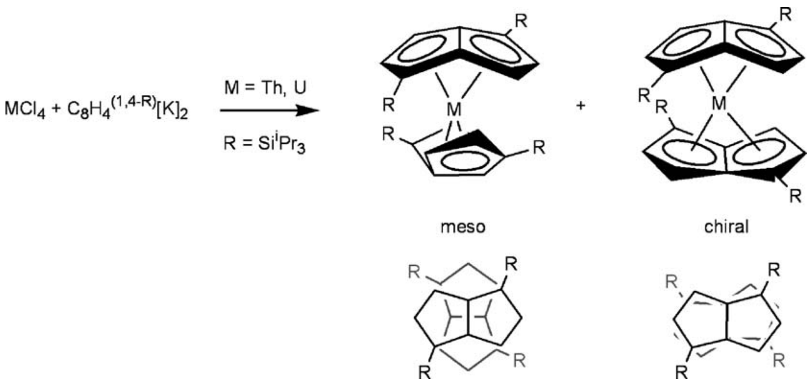


Fig. 25. Synthesis and structures of bis(pentalene)thorium(IV) and uranium(IV).

the crystal packing. The low fold angles in these compounds (M = Th, 24°, and U, 25°) reflect the large radii of the $\mathrm{M^{IV}}$ ions.

Theoretical calculations performed by Green and co-workers examined the η^8-bonding mode of pentalene with respect to that of COT, and are in good agreement with the structural data obtained experimentally [113]. Photoelectron spectra of these complexes have also been reported; in the case of the $\mathrm{U^{IV}}$ compound a band consistent with the ionization of an f-electron is observed at a relatively low energy with respect to that found in uranocene and $\mathrm{UCp_4}$. This result indicates the trialkylsilyl pentalene ligand to be a more powerful electron donor in this system than either cyclooctatetraenyl or cyclopentadienyl.

These full-sandwich compounds may be equilibrated with an equimolar quantity of $\mathrm{MCl_4}$ to give the half-sandwich species $\mathrm{M}(\eta^8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})\mathrm{Cl_2}$ (M = Th and U), potentially useful precursors to further actinide pentalene complexes. The crystal structure of the thorium compound reveals an intriguing tetrameric structure as shown in Fig. 26 [2].

Although uranocene and thorocene are undoubtedly tetravalent, the case is not so clear for cerocene, and there continues to be much debate about its formal oxidation state. Theoretical studies by Dolg et al. suggest a trivalent system with each ligand assigned a 1.5-charge [114,115], a model supported by XANES data [116]. However, photoelectron spectroscopy data and DFT calculations are more consistent with a covalent cerium(IV) system [110,117].

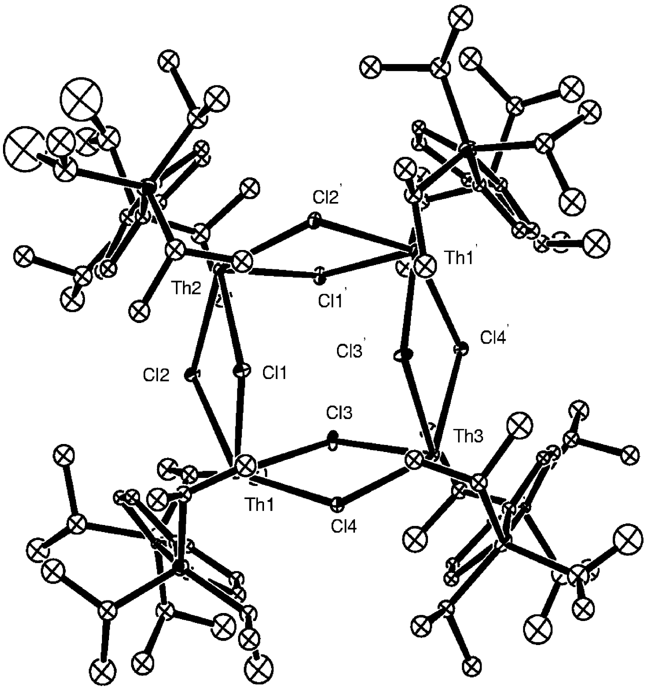


Fig. 26. Solid-state structure of $[\mathrm{Th}(\eta_8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})\mathrm{Cl_2}]_4$.

We have isolated the pentalene analogue of cerocene $\mathrm{Ce}(\eta^8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})_2$ in our laboratory via oxidation of the $\mathrm{Ce^{III}}$ species $\mathrm{Ce}(\eta^8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})_2[\mathrm{K(THF)_2}]$ using $\mathrm{AgBPh_4}$ (see Fig. 27) [118]. The anionic compound was formed in moderate yield from $\mathrm{C_8H_4}^{(1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3)}[\mathrm{K}]_2$ and $\mathrm{CeCl_3}$, and crystallographic data obtained for the 18-crown-6 salt show full η^8-coordination for both pentalene ligands. In a totally ionic system one might expect only three of the four anionic faces to bind to the $\mathrm{Ce^{III}}$ ion, yet this result suggests a degree of covalency within the bonding in the solid-state structure. A mixture of meso and rac isomers is found in the same crystal for both $\mathrm{Ce}(\eta^8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})_2[\mathrm{K(18\text{-}crown\text{-}6)(pyr)_2}]$ and $\mathrm{Ce}(\eta^8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})_2$, as for the uranium and thorium bis(pentalene) analogues (Fig. 25), and has fold angles of 22° and 26°, respectively, reflecting the change in ionic radius. Interestingly, magnetic measurements and DFT calculations for $\mathrm{Ce}(\eta^8\text{-}\mathrm{C_8H_4}^{1,4\text{-}\mathrm{Si}^i\mathrm{Pr}_3})_2$ indicate that this com-

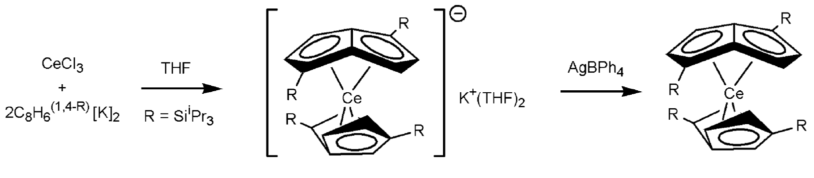
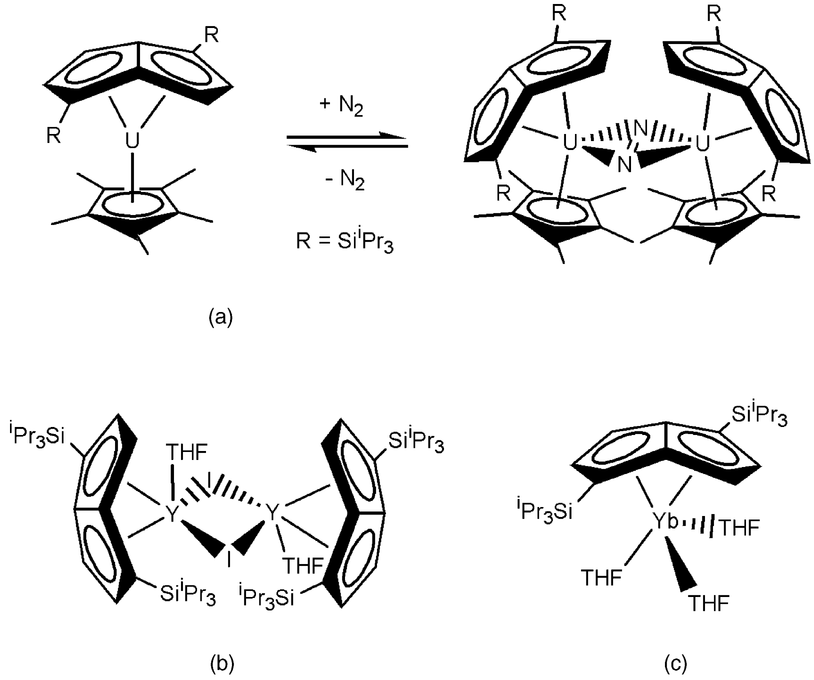


Fig. 27. Synthesis of bis(pentalene)cerium(IV).



(a)

(b)

(c)

Fig. 28. (a–c) Examples of f-element pentalene complexes.

pound is best considered as containing a formal $\mathrm{Ce^{IV}}$ centre [118].

The potential of pentalene to stabilise reactive f-element centres is further illustrated by the isolation of the sterically unsaturated $\mathrm{U^{III}}$ complex $\mathrm{U(\eta^8\text{-}C_8H_4{}^{1,4\text{-}Si^{\mathit{i}}Pr_3})Cp^*}$, afforded from $\mathrm{UI_3}$, $\mathrm{KCp^*}$ and $\mathrm{C_8H_4{}^{(1,4\text{-}Si^{\mathit{i}}Pr_3)}[K]_2}$ in “base-free” conditions [119,120]. This species is stable under an argon atmosphere, but has been shown to reversibly bind, and doubly reduce, dinitrogen (Fig. 28(a)). X-ray data show a fold angle of 26° in the monomer, and two different angles of 26.0° and 22.5° for the two ligands in the dimer; however, aside from this, no major differences in the pentalene geometry occur upon complexation of $\mathrm{N_2}$.

Reaction of $\mathrm{C_8H_4{}^{(1,4\text{-}Si^{\mathit{i}}Pr_3)}[K]_2}$ with $\mathrm{YI_3}$ in THF yields a very reactive species, $\mathrm{[Y(\eta^8\text{-}C_8H_4{}^{1,4\text{-}Si^{\mathit{i}}Pr_3})(THF)(\mu\text{-}I)]_2}$ [2,118]. Structural determination reveals a single isomer with eclipsed trialkylsilyl groups, as shown in Fig. 28(b), qualitatively similar to the geometry of $\mathrm{[Ta(\eta^8\text{-}C_8H_4{}^{1,4\text{-}Si^{\mathit{i}}Pr_3})Cl(\mu\text{-}CH_2)]_2}$. Unfortunately, further derivatisation of the Y–I bond has proved challenging, possibly due to the high reactivity of the $\mathrm{Y^{III}}$ centre in this system.

Reaction of a metal dihalide $\mathrm{MX_2}$ with an equimolar quantity of $\mathrm{C_8H_6[Li]_2}$ or $\mathrm{C_8H_4{}^{(1,4\text{-}Si^{\mathit{i}}Pr_3)}[K]_2}$ typically gives bimetallic sandwich species $\mathrm{M_2(\eta^5\text{-}pentalene)_2}$ for d-block metals (e.g. cobalt, nickel, palladium and rhodium; vide supra) [2,64,65]. In the case of the divalent f-element, ytterbium(II), the monomeric η^8-bound species $\mathrm{Yb(\eta^8\text{-}C_8H_4{}^{1,4\text{-}Si^{\mathit{i}}Pr_3})(THF)_3}$ is obtained from the reaction of $\mathrm{C_8H_4{}^{(1,4\text{-}Si^{\mathit{i}}Pr_3)}[K]_2}$ with one equivalent $\mathrm{YbI_2}$ in THF (Fig. 28(c)) [2]. In this compound, pentalene acts as the only charged ligand present, leaving an open coordination sphere to accommodate three THF solvent molecules, presumably a reflection of the larger size of the lanthanide with respect to the transition metals. The very large ionic radius of the ytterbium(II) centre gives the smallest fold angle (19.5°) currently reported for an η^8-bound pentalene species.

6. Conclusions and perspectives

It is evident that the practical difficulties in preparing and handling pentalene derivatives, which initially impeded progress in their use as ligands, have, to a fair extent, been overcome in recent years. The resultant metal complexes demonstrate the remarkable flexibility of this bicyclic ligand, which is capable of binding in ways similar to cyclopentadienyl and allyl ligands, in a folded η^8-bonding mode with larger or electron deficient metal centres, or as a bridging ligand in bimetallic systems. Thus, pentalene-based ligands offer a remarkable variety of coordination modes, unparalleled amongst currently known hydrocarbon ligand systems. The bonding modes reflect the electronic and steric considerations of the metal centre, acting in an adaptive manner rather than enforcing a predictable and inflexible coordination sphere. These properties make pentalene an excellent ligand for stabilising reactive metal centres. The ligand may also stabilise polymetallic systems, acting either as a ‘capping’ sandwich-type ligand or as a bridging ligand. These abilities have been shown to promote metal–metal bonding in *syn*-bimetallics, whereas its role as a bridging ligand in *anti*-bimetallics has been shown to induce very strong electronic delocalisation and coupling effects through the planar π system. These properties show high promise for the design of conductive or magnetic ‘nanowires’ in oligomeric or polymeric pentalenyl materials.

Acknowledgements

We would like to thank Dr. Simon Jones for his helpful comments and suggestions, and the EPSRC for the financial support of research carried out in our laboratory.

Appendix A

See Table A.1.

Table A.1
Fold angles for η^8-bound pentalene and η^9-bound indenyl ligands in organometallic complexes

Complex	Fold angle (°)[a]	Reference
d-Block		
$\mathrm{Ti(C_8H_6)Cp}$	37	[47]
$\mathrm{Ti(C_8H_6)CpCl}$	33	[47]
$\mathrm{Zr(C_8H_6)CpCl}$	33	[47]
$\mathrm{Zr(C_8H_6)Cl_2(THF)_2}$	30	[47]
$\mathrm{Zr(COT^{1,4\text{-}SiMe_3})(C_8H_4{}^{1,4\text{-}SiMe_3})}$	28	[54]
$\mathrm{Zr(\eta^9\text{-}C_9H_5{}^{1,3\text{-}SiMe_2{}^tBu})(\eta^5\text{-}C_9H_5{}^{1,3\text{-}SiMe_2{}^tBu})}$[b]	37.1	[94(a)]
$\mathrm{Zr(\eta^9\text{-}C_9H_5{}^{1,3\text{-}CHMe_2})(\eta^5\text{-}C_9H_5{}^{1,3\text{-}CHMe_2})}$[b]	37.6	[94(a)]
$\mathrm{V(C_8H_6)Cp}$	43	[57]
$\mathrm{V(C_8H_6)Cp^*}$	43	[57]
$\mathrm{V(C_8H_6{}^{2\text{-}Me})Cp^*}$	43	[57]
$\mathrm{Ta(C_8H_4{}^{1,4\text{-}Si^iPr_3})Me_3}$	29.2	[59]
$\mathrm{Ta(C_8H_4{}^{1,4\text{-}Si^iPr_3})Me_2Cl}$	31.2	[59]
$\mathrm{Ta(C_8H_4{}^{1,4\text{-}Si^iPr_3})MeCl_2}$	32.5	[59]
$\mathrm{Ta(C_8H_4{}^{1,5\text{-}SiMe_3})Cl_3}$	33.0	[58]
f-Block		
$\mathrm{[Y(C_8H_4{}^{1,4\text{-}Si^iPr_3})(THF)I]_2}$	26	[121]
$\mathrm{Ce(C_8H_4{}^{1,4\text{-}Si^iPr_3})_2[K(18\text{-}crown\text{-}6)(pyr)_2]}$	22	[118]
$\mathrm{Ce(C_8H_4{}^{1,4\text{-}Si^iPr_3})_2}$	26	[118]
$\mathrm{Yb(C_8H_4{}^{1,4\text{-}Si^iPr_3})(THF)_3}$	20	[121]
$\mathrm{Th(C_8H_4{}^{1,4\text{-}Si^iPr_3})_2}$	24	[112]
$\mathrm{[Th(C_8H_4{}^{1,4\text{-}Si^iPr_3})Cl_2]_4}$	28.1, 28.1 24.7, 24.6	[121]
$\mathrm{U(C_8H_4{}^{1,4\text{-}Si^iPr_3})_2}$	25	[121]
$\mathrm{U(C_8H_4{}^{1,4\text{-}Si^iPr_3})Cp^*}$	26	[119]
$\mathrm{U(C_8H_4{}^{1,4\text{-}Si^iPr_3})Cp^*(THF)}$	25	[121]
$\mathrm{[U(C_8H_4{}^{1,4\text{-}Si^iPr_3})Cp^*]_2(\mu\text{-}\eta^2,\ \eta^2\text{-}N_2)}$	26.0, 22.5	[119]

[a] See Section 3.1 for definition of fold angle.
[b] Indenyl sandwich complexes, see reference [94].

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