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Note

The synthesis and characterization of 1-formyl-2-acylcyclopentadienylthallium compounds

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Abstract

The reaction of sodium cyclopentadienide with RCOOEt (R = Me, Ph, 2-thienyl, or OEt) or Bu^{t}COCl followed by Vilsmeier reagent in the presence of excess sodium methoxide produces the 2-substituted-6-dimethylaminofulvenes **1a**–**e** in modest yields. Basic hydrolysis results in the formation of 2-substituted-6-hydroxyfulvenes **2a**–**e** in very good yields. Subsequent deprotonation with TlOEt yields the 1-formyl-2-acyl or carboethoxy cyclopentadienylthallium compounds **3a**–**e**.

Keywords: Thallium; Cyclopentadienide; Vilsmeier; Formyl; Acyl; Carboethoxy

1. Introduction

Complexes of specifically polysubstituted cyclopentadienyl ligands play an important role in modern organometallic chemistry. The development of metallocene catalysts for alkene polymerization has driven efforts to tune catalyst specificity with suitably substituted cyclopentadienyl ligands [1,2]. In materials applications, substituted metallocenes can display NLO properties [3–6], electrical conductivity [7,8] or electrochromism [9]. Unfortunately, electrophilic substitution reactions carried out on metallocenes have poor selectivity. Even as simple a reaction as disubstitution typically leads to a mixture of 1,1′, 1,2 and 1,3 products, with the 1,2-substitution product obtained in the lowest yield. The method described here leads regioselectively to 1,2-disubstituted cyclopentadienyl ligands prior to attaching them to a transition metal.

The utility of cyclopentadienylthallium reagents for the synthesis of new organometallic compounds has been known for many years [10–19]. Despite their toxicity, cyclopentadienylthallium reagents offer advantages over their alkali-metal counterparts. They are generally more stable to air and water, and the extremely low solubility of thallium(I) halide by-products drives reactions to completion and facilitates workup. Our efforts focus on synthesizing precursors to new metallocene-fused thiophene, pyrrole and furan derivatives [20,21]. In this paper, we report the synthesis of thallium transfer compounds designed for the preparation of 1-formyl-2-acylmetallocenes, which can in principle be closed to organometallic heterocycles [22,23].

2. Results and discussion

2.1. Synthesis of 1-formyl-2-acylcyclopentadienylthallium compounds

The sequential reaction of sodium cyclopentadienide with an ester, RCOOEt (R = Me, Ph, Tp; Tp = 2-thienyl) or pivaloyl chloride followed by Vilsmeier reagent in the presence of excess sodium methoxide produces the 2-substituted-6-dimethylaminofulvenes **1a**–**d** (Scheme 1). This synthesis essentially follows the

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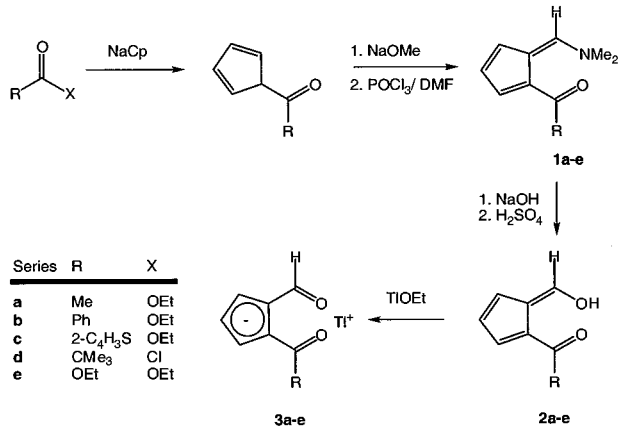
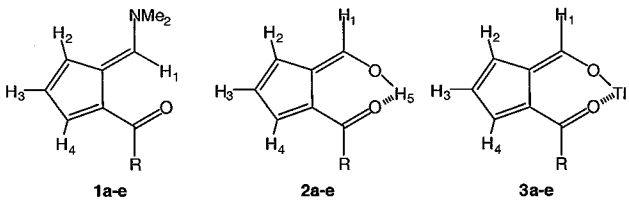
method of Fujisawa and Sakai [24], who reported a similar method for the synthesis of 2-acetyl-6-dimethylaminofulvene (**1a**) and 2-carboethoxy-6-dimethylaminofulvene (**1e**), but did not fully characterize the compounds. Although the *tert*-butyl compound (**1d**) was not formed by using ethyl pivalate, more reactive pivaloyl chloride gives the desired product in low yield. Anderson [25] used acetyl chloride and dimethyl sulfate in DMF to produce **1a** in a similar synthesis. Dreiding [26] prepared 2-isobutyryl-6-dimethylaminofulvene from dimethylaminofulvene and isobutyryl chloride in triethylamine, but we were unable to obtain 2-acyl-6-dimethylaminofulvenes by this method.



Scheme 1. Synthesis of compounds **1a**–**e**, **2a**–**3** and **3a**–**e**.

Table 1
^{1}H-NMR shifts (ppm) for compounds **1**, **2** and **3**



	R	H_1	H_2	H_3	H_4	H_5
1a	Me	8.97	7.10	6.38	6.85	–
1b	Ph	8.88	6.98	6.44	6.83	–
1c	Tp	8.68	7.16	6.45	6.95	–
1d	Bu^t	8.80	7.22	6.39	6.83	–
1e	OEt	8.82	7.14	6.39	6.80	–
2a	Me	8.33	7.49	6.47	7.28	17.10
2b	Ph	8.75	7.41	6.53	7.28	17.37
2c	Tp	8.63	7.73	6.55	7.36	17.30
2d	Bu^t	8.37	7.71	6.45	7.13	17.67
2e	OEt	7.70	7.40	6.36	6.85	14.80
3a	Me	10.0	6.49	5.70	6.49	–
3b	Ph	10.0	6.37	5.76	6.11	–
3c	Tp	9.95	6.62	5.80	6.53	–
3d	Bu^t	9.92	6.54	5.68	6.42	–
3e	OEt	9.90	6.41	5.70	6.41	–

Compounds **1** and **2** in $CDCl_3$; compounds **3** in DMSO-d_6.

The yields of the fulvene compounds **1a**–**d** are rather low, especially for the sterically demanding *tert*-butyl compound **1d**. Fortunately the starting materials are inexpensive, the reactions can be run on fairly large scales and the yields of subsequent steps (vide infra) are much higher. We attribute the low isolated yields to competitive formation of mixtures of 1,2, 1,3 and perhaps more highly substituted products. Because of their stability to chromatography on alumina and their crystallinity, the 1,2-disubsitution products can be purified from the mixtures.

Subsequent hydrolysis of the 1-acyl-2-dimethylaminofulvenes **1a**–**d** with NaOH at 60–80 °C produced 2-acyl-6-hydroxyfulvenes **2a**–**d** in very good yields. Finally, deprotonation of **2a**–**d** with thallous ethoxide yielded the corresponding 1-formyl-2-acylcyclopentadienylthallium compounds **3a**–**d** nearly quantitatively (Scheme 1).

The organic [27] and organometallic [28] chemistry of cyclopentadienes with multiple ester substituents have been extensively investigated. Previous researchers found it difficult to obtain 1,2-di(carboalkoxy)cyclopentadiene free of its 1,3-isomer or 1,2,4-triester [29,27]. Although we also find that the ester compounds are more difficult to purify and handle than the acyl compounds, we obtained 1-formyl-2-carboethoxycyclopentadienylthallium (**3e**) according to Scheme 1. Unlike the acyl compounds, 2-carboethoxy-6-dimethylaminofulvene (**1e**) decomposed during purification attempts and was therefore used in crude form. Subsequent base hydrolysis of **1e** produced carboethoxy compound **2e** that was also difficult to purify and was used in crude form, so that yields for **1**–**3e** are approximate. Subsequent deprotonation of **2e** with thallous ethoxide yielded 1-formyl-2-carboethoxycyclopentadienylthallium (**3e**), which is surprisingly more sensitive to air than **3a**–**d** and was therefore handled in a dry box or with Schlenk techniques. The yields of the ester compounds **1e**, **2e** and **3e** are generally lower than the acyl compounds.

The thallium compounds consistently analyzed low in carbon. This is possibly due to the formation of an inert thallium carbide phase. Compounds **3a**–**e** are moderately soluble in DMSO but very insoluble in most other organic solvents and decompose during attempted sublimation, making purification of analytical samples difficult.

2.2. Spectroscopic data

Key ^{1}H-NMR data for compounds **1**, **2** and **3** are listed in Table 1. Each dimethylaminofulvene (**1a**–**e**) displays a characteristic fulvene resonance between 8.6 and 9.0 ppm, in addition to three one-proton multiplets for the cyclopentadienyl protons and two singlets for the inequivalent methyl groups. Each 2-acyl-6-hydroxy-

fulvene (**2a**–**d**) shows a characteristic one-proton doublet between 16 and 18 ppm for the acidic hydroxyl proton. However, the hydroxyl proton resonance of 2-carboethoxy-6-hydroxyfulvene (**2e**) is shifted about 2–3 ppm upfield of the acyl derivatives. The hydrogen bonding may be decreased due to the electron-withdrawing effect of the ethoxy group compared to an alkyl or aryl group, thus revealing a more typical hydroxyl proton shift. Compound **2e** also displays its formyl proton ($\delta_H = 7.70$ ppm) considerably upfield of the acyl compounds (8.3–8.8 ppm). The formyl resonances of the thallium derivatives (**3a**–**e**) are shifted to considerably lower field (9.9–10.0 ppm), and their cyclopentadienyl multiplets are shifted by 0.5–1.5 ppm upfield from **2a**–**e,** consistent with more negative charge on the cyclopentadienyl ring [30].

3. Conclusion

The method of Fujisawa is applicable to a variety of acyl or carboalkoxy groups for the synthesis of 2-substituted-6-dimethylaminofulvenes and their hydroxyl derivatives. The 2-acyl and 2-carboethoxy-6-hydroxyfulvenes are useful precursors for asymmetric, 1,2-disubstituted cyclopentadienylthallium compounds. Utilization of these compounds as Cp-transfer reagents toward a variety of transition metal centers will be reported in due course.

4. Experimental

4.1. General methods and sources

Reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere or in a Braun MB 120-G dry box unless otherwise noted. Solvents were dried and distilled under nitrogen, including methanol over calcium hydride, DMF over calcium or magnesium sulfate and THF over sodium benzophenone ketyl. $CDCl_3$ and Me_2SO-d_6 were used as received from Cambridge Isotopes. Phosphorus oxytrichloride (Baker), ethyl acetate (Fisher), ethyl pivalate (Aldrich), ethyl benzoate (Baker), pivaloyl chloride (Aldrich) and diethyl carbonate (Aldrich) were distilled under nitrogen before use. Ethyl-2-thiophene carboxylate and thallous ethoxide were used as received from Aldrich. Proton and carbon NMR spectra were obtained on Varian Gemini 200 or Varian VXR-400 NMR spectrometers. Infrared spectra were obtained on a Mattson Galaxy Series FTIR 5000. Melting points are uncorrected. Elemental analyses were performed at the University of Illinois, Urbana. Mass spectra were collected at the University of Kentucky Mass Spectrometry Center.

4.2. Synthesis of 2-substituted-6-dimethylaminofulvenes

4.2.1. 1,2-$C_5H_3(HCNMe_2)(COMe)$ (**1a**)

In a dry, N_2-purged Schlenk flask cooled to 0 °C in an ice bath, THF (100 ml), sodium metal (1.44 g, 0.063 mol) and freshly cracked cyclopentadiene (5.0 ml, 0.063 mol) were added and stirred for 4–5 h, when most of the sodium had been consumed. To the resulting pale red sodium cyclopentadienide solution was added ethyl acetate (6.16 ml, 0.063 mol). The mixture was refluxed for 15–20 h under N_2, then cooled to room temperature (r.t.). Fresh sodium methoxide was prepared by adding sodium metal (5.0 g, 0.19 mol) to 100 ml of dry methanol at 0 °C. The solution was stirred and allowed to warm slowly overnight. The methanol was then removed in vacuo, leaving white sodium methoxide powder. The reaction mixture was added to the sodium methoxide via cannula. Vilsmeier reagent was prepared by adding freshly distilled $POCl_3$ (5.8 ml, 0.063 mol) at 0 °C to DMF (20 ml) in a Schlenk flask, then stirring at r.t. for 15–30 min to give a deep orange solution. The Vilsmeier reagent was added to the deep brown cyclopentadienide reaction mixture dropwise at 0 °C over 15 min, followed by stirring for 4 h at r.t. The reaction mixture was quenched with water and extracted with ethyl ether. The extracts were dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The orange solid **1a** (2.3 g, 0.014 mmol) was obtained in 22% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.97 (s, 1H, C*H*N), 7.10 (dd, 1H, C*H*CCHN), 6.85 (dd, 1H, COCC*H*), 6.38 (dd, 1H, COCCHC*H*), 3.38 (s, 3H, NMe), 3.28 (s, 3H, NMe). Lit. [24,25].

4.2.2. 1,2-$C_5H_3(HCNMe_2)(COPh)$ (**1b**)

As described for **1a**, sodium cyclopentadienide was prepared from sodium (1.44 g, 0.063 mol) and cyclopentadiene (5.0 ml, 0.063 mol) in THF (100 ml). To the resulting pale red solution was added ethyl benzoate (9.0 ml, 0.063 mol). The mixture was refluxed for 15–20 h under N_2 then cooled to r.t. The reaction mixture was added via cannula to sodium methoxide, prepared from sodium (5.0 g, 0.19 mol) in 100 ml of dry methanol. Vilsmeier reagent, prepared from $POCl_3$ (5.8 ml, 0.063 mol) and DMF (20 ml), was added to the deep brown reaction mixture dropwise at 0 °C over 15 min, followed by stirring for 4 h at r.t. The reaction mixture was quenched and worked up as described for **1a**, followed by column chromatography with ethyl ether eluent on alumina (Act. III) to give the orange solid **1b** (2.2 g, 0.010 mol) in 16% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.88 (s, 1H, $CHNMe_2$), 7.76 (m, 2H, Ph), 7.43 (m, 3H, Ph), 6.98 (dd, 1H, CNCC*H*, $^3J_{HH} = 4.4$ Hz, $^4J_{HH} = 1.6$ Hz), 6.83 (dd, 1H, CHOCCH, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.6$ Hz), 6.44 (dd, 1H, CHCHCH, $^3J_{HH} = 3.6$, 3.6 Hz), 3.40 (s, 3H, NMe), 3.33 (s, 3H, NMe); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$,

ppm) δ 154.8 (CHO), 141.9 (CN), 133.9 (*p*-Ph), 130.4 (Cp), 129.8 (CHO*C*CH), 129.2 (*o*-Ph), 128.3 (CN*C*CH), 127.7 (*m*-Ph), 123.8 (Cp), 121.2 (Cp), 115.2 (*i*-Ph), 48.0 (NMe), 40.8 (NMe); IR (neat, cm^{-1}) 1621 (CO); m.p. = 113–114 °C; MS (EI) [M^+] for $^{12}C_{15}^{1}H_{15}^{14}N^{16}O$, m/z 225, isotope pattern matches calculated pattern. Anal. Calc. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.28; H, 6.63; N, 5.09%.

4.2.3. 1,2-C_5H_3(HCNMe$_2$)(COTp) (**1c**; Tp = 2-thienyl)

As described for **1a**, sodium cyclopentadienide was prepared from sodium (0.73 g, 0.032 mol) and cyclopentadiene (2.5 ml, 0.032 mol) in THF (100 ml). To the resulting pale red solution was added 2-thiophene carboxylate (4.3 ml, 0.032 mol). The mixture was refluxed for 15–20 h under N_2 then cooled to r.t. The reaction mixture was added via cannula to sodium methoxide, prepared from sodium (2.5 g, 0.095 mol) in 50 ml of dry methanol. Vilsmeier reagent, prepared from $POCl_3$ (2.9 ml, 0.032 mol) and DMF (10 ml), was added to the deep brown reaction mixture dropwise at 0 °C over 15 min, followed by stirring for 4 h at r.t. The reaction mixture was quenched, worked up and chromatographed as described for **1b** to give the orange solid **1c** (1.1 g, 4.7 mmol) in 15% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.68 (s, 1H, C*H*N), 7.70 (dd, 1H, COCC*H*CHCHS, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.1$ Hz), 7.53 (dd, 1H, COCCHCHC*H*S, $^3J_{HH} = 5.1$ Hz, $^4J_{HH} = 1.1$ Hz), 7.16 (dd, 1H, CHNCC*H*CHCH, $^3J_{HH} = 3.7$ Hz, $^4J_{HH} = 1.7$ Hz), 7.09 (dd, 1H, COCCHC*H*CHS, $^3J_{HH} = 5.1$ Hz, $^3J_{HH} = 3.6$ Hz), 6.95 (dd, 1H, CHNCCHCH*C*H, $^3J_{HH} = 3.7$ Hz, $^4J_{HH} = 1.7$ Hz), 6.45 (dd, 1H, CHNCCHC*H*CH, $^3J_{HH} = 3.7$ Hz, $^4J_{HH} = 3.7$ Hz), 3.35 (s, 3H, NMe), 3.29 (s, 3H, NMe); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ 183.1 (*C*OTp), 154.2 (*C*HN), 146.8 (CO*C*CH), 131.6, 131.1, 130.9, 129.9 (S*C*CO), 127.1, 123.4, 121.1, 114.9 (TpCO*C*), 48.0 (N*C*H$_3$), 40.8 (N*C*H$_3$); IR (Neat, cm^{-1}) 1619 (CO); m.p. = 105–106 °C; MS (EI) [M^+] for $^{12}C_{13}^{1}H_{13}^{14}N^{16}O^{32}S$, m/z 231, isotope pattern matches calculated pattern. Anal. Calc. for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.05. Found: C, 67.40; H, 5.65; N, 5.72%.

4.2.4. 1,2-C_5H_3(HCNMe$_2$)(COBu^t) (**1d**)

As described for **1a**, sodium cyclopentadienide was prepared from sodium (1.44 g, 0.063 mol) and cyclopentadiene (5.0 ml, 0.063 mol) in THF (100 ml). To the resulting pale red solution was added pivaloyl chloride (7.7 ml, 0.063 mol). The mixture was refluxed for 15–20 h under N_2 then cooled to r.t. The reaction mixture was added via cannula to sodium methoxide, prepared from sodium (5.0 g, 0.19 mol) in 100 ml of dry methanol. Vilsmeier reagent, prepared from $POCl_3$ (5.8 ml, 0.063 mol) and DMF (20 ml), was added to the deep brown reaction mixture dropwise at 0 °C over 15 min, followed by stirring for 4 h at r.t. The reaction mixture was quenched and worked up as described for **1b**, except that chromatography was carried out with hexane eluent to give the bright yellow solid **1d** (0.65 g, 3.1 mmol) in 5% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.8 (s, 1H, CHNMe$_2$), 7.22 (m, 1H, Cp), 6.83 (m, 1H, Cp), 6.39 (m, 1H, Cp), 3.36 (s, 3H, NMe), 3.29 (s, 3H, NMe), 1.38 (s, 9H, ^{t}Bu); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ 204.4 (*C*O^{t}Bu), 155.2 (*C*HNMe$_2$), 128.7 (Cp), 127.1 (q-Cp), 121.5 (Cp), 120.2 (Cp), 115.7 (q-Cp), 48.0 (NMe), 44.3 (*C*(CH$_3$)), 40.9 (NMe), 29.4 (C(*C*H$_3$)); IR (neat, cm^{-1}) 1620 (CO); m.p. = 43–44 °C; MS (EI) [M^+] for $^{12}C_{13}^{1}H_{19}^{14}N^{16}O$, m/z 205, isotope pattern matches calculated pattern. Anal. Calc. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.54; H, 9.08; N, 6.42%.

4.2.5. 1,2-C_5H_3(HCNMe$_2$)(COOEt) (**1e**)

As described for **1a**, sodium cyclopentadienide was prepared from sodium (1.44 g, 0.063 mol) and cyclopentadiene (5.0 ml, 0.063 mol) in THF (100 ml). To the resulting pale red solution was added diethyl carbonate (7.4 ml, 0.063 mol). The mixture was refluxed for 15–20 h under N_2 then cooled to r.t. The reaction mixture was added via cannula to sodium methoxide, prepared from sodium (5.0 g, 0.19 mol) in 100 ml of dry methanol. Vilsmeier reagent, prepared from $POCl_3$ (5.8 ml, 0.063 mol) and DMF (20 ml), was added to the deep brown reaction mixture dropwise at 0 °C over 15 min, followed by stirring for 4 h at r.t. The reaction mixture was quenched and worked up as described for **1a** to give the orange solid **1e** (0.55 g, 2.8 mmol) in 5% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 8.82 (s, 1H, C*H*N), 7.14 (m, 1H, C*H*CCHN), 6.80 (m, 1H, COCC*H*), 6.39 (m, 1H, COCCHC*H*), 4.22 (q, 2H, Et), 3.35 (bs, 6H, NMe), 1.32 (t, 3H, Et); lit. [24] (synthesis but no spectroscopic data).

4.3. Synthesis of 2-substituted-6-hydroxyfulvenes

4.3.1. 1,2-C_5H_3(CHOH)(COMe) (**2a**)

Excess aq. NaOH (100 ml, 2 M) was added to 1,2-C_5H_3(HCNMe$_2$)(COMe) (**1a**, 2.3 g, 0.014 mol) in a round-bottom flask, and the mixture was heated to 60–80 °C for 4 h with a slow nitrogen purge. A yellow precipitate formed when the reaction was acidified with concentrated sulfuric acid. The mixture was extracted with ethyl ether and the extract was rinsed with water. The organic layer was dried over $MgSO_4$, filtered and the solvent removed in vacuo to yield the yellow–orange oil **2a** (1.9 g, 0.014 mol) in quantitative yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 17.1 (d, 1H, CHO*H*, $^3J_{HH} = 7.6$ Hz), 8.33 (dd, 1H, CHO, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.0$ Hz), 7.49 (m, 1H, CHOC*H*), 7.28 (dd, 1H, C*H*CCOCH$_3$, $^3J_{HH} = 3.7$ Hz, $^3J_{HH} = 1.8$ Hz), 6.47 (dd, 1H, CHC*H*CH, $^3J_{HH} = 3.7$, 3.7 Hz), 2.53 (s, 3H, COCH$_3$); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ

188.5 ($COCH_3$), 175.6 (COH), 139.5 (Cp), 138.6 (Cp), 125.8 (CH*C*CHO), 124.8 (CH*C*$COCH_3$), 123.3 (CH*C*HCH), 23.1(CH_3); lit. [24] ^{1}H-NMR 17.1 (s, CHO*H*).

4.3.2. 1,2-C_5H_3(CHOH)(COPh) (2b)

4.3.2.1. Method A. 1,2-C_5H_3(HCNMe$_2$)(COPh) (**1b**, 2.2 g, 0.01 mol) was treated with aq. NaOH (100 ml, 2 M) as described for **2a** with a reaction time of 6 h. An identical workup to **2a** gave the yellow–orange oil **2b** (1.98 g, 0.01 mol) in quantitative yield.

4.3.2.2. Method B. [Tl{C_5H_3(CHOH)(COPh)}] (**3b**, 0.20 g, 0.50 mmol) was placed in a round-bottom flask with ethyl ether (15 ml) and water (15 ml). Concentrated hydrochloric acid (2–4 drops) was added and the reaction was stirred for 5 h at r.t. The reaction was extracted with ethyl ether and water. The yellow organic layer was filtered, dried with $MgSO_4$, filtered and the solvent removed in vacuo to give the yellow oil **2b** (0.095 g, 0.48 mmol) in quantitative yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 17.37 (d, 1H, CHO*H*, $^3J_{HH} = 7.0$ Hz), 8.75 (dd, 1H, CHO, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.2$ Hz), 7.87 (m, 2H, Ph), 7.55 (m, 3H, Ph), 7.41 (dd, 1H, Cp, $^3J_{HH} = 3.9$ Hz, $^4J_{HH} = 1.8$ Hz), 7.28 (m, 1H, Cp), 6.53 (dd, 1H, Cp, $^3J_{HH} = 3.9$, 3.9 Hz); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ 184.3 (CO), 176.9 (CHOH), 141.7 (Cp), 141.1 (Cp), 136.9 (*i*-Ph), 131.6 (Ph), 130.2 (q-Cp), 129.6 (Ph), 128.3 (Ph), 127.2 (q-Cp), 124.2 (Cp); IR (neat, cm^{-1}) 1598 (br, CO); MS (EI) [M$^+$] for $^{12}C^1_{13}H^{16}_{10}O_2$, m/z 198, isotope pattern matches calculated pattern. Anal. Calc. for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08. Found: C, 71.80; H, 4.69%.

4.3.3. 1,2-C_5H_3(CHOH)(COTp) (2c)

1,2-C_5H_3(HCNMe$_2$)(COTp) (**1c**, 1.1 g, 4.7 mmol) was treated with aq. NaOH (100 ml, 2 M) as described for **2a** with a reaction time of 6 h. A workup identical to **2a** gave the yellow–orange oil **2c** (0.95 g, 4.7 mmol) in quantitative yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 17.3 (d, 1H, CHO*H*, $^3J_{HH} = 8.0$ Hz), 8.63 (dd, 1H, CHO, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz), 7.87 (dd, 1H, COCC*H*CHCHS, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.2$ Hz), 7.73 (m, 1H, CHOHCC*H*CHCH), 7.68 (dd, 1H, COCCHCHC*H*S, $^3J_{HH} = 5.2$ Hz, $^4J_{HH} = 1.2$ Hz), 7.36 (dd, 1H, CHOHCCHCHC*H*, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.2$ Hz), 7.18 (dd, 1H, COCCHC*H*CHS, $^3J_{HH} = 5.2$ Hz, $^3J_{HH} = 3.7$ Hz), 6.55 (dd, 1H, CHOHCCHC*H*CH, $^3J_{HH} = 3.6$, 3.6 Hz); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ 175.8 (CO), 175.6 (CHOH), 140.5 (Tp), 139.6 (Tp), 133.5 (Tp), 132.7 (Cp), 128 (COCCHCHCHS), 127.9 (Cp), 126.7 (CHOH*C*CH), 124.2 (Cp), 123.3 (CO*C*CH); IR (neat, cm^{-1}) 1623 (br, CO); MS (EI) [M$^+$] for $^{12}C^1_{11}H^{16}_8O^{32}_2S$, m/z 204, isotope pattern matches calculated pattern. Anal. Calc. for $C_{11}H_8O_2S$: C, 64.69; H, 3.95. Found: C, 65.40; H, 3.85%.

4.3.4. 1,2-C_5H_3(CHOH)(CO^{t}Bu) (2d)

1,2-C_5H_3(HCNMe$_2$)(COBu^t) (**1d**, 0.650 g, 3.17 mmol) was treated with aq. NaOH (100 ml, 2 M) as described for **2a**. A workup identical to **2a** gave the yellow–orange oil **2d** (0.536 g, 3.01 mmol) in 95% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 17.67 (d, 1H, CHO*H*, $^3J_{HH} = 8.8$ Hz), 8.37 (dd, 1H, C*H*OH, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 1.6$ Hz), 7.71 (m, 1H, Cp), 7.13 (dd, 1H, Cp, $^3J_{HH} = 4.0$ Hz, $^4J_{HH} = 1.6$ Hz), 6.45 (dd, 1H, Cp, $^3J_{HH} = 4.0$, 4.0 Hz), 1.45 (s, 9H, ^{t}Bu); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ 200.6 (CO^{t}Bu), 173.0 (CHO), 138.8 (Cp), 137.7 (Cp), 125.8 (q-Cp), 122.9 (q-Cp), 122.6 (Cp), 42.5 ($C(CH_3)_3$), 29.9 (C(CH_3)$_3$); IR (neat, cm^{-1}) 1628 (br, CO); MS (EI) [M$^+$] for $^{12}C^1_{11}H^{16}_{14}O_2$, m/z 178, isotope pattern matches calculated pattern. Anal. Calc. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.94; H, 6.63%.

4.3.5. 1,2-C_5H_3(CHOH)(COOEt) (2e)

Crude 1,2-C_5H_3(HCNMe$_2$)(COOEt) (**1e**) was treated with aq. NaOH (100 ml, 2 M) as described for **2a**. A workup identical to **2a** gave the yellow–orange oil **2e** in over 90% yield. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) δ 14.8 (d, 1H, $^3J_{HH} = 14.8$ Hz), 7.7 (d, 1H, $^3J_{HH} = 14.8$ Hz), 7.4 (m, 1H), 6.85 (m, 1H), 6.36 (m, 1H), 4.35 (q, 2H, CH_2), 1.37 (t, 3H, CH_3); ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$, ppm) δ 163.0 (CO), 138.7 (COC*C*HCHCH), 133.4 (COCCHCH*C*H), 123.3 (CH*C*HCH), 61.7 (CH_2), 14.2 (CH_3); lit. [24] (synthesis but no spectroscopic data).

4.4. Synthesis of 1,2-substituted cyclopentadienylthallium compounds

4.4.1. [Tl{1,2-C_5H_3(CHO)(COMe)}] (3a)

Thallous ethoxide (3.0 g, 0.012 mol) was added via syringe to a solution of 1,2-C_5H_3(CHOH)(COMe) (**2a**, 1.66 g, 0.012 mol) in THF (50 ml). A precipitate formed quickly and the reaction mixture was stirred at r.t. overnight. The THF was removed in vacuo and ethyl ether (ca. 50 ml) was added. The tan, solid product **3a** (4.0 g, 0.012 mol) was filtered out of the suspension in quantitative yield. ^{1}H-NMR (200 MHz, Me_2SO, ppm) δ 10.0 (s, 1H, C*H*O), 6.49 (m, 2H, C*H*CHC*H*), 5.7 (dd, 1H, CHCHCH, $^3J_{HH} = 3.4$, 3.4 Hz), 2.21 (s, 3H, COC*H*$_3$); ^{13}C{^{1}H}-NMR (50 MHz, Me_2SO, ppm) δ 191.3 (*C*HO), 185.6 (*C*OCH_3), 126.5 (CH*C*COMe), 126.4 (CHO*C*CH), 122.4 (CHOC*C*H), 117.3 (CH*C*HCH), 112.4 ($COCH_3C$*C*H), 27.5 (CO*C*H_3); IR (Nujol, cm^{-1}) 1622, 1585 (CO); m.p. >170 °C (dec.); MS (EI) [M$^+$] for $^{12}C^1_8H^{16}_7O^{204}_2Tl$, m/z 340 [MH$^+$], isotope pattern matches calculated pattern. Anal. Calc. for $C_8H_7O_2Tl$: C, 28.30; H, 2.07. Found: C, 28.91; H, 2.05%.

4.4.2. [Tl{1,2-C_5H_3(CHO)(COPh)}] (3b)

As described for **3a**, thallous ethoxide (0.75 g, 3.0 mmol) reacted with 1,2-C_5H_3(CHOH)(COPh) (**2b**, 0.54 g, 2.7 mmol) in THF (50 ml). The same workup gave the tan solid **3b** (1.0 g, 2.6 mmol) in over 95% yield. ^{1}H-NMR (200 MHz, Me_2SO, ppm) δ 10.0 (s, 1H, CHO), 7.57 (m, 2H, Ph), 7.37 (m, 3H, Ph), 6.37 (dd, 1H, Cp, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.8$ Hz), 6.11 (dd, 1H, Cp, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.8$ Hz), 5.76 (dd, 1H, Cp, $^3J_{HH} = 3.6$, 3.6 Hz); ^{13}C{^{1}H}-NMR (50 MHz, Me_2SO, ppm) δ 189 (COPh), 185.4 (CHO), 143.6 (*i*-Ph), 129.0 (Ph), 128.6 (q-Cp), 128.5 (Ph), 127.5 (q-Cp), 127.3 (Ph), 125.3 (Cp), 117.8 (Cp), 112.9 (Cp); IR (Nujol, cm^{-1}) 1585 (CO); m.p. >180 °C (dec.); MS (EI) [M^+] for $^{12}C^1_{13}H^{16}_9O^{204}_2Tl$, observed decomposition products only. Anal. Calc. $C_{13}H_9O_2Tl$: C, 38.88; H, 2.26. Found: C, 37.28; H, 2.32%.

4.4.3. [Tl{1,2-C_5H_3(CHO)(COTp)}] (3c)

As described for **3a**, thallous ethoxide (0.93 g, 3.7 mmol) reacted with 1,2-C_5H_3(CHOH)(COTp) (**2c**, 0.76 g, 3.7 mmol), in THF (50 ml). The same workup gave the tan solid **3c** (1.3 g, 3.3 mmol) in 89% yield. ^{1}H-NMR (200 MHz, Me_2SO, ppm) δ 9.95 (s, 1H, CHO), 7.67 (d, 1H, Tp, $^3J_{HH} = 5.1$ Hz), 7.55 (d, 1H, Tp, $^3J_{HH} = 3.3$ Hz), 7.1 (dd, 1H, Tp, $^3J_{HH} = 4.0$, 4.0 Hz), 6.62 (m, 1H, Cp), 6.53 (m, 1H, Cp), 5.8 (dd, 1H, Cp, $^3J_{HH} = 3.3$, 3.3 Hz); ^{13}C{^{1}H}-NMR (50 MHz, Me_2SO, ppm) δ 185.27 (CHO), 179.81 (COTp), 148.6 (q-Tp), 129.75 (Tp), 129.59 (Tp), 127.60 (q-Cp), 127.21 (Tp), 125.25 (q-Cp), 123.27 (Cp), 117.89 (Cp), 113.20 (Cp); IR (Nujol, cm^{-1}) 1571 (CO); m.p. >150 °C (dec.); MS (EI) [M^+] for $^{12}C^1_{11}H^{16}_7O^{32}_2S^{204}Tl$, observed decomposition products only. Anal. Calc. for $C_{11}H_7O_2STl$: C, 32.41; H, 1.73. Found: C, 28.01; H, 1.61%.

4.4.4. [Tl{1,2-C_5H_3(CHO)(CO^{t}Bu)}] (3d)

As described for **3a**, thallous ethoxide (0.49 g, 1.9 mmol) reacted with 1,2-C_5H_3(CHOH)(CO^{t}Bu) (**2d**, 0.350 g, 1.9 mmol) in THF (50 ml). The same workup gave the tan solid **3d** (0.40 g, 1.0 mmol) in 55% yield. ^{1}H-NMR (200 MHz, Me_2SO, ppm) δ 9.92 (s, 1H, CHO), 6.54 (dd, 1H, Cp, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.8$ Hz), 6.42 (dd, 1H, Cp, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.8$ Hz), 5.68 (ddd, 1H, CHC*H*CHCCHO, $^3J_{HH} = 3.6$, 3.6 Hz, $^5J_{HH} = 0.8$ Hz), 1.25 (s, 9H, ^{t}Bu); ^{13}C{^{1}H}-NMR (50 MHz, Me_2SO, ppm) δ 200.2 (*C*O^{t}Bu), 186.2 (CHO), 127.9 (q-Cp), 123.1 (q-Cp), 120.0 (Cp), 115.1 (Cp), 111.7 (Cp), 42.8 ($C(CH_3)_3$), 29.7 (C(*C*H$_3$)$_3$); IR (Nujol, cm^{-1}) 1594 (CO); m.p. >170 °C (dec.); MS (EI) [M^+] for $^{12}C^1_{11}H^{16}_{13}O^{204}_2Tl$, m/z 382, isotope pattern matches calculated pattern. Anal. Calc. for $C_{11}H_{13}O_2Tl$: C, 34.62; H, 3.43. Found: C, 29.36; H, 2.76%.

4.4.5. [Tl{1,2-C_5H_3(CHO)(COOEt)}] (3e)

As described for **3a**, thallous ethoxide (0.75 g, 3.0 mmol) reacted with 1,2-C_5H_3(CHOH)(COOEt) (**2e**, 0.50 g, 3.0 mmol) in THF (50 ml). The same workup gave the air-sensitive, brown solid **3e** (0.85 g, 2.3 mmol) in 76% yield. ^{1}H-NMR (200 MHz, Me_2SO, ppm) δ 9.9 (d, 1H, CHO, $^4J_{HH} = 1.0$ Hz), 6.41 (overlapping dd, 2H, C*H*CHC*H*), 5.7 (ddd, 1H, CHC*H*CH, $^3J_{HH} = 3.8$, 3.8 Hz, $^5J_{HH} = 1.0$ Hz), 4.04 (q, 2H, CH_2), 1.2 (t, 3H, CH_3); ^{13}C{^{1}H}-NMR (50 MHz, Me_2SO, ppm) δ 183.9 (CHO), 165.5 (COO), 126.1 (CHO*C*), 120.0 (COOC-*C*H), 115.2 (CHOCCH*C*HCH), 114.8 (COO*C*CH), 112.0 (CHOC*C*HCH), 57.2 (CH_2), 14.8 (CH_3); IR (Nujol, cm^{-1}) 1646 (m), 1570 (b, s), 1460 (b, s); m.p. >100 °C (dec.); MS (EI) [M^+] for $^{12}C^1_9H^{16}_9O^{204}_3Tl$, 370 [$MH^+$], isotope pattern matches calculated pattern. Anal. Calc. for $C_9H_9O_3Tl$: C, 29.25; H, 2.45. Found: C, 24.20; H, 2.01%.

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