A Convenient Synthesis of $C_5(CD_3)_5H$. Synthesis and Characterisation of $Fe\{\eta^5\text{-}C_5(CD_3)_5\}_2$

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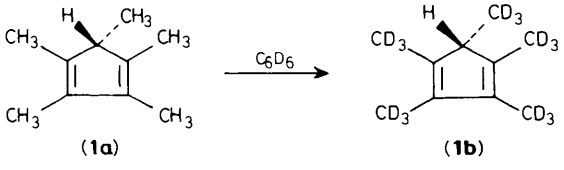
The large scale synthesis of deuterio(pentamethylcyclopentadiene), $C_5(CD_3)_5H$ ($[^2H_{30}]Cp^*H$), and subsequent synthesis of $[^2H_{30}][Fe(\eta\text{-}Cp^*)_2]$ is described, together with i.r., Raman, and solid state ^2H n.m.r. spectroscopic characterisation.

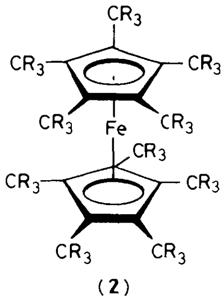
Since the discovery and structural characterization of ferrocene, at least one cyclopentadienyl, Cp, derivative of every main group, transition, and f-block metal has been reported.[1] Catalytic H/D exchange of the C–H bonds of cyclopentadiene[2] has been known for some time and has been beneficially used to synthesize labelled metallocyclopentadienyl complexes for use in n.m.r., e.p.r., matrix isolation, kinetic, and mechanistic studies. These experiments have proven vital to the understanding of the structure and bonding in organometallic complexes as well as providing definitive evidence for the mechanism of many fundamental reactions involving organometallic compounds. Extensive study of metallopermethylcyclopentadienyl compounds was not practical until the development of efficient synthetic routes to pentamethylcyclopentadiene, Cp*H.[3] Subsequently, many papers demonstrating the dramatic differences between the structure and chemistry of Cp and Cp* have appeared.[4]

Although intramolecular H/D exchange of the methyl hydrogens of the Cp* ligands in complexes such as $[(\eta\text{-}Cp^*)_2MH$; M = Hf,[5] Sc[6]] have been reported, these are stoicheiometric reactions and decomplexation of $[^2H_{15}]Cp^*$ is problematic. Herein we report the bulk catalytic synthesis of $C_5(CD_3)_5H$, and the characterisation of $[^2H_{30}][Fe(\eta\text{-}Cp^*)_2]$.

At elevated temperature under a D_2 atmosphere, $(\eta\text{-}Cp^*)_2ScD$ (readily prepared in a three step synthesis from anhydrous $ScCl_3$)[6] catalyses multiple H/D exchanges of



(1a) (1b) (1)



(2)

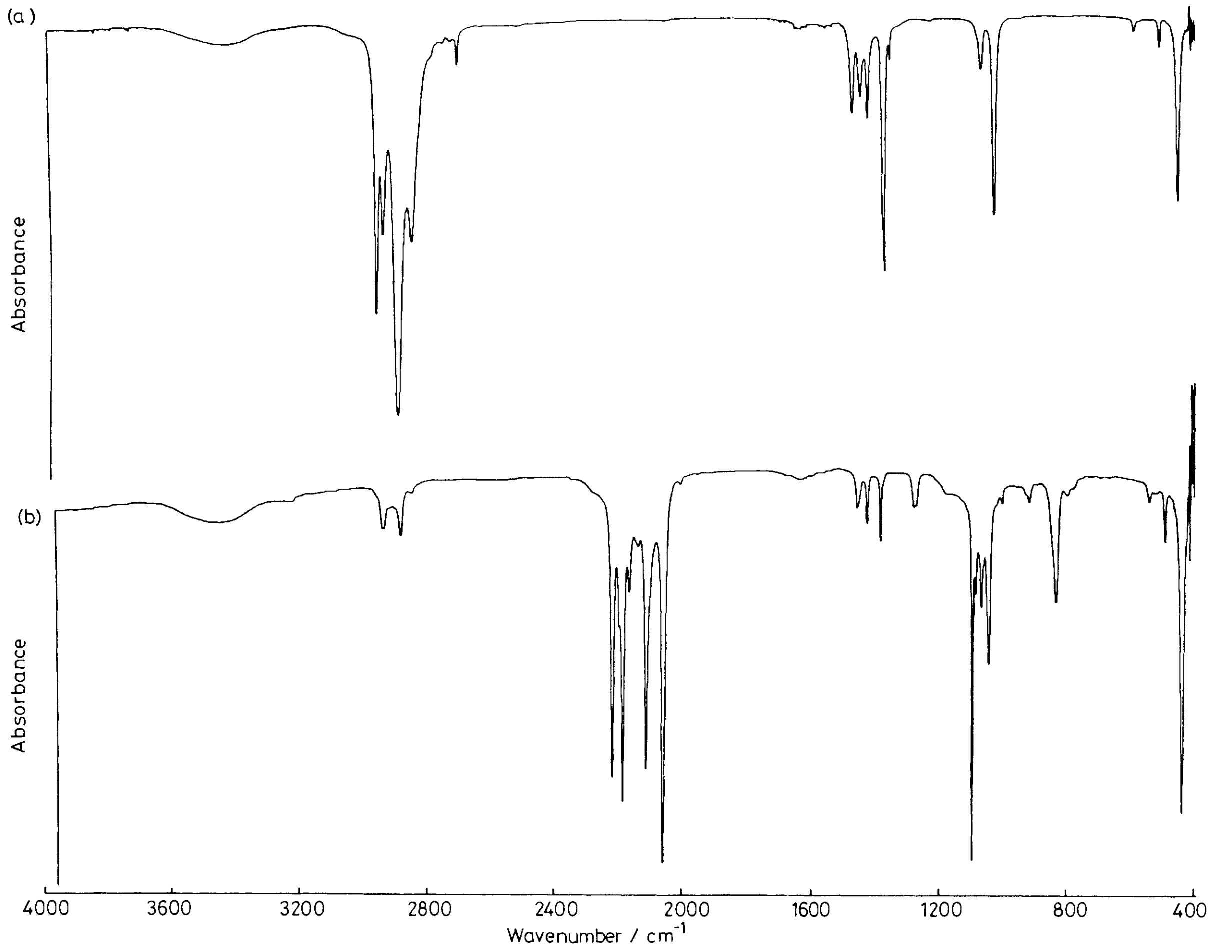


Figure 1. The infrared spectra of (a) (**2a**) and (b) (**2b**) in KBr.

$C_5(CH_3)_5H$ (**1a**) with C_6D_6 (equation 1).[†] ^{1}H N.m.r. spectroscopy at 145 °C shows that the rate of H/D exchange of all the methyl hydrogens is 10 turnovers/day. Deuterium incorporation occurs in a one-at-a-time manner. This is in contrast to H/D exchange catalysts based on $[PtCl_4]^{2-}$ (ref. 7) and zirconium alkoxides,[8] which have been reported to effect multiple deuterations per interaction with the catalyst. We observe that the allylic hydrogen exchange is much slower; only after 4—5 weeks can deuterium incorporation into this position be detected by n.m.r. or mass spectroscopy.

The large scale synthesis of $C_5(CD_3)_5H$ (**1b**)[‡] can be achieved using moderate amounts of the $(\eta\text{-}Cp^*)_2ScD$ catalyst. The typical isotopic purity as calculated from the intensity distribution of isotopomers is typically 95—96% after 4—5 week reaction times. Enriched (**1b**) can be isolated from the solvent in 90% yield *via* fractional distillation. In addition, the catalyst can be recycled for use in further exchange reactions. The unexchanged allylic hydrogen can be conveniently removed with LiBu^n giving lithium perdeuteriopentamethylcyclopentadienide. The $Li^+[^2H_{15}][Cp^*]^-$ can now be used as the primary synthon for labelled transition metal Cp* complexes, *e.g.* $[^2H_{30}][Fe(\eta\text{-}Cp^*)_2]$ (**2b**) and $[^2H_{30}][Fe(\eta\text{-}Cp^*)_2]^+[BF_4]^-$ (**3b**), which were prepared and characterised.

The vibrational spectroscopy of metallocyclopentadienyls has received much attention. The i.r., Figure 1, and Raman spectra, Figure 2, of (**2a**) and (**2b**), although unassigned, exhibit C–H stretching vibrations at *ca.* 3000 cm^{-1} which are shifted upon deuteration by $(2)^{1/2}$ to *ca.* 2120 cm^{-1}. In addition the Raman spectrum, Figure 2, shows an absorption at *ca.* 640 cm^{-1} which is unshifted upon deuteration and may be assigned to a symmetrical ring mode.

^{2}H Solid state n.m.r. spectroscopy of organometallic inclusion complexes, intercalation reactions, and charge transfer salts relies on the synthesis of suitable labelled compounds. For metallocenes, it offers the opportunity of investigating the dynamics of both η-Cp* ring rotation and methyl rotation in the solid state. The room temperature solid state static ^{2}H n.m.r. spectrum of (**2b**) shows a classical axial powder spectrum with the dominant doublet feature separated by 18.3 kHz. A simulation of the powder spectrum using a model where we have both rapid methyl rotation and η-Cp* rotation (we have assumed the rigid limit quadrupole constant e^2qQ/h = 165 kHz) gives a doublet separation of 21 kHz which is in good agreement with the observed spectrum.

It is clear that the availability of deuterium labelled Cp*H

[†] 1 atm D_2, $(\eta\text{-}Cp^*)_2ScD$ (1 g, 0.1 equiv.), 150 °C, Cp*H (10 g), C_6D_6 (150 ml).

[‡] *Selected data* for (**1b**): $^2H\{^1H\}$ n.m.r. (C_6H_6) δ 1.65 (s, 2*Me*), 1.59 (s, 2*Me*), 0.85 (s, *Me*); mass spectrum, *m/z* 151 (100%, $C_{10}D_{15}H$). For (**2d**): $^2H\{^1H\}$ n.m.r. (C_6H_6) δ 1.95 (s); *m/z* 356, P$^+$. For (**3d**): $^2H\{^1H\}$ n.m.r. (MeCN) δ −34.8 (s); *m/z* 356, P$^+$.

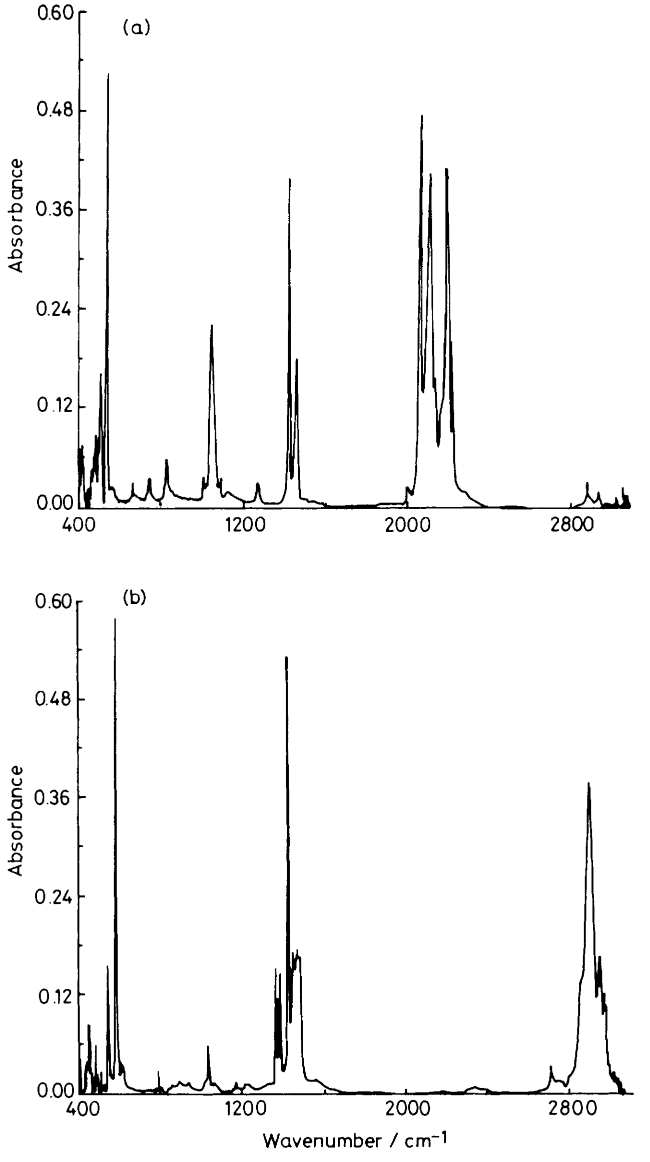


Figure 2. The Raman spectra of (a) (**2a**) and (b) (**2b**).

(**1b**) and in turn labelled metallocyclopentadienyl complexes will assist in the assignment of vibrational and magnetic resonance spectra in addition to elucidating mechanistic pathways.

Note added in proof: (**2b**) can also be prepared in greater than 99.9% isotopic purity *via* a stoicheiometric ligand exchange reaction (1). Typically, Fe(acac)$_2$ (4 g) dissolved in

$$[^2H_{30}][(\eta\text{-Cp}^*)_2ScCl] + 1.5\,Fe(acac)_2 \xrightarrow[\text{reflux}]{\text{toluene}} (\mathbf{2b}) + Sc(acac)_3 + 0.5\,FeCl_2 \quad (1)$$

acac = pentane-2,4-dionate

toluene (50 ml) was added to a solution of [$^2H_{30}$][(η-Cp*)$_2$ScCl] prepared from 4 g of [(η-Cp*)$_2$ScCl].[6] The reaction mixture was heated under reflux for 12 h, the solvent was removed under reduced pressure, and the residue was extracted with pentane. After drying the extract and sublimation, 2.5 g (62%) of (**2b**) was collected. The ^1H impurity was determined by mass spectral analysis to be <0.03%.

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