Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Improvements in the Preparation of Cyclopentadienyl Thallium and Methylcyclopentadienylthallium and in Their Use in Organometallic Chemistry

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IMPROVEMENTS IN THE PREPARATION OF CYCLOPENTADIENYL THALLIUM AND METHYLCYCLOPENTADIENYLTHALLIUM AND IN THEIR USE IN ORGANOMETALLIC CHEMISTRY

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ABSTRACT

Improved preparation methods of cyclopentadienylthallium and methylcyclopentadienylthallium, giving quantitative yields and incorporating ultrasound techniques, are described. Their use as starting materials for a wide range of organometallic syntheses is discussed and demonstrated.

INTRODUCTION

Cyclopentadienyl complexes of transition metals are generally made by the reaction between a suitable cyclopentadienide and a transition metal halide or complex[1-7]. Cyclopentadienides are generated by the reaction between a cyclopentadiene or substituted cyclopentadiene with a base, such as alkali metal hydroxides[1,2], sodium hydride[4], organic amines[3,5], n-butyllithium[6] or metallic sodium[3,8].

The generation of cyclopentadienylthallium is especially useful. This "centrally bonded" cyclopentadienyl complex reacts in a manner similar to a cyclopentadienide. It is reasonably air stable and may be isolated. Cyclopentadienylthallium is prepared by deprotonation of cyclopentadiene using potassium hydroxide in the presence of thallium salts[14,10,12], especially thallium(I) sulphate[10,12], in aqueous solution. Other methods use thallium(I) ethoxide as base and thallium source[4,6,8,9,11]. The reaction is general and has broad scope, as demonstrated principally by Rausch[6,8,11] and Bitterwolf[4,8,11] and their collaborators. It may be applied to a variety of substituted cyclopentadienes: methyl[9,10], pentamethyl, benzyl, phenyl, methoxycarbonyl, ethoxycarbonyl, formyl, acetyl, benzoyl[8], chloro[20], trimethylsilyl, methoxy[5], etc.

While thallium ethoxide is the only reagent which has been used with substituted cyclopentadienes[4,8,9,11,13,20], for unsubstituted cyclopentadiene and methylcyclopentadiene, the use of an inorganic thallium salt and potassium hydroxide is more convenient, because it may be used in aqueous solution and facilitates the isolation of the thallium cyclopentadienyl complex, prior to the subsequent reaction[10,12,14]. An additional advantage stems from the fact that thallium ethoxide is air- and water-sensitive, and its preparation is time-consuming[16].

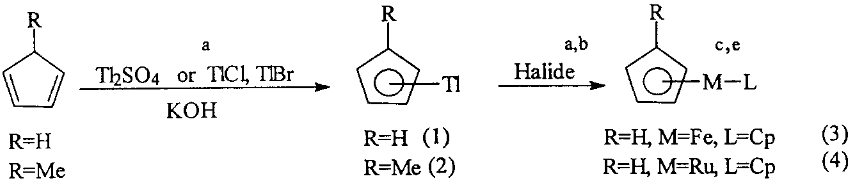
RESULTS AND DISCUSSION

In continuing studies in transition metal organometallic chemistry, we use cyclopentadienylthallium routinely as the source of cyclopentadienyl ligand for sandwich and half-sandwich complexes. On the basis of this work, we made several observations. For the preparation of cyclopentadienylthallium, the most used inorganic thallium salt is the water-soluble thallium(I) sulphate[10,12,14], which reacts with potassium hydroxide. The literature yields (confirmed in our hands) are in the range of 67-95 %, dependent on the quantities of reagents, time of reaction, speed of stirring, etc.

According to Hunt and Doyle[14], many other thallium salts may be used, including the insoluble salts such as chloride or bromide. This observation is interesting, because, after the subsequent reaction, thallium is recovered in the form of chloride or bromide. Thallium is a very toxic and relatively expensive metal and its re-utilisation is desirable. However, in our experiments, the Hunt and Doyle procedure[14], using thallium bromide or chloride (recycled or previously prepared from thallium(I) sulphate or nitrate and alkali metal chloride or bromide), gives only moderate yields (47 %) if mechanical stirring is used, and still less if magnetic stirring is used. Good yields are only obtained if thallium(I) sulphate is used.

In our initial experiments, we tested the substitution of potassium hydroxide by sodium hydroxide, but with both thallium halides and thallium sulphate the yields of the desired complex dropped down to the range 20-30 %. It seems that only potassium hydroxide is satisfactory. Another observation concerns the light-sensitivity of cyclopentadienylthallium and its derivatives. We observed that they darken when exposed to light. In fact, Hunt and Doyle reported that cyclopentadienylthallium is light-sensitive[14]. More recently, the photochemical decomposition of cyclopentadienylthallium has been studied[7]. On the basis of our observations of the sensitivity of thallium complexes and salts to light (similar to that of silver(I) salts), we carried out our reactions in flasks protected from light.

In subsequent reactions of cyclopentadienyl thallium with transition metal salts or complexes, further problems were encountered. With the thallium ethoxide method for the generation of cyclopentadienyl thallium, ethanol[4,6,8,11] is the most often used solvent. With isolated cyclopentadienyl thallium and substituted cyclopentadienylthallium, water/DMSO[9] (for the synthesis of cobalticinium salts) and benzene[4,6,8,14] have been used. In our hands, this is a source of difficulties, because benzene is a poor solvent for cyclopentadienylthallium and, also, transition metal halides are almost



R=H
R=Me

R=H (1)
R=Me (2)

[c] Yields: (1) from Tl_2SO_4 96-100%
(1) from TlCl or TlBr 87-98%
(2) from Tl_2SO_4 89%

R=H, M=Fe, L=Cp (3)
R=H, M=Ru, L=Cp (4)
R=H, M=Co, L=Cp (5)
R=H, M=Ni, L=Cp (6)
R=H, M=Co^+, L=Cp (7)[d]
R=H, M=Rh^+, L=Cp (8)[d]
R=Me, M=Fe, L=MeCp (9)
R=H, M=Mn, L=$(CO)_3$ (11)

[a] Sonication and Stirring
[b] See Table I
[c] See Table II
[d] In form of PF_6^- salts
[e] Cp is Cyclopentadienyl

Fig. 1. Synthesis of Cyclopentadienyl Complexes

insoluble in benzene. The reaction mixture is heterogeneous and considerable time of stirring and reflux is necessary. We have studied different solvent systems for the reactions. The use of polar organic solvents (such as acetonitrile, ethanol, acetone) reduces the yields. We found that benzene containing THF (25 % v/v) as co-solvent is a good choice for routine use because it permits the gradual solubilization of both the thallium complex and transition halide derivative. We also found that aqueous DMSO (5 %)[9] is satisfactory for the preparation of water-soluble metallocenes, such as cobalticinium and rhodicinium salts.

Bearing in mind that ultrasound techniques have been extensively used in organic synthesis in the last 15 years and, more recently, in analytical chemistry[17], and have been shown to be very useful in heterogeneous reactions, we decided to apply sonication in the reactions involving the synthesis of cyclopentadienylthallium and the methyl substituted analogue, and their subsequent use in reactions with transition metal complexes (Fig. 1). Ultrasound was found to be beneficial in both kinds of reactions.

In one procedure, thallium(I) sulphate reacts with potassium hydroxide and cyclopentadiene or methylcyclopentadiene in aqueous solution, with protection from light and in a nitrogen atmosphere. Using alternating periods of sonication and magnetic stirring, we obtained nearly quantitative yields of the corresponding cyclopentadienylthallium in practically pure form. The compounds could be isolated and stored. Recycled thallium bromide or chloride were also used. In this case, the reaction time is longer, but the yields are equivalent (Fig. 1, Table II).

For the synthesis of transition metal derivatives, it is convenient to react cyclopentadienylthallium with the transition metal halide or complex in benzene /THF mixture 4:1 v/v, protected from light, in a nitrogen atmosphere, and also with alternating periods of sonication/magnetic stirring. If the oxidised, water soluble metallocenes (rhodicinium, cobalticinium salts) are desired, , air is bubled into the reaction mixture, prior to isolation. The reactions carried out, reaction conditions and yields are summarised in Table I.

The obtained compounds, characteristics and melting points are summarised in Table II. Special attention is directed to the entries 9 and 10 in Table I and 7 and 9 in Table II. The reaction between a substituted cyclopentadienylthallium and $CpFe(CO)_2I$[5] is a good method to synthetise asymmetrically substituted ferrocenes.

Entry 10 refers to the reaction between cyclopentadienylthallium and $Mn(CO)_5Br$[5.19]. It is the best method to prepare laboratory quantities of cyclopentadienylmanganesetricarbonyl (11), a useful organometallic intermediate[20] difficult to synthetise by other methods [5].

Analytical and Spectral Data

All the compounds prepared are known. This demonstrates the generality of the method. Elemental Analysis Data are given in Table III. For all the compounds prepared, the spectral data are in agreement with the structure (Table IV).

TABLE I

Reactions Between Cyclopentadienylthallium and Transition Metal Halides or Complexes

Entry	Halide (mmol)	CpTl (n) (mmol)	Solvent	Conditions[d]	Time	Yields (%)	Product [c]
1	$FeCl_2$ (2)	CpTl **(1)** (4)	Benzene/THF (4:1)	reflux	3 h	76,4	Ferrocene **(3)**
2	$NiCl_2$ (2)	CpTl **(1)** (4)	Benzene/THF (4:1)	R.T.	overnight	67,2	Nickelocene **(6)**
3	$CoCl_2$ (2)	CpTl **(1)** 4)	Benzene/THF (4:1)	R.T.	overnight	81,4	Cobaltocene **(5)**
4	$RuCl_3$ (0,5)	CpTl **(1)** (1)	Benzene/THF (4:1)	reflux	6 h[a]	44,3	Ruthenocene **(4)**
5	$CoCl_2$.(dioxane) (2)	CpTl **(1)** (4)	Benzene/THF (4:1)	R.T.	overnight	78,7	Cobaltocene **(5)**
6	$CoCl_2.6H_2O$ (2)	CpTl **(1)** (4)	5%Aqueous/ DMSO	R.T.	overnight	78,2	Cobalticinium Hexafluorphosphate **(7)**
7	$RhCl_3.xH_2O$ (0.5)	CpTl **(1)** (1)	5%Aqueous/ DMSO	R.T.	overnight	64,3	Rhodicinium Hexafluorphosphate **(8)**
8	$FeCl_2$ (2)	MeCpTl **(2)** (4)	Benzene/THF (4:1)	reflux	3 h	93,5	1,1-Dimethyl Ferrocene **(10)**
9	$CpFe(CO)_2I$ (1)	MeCpTl **(2)** (1)	Benzene/THF (4:1)	reflux	3 h	55,1	Methyl Ferrocene **(9)**
10	$Mn(CO)_5Br$ [b] (1)	CpTl **(1)** (1)	Benzene/THF (4:1)	reflux	3-4 h	83,4-94 [b]	Cyclopentadienyl Manganese Tricarbonyl **(11)**

[a] Because $RuCl_3$ is poorly soluble, reaction time is increased.
[b] Several runs of this reaction were made.
[c] See Tables II, III and IV.
[d] Alternating stirring and sonication.

TABLE II

Compounds

Entry	Compound (number)	Formula[b]	M.p. (°C)[c]	Charactheristics[a]
1	Ferrocene **(3)**	CpFeCp	173-174 (lit.173-174)[2,5]	dark orange crystals.
2	Ruthenocene **(4)**	CpRuCp	198-199 (lit. 199)[18]	pale yellow crystals.
3	Cobaltocene **(5)**	CpCoCp	172 (sealed capillary)	dark violet (almost black) crystals, purple solutions.
4	Nickelocene **(6)**	CpNiCp	173-175 (lit. 173-174)[5] (sealed capillary)	olive green crystals, green solutions.
5	Cobalticinium Hexafluorphosphate **(7)**	$[CpCo^+Cp]PF_6$	> 300 (lit. > 300)[9]	bright yellow crystals.
6	Rhodicinium Hexafluorphosphate **(8)**	$[CpRh^+Cp]PF_6$	> 300	bege solid.
7	Methylferrocene **(9)**	MeCpFeCp	liquid. (lit. 35)[33]	orange-red liquid.
8	1,1'-Dimethylferrocene **(10)**	MeCpFeCpMe	liquid	dark-red liquid.
9	Cyclopentadienyl-manganese-tricarbonyl **(11)**	$CpMn(CO)_3$	75-76(lit.77)[5]	yellow crystals.
10	Cyclopentadienyl-thallium **(1)**	CpTl	dec. on heating (lit. dec. w. melt.)[12]	white or cream colored solid.
11	Methylcyclopenta-dienylthallium **(2)**	MeCpTl	108 (lit. 108.5-109; 88-89)[12d]	pale yellow solid.

[a] See Tables III and IV.
[b] Cp is cyclopentadienyl, see Fig. 1.
[c] M.p. obtained in a Kofler type plate, except for unstable to air compounds.
[d] Different m.p.s were reported in the same reference[12].

TABLE III

Analytical Data

Compound number[a]	Structure[b] (formula weight)	Yields (%)	Elemental Analyses (%)			
			Calculated		Found	
			C	H	C	H
1	C_5H_5Tl (269.48)	87-100	22.29	1.87	22.41	1.96
2	C_6H_7Tl (283.50)	89	25.42	2.49	c	c
3	$C_{10}H_{10}Fe$ (186.04)	76	64.56	5.42	64.31	5.73
4	$C_{10}H_{10}Ru$ (231.26)	44	51.94	4.36	51.70	4.71
5	$C_{10}H_{10}Co$ (189.12)	78-79	63.51	5.33	c	c
6	$C_{10}H_{10}Ni$ (188.88)	67	63.59	5.34	c	c
7	$C_{10}H_{10}CoPF_6$ (334.09)	78	35.95	3.02	35.82	3.33
8	$C_{10}H_{10}RhPF_6$ (378.06)	64	31.77	2.67	31.53	2.74
9	$C_{11}H_{12}Fe$ (200.06)	55	66.04	6.05	65.74	6.14
10	$C_{12}H_{14}Fe$ (214.09)	94	67.32	6.59	67.41	6.64
11	$C_8H_5MnO_3$ (204.06)	83-94	47.09	2.47	47.23	2.61

[a] See Table II.

[b] See fig.1.

[c] Elemental Analysis not carried out (very air-sensitive).

TABLE IV

Spectral Data

Compound number[a, b]	^{1}H NMR[c] (δ)				IR[d] (cm^{-1})					
	Cp	Subst. Cp	Subst. CH$_3$	Lit.[e]	νCH	νC-C	δCH	πCH	Other bands[f]	Lit.[e]
1[g]	-	-	-	-	3064	1585, 1430	1003	760	-	-
2[g]	-	-	-	-	3000	1572, 1410	1002	730	1370, 1170,980	-
3	4.05,s,(10H)	-	-	-	3078	1410, 1110	995	820	-	23
4	4.50,s,(10H)	-	-	18	3075	1410, 1098	1002	810	-	21; 22
5[h]	-	-	-	-	3030	1410, 1100	995	830	-	23
6[h]	-	-	-	-	3075	1430, 1100	1000	840	-	21; 22
7	5.95,s,(10H)	-	-	-	3090	1420, 1115	1010	860	760	24; 25
8	6.10,s,(10H)	-	-	9;26	3095	1412, 1110	1005	860	760	25; 26
9	4.03,s,(5H)	4.08-4.10,2t,(4H)	2.00,s,(3H)	-	3100	1420, 1120	1000	860	2950, 1450, 1050, 1030, 800	-
10		3.80-3.90(2t,8H)	1.90,s,(6H)	-	3080	1460	-	810	2940, 1360, 1035, 1020	-
11	3.98,s,(5H)	-	-	20	3130	1410, 1120	1010	870, 850	2040, 1950, 1280, 1190, 670, 650	-

[a] See Tables *II* and *III*.
[b] See Fig. 1.
[c] Brucker AC-80 Spectrometer, TMS as reference.
[d] Perkin Elmer 1420 Spectrophotometer.
[e] In agreement with reference.
[f] Due to substituent or counterion.
[g] Not sufficient soluble for NMR studies.
[h] Highly paramagnetic.

In the ^{1}H NMR analysis, the characteristic singlet of 5 equivalent protons of the unsubstituted Cp ring was observed. If the compound possesses a substituted cyclopentadienyl ring, two triplets, corresponding to α and β protons in relation to the substituent are observed. If the coupling constant is sufficiently small, the two triplets may be observed nearly juxtaposed, resembling the unsubstituted cyclopentadienyl singlet; for example, in this work, in methylferrocene (9) and dimethylferrocene (10). Other examples of the juxtaposition of peaks exist: *inter alia*, in monochloromercurioferrocene[30], monoacetoximercurioferrocene[29], methyl ferrocenyl carbinol and various ferrocenyl alcohols[31].

In all the compounds studied, the IR spectra show the characteristic ring CH bands in the 3000 cm^{-1} region, the ring C-C stretching bands (1400 and 1100 cm^{-1} regions), ring CH deformation (1000 cm^{-1} region), and π CH bands (800-750 cm^{-1} region). The bands in the 1000 and 1100 cm^{-1} regions are especially useful. These are the so-called "ferrocene bands" and their presence indicates at least one unsubstituted cyclopentadienyl ring in the complex [21,22,27,28]. If the ferrocene is 1,1-dissubstituted, the 1000 and 1100 cm^{-1} bands are absent[28,32].

Some exceptions are known, but the presence of the peaks at 1000 and 1100 cm^{-1} in a compound which does not possesses an unsubstituted Cp ring, may be due to the nature of the substituent[27,32]. For example, in our compound, 1,1 dimethyl ferrocene (10), δ CH bands exist at 1035 and 1020 cm^{-1}, but may be assigned to methyl group vibrational modes[27,28]. In agreement, in the same compound, the unsubstituted ring band at 1100 cm^{-1} does not exist.

EXPERIMENTAL

All reactions were carried out in a nitrogen atmosphere and protected from light, using standard Schlenk techniques. Sonication was carried out in a Thornton T7 bath, equipped with a low-potency ultrasound generator. The bath was filled with water and the flask was immersed in it.

Cyclopentadienylthallium (1) from Thallium(I) Sulphate (method A)

To an aqueous solution of 30% potassium hydroxide (100 mL) at ambient temperature, 12.5 g (25 mmol) of thallium(I) sulphate was added, previously suspended/dissolved in 50 mL of H_2O. The mixture was stirred and 3.3 g (50mmol) of freshly cracked cyclopentadiene was added dropwise. The mixture was sonicated for 30 min, and stirred again for 1 h and sonicated and stirred sucessively for a total period of 4 hours.

The precipitated compound was filtered off, washed with water and ethanol then dried under vacuum. It was nearly pure. For spectral studies, a small amount was purified by high vacuum sublimation. Several runs of this reaction were carried out and the yields are shown in Fig 1.The product was obtained as white, or slighly cream-coloured microcrystaline solid.

Cyclopentadienyl Thallium (1) From Recycled Thallium Chloride or Bromide (method B)

Compound (1) may also be prepared from TlCl or TlBr, in a manner similar to that described above, except that equimolar quantities of thallium salt and cyclopentadiene were used. The total reaction period was prolonged to 48 h.

Methylcyclopentadienylthallium (2)

This compound was prepared in a similar manner to that described in method A, substituting cyclopentadiene by methylcyclopentadiene. It was obtained as pale yellow crystals.The properties are similar to those of the compound (1), except that it is much more light- and air-sensitive.

Method for The Synthesis Of Air-Stable Cyclopentadienyl Complexes. Representative Preparation: Cyclopentadienylmanganesetricarbonyl (11).

0.27 g. (1 mmol) of $Mn(CO)_5Br$[5,19], was added to a suspension of cyclopentadienylthallium (0.27 g., 1 mmol) in 20 mL of benzene/THF mixture 4:1 v/v. The mixture was stirred/sonicated as described in method A, for 4 h. After this time, TlBr was filtered off, washed with benzene and the organic extracts dried (over Na_2SO_4) and evaporated. The compound was purified in a nitrogen atmosphere, by sublimation (without vacuum), using a Kugelrohr distillation unit, yielding air-stable crystals.

With essentially the same procedure, other compounds were also prepared, viz., ferrocene (3), ruthenocene (4), 1,1-dimethylferrocene (10), methylferrocene (9).

Method for the Synthesis of Air-Stable, Cationic Metallocenes: Representative Preparation of Cobalticinium Hexafluorophosphate (7).

0.48 g. (2 mmol) of $CoCl_2.6H_2O$ was added to a stirred suspension of cyclopentadienylthallium (1.0 g., 4 mmol) in 4 mL of aqueous 5% DMSO, and the mixture stirred/sonicated as in method A, for 24 h. at ambient temperature. Air was then bubbled through the mixture for 2 hours (to oxidise any cobaltocene present) and aqueous HCl (1:1) was added until acid to litmus paper. TlCl was filtered off, the filtrate extracted with hexanes for the removal of organic impurities and solid NH_4PF_6 added (0.32 g, 2 mmol or until no more precipitate was formed). The mixture was cooled and stored overnight in a refrigerator until total precipitation occurs. The precipitate was filtered off, washed with a little water and purified by dissolution in acetone and reprecipitation with warm water (subsequent cooling). Yellow, very air-stable crystals, were obtained.

In a similar manner, rhodicinium hexafluorophosphate (8) was prepared in the form of slighly cream coloured crystals which were stable in air.

Method for The Synthesis of Air Sensitive Metallocenes. Representative Preparation: Cobaltocene (5).

Anhydrous $CoCl_2$ (0.26 g., 2 mmol) or $CoCl_2$.dioxane[15] (0.44 g.,2mmol) was added to a stirred suspension of cyclopentadienyl thallium (1.0 g, 4 mmol) in a benzene/THF 4:1 mixture. The slurry was stirred/sonicated at ambient temperature similar to that described in method A for 24 h. TlCl was filtered under nitrogen atmosphere, the organic extracts were evaporated under vacuum and the residue sublimated under vacuum. Cobaltocene was isolated as a solid, dark violet, nearly black solid, which gives purple solutions in benzene and is very air-sensitive.

In a similar manner, nickelocene (6) was prepared in form of a dark green (olive green) solid, which is also air-sensitive.

Recycling of TlBr or TlCl

Thallium(I) bromide or chloride, recovered from reactions in the above preparations was washed with dilute (5%) nitric acid, then by decantation with water, 10% HCl, more water, and dried in a desiccator protected from light, and used in the procedure of method B.

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