The hexamethylpentalene dianion and other reagents for organometallic pentalene chemistry†

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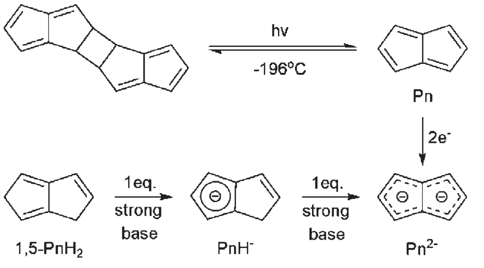
Novel permethylated pentalenide anions are reported which offer exciting new opportunities for the future development of organometallic pentalene chemistry.

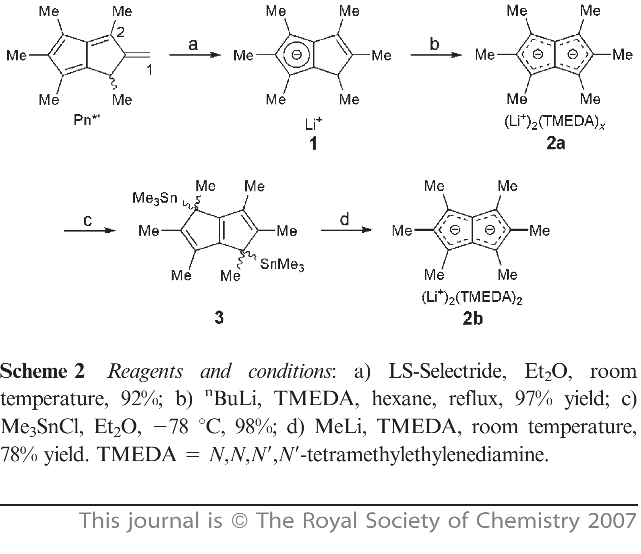
The organometallic chemistry of pentalene (C_8H_6; Pn) has developed substantially over the past decade.[1,2] Two major contributing factors to this heightened activity are the applicability of the bicyclic framework in the construction of extended organometallic networks[3,4] and the discovery that the ligand may fold about the bridgehead bond to enable a novel η^8-coordination mode,[5–7] which effectively shields an entire face of a metal's coordination sphere. Furthermore the metal-complexes of Pn have shown a diverse array of coordination modes, showing great flexibility in adapting to the electronic requirements of the metal centre. Pn itself is an extremely thermolabile 8π anti-aromatic species which dimerises at temperatures above −196 °C (Scheme 1).[8,9] Two electron reduction results in the aromatic dianion (Pn^{2-}), which is related to naphthalene as the cyclopentadienyl (C_5H_5; Cp) anion is to benzene. In practice, however, Pn^{2-} is accessed by the double deprotonation of dihydropentalene (PnH_2)[10,11] with strong bases which gives an 'anionic' synthon of Pn that can form compounds in conjunction with 'cationic' metal precursors *e.g.* metal halides.

Alternatively, mono-deprotonation affords the hydropentalenide anion (PnH^-),[12,13] a useful material for the synthesis of heterobimetallics and also a building block for the construction of organometallic macromolecules. Unfortunately the widespread development of Pn chemistry has been hampered by the lack of efficient syntheses of PnH_2, which is currently furnished from the carefully controlled flash vacuum pyrolysis of cyclooctatetraene[14] or the Skatteböl rearrangement of a geminal dibromocyclopropane-fused cycloheptatriene.[15] The only successful strategies for the synthesis of substituted pentalenes also derive from these existing protocols and neither is amenable to a polysubstituted carbocyclic structure.[16] With the knowledge of the beneficial attributes imparted to Cp* (C_5Me_5) complexes in comparison to their Cp analogues (enhanced stability, solubility and crystallisability)[17] we decided to develop a new, totally alkylated pentalene ligand system, in order to aid the development of this important ligand type. Recently we reported the facile, large-scale and solution-phase synthesis of the hydrocarbon (1,3,4,5,6-pentamethyl-2-methylene-1,2-dihydro-pentalene, Pn*′), an isomer of hexamethylpentalene (Pn*).[18] The synthesis had been achieved through the peripheral functionalisation of the bicyclo[3.3.0]octane skeleton. We now wish to communicate the successful transformation of Pn*′ into the lithium salt of the hydropermethylpentalene anion, with subsequent deprotonation to the dianion of permethylpentalene, which has been structurally characterised by X-ray crystallography.



Scheme 1 Photochemical formation of pentalene from [2 + 2] dimer (*trans*-isomer shown) and formation of the hydropentalene anion or pentalene dianion by sequential deprotonation of a dihydropentalene.

Initial attempts to reduce Pn*′ using alkali metals gave only intractable solids, indicative of extensive polymerisation. The successful conversion of the polyolefin Pn*′ into a metallated derivative suitable for use in organometallic chemistry relied on its similarities to an α,β-unsaturated carbonyl. The use of bulky trialkylborohydride reagents to effect the 1,4-reduction of these species has been documented; this pathway arises when standard 1,2-addition is hindered due to α-branching.[19] The reaction of LS-Selectride with a dried Et_2O solution of Pn*′ elegantly furnished **1** (LiPn*H), which precipitated cleanly from the solvent in good yield and on a multi-gram scale (Scheme 2). This is the first



Scheme 2 *Reagents and conditions*: a) LS-Selectride, Et_2O, room temperature, 92%; b) ^nBuLi, TMEDA, hexane, reflux, 97% yield; c) Me_3SnCl, Et_2O, −78 °C, 98%; d) MeLi, TMEDA, room temperature, 78% yield. TMEDA = *N,N,N′,N′*-tetramethylethylenediamine.

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example of regiospecific conjugate hydride delivery upon a pure hydrocarbon to produce a cyclopentadienyl anionic species. **1** is a pyrophoric solid which is insoluble in aliphatic and aromatic hydrocarbons and only sparingly soluble in THF. However, in pyridine it is sufficiently soluble to enable its characterisation by NMR spectroscopy. DFT calculations upon Pn*′ indicate that carbon atom 1 is substantially less electropositive than atom 2 (Scheme 2) and both have approximately equal orbital coefficients. This information allows the conclusion that the observed selectivity is sterically derived; indeed, substitution for the less bulky L-Selectride results in a ratio of 2 : 1 for **1** and the 1,2-addition product respectively. **1** is a very attractive building block for the construction of organometallic polymers derived from the pentalene nucleus which should demonstrate much greater solubility over their unsubstituted counterparts.

The second deprotonation of **1** is achieved by the heterogeneous reaction with ^{n}BuLi and TMEDA in hexane to form **2a** in excellent yield. **2a** is an intensely pyrophoric brown powdery solid which is insoluble in hydrocarbon and aromatic solvents and only slightly so in THF or TMEDA. The ^{1}H and ^{13}C NMR solution spectra display two (ratio 2 : 1) and five resonances respectively, indicative of a highly symmetrical species, corroborating a planar delocalised structure. **2a** is the reagent of choice for the formation of η^8-Pn* organometallic complexes using straightforward metathesis reactions.

Reaction of **2a** with two equivalents of Me$_3$SnCl furnishes a mixture of *cis* and *trans* isomers (2 : 3 ratio) of the dihydropermethylpentalene derivative **3** in near quantitative yield. Pale yellow crystals suitable for X-ray crystallography were grown from a hexane solution at −80 °C and were found to be of *cis*-(SnMe$_3$)$_2$Pn*; a view is shown in Fig. 1.‡ Although the molecule has no crystallographic symmetry the similarities between the two halves mean it approximates to local twofold rotational symmetry, through the C4–C8 bond. Each Sn atom is coordinated in a tetrahedral fashion and clearly bonded to one pentalene carbon atom only; there are well-defined localised double bonds within the ring system. The C$_5$ rings deviate slightly from planarity and are slightly bent away from the SnMe$_3$ substituents such that the angle between their best planes is 7.9°. The Sn–Me bond lengths are slightly less than the sum of the covalent radii of Sn and C (2.17 Å), yet the Sn–Pn* bonds are longer; the latter value is comparable to that found in *trans*-(SnMe$_3$)$_2$Pn [2.209(7) Å],[20] SnMe$_3$(η^1-Flu*) [2.221(3) Å][21] and SnMe$_3$(η^1-Ind*) [2.232(6) Å].[22]

The RT ^{1}H and ^{13}C NMR spectra of *cis*/*trans*-**3** show that these isomers are fluxional (presumably proceeding *via* 1,2-metallotropic rearrangements) and the results are comparable to those found by Ustynyuk on the unsubstituted system.[20] However, even at −100 °C, the spectra remain broad and it was thus not possible to ‘freeze out’ the dynamic process. The assignment of the resonances was carried out at this temperature using ^{1}H, ^{13}C, ^{119}Sn and 2D NMR (HMQC, HMBC). The process taking place in both isomers of **3** evidently proceeds at a higher rate than in the unsubstituted compounds and possibly arises from permethylation increasing the energy of the ground states of each isomer through greater bond angle and steric strain. If the excited state remains very similar or even lower in energy than in (SnMe$_3$)$_2$Pn (which is expected due to extra hyperconjugative stabilisation of the Pn* entity) then $\Delta G^‡$ would be diminished. **3** should prove an excellent alternative as a Pn* transfer agent to higher valent metal halides through Me$_3$SnX elimination when the reducing power of **2a** may become problematic.

Due to the sensitivity and poor solubility of **2a** recrystallisation from TMEDA did not prove an effective method in obtaining crystals suitable for single crystal X-ray crystallography, and a new strategy was devised which is based on Sn–Li exchange upon **3**. (SnMe$_3$)$_2$Pn* was transmetallated with halide-free MeLi in TMEDA solvent whereupon the initially pale yellow solution became deep orange–red. Large hexagonal prisms suitable for X-ray diffraction were prepared by slow cooling to −35 °C.

The pentalene ligand is located on a crystallographic centre of inversion and accordingly the two five-membered rings are exactly coplanar by symmetry, a finding which is in accordance with the criteria for a Hückel 10π aromatic (Fig. 2). No bond alternation is evident and the average C–C bond length (1.43 Å) compares well with benzene (1.40 Å) and those previously reported for the unsubstituted pentalene dianion (1.44 Å).[23] The Li atom is coordinated in an almost symmetrical manner with the Li–centroid distance found to be shorter than that in [Li(DME)]$_2$Pn (1.89 Å) . There is a slight difference in the length of the average lithium to bridgehead carbon bonds [2.255(3) Å] compared to the

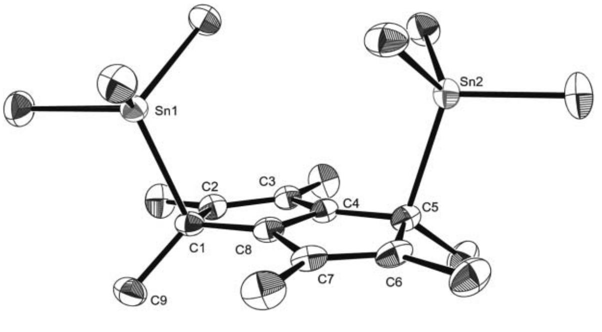

Fig. 1 X-ray crystal structure view of *cis*-**3**, (SnMe$_3$)$_2$(μ:η^1,η^1-Pn*) (thermal ellipsoids shown at 50% probability, hydrogen atoms excluded for clarity). Selected bond lengths [Å] and angles [°]: Sn1–C1 2.215(2), Sn1–Me (average) 2.148(3), C2–C3 1.371(4), C4–C8 1.374(3), C6–C7 1.369(4), C2–C1–C8 102.4(2).

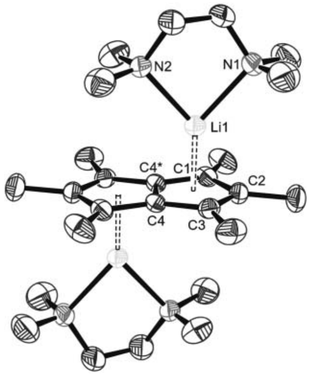

Fig. 2 X-ray crystal structure view of **2b**, *anti*-[Li(TMEDA)]$_2$(μ:η^5,η^5-Pn*) (thermal ellipsoids shown at 50% probability, hydrogen atoms excluded for clarity). Selected bond lengths [Å]: Li1–C1 2.224(3), Li1–C2 2.211(3), Li1–C3 2.217(4), Li1–C4 2.255(3), Li1–C4* 2.258(3), Li1–N1 2.189(3), Li1–N2 2.158(3), Li–Ct 1.872(3). Ct is a C$_5$ ring centroid, C4* generated by (1 − *x*, 1 − *y*, 1 − *z*) from C4.

average of the remainder [2.217(4) Å], although this is insufficient to ascribe η^3-coordination. The Li–N average [2.173(3) Å] is longer than those found in comparable lithium cyclopentadienides stabilised by the same complexing agent – Li(Ind)(TMEDA) [2.103(4) Å] and Li($C_5H_4SiMe_3$)(TMEDA) [2.131(10) Å].[24,25] This weakened bond might be explained by the high electron density conferred by the Pn^{*2-} ligand on the Li cations, which reduces their affinity for the chelator, and corroborates the experimental findings that loss of TMEDA from **2a** and **2b** is rather facile.

In conclusion we have established a large-scale and reproducible route to the lithium salts of both the hydropermethylpentalenide anion and permethylpentalene dianion using a rational synthesis. Our initial studies have recently shown that the Pn* dianion can react with lanthanide halides to give interesting bis-(η^8-Pn*) derivatives of these elements.[26] We are confident that these new anionic synthons of Pn* should ensure that the development of metal-pentalene chemistry is no longer restricted due to the availability of ligand precursors and can thus continue apace.

Notes and references

‡ Crystal data for (**2b**): $C_{26}H_{50}N_4Li_2$, M = 432.58, crystal size (mm) = 0.18 × 0.22 × 0.40, monoclinic, $P2_1/n$, a = 10.8575(2), b = 9.3133(2), c = 14.1063(3) Å, β = 90.8093(7)°, V = 1426.27(5) Å^3, Z = 2, ρ_{calcd} = 1.007 g cm^{-3}, μ = 0.058 mm^{-1}, Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), T = 150 K, $2\theta_{\max}$ = 55.0°, 14757 measured reflections (3432 independent, R_{int} = 0.033), absorption correction (multiscan), transmission factors 0.98/0.99, R = 0.0709, wR = 0.0961 refined against $|F^2|$, GOF = 1.0173, $[\Delta\rho]_{\max}$ 0.63, $[\Delta\rho]_{\min}$ −0.35 e Å^{-3}. Crystal data for (**3**): $C_{20}H_{36}Sn_2$, M = 513.89, crystal size (mm) = 0.18 × 0.18 × 0.24, triclinic, $P\bar{1}$, a = 7.8927(2), b = 10.0097(2), c = 14.9792(3) Å, α = 99.4761(7)°, β = 101.8991(7)°, γ = 102.8466(7)°, V = 1101.18(4) Å^3, Z = 2, ρ_{calcd} = 1.550 g cm^{-3}, μ = 2.265 mm^{-1}, Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), T = 150 K, $2\theta_{\max}$ = 55.0°, 16301 measured reflections (5011 independent, R_{int} = 0.024), absorption correction (multiscan), transmission factors 0.58/0.67, R = 0.0246, wR = 0.0290 refined against $|F^2|$, GOF = 1.0405, $[\Delta\rho]_{\max}$ 0.88, $[\Delta\rho]_{\min}$ −0.78 e Å^{-3}. CCDC 632847–632848. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702150j

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