Deuteriated Cyclopentadienyls of Thallium and Other Metals

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Summary C_5D_5Tl can conveniently be prepared at room temperature from C_5H_6, D_2O, and Tl_2SO_4, and can be used to synthesise a variety of deuteriated cyclopentadienyls.

THE ease of preparation and handling of cyclopentadienylthallium[1] has led to its widespread use in the preparation of metal cyclopentadienyls,[2] and its employment in a number of organic syntheses, notably prostaglandin precursors.[3] No serious attempt seems to have been made to produce a fully deuteriated analogue, however. Partially deuteriated cyclopentadiene, from C_5H_5Na and D_2O, has been used to prepare indium and thallium derivatives.[4] Our attempts to convert C_5H_5Tl directly into its deuteriated analogues by treatment with D_2O, $(CD_3)_2CO$, CD_2Cl_2, or $CDCl_3$, with or without added acid or base catalysts, met with no success, owing probably to the low solubility of the thallium compound or to competing side reactions. (Cyclopentadienylthallium is known to react with $CHCl_3$:[1] treatment of C_5H_5Tl with 8% D_2SO_4 in D_2O leads to C_5H_5D[5]). We report here a simple one-pot synthesis of C_5D_5Tl from cyclopentadiene and D_2O.

In a typical experiment, 0·6 ml of freshly distilled cyclopentadiene was added to a solution of sodium deuteroxide, prepared under nitrogen from 1·84 g of sodium metal and 20 ml of D_2O (Fluorochem Ltd., 99·8% isotopic purity). The mixture was shaken vigorously for 3·5 h at room temperature, when 1·5 g of finely-ground thallium(I) sulphate was added, and the shaking continued for several hours more. The product was obtained by filtration and sublimation at 90 °C and 0·5 Torr. Mass spectroscopic analysis showed it to contain 90% of C_5D_5Tl (*m/e* at 275 and 273, from ^{205}Tl and ^{203}Tl respectively) with C_5D_4HTl making up the remaining 10%. This ratio corresponds closely to that expected (89·4% C_5D_5Tl) from the overall ratio of D to H of the reagents employed, indicating that the base-catalysed redistribution of D and H is random. Lower ratios of D to H in the starting materials lead to the expected lower incorporation of deuterium in the final product, and this results in a more complex mixture of partially deuteriated products.

The rate of the exchange process is critically dependent on the concentration of NaOD, as would be expected from the base-catalysis mechanism (1). Thus when the amount of sodium used in experiments of the scale above is reduced to 0·3 g, maximum incorporation of deuterium into the cyclopentadiene requires 18 h at room temperature. During this time only a small fraction of the cyclopentadiene dimerises.† The high temperatures previously employed to avoid dimerisation[6] are not necessary in this method, nor is the use of such solvents as $(Me_2N)_3PO$.[7]

$$C_5H_6 + OD^- \rightleftharpoons C_5H_5^- + HOD \rightleftharpoons C_5H_5D + OH^- \text{ etc.} \quad (1)$$

The mass spectrum of C_5D_5Tl resembles that of C_5H_5Tl,[8] with a base peak of Tl^+ and a strong molecular ion. The i.r. spectrum of a polycrystalline sample shows ν(C–D) at 2280 and 2320 cm^{-1}, with the strong characteristic C–D bending modes at 769 and 540 cm^{-1} (shifted from 1000 and 727 cm^{-1} respectively for the CH modes of C_5H_5Tl[9]).

Some preliminary experiments confirm that the deuteriated thallium reagent simply transfers its cyclopentadienyl to other metals. Iron(II) chloride reacts in benzene[2a] to form $(C_5D_5)_2Fe$, previously obtained by a more difficult multi-stage route.[10] Di-μ-chloro-bis-[2-(phenylazo)phenyl-C^2N']palladium[11] is readily converted into $(PhN_2C_6H_4)Pd(C_5D_5)$. The mass spectrum of this latter compound shows a strong peak at *m/e* 249 corresponding to $C_6H_5N_2C_6H_4{\cdot}C_5D_4$ (found at *m/e* 245 in the fully protonated material), suggesting that the rearrangement involves loss of a cyclopentadienyl substituent. The ^1H n.m.r. spectrum of the palladium complexes shows a weak singlet at δ 5·8 due to the single ring proton from the small amount of the C_5D_4H material also present.

The C_5D_5Tl retains all the desirable features (air stability, ease of purification, *etc*) of the protonated analogue, and seems an obvious alternative to C_5D_5Li or C_5D_5Na which have been employed to date.[12] We believe that the 9:1 ratio of C_5D_5 to C_5D_4H obtained in our experiments is sufficiently good for most labelling requirements. A higher deuterium incorporation is theoretically possible using a greater D_2O:C_5H_6 ratio, but to make a significant improvement the expense becomes prohibitive. On a larger scale, more economic use of the D_2O can be made by using it in aliquot portions. Phase-transfer catalysis using a suitable organic solvent[13] might be advantageous under these conditions.

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† Separate n.m.r. investigations showed that 50% of pure C_5H_6 dimerised over 3 days under those conditions, but 5% solutions in $CDCl_3$ showed no change at all in this time.

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