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Das Reagenz · The Reagent

Cyclopentadienylthallium(I) as a Ligand Transfer Reagent

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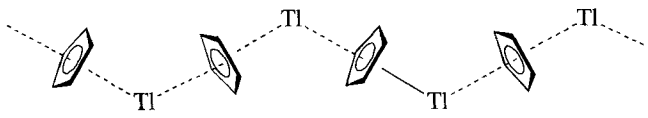
Cyclopentadienylthallium(I) compounds, in large, are often valued as ligand transfer reagents for lab-scale syntheses of cyclopentadienyl main group element and transition metal compounds as well as organic cyclopentadiene derivatives, because they are generally very mild reagents for the careful cyclopentadienyl (Cp) ligand transfer. Also, they are relatively easy to prepare and handle. Most cyclopentadienylthallium compounds can be stored for long periods under the appropriate conditions and often they exhibit at least a brief stability upon exposure to air. This then allows for the precise determination of the quantity of the cyclopentadienide ion in the initial reaction mixture. In the case of complexes prone to reduction or in the case of functionalized cyclopentadienyl ligands [1], the thallium derivatives are often better suited, *i.e.* "milder" or less reducing, for the Cp-transfer than the sodium or lithium compounds [2].

The parent compound C_5H_5Tl is commercially available or can easily be prepared in nearly quantitative yield by reaction of cyclopentadiene with a thallium(I) salt in aqueous potassium hydroxide according to equation 1. Usually thallium(I) sulfate is employed as the salt [3].

$$2\ C_5H_6 + 2\ KOH + Tl_2SO_4 \rightarrow 2\ C_5H_5Tl\downarrow + K_2SO_4 + 2\ H_2O \qquad (1)$$

C_5H_5Tl forms an ionic polymeric zig-zag chain in the solid-state (**1**) [4], in the gas phase it is monomeric with a more covalent ring–thallium bond (**2**) [5] and in solution it exists as close contact ion pairs.



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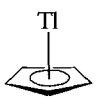


2

C_5H_5Tl is a colourless to pale yellow powdery or crystalline solid. It is weakly thermochromic, fairly air- and moisture stable and darkens only slowly on standing in air or light. The compound sublimes between 80–145 °C, depending on the quality of the vacuum. C_5H_5Tl starts blackening due to decomposition at ~60 °C in air and at ~230 °C in an evacuated capillary but does not melt below 270 °C. It is insoluble in water, somewhat soluble in polar solvents like THF, methanol, acetone and pyridine and insoluble in less polar solvents [3]. Selected applications of the use of C_5H_5Tl as a ligand transfer agent will be detailed in the following.

Most often the cyclopentadienylthallium reagent reacts with a halide containing transition metal complex in a salt elimination or metathesis reaction (equation 2) with the formation of the cyclopentadienylmetal complex, thallous halide (TlX) and in some cases elimination of additional ligands (*e.g.* CO, PR_3) as the by-products. The thallium compounds are particular suitable reagents in metathesis reactions with metal halides due to the thermodynamic driving force in favour of the formation of insoluble TlX. This method was even patented [6]. Cyclopentadienylthallium reagents are normally stirred or heated at reflux in ethereal or hydrocarbon solution with the substrate under an inert atmosphere. The insoluble thallium halide produced may be filtered from the reaction solution. For an Inorganic Synthesis preparation of $(C_5H_5)_2TiCl$ and $(C_5H_5)_2VCl$ using this route see [7], for $(C_5H_5)_3UCl$ and $(C_5H_5)_3ThCl$ see [8]. Out of a very large number of such ligand transfer reactions [9] a few specific examples are given in equation 3–7. The solvent is usually THF, diethyl ether or toluene. Substituted cyclopentadienylthallium compounds can be employed just the same way in such ligand transfer reactions.

$$C_5H_5Tl + MXL_z \rightarrow (C_5H_5)ML_z + TlX \qquad (2)$$

$$NiX_2(PR_3)_2 + C_5H_5Tl \rightarrow (C_5H_5)NiX(PR_3) + TlX + PR_3 \qquad (3)$$

X = Cl, Br, I [10]

$[RhCl(diene)]_2 + C_5H_5Tl \rightarrow (C_5H_5)Rh(diene) + TlCl$ [11] (4)

$Ta(CH_2CMe_3)_2Cl_3 + C_5H_5Tl \rightarrow (C_5H_5)Ta(CH_2CMe_3)_2Cl_2 + TlCl$ [12] (5)

$PtCl_2(PR_3)_2 + C_5H_5Tl \rightarrow (C_5H_5)PtCl(PR_3)_2 + TlCl$ [13] (6)

$UCl_4 + n\,C_5H_5Tl \rightarrow (C_5H_5)_nUCl_{4-n} + n\,TlCl$ n = 1,2,3 [14] (7)

There is, however, also the possibility for cyclopentadienylthallium to transfer the cyclopentadienyl moiety in a redox reaction with activated metal (equation 8 or 9) leading to the reduction to thallium metal. This is a particular elegant route with lanthanide metals which are activated by mercury. The addition of mercury reduces the induction time, but is not essential for the reaction to occur, nor does it affect the outcome [15, 16]. This reductive transmetallation reaction of thallium(I) cyclopentadienide has also been worked out for Inorganic Synthesis [17]. Furthermore, this redox transmetallation has also been carried out for M = Fe, Sm, and Eu in the absence of solvents, simply by mechanochemical means through ball milling [18].

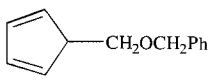
$2\,CpTl^{+1} + M^0 \rightarrow Cp_2M^{+2} + 2\,Tl^0$ (8)

M^0 = Eu,Yb [18,19]

$3\,CpTl^{+1} + M^0 \rightarrow Cp_3M^{+3} + 3\,Tl^0$ (9)

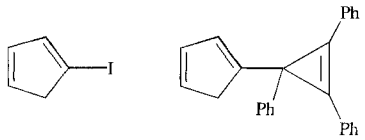
M = La, Ce, Nd, Sm, Eu, Gd, Er, Yb [15,17,19,20]

Cyclopentadienylthallium also reacts with organic halides to give an alkylated cyclopentadiene. The alkylation of C_5H_5Tl found important applications in the prostaglandin work by Corey and others. Compared to the lithium and sodium cyclopentadienide, the thallium derivative minimizes the cyclopentadiene isomers formed. Reaction of C_5H_5Tl with benzyl chloro- or bromomethyl ether affords the cyclopenta-2,4-diene isomer (**3**) exclusively (equation 10) [21].

$C_5H_5Tl + Cl\text{-}CH_2OCH_2Ph \rightarrow TlCl +$  (10)

3

Upon reaction of C_5H_5Tl with acyl iodides or triphenylcyclopropenyl perchlorate only the 1,3-isomers (**4**) are obtained [22].



4

Reaction of C_5H_5Tl with sulfenyl chlorides gives unstable *S*-alkyl or *S*-aryl cyclopentadienes (equation 11), which can be deprotonated again with TlOEt (equation 12). The thallium salts can then be *S*-alkylated to form dialkylsulfonium cyclopentadienides or alkylarylsulfonium cyclopentadienides (equation 13 and 14). The latter are, however, only stable in the form of the thallium complexes [23].

$C_5H_5Tl + RSCl \rightarrow C_5H_5SR + TlCl$ (11)

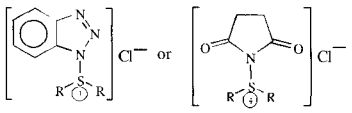
$C_5H_5SR + TlOEt \rightarrow C_5H_4(SR)Tl + EtOH$ (12)

{R = Me, Ph, -C_6H_4-4- Me, -C_6H_3(-2,4-NO_2)$_2$}

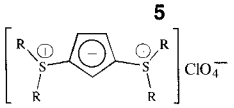
$C_5H_4(SMe)Tl + MeI \rightarrow C_5H_4^{-}\text{-}^{+}SMe_2 + TlI$ (13)

$C_5H_4(SC_6H_4R')Tl + (Me_3O)BF_4 \xrightarrow{HBF_4} [C_5H_4\{S(Me)C_6H_4R'\}Tl]^+ BF_4^- + Me_2O$ (R' = H, Me) 14)

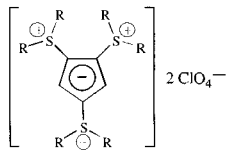
Azasulfonium salts (**5**) react with unsubstituted C_5H_5Tl to give bis(sulfonio)cyclopentadienides or tris(sulfonio)cyclopentadienides (**6**). Thallium salts of monosubstituted cyclopentadiene condense with the azasulfonium salts to form mono (sulfonio)cyclopentadienides [24].



5



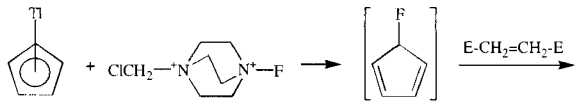
R = piperidino, morpholino, NMe_2, Me
R,R = -$(CH_2)_5$-

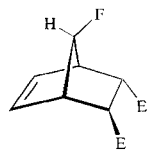


R = Me
R,R = -$(CH_2)_5$-

6

Another electrophilic substitution reaction of C_5H_5Tl takes place with the "F^+" source 1-chloro-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane which generates 5-fluorocyclopentadiene, [C_5H_5F], *in situ*, which could be trapped by suitable dienophiles, such as $(MeO_2CC)_2$, $CH_2{=}C(Cl)CN$, $CH_2{=}CHCO_2Me$, MeCH=CHCHO to give the respective Diels–Alder adduct (equation 15) [25].





(15)

A speciality is the preparation of C_5D_5Tl, from NaOD/D_2O and C_5H_6, and its use as a ligand transfer agent for the introduction of the perdeuterated cyclopentadienyl ligand [26].

A major disadvantage of these applications reported here for the cyclopentadienylthallium compounds is, however, the

discarding of the thallium salt side product which should always be treated with caution and must be especially disposed of (*e.g.* heavy metal waste for special treatment) because of the poisonous nature of thallium.

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