SYNTHESES AND ^{1}H, ^{13}C, ^{15}N, ^{17}O, [205]Tl NMR OF NEW RING-FUNCTIONALISED CHELATING HALF-SANDWICH COMPLEXES OF THALLIUM(I) CONTAINING AN N-, O- OR S-DONOR ATOM

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Novel, ring-functionalised cyclopentadienylthallium(I) complexes have been synthesised in good to moderate yields from thallium ethoxide and N-, O- and S-alkyl substituted cyclopentadienes in diethyl ether at 0 °C. The new compounds have been analysed by ^{1}H, ^{13}C, ^{15}N, ^{17}O and [205]Tl NMR, which revealed that cyclopentadienyl ring and the donor atom in the side chain are coordinated to thallium; they are mononuclear complexes. Hence, these compounds can be viewed as analogues of their parent, CpTl, but their solubility is much enhanced because of the mononuclear nature due to the presence of the side chain. The thallium(I) complexes with the (dimethylamino)ethyl, methoxyethyl and (methylsulfanyl)ethyl side chain are promising reagents for transmetallation reactions.

Keywords: Organometallic compounds; Monoalkylcyclopentadiene; Monoalkylcyclopentadienyl ligands; Thallium(I) complexes; Multinuclear NMR spectroscopy; Half-sandwich complexes.

The utility of the unsubstituted cyclopentadienylthallium(I) complex, [Tl(Cp)], as a ligand-transfer reagent for the syntheses of new cyclopentadiene and organometallic compounds has been known for many years[1–4]. [Tl(Cp)] reacts in a similar way as a cyclopentadienide and the Cp-ligand exchange generally occurs under milder and less reducing conditions than for the NaCp or LiCp analogues[2,4].

Thallium(I) complexes of mono- and polysubstituted cyclopentadiene, [Tl(R_nCp)], are very interesting because of their widely varied stability and solubility depending on the ring substituents. The R_nCp ligand in these complexes can also be easily exchanged for ligands on main-group and transition metals, and many examples of [Tl(R_nCp)] as trans-metallating agent are known[5–14]. These complexes have a high synthetic value as (ligand transfer) reagents in cases where an R_nCp–metal complex cannot be

obtained by a direct reaction between $(R_nCp)Na$ or $(R_nCp)Li$ and a main-group or transition metal salt.

Metal complexes with donor-functionalised cyclopentadienyl ligands have been intensively studied during the past decade because of their potential application as catalysts in ethylene, propylene and styrene (Ziegler–Natta) polymerisation[15–18]. Intramolecular coordination has been established for complexes of this kind. The donor atom in the side chain (e.g., N, O or S) will influence the stability, solubility and reactivity of the π-complexes by additional intramolecular coordination to the metal atom of the complex, and this chelating effect will play an important role in catalytic processes.

Much of the work on this topic relates to several R_nCp complexes of s- and p-block elements[19–22], lanthanides[20,23–26] and some transition metals[6,17,18,20,27–32]. Most of this research has been based on complexes with the [(dimethylamino)ethyl]cyclopentadienyl ligand, where the nitrogen atom is directly coordinated to the metal centre. Also, compounds derived from Cp ligands with two 2-(dimethylamino)ethyl side chains[23], a 2-(diiso-propylamino)ethyl side chain[17] or side chains with oxygen donors[24–26], which all have donating capability, are known.

In this paper we report the syntheses and analyses of a series of [Tl(RCp)] complexes with N-, O- and S-donor atoms in the side chain, which resemble the known complex [{2-(dimethylamino)ethyl}cyclopentadiene]-thallium(I) (**1a**; Fig. 1)[18,19,22]. Complex **1a** was used as the reference compound for this study. The other compounds are novel and their syntheses, structure and stability have been evaluated. We will show that the differences in stability of the complexes can be ascribed to the substituents on the donor atoms on the side chain. To the best of our knowledge, this is the first time that this type of complexes has been synthesised and studied by ^{15}N, ^{17}O, and [205]Tl NMR that has provided evidence for intramolecular coordination of the N- or O-atom to thallium.
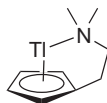
1a

FIG. 1
Proposed structure of complex **1a**

RESULTS AND DISCUSSION

Syntheses

The monosubstituted cyclopentadiene compounds **1–4** have been synthesised according to the procedure described by Rees et al.[33]; compound **5** is new. A mixture of 1- and 2-alkylcyclopentadiene isomers **I + II** of the ligands **1–5** is formed when sodium cyclopentadienide is reacted with the respective primary alkyl chlorides (Scheme 1). Distillation under reduced pressure was necessary to purify the compounds that were isolated in 12–40% yields as colourless liquids. To prevent dimerisation, the compounds **1–5** were stored at 0 °C.

The corresponding thallium(I) complexes **1a–5a** have been synthesised by reacting ligands **1–5** with thallium ethoxide in diethyl ether, starting at 0 °C, followed by warming to room temperature (Scheme 1)[22]. Evaporating the solvent and washing with pentane yielded white microcrystalline powders for **1a**, **3a** and **5a**. Complexes **2a** and **4a** were yellow to brown oils. The yields varied between 41 and 73%.

The complexes **1a**, **3a** and **5a** are soluble in apolar organic solvents and show sensitivity to air in the solid state and in solution. Although the solids turn brown on exposure to air, they can be briefly handled in air. Complexes **2a** and **4a** are soluble in some polar and apolar solvents and are very sensitive to air. The solubility of complexes like **1a** suggests, in general, monomeric or oligomeric structures in solution[19,22]. More bulky substituents on the Cp-ring can also lead to monomeric or oligomeric structures[4]
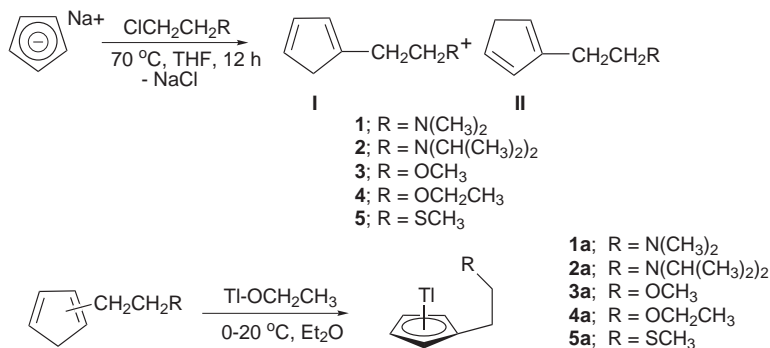
Scheme 1
Synthesis of monosubstituted cyclopentadiene compounds and the corresponding cyclopentadienylthallium(I) complexes

and will result in more covalent Cp–Tl interaction. The solids **1a**, **3a** and **5a** seem to be good precursors for, e.g., transmetallation reactions because of the ease of their isolation and their relative stability in the solid state. For details, see Experimental.

NMR Spectroscopy

The ligands **1**–**5** and their Tl(I) complexes **1a**–**5a** were analysed by ^{1}H, ^{13}C, ^{15}N, ^{17}O and [205]Tl NMR spectroscopy. No ^{13}C NMR spectrum could be obtained for complexes **4a** and **5a** because of their (partial) decomposition during the data acquisition. It was not possible to obtain [33]S NMR data of complex **5a**, probably due to the unsymmetrical environment of the S atom, leading to a short T_1 value and, hence, a very broad line.

^{1}H and ^{13}C NMR

^{1}H NMR data of cyclopentadiene compounds **1** (refs[19,28,33]), **2** (ref.[17]), **3** (ref.[33]) and **4** (ref.[33]), and the ^{13}C NMR data of **1** and **2** have been published previously. The ^{1}H and ^{13}C NMR data of ligand **5** are collected in Experimental. The occurrence of two isomers, **I** and **II**, was substantiated by the observation of two sets of signals. The ^{1}H and ^{13}C chemical shifts of the known compounds match the published values.

Concerning the cyclopentadienyl complexes **1a**–**5a**, only ^{1}H and ^{13}C NMR data of **1a** have been published earlier[18,19,22]. Complete NMR data, including ^{15}N, ^{17}O and [205]Tl NMR signals of complexes **2a**–**5a**, have been collected in Experimental. Selected ^{1}H and ^{13}C NMR data of **1a**–**5a** are collected in Table I.

No [(203)205]Tl-^{1}H/^{13}C couplings have been observed, which, in agreement with the literature[22,34], may indicate ionic character of the thallium–cyclopentadienyl bonding. Still, the nature of bonding in the [Tl(RCp)] complexes is unclear. Koridze et al.[35,36] suggest an intermediate structure were the bond is neither purely ionic nor purely covalent. On the other hand, others[4] suggest that from the absence of [(203)205]Tl-^{1}H/^{13}C spin-spin couplings, it does not necessarily follow that the thallium–Cp interaction is predominantly ionic. The absence of [205]Tl-^{1}H/^{13}C couplings could also be due to fast intermolecular exchange of the Cp groups between the molecular complexes.

Coordination-induced shifts of relevant ^{1}H and ^{13}C nuclei in **1a**–**5a** have been observed, which may be indicative of a change in their environments due to coordination of the heteroatom of the side chains for these com-

pounds. Indeed, a significant shift of the α-protons to higher frequencies is observed for **1a** and **2a**, but for **3a** and **4a** a shift to lower frequencies is noted instead. The same trend is found for the carbons in α and α′ positions. For **5a**, there is no apparent change. For other metal complexes with **1** as the coordinating ligand[17,19–22], even with other group 13 metals (Al, Ga and In), the authors show that intramolecular coordination will lead to a shift of both the α and α′ protons to higher frequencies. On the other hand, the appreciable low-frequency shift of the α′ protons observed for complex **1a**, has been put forward as an indication that the heteroatoms are coordinated to the thallium centre[19,22]. However, the same authors state in a later paper that "there is no conclusive evidence for intramolecular coordination in complex **1a**" (ref.[19]). We are inclined to say, that the induced ¹H and ¹³C shifts for the atoms remote from the metal centre and from the coordinating group are circumstantial evidence for the coordination of the heteroatoms in case of **1a**–**4a**.

TABLE I
Selected ^{1}H and ^{13}C NMR data of cyclopentadienes[a] and their Tl(I) complexes[b]

Ligand/complex	^{1}H δ, ppm		^{13}C δ, ppm	
	N(**CH**$_3$)$_2$	**CH**$_2$N	N(**C**H$_3$)$_2$	**C**H$_2$N
1	2.26, 2.27	2.47 br	59.3, 59.9	28.5, 29.3
1a	1.61	2.52	43.3	60.7
	N(**CH**(CH$_3$)$_2$)$_2$	**CH**$_2$N	N(**C**H(CH$_3$)$_2$)$_2$	**C**H$_2$N
2	3.02 br	2.59 br	49.0	41.5, 43.9
2a	2.91	2.72	48.4	47.9
	O**CH**$_3$	**CH**$_2$O	O**C**H$_3$	**C**H$_2$O
3	3.37	3.56	58.6	72.1, 72.6
3a	2.90	3.25	57.9	75.1
	O**CH**$_2$CH$_3$	**CH**$_2$O	O**C**H$_2$CH$_3$	**C**H$_2$O
4	3.48	3.57	66.3	70.1, 70.7
4a	3.27	3.42	–	–
	S**CH**$_3$	**CH**$_2$S	S**C**H$_3$	**C**H$_2$S
5	2.08	2.68	15.9	33.7, 33.4
5a	1.65	2.69	–	–

δ relative to residual: ^{a} CHCl$_3$ at δ 7.24 at 300 MHz, ^{b} C$_6$H$_6$ at δ 7.11 at 300 MHz.

Apart from the ^{1}H and ^{13}C NMR coordination shifts, one may also involve the coordination shifts of the heteroatoms. Hence, we have measured the ^{205}Tl, ^{15}N and ^{17}O NMR spectra for compounds **1a**–**5a**. To the best of our knowledge, this has never been done before for this type of compounds.

^{205}Tl NMR

Thallium is easy to detect (the sensitivity of ^{205}Tl is 0.1355 relative to ^{1}H) and several thallium NMR studies, mostly of Tl(III) compounds, but also of some Tl(I) salts, have been published[37–40]. Due to the highly ionic nature of Tl(I) complexes, only a few coupling constants of such species have been observed ($^1J_{Tl,H}$ = 6000 Hz, $^1J_{Tl,C}$ > 10 000 Hz, $^2J_{Tl,C}$ = 96–100 Hz)[38,39]. ^{205}Tl-^{203}Tl coupling constants are very large (ca. 2 kHz) and easily observed when present. The absence of ^{205}Tl-^{203}Tl couplings in our complexes is in agreement with their mononuclear nature. The results of our ^{205}Tl NMR study have been compiled in Table II. The ^{205}Tl shifts of the complexes **1a**–**3a** and **5a** are observed in the region similar to that published for some Tl(I) nitrates and several solid Tl(I) compounds[38]. The ^{205}Tl shift of complex **3a** is comparable with the ^{205}Tl shift found for thallium(I) ethoxide in ben-

TABLE II
^{15}N, ^{17}O and ^{205}Tl NMR data of the ligands **1**–**5** and their thallium complexes[a]

	Ligand/complex	^{15}N or ^{17}O δ, ppm	δ ^{205}Tl, ppm
1	Cp-CH$_2$CH$_2$**N**(CH$_3$)$_2$	–354	
1a	[Tl(Cp-CH$_2$CH$_2$**N**(CH$_3$)$_2$])]	–344 (Δδ = +10)	–460
2	Cp-CH$_2$CH$_2$**N**(i-Pr)$_2$	–327	
2a	[Tl(Cp-CH$_2$CH$_2$**N**(i-Pr)$_2$)]	–321 (Δδ = +6)	–667
3	Cp-CH$_2$CH$_2$**O**CH$_3$	–16	
3a	[Tl(Cp-CH$_2$CH$_2$**O**CH$_3$)]	–11 (Δδ = +5)	–790
4	Cp-CH$_2$CH$_2$**O**C$_2$H$_5$	11	
4a	[Tl(Cp-CH$_2$CH$_2$**O**C$_2$H$_5$)]	14 (Δδ = +3)	–123
5a	[Tl(Cp-CH$_2$CH$_2$**S**CH$_3$)]	–	–750

[a] ^{15}N NMR spectra were obtained at 30.40 MHz, ^{17}O NMR spectra at 67.78 MHz, ^{205}Tl NMR spectra at 57.78 MHz.

zene: –605 ppm [40]. Because of its insolubility, [205]Tl NMR of unsubstituted [Tl(Cp)] could not, unfortunately, be measured to compare its shift with the [205]Tl shifts of complexes **1a**–**5a**. Hence, it is difficult to draw conclusions concerning the presence or absence of intramolecular coordination of the heteroatom to thallium in **1a**–**5a** from the [205]Tl NMR experiments. We note a substantially different [205]Tl shift for complex **4a**, which is difficult to attribute because of the fact that we cannot obtain [205]Tl shift data for the parent compound and that several factors will contribute to this shift. One may argue, however, that complex **4a** is different from the rest of the series.

^{15}N and ^{17}O NMR

The results of the ^{15}N and ^{17}O NMR experiments are outlined in Table II. The ^{15}N chemical shifts are in the range of those for amine nitrogen atoms[41]. The observed [17]O chemical shifts lie in the range expected for ether groups (–40 to 70 ppm)[42–44]. There is a small high-frequency shift of the heteroatoms for complexes **1a**–**4a**, which indicates rather modest overall changes in the geometry at the heteroatom and the electron density on this atom. Indeed, this has been observed before for Tl(I) compounds; however, for thallium bis(2-pyridyl)amido complexes, a ^{15}N coordination shift of 50 ppm to higher frequency has been reported[45]. Nevertheless, our NMR data indicate that a change in the coordination and electronic environment of these heteroatoms relative to the free ligands has occurred. Hence, it seems reasonable to assume that the N or O atoms are indeed coordinated to the thallium atom in complexes **1a**–**4a**.

Mass Spectrometry

The complexes **1a** and **3a** have been analysed by FAB-MS. The molecular mass peak could not be observed. Three [Tl$_2$(RCp)]$^+$ peaks (1:5:6) for each compound were found, reflecting the thallium isotope composition. Similar fragmentation behaviour is known from the literature[4] when using chemical ionisation or fast atom bombardment mass spectroscopy methods. The authors state that the zig-zag chain of the [Tl(RCp)] complexes is not entirely disrupted, as indicated by the formation of [Tl$_2$(RCp)]$^+$ and [Tl(RCp)$_2$]$^-$ species. Although this would point to a chain-like structure for **1a** and **3a**, it is more likely that the fragments generated from one mononuclear [Tl(RCp)] complex re-aggregate with another [Tl(RCp)] during the mass measurement, or from fragmentation of dimers. Hence, the mass spectrometric results are in agreement with the proposed structures of **1a** and

3a, yet they do not warrant an unequivocal conclusion with respect to the coordination behaviour of the ligands in the solid state.

CONCLUSIONS

A new ligand, as a mixture of 1- and 2-[2-(methylsulfanyl)ethyl]cyclopenta-1,3-diene (**5**), and several new thallium complexes, **2a**–**5a**, have been synthesised in reasonable to good yields. Their ^{1}H and ^{13}C NMR are comparable with data published earlier. New [205]Tl NMR data have been collected. Complementing heteronuclear NMR data have been collected for the ligands **1**–**5** and their corresponding complexes, which indicate that the environment of the heteroatoms changes for most of the [Tl(RCp)] complexes as compared with the corresponding cyclopentadiene ligands. These findings imply that in solution the heteroatoms of **1a**–**4a** are probably coordinated to thallium. The fact that the coordination-induced chemical shifts are small may be a consequence of the more ionic rather than covalent character of the Tl–Cp bonding. Finally, the [Tl(RCp)] complexes **1a**, **3a** and **5a** seem to be promising precursors for transmetallation reactions because of the ease of their preparation and isolation, as well as their relative stability.

EXPERIMENTAL

General

All reactions were carried out under an inert atmosphere of dry nitrogen. The solvents used, diethyl ether, pentane and THF, were dried by distillation from sodium wire immediately prior to use. Deuterated benzene-d^6 was distilled from CaH_2 and deoxygenated by freeze-pump-thaw cycles. Chemicals where purchased from Acros, Aldrich and Merck. ^{1}H and ^{13}C NMR measurements of the ligands and their complexes were carried out on a Varian Mercury 300 spectrometer at 300.13 MHz in $CDCl_3$ and on a Varian Inova 500 spectrometer at 125.69 MHz in C_6D_6, respectively. ^{15}N NMR spectra of the ligands and complexes were measured on a Bruker DRX 300 spectrometer at 30.42 MHz in dry C_6D_6. The ^{17}O NMR spectra of the ligands and complexes were obtained on a Varian Inova 500 spectrometer at 67.76 MHz in dry C_6D_6. [205]Tl NMR was measured in dry C_6D_6 on a Bruker AMX 100 spectrometer at 57.72 MHz. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Fast atom bombardment (FAB) mass spectroscopy was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. The samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements, a resolving power of 10 000 (10% valley definition) was used.

Syntheses of the Cyclopentadiene Derivatives

Mixture of 1- and 2-[2-(dimethylamino)ethyl]cyclopenta-1,3-diene (**1**). To a solution of NaCp in dry THF, a slight excess of 2-(dimethylamino)ethyl chloride (commercially available as its chloride hydrochloride, which was treated with NaOH in water prior to use) was added and heated under reflux for 24 h. The white suspension was treated with H_2O and the reaction mixture was extracted with diethyl ether. Evaporating the ether gave a yellow oil which was purified by distillation (b.p. 39 °C/2 mm Hg). Yield 23%. ^{15}N NMR (C_6D_6): –354.

Mixture of 1-and 2-[2-(diisopropylamino)ethyl]cyclopenta-1,3-diene (**2**). Analogously to **1**, using 2-(diisopropylamino)ethyl chloride hydrochloride. B.p. 48 °C/0.5 mm Hg. Yield 30%. ^{15}N NMR (C_6D_6): –327.

Mixture of 1- and 2-(2-methoxyethyl)cyclopenta-1,3-diene (**3**). Analogously to **1**, using chloroethyl methyl ether. B.p. 45 °C/3 mm Hg. Yield 22%. ^{13}C NMR (CDCl$_3$): 146.1, 143.8 (ring C$_q$); 134.6, 133.9 132.5 132.1 127.7, 127.4 (ring HC=CH); 72.6, 72.1 (CH$_2$O); 58.6 (OCH$_3$); 43.7, 41.4 (CH$_2$), 31.1, 30.3 (ring CH$_2$). ^{17}O NMR (C_6D_6): –16.

Mixture of 1- and 2-(2-ethoxyethyl)cyclopenta-1,3-diene (**4**). Analogously to **1**, using chloroethyl ethyl ether. B.p. 42 °C/3 mm Hg. Yield 31%. ^{13}C NMR (CDCl$_3$): 146.4, 143.9 (ring C$_q$); 134.9, 133.9, 132.6, 132.2, 127.7, 127.4 (ring HC=CH); 70.7, 70.1 (CH$_2$**C**H$_2$O); 66.4 (O**C**H$_2$CH$_3$); 43.9, 41.4 (ring CH$_2$); 31.4, 30.6 (**C**H$_2$CH$_2$O); 15.4 (OCH$_2$**C**H$_3$). ^{17}O NMR (C_6D_6): 11.

Mixture of 1- and 2-[2-(methylsulfanyl)ethyl]cyclopenta-1,3-diene (**5**). Analogously to **1**, using 2-chloroethyl methyl sulfide. B.p. 68 °C/3.5 mm Hg. Yield 13%. ^{1}H NMR (CDCl$_3$): 6.42, 6.26, 6.21, 6.07 (multiplets, 3 H, HC=CH); 2.96, 2.90 (m, 2 H, ring CH$_2$); 2.68 (br, 4 H, CH$_2$**C**H$_2$S); 2.11, 2.10 (SCH$_3$) ^{13}C NMR (CDCl$_3$): 148.0, 144.8 (ring C$_q$); 134.5, 134.3, 132.0, 131.3, 127.7, 127.2 (ring HC=CH); 43.4, 41.6 (ring CH$_2$); 34.4, 33.7 (CH$_2$**C**H$_2$S); 30.8, 30.1 (**C**H$_2$CH$_2$S); 15.8 (SCH$_3$).

Syntheses of the Thallium(I)cyclopentadienyl Complexes

{[2-(Dimethylamino)ethyl]cyclopentadienyl}thallium(I) (**1a**). A solution of thallium ethoxide (1.76 g, 7.06 mmol) in dry Et$_2$O (0.5 ml) was cooled to 0 °C and Cp ligand **1** (10.6 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 16 h. A white suspension was formed. Evaporating the volatiles and washing with dry pentane gave a white microcrystalline solid in 41% yield. The solid decomposes in air, giving a brown colour. ^{15}N NMR (C_6D_6): –343.8. ^{205}Tl NMR (C_6D_6): –459.7. MS (FAB$^+$): 546.1 [C$_9$H$_{14}$N^{205}Tl$_2$]$^+$, 544.1 [C$_9$H$_{14}$N^{205}Tl^{203}Tl]$^+$, 542.1 [C$_9$H$_{14}$N^{203}Tl$_2$]$^+$, 358 [(C$_6$H$_5$)$_2$^{205}Tl], 356 [(C$_6$H$_5$)$_2$^{203}Tl], M$^+$ = 342.09 [C$_9$H$_{14}$N^{205}Tl], 340.09 [C$_9$H$_{14}$N^{203}Tl], 205 [^{205}Tl], 203 [^{203}Tl].

{[2-(Diisopropylamino)ethyl]cyclopentadienyl}thallium(I) (**2a**). Cp ligand **2** (1.6 ml, 8.47 mmol) was added dropwise to a solution of thallium ethoxide (1.76 g, 7.06 mmol) in dry Et$_2$O (0.5 ml) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 h. Evaporation of the volatiles and washing with dry pentane gave a yellow oil. NMR spectra were recorded in situ. Yield was not determined because of fast decomposition of the compound. ^{1}H NMR (C_6D_6): 6.07 (m, 4 H, ring HC=CH); 2.91 (septet, 2 H, ^{3}J(HH) = 6.6, C**H**(CH$_3$)$_2$); 2.72 (m, 2 H, CH$_2$**C**H$_2$N); 2.60 (m, 2 H, C**H**$_2$CH$_2$N); 0.89 (d, 12 H, ^{3}J(HH) = 6.6, CH(C**H**$_3$)$_2$). ^{13}C NMR (C_6D_6): 107.6, 106.9 (ring HC=CH); 48.4 (**C**H(CH$_3$)$_2$); 47.9 (CH$_2$**C**H$_2$N); 29.9 (**C**H$_2$CH$_2$N); 20.8 (CH(**C**H$_3$)$_2$). ^{15}N NMR (C_6D_6): –321.5. ^{205}Tl NMR (C_6D_6): –667.

[2-(Methoxyethyl)cyclopentadienyl]thallium(I) (**3a**). A solution of Cp ligand **3** (12 g, 9.7 mmol) in dry Et$_2$O (0.5 ml) was cooled to 0 °C. An equimolar amount of thallium ethoxide (0.7 ml,

2.4 g, 9.7 mmol) was filtered and added dropwise with a syringe. The solid formed after 1 h was purified by decanting the solvents and washing with dry diethyl ether. This gave crystalline white to colourless plates in 73% yield. ^{1}H NMR (C$_6$D$_6$): 6.06 (t, ^3J(HH) = 1.2, 2 H, ring HC=CH); 6.02 (t, ^3J(HH) = 1.5, 2 H, ring HC=CH); 3.32 (t, 2 H, ^3J(HH) = 3.6, CH$_2$C**H**$_2$O); 2.98 (s, 3 H, OCH$_3$); 2.78 (t, 2 H, ^3J(HH) = 3.6, C**H**$_2$CH$_2$O). ^{13}C NMR (C$_6$D$_6$): 122.5 (ring C$_q$); 108.6, 107.7 (ring HC=CH); 75.1 (CH$_2$**C**H$_2$O); 57.9 (OCH$_3$); 30.4 (**C**H$_2$CH$_2$O). ^{17}O NMR (C$_6$D$_6$): –11. ^{205}Tl NMR (C$_6$D$_6$): –789. MS (FAB$^+$): 533 [C$_8$H$_{11}$O^{205}Tl$_2$]$^+$, 531 [C$_8$H$_{11}$O^{205}Tl^{203}Tl]$^+$, 529 [C$_8$H$_{11}$O^{203}Tl$_2$]$^+$, 358 [(C$_6$H$_5$)$_2$^{205}Tl], 356 [(C$_6$H$_5$)$_2$^{203}Tl], M$^+$ = 329.06 [C$_8$H$_{11}$O^{205}Tl], 327.06 [C$_8$H$_{11}$O^{203}Tl], 205 [^{205}Tl], 203 [^{203}Tl].

[2-(Ethoxyethyl)cyclopentadienyl]thallium(I) (**4a**). A solution of Cp ligand **4** (10 g, 7.2 mmol) in dry Et$_2$O (0.5 ml) was cooled to 0 °C. An equimolar amount of thallium ethoxide (0.5 ml, 1.8 g, 7.2 mmol) was filtered and added dropwise with a syringe. The reaction mixture was stirred for 2 days. A yellow oil was formed at the bottom of the flask, which was quickly separated from the supernatant. The ^{1}H NMR was in agreement with the structure of **4a**. Yield was not established because of the fast decomposition of the complex. ^{1}H NMR (C$_6$D$_6$): 5.84 (br, 2 H, ring HC=CH); 5.73 (br, 2 H, ring HC=CH); 3.42 (t, ^3J(HH) = 5.1, 2 H, CH$_2$C**H**$_2$O); 3.27 (m, 2 H, OC**H**$_2$CH$_3$); 2.75 (m, 2 H, C**H**$_2$CH$_2$O); 1.09 (t, 3 H, ^3J(HH) = 7.2, OCH$_2$C**H**$_3$). ^{17}O NMR (C$_6$D$_6$): 14. ^{205}Tl NMR (C$_6$D$_6$): –122.7.

{[2-(Methylsulfanyl)ethyl]cyclopentadienyl}thallium(I) (**5a**). A solution of Cp ligand **5** (0.5 g, 3.8 mmol) in dry Et$_2$O (0.5 ml) was cooled to 0 °C. An equimolar amount of thallium ethoxide (0.3 ml, 0.9 g, 4 mmol) was filtered and added dropwise with a syringe. A white solid was formed, after solvents decantation, was washed with dry pentane. Yield could not be established because of fast decomposition of the complex. ^{1}H NMR (C$_6$D$_6$): 6.01 (br, 4 H, ring HC=CH); 2.69 (t, 2 H, ^3J(HH) = 6.9, CH$_2$C**H**$_2$S); 2.47 (t, 2 H, ^3J(HH) = 6,9, C**H**$_2$CH$_2$S); 1.65 (s, 3 H, SCH$_3$). ^{205}Tl NMR (C$_6$D$_6$): –750.3.

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