Check for updates

Synthesis of organometallic pentalenide complexes

Stuart M. Boyt, [iD] [a] Niko A. Jenek [iD] [a] and Ulrich Hintermair [iD] *[a,b]

While a number of reports have established the unique structures and electronic properties of mono- and dinuclear pentalenide complexes of s, p, d and f block elements, access to these intriguing compounds is restricted by synthetic challenges. Here we review various strategies for the synthesis, functionalisation and (trans)metalation of pentalenide complexes from a practical point of view, pointing out promising avenues for future research that may allow wider access to novel pentalenide complexes for application in many different areas.

1. Introduction

Pentalene (**Pn**, C_8H_6) has long fascinated theoretical and synthetic organic chemists for its anti-aromatic 8π system.[1] Unlike the flexible 8π cyclooctatetraene (**COT**, C_8H_8) **Pn** is planar due to its bicyclic ring structure, enforcing its anti-aromaticity. As a result, it readily dimerises above −196 °C to form two fulvene units isolated from each other by a cyclobutane linkage (Fig. 1).[2]

Due to its inherent instability, **Pn** itself is of limited use for applications in synthetic chemistry.† However, similar to other 8π *anti*-aromatics like **COT**, double reduction of **Pn** to pentalenide (**Pn²⁻**, $C_8H_6{}^{2-}$) generates a stable 10π aromatic system that presents itself as a useful π ligand for organometallic chemistry.[4] Its dianionic nature makes it a stronger donor for Lewis-acidic metals than neutral 10π hydrocarbons such as

*[a]Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK.
E-mail: u.hintermair@bath.ac.uk*
[b]Centre for Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath BA2 7AY, UK

†Electronically stabilized benzopentalenes have proven useful compounds for organic materials chemistry (see ref. 3 for a recent overview) but are beyond the scope of this review.

Stuart M. Boyt, Niko A. Jenek, Ulrich Hintermair

Stuart M. Boyt *graduated from the University of Warwick with an MChem in Chemical Biology but developed a taste for organometallic chemistry after a masters thesis with Adrian Chaplin looking at NHC complexes of group 9 metals. In 2015 he moved to the University of Bath to pursue his PhD in the Hintermair lab.*

His project involves synthesizing new pentalenide ligands from readily available precursors and investigating their reactivity towards a range of s-, d- and p-block compounds.

Niko A. Jenek *obtained his BSc in Chemistry from the University of Stuttgart in 2013, after which he moved to the University of Freiburg to finish his master's studies with a thesis on the fluorination of silicon surfaces with Ingo Krossing in 2017. After further fluorination adventures at the Fraunhofer Institute for Solar Energy Systems he joined the Hintermair group at the University of Bath for his PhD on novel pentalenide complexes for catalysis.*

Ulrich Hintermair *studied Chemistry and Chemical Engineering in Würzburg and Lyon with a stint at the University of St Andrews. After completing his PhD with Walter Leitner at Aachen he was a Humboldt postdoctoral fellow with Bob Crabtree at Yale University. In 2013 he started his independent academic career at the CSCT in Bath where he currently holds a Royal Society University Research Fellowship. Research in his group revolves around catalysis with metal complexes, including organometallic chemistry and real-time spectroscopy for mechanistic investigations.*

Fig. 1 Reversible dimerisation of pentalene.

Fig. 2 Charge distribution in the 10π aromatic pentalenide dianion.

naphthalene, and the two five-membered ring systems enable symmetrical charge distribution for reversible hapticity shifts of the metals bound to it (Fig. 2).

Due to this facile hapticity shift and a large degree of flexibility around the central C–C bridge, Pn^{2-} ligands exhibit some uniquely adaptive coordination abilities that neither **COT** nor naphthalene derivatives display. Pn^{2-} may wrap itself around, electron-deficient metal centres in η^8 coordination mode, or form doubly η^5/η^3 coordinated homo- and hetero-bimetallic complexes with direct metal–metal interactions within *syn*-bimetallics and strong electronic coupling in *anti*-bimetallic systems.[5] Given these intriguing properties it may appear surprising that organometallic Pn^{2-} chemistry is far less explored and developed than that of its 6π congener cyclopentadienide (Cp^-, $C_5H_5^-$), arguably the most important and most widely used organometallic ligand to date.[6] Whereas thousands of Cp^- complexes including almost every metal in the periodic table are known[7] and widely used in numerous applications including sensing, electrochemistry, magnetism, material synthesis, and of course catalysis, only about 150 examples of variously substituted Pn^{2-} and HPn^- complexes (including precursor salts) have been reported so far. This limitation is in no small part due to the practical challenges associated with accessing suitable synthons for Pn^{2-} chemistry. Historically, only few dedicated organometallic labs have developed the expertise and equipment required for pentale-

nide chemistry, each following their own preferred synthetic method. However, a number of routes to suitable precursors have emerged in different parts of the chemical literature over the past 50 years. Here we summarise and compare various strategies for the synthesis and functionalisation of Pn^{2-} complexes that promise to give more facile access to a wider range of precursors, and thus hopefully allow more widespread exploration of the intriguing properties of organometallic pentalenide complexes in different areas in the future.

2. Synthesis of pentalenides

In the context of discussing synthetic pentalenide chemistry, it is useful to distinguish the 8π antiaromatic pentalene (Pn, C_8H_6), the non-aromatic dihydropentalene (H_2Pn, C_8H_8 existing as several double-bond isomers[8]), the 6π aromatic hydropentalenide (HPn^-, $C_8H_7^-$), and the 10π aromatic pentalenide (Pn^{2-}, $C_8H_6^{2-}$). Their structures and interconversion pathways are laid out in Fig. 3.

2.1. Deprotonation of dihydropentalenes

Mono-anionic 6π HPn^- can easily be generated by deprotonation of H_2Pn using a weak base, as demonstrated by Katz and Mrowca.[9] They showed that an isomeric mixture of H_2Pn would react with KOH and Tl_2SO_4 in water to furnish $TlPnH$ as a precipitate in moderate yields (Fig. 4). In contrast to the neutral, unsubstituted H_2Pn, HPn^- salts are thermally stable and can be isolated and stored at room temperature like the related MCp salts (M = Li, Na, K). Jones *et al.* later showed TlOEt in pentane to be equally effective in generating $TlPnH$ from H_2Pn.[10] The first pK_a of H_2Pn must therefore be below 14, showing it to be slightly more acidic than HCp.[11]

Presumably due to charge effects, deprotonation of the second ring in HPn^- to furnish the fully 10π delocalised Pn^{2-} requires a stronger base. Katz *et al.* showed that Li_2Pn can be prepared by double deprotonation of H_2Pn with an excess of [n]butyllithium at −78 °C (Fig. 5).[12] Although the second pK_a value of H_2Pn is not known with certainty, using two (or more) equivalents of bases with pK_a values >25 usually leads to quantitative double deprotonation of all H_2Pn double-bond isomers. While Katz's original preparation used heptane

Fig. 3 Nomenclature and interconversion of pentalene derivatives.

Fig. 4 Synthesis of dilithium pentalenide by double deprotonation of dihydropentalenes.

Fig. 5 Synthesis of dilithium pentalenide by double deprotonation of dihydropentalenes.

to precipitate **Li₂Pn**, Stezowski *et al.* later used dimethoxy-ethane (DME) to obtain single crystals of η^5[**Li(DME)**]₂**Pn** that showed both metals to adopt *anti* configuration around the planar **Pn²⁻** in the solid state.[13] A recent computational study confirmed this to be the preferred geometry for all alkali–metal **Pn²⁻** complexes in solution.[14]

While these reactions look appealingly straightforward, and the utility of **HPn⁻** and **Pn²⁻** salts for transmetalation reactions is well documented (see section 3), the difficulty lies in generating the **H₂Pn** starting material. In the following subsections we review the most prominent methods reported.

2.2. Pyrolytic routes to dihydropentalenes

H₂Pn can be obtained from controlled, anaerobic pyrolysis of suitable precursors such as isodicyclopentadiene in Katz's method (Fig. 6).[15] Isodicyclopentadiene was formed by treating dihydrodicyclopentadiene (obtained from partial hydrogenation of dicyclopentadiene) with acetic anhydride and selenium dioxide, followed by dehydration of the resulting alcohol by passing over alumina at 300 °C.[16] Anaerobic pyrolysis of isodicyclopentadiene at 575 °C lead to the formation of **1,4-H₂Pn** (through release of ethylene) in ~30% yield, to which hydroquinoline had to be added immediately to prevent polymerisation. However, Kazennova *et al.* later reported that passing the pyrolysis distillate through a plug of solid potassium hydroxide provided pure **H₂Pn** samples that were stable to

polymerisation at −78 °C.[17] They also demonstrated an improved synthesis of isodicyclopentadiene, reporting a 40% overall yield of **H₂Pn** starting from **HCp**.

An alternative precursor was reported by Jones and Schwab, who showed that **COT** undergoes thermal rearrangement between 400–665 °C to give **H₂Pn** (Fig. 6) in addition to acetylene, benzene and styrene.[18] The selectivity to **H₂Pn** was found to be highly temperature-dependent, with the optimum conversion occurring between 500–600 °C. An optimised procedure was later reported by Cloke *et al.*, in which a 87% yield was achieved thanks to precise temperature and residence time control during the continuous-flow pyrolysis.[19] In this set-up, the resulting **H₂Pn** were condensed into a *n*butyllithium solution in DME/hexane at −78 °C to be directly converted to the more stable [**Li₂(DME)$_x$**]**Pn** salts that precipitate to be further purified by washing with cold hexane.

While both routes are reasonably well established (with lower yields and more synthetic steps starting from inexpensive (**HCp**)₂, or fewer steps and higher yields starting from the more valuable **COT**), they are limited to the synthesis of the parent (unsubstituted) **H₂Pn**. Substituted iso-**CpH** or **COT** have not been explored as pyrolysis precursors for substituted **H₂Pn**, likely due to the difficulty and expense of synthesising the starting materials and/or unwanted thermal rearrangement pathways. A slightly more versatile pyrolytic method has been reported by Griesbeck, who showed the use of two protected vinyl fulvenes, synthesised by Diels–Alder reaction of **HCp** and acroleins followed by pyrrolidine-facilitated Knoevenagel condensation with an additional equivalent of **HCp** (Fig. 7).[20]

Anaerobic pyrolysis of these compounds at 520 °C furnished **H₂Pn** (88% yield) or **2-Me-PnH₂** (50% yield) through thermal cyclisation accompanied by loss of **HCp**. This methodology is appealing as the precursors are straightforward to synthesise from inexpensive starting materials, and potentially provide a route to other substituted **H₂Pn** through use of substituted acroleins in the first step and/or substituted **HCp** in the second step. However, the final pyrolysis may require optimisation for each protected vinyl fulvene.

Another pyrolytic route to **H₂Pn** and **2-Me-PnH₂** has been reported by Stapersma *et al.*, who showed that tetracyclo-oct-7-enes may be rearranged by anaerobic heating between 250 °C and 500 °C.[21] These starting materials, derived from photolytic rearrangements of 7-carbomethoxynorbornadienes,[22] are comparatively difficult to prepare, and their pyrolysis reactions gave relatively low **H₂Pn** yields of 7–16% due to the formation of a large number of side products.

Fig. 6 Synthesis of dihydropentalene by anaerobic flash vacuum pyrolysis.

Fig. 7 Flash vacuum pyrolysis of protected vinyl fulvenes derived from cyclopentadiene and acroleins.

Fig. 8 Thermal cyclisation of vinyl fulvenes to dihydropentalenes.

2.3. Thermal cyclisations of vinyl fulvenes

A mild thermal synthesis of **H₂Pn** has been described by Gajewski and Cavender, who found that neat 6-vinyl fulvene will undergo thermal cyclisation at 110 °C (Fig. 8).[23] This procedure gave exclusively the **1,5-PnH₂** isomer due to facile 1,5-hydride shifts occurring.

6-Propenylfulvene was reported to undergo a thermal reaction at 65 °C, however, analysis of the products obtained was limited and no isolated yields were reported. The relatively low temperatures required to induce these rearrangements promise practical benefits over the higher temperature pyrolysis reactions discussed above. However, 6-vinyl fulvene is

again not trivial to synthesise. Neuenschwander reported two preparations: the first reacting 1-hydroxymethyl-spiro-[2,4]-hepta-4,6-diene with HCl,[24] the second reacting **NaCp** with 3-acetoxy-3-chloro-1-propene.[25] Both routes give low yields (10% and 20%, respectively) due to significant side reactions occurring. Erden *et al.* describe an improved protocol, starting with condensation of **HCp** with 3-(methylthio)propanal, followed by oxidation with NaIO₄ and sulfoxide elimination with DBU. The reported yield across the three steps was 37% including a purification after each step.[26]

Kaiser and Hafner showed that 6-(2-aminovinyl)fulvenes would undergo a solution-phase thermal cyclisation and isomerisation in boiling piperidine to give **3-amino-PnH₂** in high yields (Fig. 9).[27] These species could be reduced with LiAlH₄ to give an organoaluminium species that, upon hydrolysis, underwent amine elimination at room temperature to yield **H₂Pn**. The syntheses of some mono- and di-substituted **H₂Pn** were also described, using 6-substituted amino fulvenes in the first step, and using alkyl/aryl lithiums in the following reduction/elimination step. However, purification procedures for these compounds were not described.

Similar to the above case of vinyl fulvenes, the amino-vinyl fulvene starting materials (derived from condensation of **HCp**

Fig. 9 Thermal rearrangement of aminovinyl-fulvenes and subsequent reduction to dihydropentalenes.

with di(alkyl)-aminoacroleins) are difficult to handle due to their thermal instability.[28] In theory, starting from substituted **HCp** could produce more stable amino-vinyl fulvenes and provide access to more highly substituted **H₂Pn**. However, it is difficult to predict whether these species would follow the same thermal rearrangement pathways.

While some of the thermal routes reviewed above have been shown to be quite efficient in generating **H₂Pn** precursors suitable for double deprotonation to **Pn²⁻**, the limitations of these rearrangement reactions are obvious: their precursors rely on multi-step syntheses and/or utilise expensive starting materials, they often require special apparatus, conditions need to be carefully controlled and optimised, and they are rather limited in scope.

2.4. Solution-phase rearrangement reactions

Several solution-phase syntheses of **H₂Pn** that do not involve pyrolytic steps have been described in the literature. Jones *et al.* reported the synthesis of **Li₂Pn** starting with the conversion of cycloheptatriene to 8,8-dibromobicyclo[5.1.0]octa-2,4-diene using bromoform and KO*t*Bu (Fig. 10).[10] Reacting this species with methyllithium triggered a carbene-induced rearrangement to give **H₂Pn** which was trapped with *ⁿ*butyllithium in DME/pentane to give [**Li₂(DME)ₓ]Pn**. Although the overall yields are quite low (<12%), this solution-phase method can be performed with standard laboratory equipment.

The Skattebøl rearrangement of the transient carbene generated from the geminal dihalo-cyclopropane unit allows for some variability in the substitution pattern. Cycloheptatriene can be converted to 7-alkylcycloheptatrienes through hydride abstraction, formation of the ethyl ether with EtOH and NaHCO₃, then finally substitution of the ether with a Grignard reagent. Although 7-*tert*-butyl-cycloheptatriene was found not to react with CHBr₃ and KO*t*Bu, the methyl, ethyl and isopropyl variants did undergo this transformation (albeit with low

yields of 9–15%). Treating the *gem*-dibromo cyclopropane unit in these species with methyllithium furnished 1-alkyl substituted **H₂Pn**, which gave high yields of **Li₂[1-alkyl-Pn]** upon double deprotonation with *ⁿ*butyllithium (53–70%).[10]

Another synthesis of **H₂Pn** *via* carbene rearrangement has been reported by Brinker and Fleischhauer.[29] *trans*-1,2-Bis(2.2-dibromocyclopropyl)ethane, formed by twofold reaction of *trans*-1,3,5-hexatriene with CHBr₃ and KO*t*Bu, was found to rearrange to **H₂Pn** when treated with methyllithium in diethyl ether. However, significant side products were formed, and attempts to separate the mixture using vapour-phase chromatography proved unsuccessful.

Ashley *et al.* developed a solution-phase synthesis of hexamethylpentalenide, **Pn*²⁻**, the pentalenide analogue of pentamethylcyclopentadienide (**Cp*⁻**).[30] The starting material for this preparation is the so-called 'Weiss-H₄' compound, obtained from reaction of dimethyl-1,3-acetonedicarboxylate with glyoxal.[31] Reacting the 'Weiss-H₄' compound with an excess of methyl iodide and K₂CO₃, followed by hydrolysis/decarboxylation with concentrated HCl yielded 2,4,6,8-tetramethylbicyclo[3.3.0]octane-3,7-dione (Fig. 11). The so-obtained diketone could be oxidised with bromine in MeOH, then reacted with 'methylcerium dichloride' (derived from methyllithium and cerium trichloride) at −78 °C in THF. The resulting alcohol is prone to polymerisation and thus extremely sensitive to acid. The final dehydration reaction therefore required an aprotic method, and it was found that LiCl in DMSO was effective in producing 1,3,4,5,6-pentamethyl-2-methylene-1,2-dihydropentalene, **Me₆-Pn** or **Pn***, an exocyclic isomer of hexamethylpentalene. This compound is stable due to its vinylic fulvene structure preventing cyclic conjugation of an otherwise anti-aromatic 8π system, and marks the only pentalenide synthon where the 8π **Pn*** is stable whereas the non-aromatic **H₂Pn*** is unknown. As outlined in Fig. 3, to transform the **Pn*** into **Pn*²⁻** it must be doubly reduced. Direct reaction with alkali metals lead to degradation of the starting material

Fig. 10 Synthesis of dilithium pentalenides from cycloheptatrienes.

Fig. 11 Synthesis of an exocyclic hexamethylpentalene isomer from 'Weiss-H₄'.

Fig. 12 Reduction of hexamethylpentalene to lithium hexamethylhydropentalenide, and its subsequent deprotonation to dilithium hexamethylpentalenide.

through polymerisation, but reaction with a bulky trialkyl borohydride (LS-selectride) allowed for 1,4-addition of a hydride to yield **LiHPn*** (Fig. 12).[32] Use of the less sterically demanding L-selectride resulted in a mixture of 1,2- and 1,4-addition products.

LiHPn* is reportedly insoluble in most organic solvents, requiring solubilisation with pyridine for NMR analysis. The final deprotonation of **LiHPn*** however was performed in a refluxing hexane slurry with ^{n}butyllithium and TMEDA to afford the TMEDA adduct of **Li$_2$Pn***. In order to obtain single crystals suitable for XRD analysis [**Li$_2$(TMEDA)$_x$]Pn*** had to be converted into a bis-stannyl derivative using Me$_3$SnCl (see Fig. 39, section 3.3), and transmetallated again using methyllithium in neat TMEDA.[32]

Despite requiring multiple steps involving several sensitive intermediates, the overall synthesis of **[Li$_2$(TMEDA)$_x$]Pn*** is well developed and gives access to a valuable synthon for organometallic pentalenide chemistry without the use of special apparatus. Using different electrophiles (for example, ethyl iodide or isopropyl bromide) in the first step could in principle allow for incorporation of different substituents into these four positions, but this change would likely require downstream modification of the overall synthesis. So far there is no report of such variants.

2.5. Annulation reactions of cyclopentadienes

As already exemplified in some of the previous thermal rearrangement reactions, **HCp** provide a convenient starting material for the synthesis of pentalene derivatives. In the following section we review examples where selective 1,2 annulation reactions of **HCp** have been accomplished via mild solution-phase methods. An early example was provided by Hafner

and Süss, who used **Li[^{t}BuCp]** to synthesise ^{t}**Bu$_3$Pn** through its reaction with an iminium salt derived from 5-dimethylamino-2,2,6,6-tetramethyl-4-hepten-3-one and triethyloxonium tetra-fluorborate (Fig. 13).[33]

The resulting deep blue species had to be purified by chromatography on alumina at −75 °C using pentane as the eluent. Kitschke and Lindner were later able to obtain crystals of ^{t}**Bu$_3$Pn** for XRD analysis by recrystallisation from hexane.[34] Its stability is interesting in that although normally one would not approach the synthesis of an organometallic **Pn^{2-}** ligand via its 8π **Pn** version, this might be a viable approach in the case of sterically demanding substitution patterns such as 1,3,5-tris(*tert*-butyl) that are effective in blocking dimerization pathways. Ashley *et al.* have shown that a permethylated **Pn** system may be reduced using a bulky borohydride to give **HPn$^-$** and then **Pn^{2-}** upon deprotonation (Fig. 11),[32] so similar chemistry might be possible with other bulky **Pn** such as Hafner's ^{t}**Bu$_3$Pn**.

Due to their known stability and ease of deprotonation, routes that give access to **H$_2$Pn** synthons are still preferable in most cases. Retrosynthetic analysis shows that Hafner's **HCp** annulation strategy to synthesise ^{t}**Bu$_3$Pn** is well suited to give access to **H$_2$Pn** as well: 1,4-Michael addition by a **Cp$^-$** to an electrophilic conjugated carbonyl species would yield a β-cyclopentadiene-functionalised ketone/aldehyde intermediate that is set up to undergo an intramolecular Knoevenagel condensation (Fig. 14). Compatible **HCp** merely require two adjacent unsubstituted carbons in order to accommodate the final ring-closing step. Thus, a wide range of mono-, 1,2 and 1,3 di-, as well as 1,2,3-trisubstituted **HCp** may be transformed into the corresponding **H$_2$Pn** pro-ligands by reaction with simple enones (chalcones).
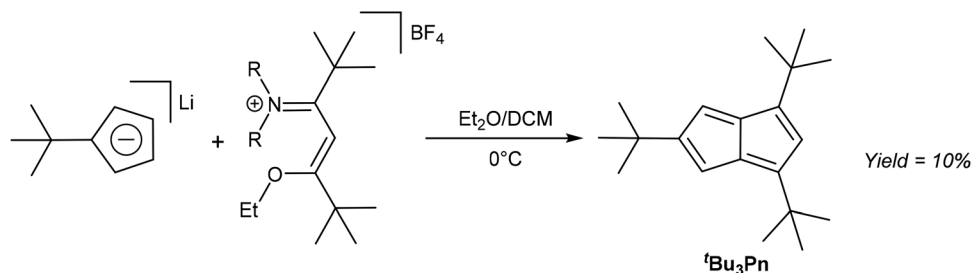

Fig. 13 Synthesis of 1,3,5-tris(^{t}butyl)pentalene from lithium ^{t}butylcyclopentadienide.
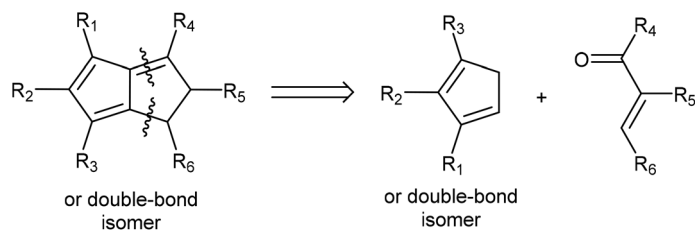
Fig. 14 Retrosynthesis of substituted dihydropentalenes from cyclopentadienes and enones.

The simplest unsubstituted **H₂Pn** is currently not accessible by such a transformation, as **HCp** and acrolein are known to undergo a Diels–Alder reaction instead of the required Michael addition.[35] However, Griesbeck showed that moving to slightly higher substituted reaction partners, and using pyrrolidine to activate the chalcone towards 1,4 nucleophilic attack *via* its enamine, indeed furnishes substituted **H₂Pn** in good yields from a single step reaction under mild conditions (Fig. 15).[36]

The six different 1,3-disubstituted **H₂Pn** thus prepared were air-stable compounds that did not polymerise and could be purified by high-vacuum distillation. The initially obtained 1,2 double-bond isomers were found to isomerise to the more stable 1,5 form when contacted with Brønsted acids (*e.g.* trifluoroacetic acid or activated alumina) or when heated above 500 °C. Curiously, none of the 1,3-disubstituted **H₂Pn** reported in this study have been taken forward to the **Pn²⁻** form by double deprotonation or used as organometallic synthons in other reports so far.

Another, more highly substituted example of this strategy has been reported by Le Goff,[37] who reported the fluoride-catalysed condensation of **1,2,3-Ph₃CpH** and 1,2,3-triphenylenone to yield **Ph₆PnH₂** (Fig. 16). Oxidation with N-bromosuccinimide reportedly afforded the corresponding

Ph₆Pn as another example of an 8π pentalene stabilised by suitable substitution pattern, as inferred from its UV-vis spectrum.

Its corresponding **Ph₆Pn²⁻** would make an interesting organometallic ligand, however, this two-page single-author communication does not contain any synthetic or analytical details, and the synthesis has never been replicated in later literature.

2.6. Annulation reactions of fulvenes

In cases where the required chalcone is either difficult to access or does not display the desired reactivity, a step-wise approach to **H₂Pn** synthesis *via* **HCp** annulation is also possible. Condensation of a **HCp** with an aldehyde yields a 6-substituted fulvene that may be attacked by an enolate to ring-close *via* an intramolecular Knoevenagel condensation (Fig. 17). Although apparently introducing an additional reaction step, it eliminates the need for synthesising the enone in the first place. Formation of the fulvene intermediate from **HCp** and aldehyde follows a straightforward condensation reaction using pyrrolidine in MeOH as described by Stone and Little (Fig. 18).[38]
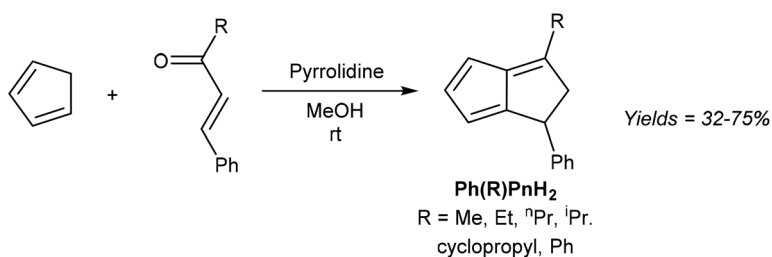

Fig. 15 Synthesis of di-substituted dihydropentalenes by pyrrolidine–facilitated condensation of cyclopentadiene and substituted enones.
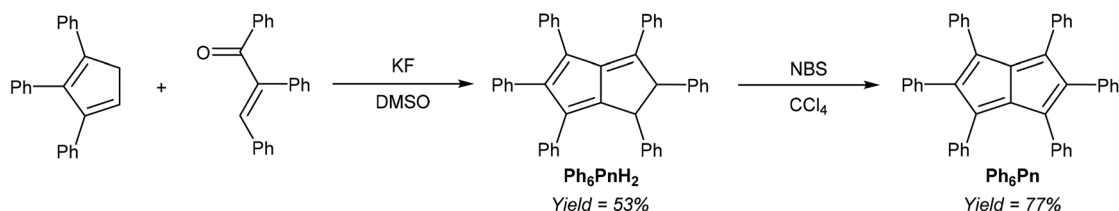

Fig. 16 Synthesis of hexaphenyldihydropentalene, and its oxidation into hexaphenylpentalene.

Fig. 17 Retrosynthesis of substituted dihydropentalenes from cyclopentadienes, aldehydes and ketones.
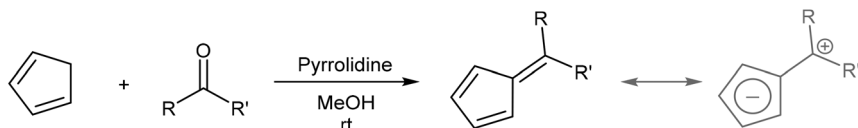

Fig. 18 Synthesis of fulvenes from cyclopentadiene and carbonyl compounds and their resonance structure.

Yields = 40–91%

1,3-(R)Me-PnH$_2$
R = Me, Et, iPr, Ph, p-Tosyl, p-Anisyl,
Vanilyl, p-Chlorophenyl

Fig. 19 Synthesis of 1,3-disubstituted dihydropentalenes from 6-substituted fulvenes and acetone.

6-Substituted fulvenes are stable enough to be isolated, however, with their exocyclic double bond being polarised to enable nucleophilic attack by a range of nucleophiles (Fig. 18).[28] Coskun *et al.* have demonstrated the utility of this reactivity for **H$_2$Pn** synthesis (Fig. 19).[39] Reaction of **HCp** with a range of different aldehydes afforded 6-substituted fulvenes that cleanly condensed with acetone (used as the solvent for this transformation) at room temperature in the presence of pyrrolidine to give variously substituted **1,3-RMe-PnH$_2$** in good yields. The air-stable products were obtained after evaporation of solvent and side products (mainly from cross-condensation of acetone) followed by flash chromatography on silica, which was reported not to induce any double bond isomerisation.

Again, none of the **H$_2$Pn** synthesised have been deprotonated to the corresponding **Pn^{2-}** in this or other studies. Coskun *et al.* only describe the reactivity of 6-methyl fulvene, but it could be supposed that fulvenes derived from substituted **HCp** and various aldehydes could be reacted in an analogous manner to give a variety of more highly substituted **H$_2$Pn** as outlined in Fig. 16. However, like the concerted double-condensation reaction using chalcones described above, the parent (unsubstituted) **H$_2$Pn** is not likely to be accessible *via* this step-wise condensation method either due to the instability of its hypothetical reaction partners (unsubstituted fulvene and acetaldehyde).

2.7. Acetylene oligomerisation

Akin to alkyne trimerization to give variously substituted 6π aromatics (Reppe chemistry),[40] there are also some reports of alkyne oligomerisation reactions that produce pentalene scaffolds. Kuwabara *et al.*[41] and Saito *et al.*[42] reported the synthesis of bis-silylated dibenzopentalenides through reduction of phenylacetylenes with alkali metals (Fig. 20). When phenyl

$R_3 = (^iPr)_3, (Me)_3, (^tBuMe_2)$

Yield = 35–89%

(SiR$_3$)$_2$Bn$_2$Pn^{2-}

Fig. 20 Formation of dibenzopentalenides by reaction of phenylsilylacetylenes with potassium.

Fig. 21 Palladium-mediated cyclotetramerization of phenylacetylene to tetraphenyldihydropentalenes.

(tris^{i}propylsilyl)acetylene was reacted with metallic lithium in Et$_2$O only a small amount of **Li$_2$[Bn$_2$Pn]** was obtained. The major product of this reaction, a 1,4-dilithio-1,3-butadiene, could be reacted with Ba(HMDS)$_2$ to give **Ba[Bn$_2$Pn]**, the hydrolysis of which yielded the silyl-substituted **Bn$_2$PnH$_2$**.[43] Reduction of phenyl(tris^{i}propylsilyl)acetylene with metallic potassium directly gave **K$_2$[Bn$_2$Pn]** in high yields, with other silyl-substituted phenylacetylenes reacting in the same manner (Fig. 20).

In another example, Bailey et al.[44] described the PdCl$_2$ catalysed cyclotetramerisation of phenylacetylene to **Ph$_4$PnH$_2$** (Fig. 21). However, of the two isomeric products obtained from this reaction only one would be suitable for deprotonation into a **Ph$_4$Pn^{2-}**, and the report does not include methods of preparative work up and isolation.

Although interesting examples of an alternative, potentially elegant synthetic approach of accessing **H$_2$Pn** from simple alkyne starting materials, the generality and versatility of these methods remain to be explored more systematically.

2.8. Functionalisation of pentalenides

Although most solution-phase syntheses of **H$_2$Pn** are easier for more highly substituted starting materials, the opposite is true for pyrolytic pathways. However, post-synthetic functionalisation of the parent (unsubstituted) **H$_2$Pn** obtained from e.g. FVP is also possible to some degree. Cloke et al. for instance

demonstrated the functionalisation of **Li$_2$Pn** with of trialkyl-silyl-groups (Fig. 22), which in addition to modifying their electronic and steric parameters imparts the complexes with enhanced solubility in hydrocarbon solvents.[19]

[Li(DME)]$_2$Pn was shown to react regio-selectively with two equivalents of TMS-Cl in THF to give **1,4-TMS$_2$PnH$_2$** as a mixture of syn and anti isomers. These could be doubly deprotonated again with ^{n}butyllithium in DME/pentane to give the corresponding **[Li(DME)]$_2$[1,4-TMS$_2$Pn]** for subsequent transmetalation reactions. When introduction of additional substituents was attempted at this stage, by further reaction of **1,4-TMS$_2$Pn^{2-}** with another two equivalents of TMS-Cl, **1,1,4,4-TMS$_4$PnH$_2$** was obtained exclusively. Due to the two bis-silylated sp^3 carbons in the 1 and 4 positions this compound cannot be converted into a **Pn^{2-}** by way of deprotonation any more, limiting how much functionality may be introduced through this strategy. **[Li(DME)]$_2$Pn** failed to react analogously with tris(^{i}propyl)silyl chloride, but did react with the more activated tris(^{i}propyl)silyl triflate to give the corresponding **1,4-TIPS$_2$PnH$_2$**, forming the anti isomer only, presumably due to steric reasons in this case. Reacting this compound with KNH$_2$ in Et$_2$O gave high yields of **K$_2$[1,4-TIPS$_2$Pn]**, a useful ligand for use in f-block chemistry where lithium salts tend to form 'ate' complexes (see section 3.3).[19]

The regioselectivity of the reaction of **Pn^{2-}** with hard electrophiles is a consequence of its charge distribution. In

Fig. 22 Reaction of dilithium pentalenide with silyl-electrophiles, and deprotonation of the resulting disilyl-dihydropentalenes.

Fig. 23 Resonance structures of the pentalenide dianion.

Fig. 24 Reaction of pentalene dimer with diiron nonacarbonyl.

addition to the fully delocalised (aromatic) η^8 form and the partially delocalised (allylic) η^3 form that govern reactivity with soft Lewis acids, its ground state η^1 resonance structure conjugates both charges to the 1 and 4 positions (Fig. 23). Thus, post-synthetic functionalisation of Pn^{2-} is often limited to these two positions.

3.   Synthesis of pentalenide complexes of p-, d- and f-block metals

As mentioned in section 2.1 (Fig. 4 and 5), deprotonative metalation of H_2Pn with suitably strong bases gives straightforward access to stable HPn^- and Pn^{2-} salts that can be used for transmetalation on to p-, d-, and f-block metals in the desired oxidation state. Before we review selected cases of these in section 3.3, there are also some examples of direct metalation reactions of neutral precursors *via* redox reactions (as in related **HCp** chemistry) that deserve mentioning. At present these appear less generally applicable than transmetalation from HPn^- and Pn^{2-} salts, but serve to illustrate the rich coordination chemistry of pentalenide ligands.

3.1.   Pentalenide and hydropentalenide complexes through direct metalation of neutral precursors

An early example of a direct redox metalation of **Pn** with a transition metal has been provided Hafner and Weidemüller,[45] who reported that the reaction of Pn_2 with an iron(0) precursor produced a small amount of $(CO)_5Fe_2Pn$ (Fig. 24). According to the contemporary ionic electron counting model, and in line with the thermodynamic driving force of forming a 10π aromatic, this reaction implies a double reduction of **Pn** to Pn^{2-} accompanied by cleavage of the dimer and oxidation of two Fe^0 centres to Fe^I. Heating Pn_2 to 50 °C in methylcyclohexane in the presence of $Fe_2(CO)_9$ resulted in the formation of a yellow crystalline solid, supposed to be the *syn*-diiron pentalenide complex shown based on its NMR spectro-

scopic and mass spectrometric signatures. However, no XRD analysis is available to confirm the geometry, and work up details were not provided in the original paper. A mixture of isomers of $[1,3\text{-}Me_2Pn]_2$ was reacted in a similar fashion to give an unidentified green diiron complex in 21% reported yield.[45]

In related examples of directly metalating H_2Pn precursors, Hunt and Russel[46] reported that reacting $3\text{-}Me_2N\text{-}PnH_2$ or $3\text{-}Ph\text{-}PnH_2$ with $Fe(CO)_5$ would produce analogous *syn* bimetallic $(CO)_5Fe_2Pn$ complexes in similar yields (Fig. 25). However, none of the geometries have been confirmed by XRD either.

Similar to direct metalation reactions of **HCp** with zerovalent metal precursors to give $M(I)Cp$ complexes, this conversion of a H_2Pn into a bimetallic Pn^{2-} complex implies a double deprotonation and proton reduction to H_2 to give two Fe^I centres in the resulting complex.

Another redox metalation of a **Pn** has been reported by Ashley *et al.*[47] Refluxing **Pn*** (Fig. 11) with an excess of $Fe_2(CO)_9$ in toluene (added in portions) furnished a brown solid upon filtration and washing. Recrystallisation from toluene/hexane produced the η^5 $(CO)_5Fe_2Pn^*$ complex shown in Fig. 26 in good yields. In this case the *syn* geometry of the two metal centres has been established by XRD analysis. The same procedure could be applied to synthesise a related dicobalt complex using a stoichiometric amount of $Co_2(CO)_8$ (Fig. 26). Notably, both compounds could be synthesised on a multigram scale.

Both reactions involve a formal double reduction of the **Pn*** scaffold by the metal(0) precursors, accompanied by a two-bond hydrogen shift to the exocyclic methylene group. The similar reactivity but increased stability and enhanced crystallinity of these Pn^{*2-} compounds compared to the parent Pn^{2-} complexes are promising and provide motivation for further exploration of other substitution patterns in organometallic pentalenide chemistry.

Redox metallations of **COT** accompanied by skeletal rearrangement to Pn^{2-} are also known for some d-block metal

Fig. 25 Reaction of mono-substituted dihydropentalenes with iron pentacarbonyl.

Fig. 26 Reaction of hexamethylpentalene with diiron nonacarbonyl and dicobalt octacarbonyl.

Fig. 27 Rearrangement redox reaction of cyclooctatetraene with $Ru(CO)_4(GeMe_3)_2$.

Fig. 28 Reaction of acetylene with dimanganese decacarbonyl.

complexes. Brookes *et al.*[48] reported the reaction of *cis*-[Ru (CO)$_4$(GeMe$_3$)$_2$] with **COT** in refluxing heptane or octane (Fig. 27). Of the several compounds produced from this reaction, a small amount of the pale yellow *syn* bimetallic **Ru$_2$Pn** complex shown in Fig. 27 could be isolated and analysed by XRD.

Similarly, Howard *et al.*[49] reported that **COT** would react with Ru$_3$(CO)$_{10}$ in refluxing heptane to give a trinuclear **RuPn** complex, albeit in low yields and in a mixture with various other **RuCOT** complexes. Silyl-substituted **COT** have been reported to react in an analogous manner, giving the correspondingly substituted trinuclear **RuPn** complexes.[50] All of these reactions were very low yielding and no work up procedures are available, so the synthetic utility of these transformations appears limited.

Akin to the alkali metal induced and palladium catalysed alkyne oligomerisation reactions that produce substituted **H$_2$Pn** (section 2.7), the direct formation of **HPn$^-$** complexes from cyclotetramerization of acetylenes has also been reported. For example, Coffield *et al.*[51] showed that heating Mn$_2$(CO)$_{10}$ in THF under a pressure of acetylene resulted in the formation of η^5 **(CO)$_3$MnPnH** as a viscous yellow oil that was purified by distillation (Fig. 28). The same transformation could also be accomplished using MeMn(CO)$_5$ but with lower yields of 27%. Further deprotonation of the bound **HPn$^-$** was not attempted.

Komatsu *et al.* reported the formation of η^5 **RhPnH** complexes through Rh^I mediated tetramerisation of bulky monosubstituted alkynes (Fig. 29). The reaction of ^{t}butylacetylene with [Rh(COD)Cl]$_2$ and NEt$_3$ in cyclohexane furnished η^5 **(COD)Rh[^{t}bu$_4$PnH]** in 13% yield after purification by chromatography on alumina followed by recrystallization from EtOH.[52]

The analogous reaction of TMS-acetylene with [Rh(COD) Cl]$_2$ gave the corresponding η^5 **(COD)Rh[TMS$_4$PnH]** complex in 50% isolated yield. Interestingly, whereas tetramerization of

Fig. 29 Reaction of substituted acetylenes with [Rh(COD)Cl]$_2$.

Fig. 30 Synthesis of di(hydropentalenide)iron from dihydropentalene.

Fig. 31 Transmetalation reactions of thallium hydropentalenide.

^{t}butylacetylene produced **1,1,3,5-R$_4$PnH$^-$**, TMS-acetylene yielded the **1,2,4,6-R$_4$PnH$^-$** regio-isomer. While not possible with the former, the latter could in principle allow for a second deprotonation to a **1,2,4,6-R$_4$Pn^{2-}**. However, this has not been reported yet.

3.2. Hydropentalenide complexes through transmetalation of hydropentalenides

As shown in Fig. 3 and section 2.4, and illustrated in some of the examples in section 3.1, the monoanionic, 6π aromatic **HPn$^-$** synthon may be obtained from either hydride addition to a stable **Pn** or mono-deprotonation of **H$_2$Pn**. Katz and Rosenberger provided an early demonstration of its utility as a transmetalation agent: *in situ* generation from **H$_2$Pn** with 1.1 equivalents of ^{n}butyllithium in THF/hexane followed by addition of iron(II) precursors yielded the ferrocene analogue η^5 **Fe[PnH]$_2$** as a mixture of two isomers (Fig. 30).[53] The stable compound was obtained in 54% yield after aqueous work up followed by sublimation and recrystallisation from hexane.

TlCp is known to be a useful transmetalation agent in instances where alkali metal **Cp$^-$** salts are too reducing.[54] In the same manner, **TlPnH** (Fig. 4) has been shown to act as an efficient, mild transmetalating agent with d-block metal precursors: reaction with FeCl$_2$ in THF was shown to give the

ferrocene derivatives shown in Fig. 30 in 47% isolated yield.[9] Similalry, reaction of **TlPnH** with [Rh(COD)Cl]$_2$ in THF smoothly yielded η^5 **(COD)Rh[PnH]** (Fig. 31).[9] The TlCl by-product was easily removed by filtration, and sublimation of the product gave the pure Rh^I complex in high yield. The same study also demonstrated the successful reaction of **TlPnH** with Me$_3$PtI, but the **Me$_3$Pt[PnH]** complex produced required gas-phase chromatography in order to furnish pure product.

Reaction of **TlPnH** with a suspension of [Re(CO)$_3$(THF)Br]$_2$ in THF in the absence of light gave η^5 **(CO)$_3$Re[PnH]** as a colourless solid after purification by chromatography on silica (Fig. 31).[10] Recrystallisation from Et$_2$O yielded crystals suitable for XRD analysis. The analogous manganese complex could also be prepared through the reaction of [Mn(CO)$_3$(py)$_2$Br] with **TlPnH** in THF to give the same product of the cyclotetra-merisation of acetylene with Mn$_2$(CO)$_{10}$ (Fig. 28).[5a] Reacting a mixture of **Tl[MePnH]** isomers with [Re(CO)$_3$(THF)Br]$_2$ in THF yielded the corresponding η^5 **(CO)$_3$Re[MePnH]** complexes as a mixture of double bond isomers.[10] Although good combined yields were obtained after purification on silica, the isomers (distinguishable by NMR) could not be separated by chromato-graphy or fractional crystallisation.

Direct metalation reactions of **H$_2$Pn** with other heavy p-block metal bases has also been achieved. Ustynyuk *et al.* reported the synthesis of mono- and bis-Me$_3$Sn derivatives of **H$_2$Pn** using tin amides.[55] The reaction of **H$_2$Pn** with one equivalent of Me$_3$Sn(NEt$_2$) in boiling hexane produced, after distillation, a mixture of 1- and 2-η^1-**(Me$_3$Sn)PnH** (Fig. 32). Higher yields were obtained by stirring the reagents in heptane at room temperature for 48 hours. According to Fig. 23, the 1-isomer would be the primary reaction product from formal addition of a Me$_3$Sn$^+$ moiety to the **HPn$^-$** intermediate, and NMR analysis indeed showed rapid suprafacial 1–2–3 shifts of the TMT group within **(Me$_3$Sn)PnH** (as also observed in related η^1-TMT **Cp** and **Ind** complexes[56]) to be responsible for formation of the 2-isomer.

The same reaction with two equivalents of Me$_3$Sn(NEt$_2$) produced **1,4-(Me$_3$Sn)$_2$Pn** in high yield without purification. A 6 : 1 mixture of *anti*- and *syn*-isomers was obtained which did not interconvert; although VT ^{13}C NMR analysis showed supra-facial Me$_3$Sn shifts to be possible within each **(Me$_3$Sn)$_2$Pn** isomer there was no evidence for superfacial migration or intermolecular exchange. A pure sample of the *anti*-isomer could be obtained after separation by fractional distillation

Fig. 32 Reactions of dihydropentalene with trimethyltin–diethylamide.

and crystallisation from pentane, enabling structural analysis by XRD. The authors also showed how the *anti-* and *syn-* isomers may be distinguished by their ^{119}Sn chemical shift values and assigned *via* characteristic ^{119}Sn–^{117}Sn coupling constants within a mixture in solution.

Similar to the η^5 thallium reagents, η^1 stannylated **Pn** act as mild transmetalation agents in cases where alkali metal **Pn^{2-}** salts are too reducing (see below). This reactivity is not seen with the structurally related but non-fluxional η^1 silylated **Pn** derivatives discussed in section 2.8 due to the strength of the covalent Si–C bond, preventing the trisalkylsily substituent from acting as a leaving group.

Turner *et al.* demonstrated the use of mono-stannylated **HPn*$^-$** as a ligand transfer agent for synthesising hydropentalenide complexes of group 4 metals (Fig. 33).[57] The reaction of **LiHPn*** with SnMe$_3$Cl in pentane gave η^1 (**Me$_3$Sn)HPn*** as a 1:1 mixture of *syn* and *anti* isomers in near quantitative yields after isolation by filtration.

Reacting (**Me$_3$Sn)HPn*** with TiCl$_4$(THF)$_2$ in refluxing benzene gave a single isomer of η^5 **TiCl$_3$[HPn*]** in high yields, and single crystals for XRD analysis could be grown from diethyl ether. Chlorine-bridged, mono-nuclear zirconium and hafnium **HPn*** dimer complexes could also be prepared from (**Me$_3$Sn)HPn***.[57] Although deprotonation of the bound **HPn***

ligand in the Ti complex was not attempted, the reverse reaction (mono-protonation of a titanium **Pn*$^{2-}$** complex) was later reported by the same group (see Fig. 40).

3.3. Pentalenide complexes through transmetalation of pentalenides

Due to their stability and ease of preparation, alkali metal **Pn^{2-}** salts are the most prevalent reagents for synthesising organometallic pentalenide complexes. Again similar to **MCp** chemistry, Jonas *et al.* reported that [**Li$_2$(DME)$_x$]Pn** would react cleanly with Cp$_2$VCl by substitution of one **Cp$^-$** ligand and chloride.[58] The resulting η^5CpVη^8**Pn** complex (Fig. 34) is air sensitive but could be sublimed under vacuum to give pure product in high yields. η^5**Cp*Vη^8Pn** and η^5**IndVη^8Pn** could be prepared in the same manner, and recrystallisation from hexane at low temperatures gave samples suitable for XRD analysis.

The reaction of CpTiCl$_2$ with [**Li$_2$(DME)$_x$]Pn** yielded η^5**CpTiη^8Pn** in high yield, and the analogous reaction of Cp$_2$ZrCl$_2$ gave η^5**CpClZrη^8Pn** (Fig. 34).[59] However, details of solvents for these transformations is missing from these reports.

Jones *et al.* managed to access several new bimetallic group 7 carbonyl **Pn^{2-}** complexes by way of transmetalation.[60] The reaction of [**Li$_2$(DME)$_x$]Pn** with 2 equivalents of

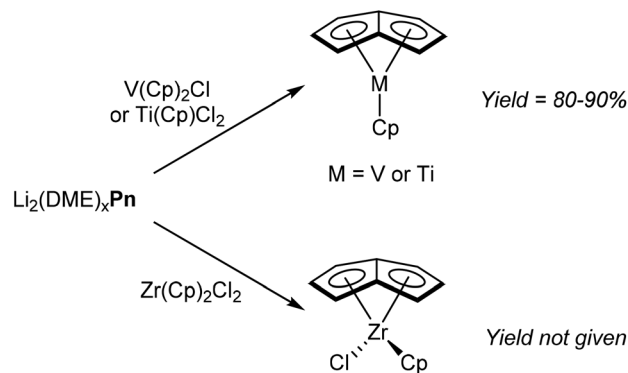**Fig. 33** Synthesis of a stannylated derivative of HPn*$^-$ and its reaction with a titanium(IV) precursor.

Fig. 34 Transmetalation reactions of dilithium pentalenide with early d-block metals.

[Mn(CO)$_3$(py)$_2$Br] in THF gave exclusively the *anti*-isomer of η^5 [(CO)$_3$Mn]$_2$Pn (Fig. 35), which after extraction and filtration in air was purified by chromatography on silica. When the analogous reaction was performed with one equivalent of [Re(CO)$_3$(THF)Br]$_2$, a mixture of *syn*- and *anti* η^5 [(CO)$_3$Re]$_2$Pn was obtained, with the ratio being dependent on the reaction temperature. The two isomers could be separated through fractional crystallisation.

Katz *et al.* showed that dinuclear Pn^{2-} sandwich complexes of cobalt and nickel could be synthesised by reacting their respective dihalide salts with [Li$_2$(DME)$_x$]Pn in THF (Fig. 35).[61] Both compounds were obtained in low yields after purification by sublimation. The analogous reaction with FeCl$_2$ however did not produce the analogous dinuclear sandwich complex ("double ferrocene"),[61b] but a mononuclear sandwich complex with two bridging HPn$^-$ ligands instead.[62] Binding *et al.* were later able to synthesise the dinuclear sandwich complex [FePn*]$_2$ by reacting [Li$_2$(TMEDA)$_x$]Pn* with Fe(acac)$_2$ in THF at room temperature,[63] providing yet another example of the utility of more highly substituted pentalenide scaffolds.

Manriquez *et al.* showed that Cp*Fe(acac), generated *in situ* from LiCp* and Fe(acac)$_2$ in THF, would react smoothly with [Li$_2$(DME)$_x$]Pn to produce *anti* η^5[Cp*Fe]η^{8}Pn (Fig. 35).[64] The complex was obtained in high yields after recrystallization from toluene; analogous cobalt, nickel and ruthenium complexes could be prepared in the same manner.

Exploring Pn^{2-} complexes of f-block metals, Cloke *at al* successfully synthesised thorium and uranium complexes of 1,4-(TIPS)$_2$Pn^{2-} by way of transmetallation.[65] The reaction of ThCl$_4$ and K$_2$[1,4-(TIPS)$_2$Pn] suspended in THF yielded a bright orange solid containing a mixture of staggered and eclipsed isomers of η^8 [1,4-(TIPS)$_2$Pn]$_2$Th (Fig. 36). The product could be purified by sublimation, and crystals for XRD analysis were grown from pentane. The same reaction with UCl$_4$ produced a dark green product as the analogous isomeric mixture of η^8 [1,4-(TIPS)$_2$Pn]$_2$U again in high yields.

Fig. 35 Transmetalation reactions of dilithium pentalenide with late d-block metals.

Fig. 36 Transmetalation of dipotassium bis(trimethylsilyl) pentalenide with f-block metal halides.

Fig. 37 Reactions of dilithium hexamethylpentalenide with group IV metal halides.

Balazs *et al.* synthesised the anionic cerium(III) sandwich complex **K[Ce(1,4-TIPS₂Pn)₂]** by reacting **K₂[1,4-TIPS₂Pn]** with CeCl₃ in THF at room temperature.[66] This sand-coloured species was purified by filtration and washing with pentane, and characterised crystallographically by complexing the potassium ion with 18-crown-6 and recrystallising the resulting solid from toluene. The oxidation of **K[Ce(1,4-TIPS₂Pn)₂]** was shown using a slurry of AgBPh₄ in THF, and the resulting cerium(IV) sandwich complex **[Ce(1,4-TIPS₂Pn)₂]** was purified by extraction with pentane and crystallisation. Ashley *et al.* showed the analogous synthesis of **CePn*₂** by reacting **[Li₂(TMEDA)ₓ]Pn*** and CeCl₃ in THF at room temperature, followed by oxidation of the intermediate **Li[CePn*₂]** using an excess of dichloroethane.[67]

In another example of a substituted **Pn²⁻** transmetallation reaction, Cooper *et al.* described the reactivity of **Pn*²⁻** with group 4 metal halides.[68] ZrCl₄ and HfCl₄ mixed with **[Li₂(TMEDA)ₓ]Pn*** in benzene gave, after filtration and recrystallization, halide-bridged dinuclear η⁸ complexes of zirconium and hafnium as LiCl adducts (Fig. 37). Attempts to remove coordinated THF *via* high vacuum lead to decomposition.

When the analogous reaction was performed with titanium(IV) precursors, no titanium complex could be obtained but ligand degradation was observed instead. Reaction of **[Li₂(TMEDA)ₓ]Pn***

with TiCl₃ and subsequent oxidation with PbCl₂ did give a dinuclear Ti^IV complex, however, only in 8% yield.

In order to access **Ti^IV₂Pn*** complexes, less reducing transmetalation agents were required. **[Li₂(TMEDA)ₓ]Pn*** was thus reacted with two equivalents of Me₃SnCl to give η¹ **(Me₃Sn)₂Pn*** derivatives (Fig. 38), analogous to those reported for the parent **H₂Pn** (section 3.2, Fig. 32), in an extension to the η¹ **(Me₃Sn)HPn*** shown in Fig. 33.[68]

Interestingly, the use of a non-polar solvent such as benzene lead to formation of the *syn* product, whereas the use of THF exclusively gave the *anti*-isomer. Both could be isolated in very high yields after filtration and recrystallisation from toluene or pentane. It was proposed that the second lithiation step in the synthesis of **[Li₂(TMEDA)ₓ]Pn*** initially precipitated the *syn* dilithio complex as the kinetic product, which when reacted further in a benzene slurry produced *syn* TMT derivatives, whereas the use THF allowed interconversion to the thermodynamic *anti* dilithio configuration during the dissolution, producing *anti* TMT derivatives. This represents an interesting opportunity to steer the face selectivity of **M₂Pn** reagents in transmetalation reactions in general, but remains to be explored for other pentalenide reagents than **[Li₂(TMEDA)ₓ]Pn***.

In terms of transmetalation ability, reaction of *syn* η¹ **(Me₃Sn)₂Pn*** with TiCl₄ in toluene indeed smoothly produced η⁸ **[TiCl₂Pn*]₂** in high yields after recrystallization (Fig. 39).[68] The

Fig. 38 Synthesis of bis-stannylated hexamethylpentalenides.

Fig. 39 Reactions of bis(trimethylstannyl)-hexamethylpentalenide with group IV metal halides.

analogous reactions with ZrCl$_4$ and HfCl$_4$ failed to produce the desired complexes, suggesting the presence of LiCl is required to stabilise the Zr/Hf **Pn*** complexes shown in Fig. 37.

In a controlled hydrolysis experiment, Clement *et al.* showed that reacting **[TiCl$_2$Pn*]$_2$** with one equivalent of 2,6-xylenol (pK_a ~10) in toluene resulted in clean mono-protonation of the bound **Pn*** ligand and cleavage of the dimer by coordination of the alkoxide (Fig. 40), giving a single isomer of the mono-nuclear hydropentalenide complex **Ti(OR)Cl$_2$[HPn*]** in 68% yield.[69] This transformation represents an interesting

example of accessing a **HPn$^-$** complex *via* protonation of a **Pn^{2-}** complex, but on its own does not allow commenting on the reversibility of the reaction.

In a further demonstration of the usefulness of **(Me$_3$Sn)$_2$Pn*** as mild transmetalation agent, Chadwick *et al.* successfully synthesised dinuclear **Pn*$^{2-}$** complexes of easily reducible rhodium(I) and iridium(I) precursors.[70] Reactions of [M(CO)$_2$Cl]$_2$ (M = Rh, Ir) with *syn* η^1 **(Me$_3$Sn)$_2$Pn*** (generated *in situ*) selectively produced the corresponding *syn* η^5 **[(CO)$_2$M]$_2$Pn*** complexes (Fig. 41). Both the rhodium and
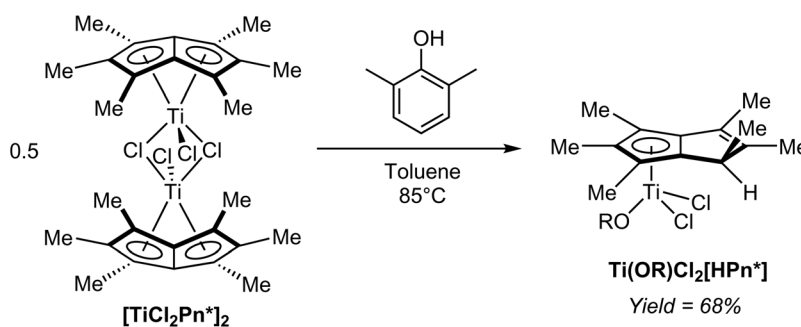

Fig. 40 Partial hydrolysis of a titanium(IV) **Pn*** complex with 2,6-xylenol.

Fig. 41 Reactions of bis(trimethylstannyl)hexamethylpentalenide with group IX metal carbonyl dimers.

iridium complexes have been analysed by XRD, with suitable crystal samples grown from hexane at low temperatures.

Whether the observed *syn* selectivity of the transmetalation was a result of using *syn* **(Me₃Sn)₂Pn*** or due to the dimeric nature of the metal precursor is not clear, however.

4. Conclusion

From the selected examples reviewed it is clear that a number of different synthetic routes to pentalenide complexes exist. Unsubstituted **H₂Pn** is mostly synthesised by controlled anaerobic pyrolysis of various starting materials, whereas several relatively straightforward solution-phase methods for substituted **H₂Pn** exist. It is interesting that not all of these, mostly developed in the realm of organic synthesis, have been put to use in organometallic pentalenide chemistry yet. Symmetrically substituted **H₂Pn** appear most desirable to reduce the number of possible isomers, which may be hard to separate or transform selectively from a mixture. Given that their reactivity is mostly governed by their core π electronic system, it is not unreasonable to expect that most new substituted **H₂Pn** would be amenable to the same deprotonation, functionalisation and transmetalation methods developed for the two archetypical synthons, unsubstituted **H₂Pn** and permethylated **Pn***. This would allow a wider range of novel **Pn²⁻** complexes to be synthesised for a more systematic study of **Pn²⁻** ligand effects on their electronic structure and reactivity. Thallium salts and Me₃Sn derivatives have proven to be mild and effective transmetalation agents in addition to the alkali metal salts, but the development of less toxic alternatives would be desirable for practical reasons. The prospect of controlling the face selectivity of **Pn²⁻** double metalation *via* either kinetically controlled deprotonation or installation of *syn*-configured leaving groups represents an exciting opportunity for selectively synthesising *syn*-dinuclear half-sandwich complexes with interesting properties for binding and activating various ligands across the two metal sites. The stability of mono-deprotonated **HPn⁻** and its metal complexes may even allow consecutive installation of different metals to synthesise heterodinuclear compounds in a controlled manner. In general, the flexible and adaptive nature of **Pn²⁻** to bind a range of different metals together with the ability of bringing two metals together in close proximity with electronic coupling hold great potential for future applications in sensing, electrochemistry, and homogeneous catalysis.

Conflicts of interest

The authors declare no conflict of interests.

Acknowledgements

References

1 H. J. Lindner, in *Houben-Weyl Methods of Organic Chemistry, Vol. 5: Carbocyclic p-Electron Systems*, Georg Thieme Verlag, Stuttgart, 4th edn, 1985, pp. 103–122.

2 T. Bally, S. Chai, M. Neuenschwander and Z. Zhu, *J. Am. Chem. Soc.*, 1997, **119**, 1869–1875.

3 H. Hopf, *Angew. Chem., Int. Ed.*, 2013, **52**, 12224–12226.

4 S. A. R. Knox and F. G. A. Stone, *Acc. Chem. Res.*, 1974, **7**, 321–328.

5 (*a*) O. T. Summerscales and F. G. N. Cloke, *Coord. Chem. Rev.*, 2006, **250**, 1122–1140; (*b*) F. G. N. Cloke, J. C. Green, A. F. R. Kilpatrick and D. O'Hare, *Coord. Chem. Rev.*, 2017, **344**, 238–262.

6 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley & Sons, 6th edn, 2014.

7 J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding To Catalysis*, University Science Books, Sausalito, California, 2010.

8 A. Pauli, H. Kolshorn and H. Meier, *Chem. Ber.*, 1987, **120**, 1611–1616.

9 T. J. Katz and J. J. Mrowca, *J. Am. Chem. Soc.*, 1967, **89**, 1105–1111.

10 S. C. Jones, P. Roussel, T. Hascall and D. O'Hare, *Organometallics*, 2006, **25**, 221–229.

11 A. V. Bandura and S. N. Lvov, *J. Phys. Chem. Ref. Data*, 2006, **35**, 15–30.

12 T. J. Katz and M. Rosenberg, *J. Am. Chem. Soc.*, 1962, **84**, 865–866.

13 J. J. Stezowski, H. Hoier, D. Wilhelm, T. Clark and P. V. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1263–1264.

14 J. Barroso, S. Mondal, J. L. Cabellos, E. Osorio, S. Pan and G. Merino, *Organometallics*, 2017, **36**, 310–317.

15 T. J. Katz, R. K. Ohara and M. Rosenberg, *J. Am. Chem. Soc.*, 1964, **86**, 249–252.

16 K. Alder, F. H. Flock and P. Janssen, *Chem. Ber.*, 1956, **89**, 2689–2697.

17 N. B. Kazennova, A. K. Shestakova, V. A. Chertkov, N. A. Ustynyuk and Y. A. Ustynyuk, *Zh. Org. Khim.*, 1986, **22**, 2108–2111.

18 M. Jones and L. O. Schwab, *J. Am. Chem. Soc.*, 1968, **90**, 6549–6550.

19 F. G. N. Cloke, M. C. Kuchta, R. M. Harker, P. B. Hitchcock and J. S. Parry, *Organometallics*, 2000, **19**, 5795–5798.

20 A. G. Griesbeck, *Synthesis*, 1990, 144–147.

21 J. Stapersma, I. D. C. Rood and G. W. Klumpp, *Tetrahedron*, 1982, **38**, 2201–2211.

22 J. Stapersma, I. D. C. Rood and G. W. Klumpp, *Tetrahedron*, 1982, **38**, 191–199.

23 J. J. Gajewski and C. J. Cavender, *Tetrahedron Lett.*, 1971, 1057.

24 M. Neuenschwander, H. Schaltegger and D. Meuche, *Helv. Chim. Acta*, 1963, **46**, 1760–1765.

25 R. Kyburz, H. Schaltegger and M. Neuenschwander, *Helv. Chim. Acta*, 1971, **54**, 1037–1046.

26 I. Erden, J. Sabol, A. Gubeladze and A. Ruiz, *Turk. J. Chem.*, 2013, **37**, 519–524.

27 R. Kaiser and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 892.

28 K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm and K. H. Vöpel, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 123–134.

29 U. H. Brinker and I. Fleischhauer, *Tetrahedron*, 1981, **37**, 4495–4502.

30 A. E. Ashley, A. R. Cowley and D. O'Hare, *Eur. J. Org. Chem.*, 2007, 2239–2242.

31 S. H. Bertz, J. M. Cook, A. Gawish and U. Weiss, *Org. Synth.*, 1986, **64**, 27–38.

32 A. E. Ashley, A. R. Cowley and D. O'Hare, *Chem. Commun.*, 2007, **15**, 1512–1514.

33 K. Hafner and H. U. Süss, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 575–577.

34 B. Kitschke and H. J. Lindner, *Tetrahedron Lett.*, 1977, **18**, 2511–2514.

35 A. G. Griesbeck, *J. Org. Chem.*, 1989, **54**, 4981–4982.

36 A. G. Griesbeck, *Chem. Ber.*, 1991, **124**, 403–405.

37 E. Le Goff, *J. Am. Chem. Soc.*, 1962, **84**, 3975–3976.

38 K. J. Stone and R. D. Little, *J. Org. Chem.*, 1984, **49**, 1849–1853.

39 N. Coskun, J. X. Ma, S. Azimi, C. Gartner and I. Erden, *Org. Lett.*, 2011, **13**, 5952–5955.

40 N. E. Schore, *Chem. Rev.*, 1988, **88**, 1081–1119.

41 T. Kuwabara, K. Ishimura, T. Sasamori, N. Tokitoh and M. Saito, *Chem. – Eur. J.*, 2014, **20**, 7571–7575.

42 M. Saito, M. Nakamura, T. Tajima and M. Yoshioka, *Angew. Chem., Int. Ed.*, 2007, **46**, 1504–1507.

43 H. Li, B. Wei, L. Xu, W.-X. Zhang and Z. Xi, *Angew. Chem., Int. Ed.*, 2013, **52**, 10822–10825.

44 P. M. Bailey, B. E. Mann, I. D. Brown and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1976, 238–239.

45 W. Weidemüller and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 925–925.

46 (*a*) D. F. Hunt and J. W. Russell, *J. Am. Chem. Soc.*, 1972, **94**, 7198–7199; (*b*) D. F. Hunt and J. W. Russell, *J. Organomet. Chem.*, 1972, **46**, C22–C24.

47 A. E. Ashley, G. Balazs, A. R. Cowley, J. C. Green and D. O'Hare, *Organometallics*, 2007, **26**, 5517–5521.

48 A. Brookes, F. Gordon, J. Howard, S. A. R. Knox and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1973, 587–589.

49 J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1974, 452–453.

50 J. A. K. Howard, S. A. R. Knox, F. G. A. Stone, A. C. Szary and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1974, 788–789.

51 T. H. Coffield, K. G. Ihrman and W. Burns, *J. Am. Chem. Soc.*, 1960, **82**, 4209–4210.

52 H. Komatsu, Y. Suzuki and H. Yamazaki, *Chem. Lett.*, 2001, **16**, 998–999.

53 T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, 1963, **85**, 2030–2031.

54 C. Janiak, *Coord. Chem. Rev.*, 1997, **163**, 107–216.

55 Y. A. Ustynyuk, A. K. Shestakova, V. A. Chertkov, N. N. Zemlyansky, I. V. Borisova, A. I. Gusev, E. B. Tchuklanova and E. A. Chernyshev, *J. Organomet. Chem.*, 1987, **335**, 43–57.

56 N. M. Sergeyev, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1973, **9**, 71–144.

57 Z. R. Turner, J.-C. Buffet and D. O'Hare, *Organometallics*, 2014, **33**, 3891–3903.

58 K. Jonas, B. Gabor, R. Mynott, K. Angermund, O. Heinemann and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1712–1714.

59 K. Jonas, P. Korb, G. Kollbach, B. Gabor, R. Mynott, K. Angermund, O. Heinemann and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1714–1718.

60 S. C. Jones, T. Hascall, S. Barlow and D. O'Hare, *J. Am. Chem. Soc.*, 2002, **124**, 11610–11611.

61 (*a*) T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, 1972, **94**, 3281–3283; (*b*) T. J. Katz, N. Acton and J. Mcginnis, *J. Am. Chem. Soc.*, 1972, **94**, 6205–6206.

62 M. R. Churchill and K. K. G. Lin, *Inorg. Chem.*, 1973, **12**, 2274–2279.

63 S. C. Binding, J. C. Green, W. K. Myers and D. O'Hare, *Inorg. Chem.*, 2015, **54**, 11935–11940.

64 J. M. Manriquez, M. D. Ward, W. M. Reiff, J. C. Calabrese, N. L. Jones, P. J. Carroll, E. E. Bunel and J. S. Miller, *J. Am. Chem. Soc.*, 1995, **117**, 6182–6193.

65 (*a*) F. G. N. Cloke, J. C. Green and C. N. Jardine, *Organometallics*, 1999, **18**, 1080–1086; (*b*) F. G. N. Cloke and P. B. Hitchcock, *J. Am. Chem. Soc.*, 1997, **119**, 7899–7900.

66 G. Balazs, F. G. N. Cloke, J. C. Green, R. M. Harker, A. Harrison, P. B. Hitchcock, C. N. Jardine and R. Walton, *Organometallics*, 2007, **26**, 3111–3119.

67 A. Ashley, G. Balazs, A. Cowley, J. Green, C. H. Booth and D. O'Hare, *Chem. Commun.*, 2007, **15**, 1515–1517.

68 R. T. Cooper, F. M. Chadwick, A. E. Ashley and D. O'Hare, *Organometallics*, 2013, **32**, 2228–2233.

69 D. D. Clement, S. C. Binding, T. A. Q. Arnold, F. M. Chadwick, I. J. Casely, Z. R. Turner, J.-C. Buffet and D. O'Hare, *Polyhedron*, 2019, **157**, 146–151.

70 F. M. Chadwick, A. E. Ashley, R. T. Cooper, L. A. Bennett, J. C. Green and D. M. O'Hare, *Dalton Trans.*, 2015, **44**, 20147–20153.