

COMMUNICATION

Selective Mono- and Dimetallation of a Group 3 Sandwich Complex

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Abstract: The scandium Cp/COT hybrid sandwich compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$ is resistant to metallation via conventional alkylolithium and lithium amide bases. In this work, clean, selective, stoichiometric and high-yielding mono- and dimetallation is accomplished using tandem *trans*-metal-trapping (TMT) involving LiTMP and *i*Bu₂AlTMP with deprotonation occurring selectively at the Cp and Cp/COT rings respectively, providing the first example of selective metallation of a sandwich complex featuring a Group 3 element.

While the functionalization of ferrocene¹ and related Cp (C₅H₅⁻, cyclopentadienyl)-based metallocenes is well established, the functionalization of sandwich complexes with COT (C₈H₈²⁻, cyclooctatetraendiide) ligands is significantly more challenging and therefore known methods are still relatively scarce.² Deprotonative metallation is a common tool used for opening up carbon sites in sandwich compounds for functionalization.³ Ferrocene can be monometallated or dimetallated with varying degrees of selectivity depending on the choice of polar organometallic base [e.g., *n*BuLi·TMEDA, *t*BuLi·(KOTBu)].⁴ Its controlled tetrametallation is achievable via the synergistic bimetallic mixture⁵ *n*BuNa/*n*,*s*Bu₂Mg/3*i*Pr₂NH,⁶ while excess *n*BuK can allow attachment of up to eight metal atoms on its carbon scaffold.⁷ Selective dimetallation is particularly attractive since it can provide access to *ansa* complexes, which

are convenient monomers for ring-opening polymerization (ROP) reactions.⁸ This reaction protocol has been successfully transferred to heteroleptic ligand systems, i.e. complexes of the composition $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^7\text{-C}_7\text{H}_7)]$, of which both *ansa* complexes and ring-opened polymers have been reported.⁹ In 2011 the group of Braunschweig used a metallation protocol consisting of *n*BuLi and the activating oligoamine *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDTA) in *n*-hexane to synthesize a unique *ansa*-bridged cyclooctatetraenide complex of composition $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})(\eta^8\text{-C}_8\text{H}_7\text{Li})\cdot\text{PMDTA}]$,² and this ligand system is of particular interest due to its widespread use in *d*-block metal chemistry.¹⁰ However, this same approach was unsuccessful when applied to the heteroleptic scandium Cp/COT sandwich compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$ (**1**).¹¹ Varying the organolithium reagent used (*n*BuLi, *t*BuLi, LiNiPr₂, *n*BuLi·KOTBu), its stoichiometric excess, the activating donor molecule (TMEDA, PMDTA, THF), and the reaction conditions (temperatures and reaction time, some even up to 5-7 days) also proved ineffective, providing either no metallation at all or poor yields of dimetallated products (3-11%) in complex mixtures. Thus we turned our attention to the accomplished toolbox of metallating agents developed by the group of Mulvey, which includes examples specifically engineered for effecting efficient dimetallation.¹² Herein we report the outcomes of reacting a selection of these agents with $[(\eta^5\text{-C}_5\text{H}_5)\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$ (**1**).

First, the reactivity of **1** with the heterobimetallic sodium magnesiate $[(\text{TMEDA})\text{Na}(\textit{n}\text{Bu})(\text{TMP})\text{Mg}(\text{TMP})]$ ¹³ and $[\text{Na}_6\text{Mg}_2\text{TMP}_6\textit{n}\text{Bu}_2]$ ¹⁴ (TMP = 2,2,5,5-tetramethylpyrrolidide) was studied, with the latter chosen due to its template ring structure that has been found a perfect fit to selectively dimetallate a series of arenes. Unfortunately, in both cases the resulting experimental data did not show promise as mixtures were obtained under diverse stoichiometries and reaction conditions. Second, the reactivity of **1** with bulky lithium amides was explored.¹⁵ Equimolar amounts of **1** and LiTMP¹⁶ in *n*-hexane gave only low in situ yields (9% or 11% after 24 h at room temperature or 12 h under reflux conditions, respectively, as evidenced by in situ ¹H-NMR monitoring) of the singly

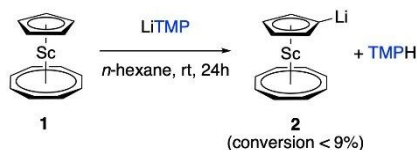
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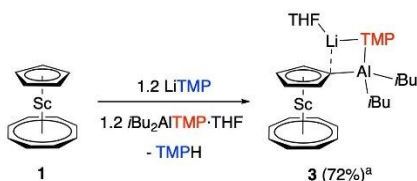
Electronic Supplementary Information (ESI) available: synthetic, spectroscopic, computational and crystallographic details. See DOI: 10.1039/x0xx00000x

metallated product $[\text{Li}\{\{\eta^5\text{-C}_5\text{H}_4\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)\}]$ **2** (Scheme 1). Here monolithiation occurs preferentially at the Cp ring, leaving the COT ring untouched.



Scheme 1. Metallation of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$ with LiTMP to give $[\text{Li}\{\{\eta^5\text{-C}_5\text{H}_4\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)\}]$.

This modest but significant result was promising as *trans*-metal-trapping (TMT) protocols can promote enhanced metallation in reactions where the conversion is low.¹⁷ In TMT, LiTMP remains separated from $i\text{Bu}_2\text{AlTMP}$ in hydrocarbon solution or THF solution rather than forming an ate complex of type “ $(\text{THF})_n\text{Li}(\text{TMP})\text{Al}(i\text{Bu})_2(\text{TMP})$ ”. Thus, free LiTMP can operate as a base to lithiate substrates in low yields, while the more carbophilic $i\text{Bu}_2\text{AlTMP}\cdot\text{THF}$ can trap and stabilize the generated carbanion and drive equilibria to the product side to achieve much higher lithiation conversions. Given the success of the TMT strategy with other systems, we sought to determine if a similar strategy could enable metallation of the challenging scandium sandwich compound **1**. Thereby, reaction of LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ (1.2 equiv.) with **1** (1 equiv.) yielded monometallated $[\text{THF}\cdot\text{Li}(\mu\text{-TMP})\{\mu\text{-}\{\eta^5\text{-C}_5\text{H}_5\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)\}\text{Al}(i\text{Bu})_2\}]$ **3** in near quantitative *in situ* yield in refluxing *n*-hexane for 12 hours (Scheme 2).



Scheme 2. Metallation of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$ **1** with LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ (1.2 equiv) to give **3**. ^a Isolated yield, full conversion by NMR.

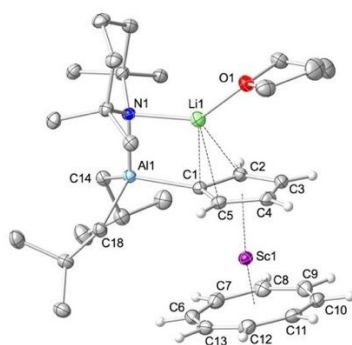
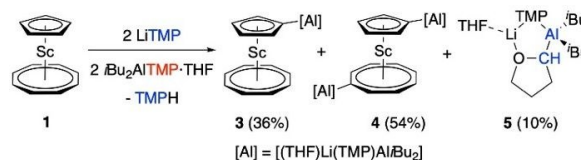


Figure 1. Molecular structure of $[\text{THF}\cdot\text{Li}(\mu\text{-TMP})\{\mu\text{-}\{\eta^5\text{-C}_5\text{H}_5\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)\}\text{Al}(i\text{Bu})_2\}]$ (**3**). Displacement ellipsoids are displayed at 35% probability. Hydrogen atoms, except those on the $\{\eta^5\text{-C}_5\text{H}_5\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)$ unit, are omitted for clarity. Dashed lines illustrate Li...C and Sc...centroid interactions.

Complex **3**, isolated as a solid (72%) or as crystals (66%), was characterized in the solid state by X-ray diffraction analysis (Figure 1) and in solution by ^1H , ^{13}C and ^7Li NMR spectroscopy (Figures S2-S8, spectroscopic assignments were performed, in some cases, via $^{13}\text{C}\{^1\text{H}\}$ -DEPT135, $^1\text{H}, ^1\text{H}$ -COSY, $^1\text{H}, ^{13}\text{C}$ -HMQC and $^1\text{H}, ^{13}\text{C}$ -HMBC experiments). Also, the aggregation of **3** in $[\text{D}_8]\text{THF}$ was studied by ^1H DOSY NMR spectroscopy (Figure S22) with the MW_{DOSY} determinations (within experimental error < 10%) suggesting that the solid-state structure of **3** is retained in solution.¹⁸ Satisfactory elemental analyses were also obtained for **3**. Attempts to dimetallate **1** with two equivalents of the TMT system LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ in all cases gave mixtures of the monometallated and dimetallated species **3** and $[\{\text{THF}\cdot\text{Li}(\mu\text{-TMP})\text{Al}(i\text{Bu})_2\}_2\{\mu\text{-}\{\eta^5\text{-C}_5\text{H}_4\}\text{Sc}(\eta^8\text{-C}_8\text{H}_7)\}]$ (**4**), in an approximately 0.4:0.6 molar ratio, as shown by NMR spectroscopy (Figure S17, S18, S20). Both *n*-hexane and methylcyclohexane were the solvents of choice for the studies and the reactions were tested under reflux conditions with varying reaction times. On reaching the 0.4:0.6 molar ratio the reaction did not progress towards **4**, even with longer reaction times in refluxing *n*-hexane (bp 68 °C) or methylcyclohexane (bp 101 °C). A second process occurring in solution was found to consume the base-trap mixture LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ by approximately 20% under these reaction conditions. A more rigorous NMR study of the *in situ* reaction revealed that α -metallation of THF was in competition with metallation of **1** under these reaction conditions.¹⁹ Compound **5**, $[\{\text{THF}\cdot\text{Li}(\mu\text{-TMP})\text{Al}(i\text{Bu})_2\}(\mu\text{-C}_4\text{H}_7\text{O})]$, was detected in approximately 10% with respect to **3** and **4** by NMR spectroscopic investigations (Figure S20).²⁰ To form **5** two THF molecules are required; therefore, a maximum 10% of **5** can be formed. Free LiTMP and $i\text{Bu}_2\text{AlTMP}$ (10% both) balance the equation (Scheme 3).

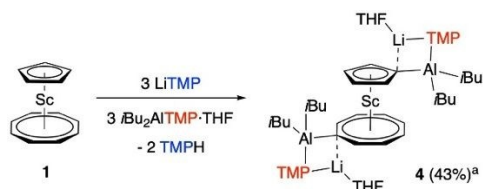


Scheme 3. Metallation of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$ (**1**) with LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ (2 equiv.) to give **3**, **4** and **5**.

Next, three molar equivalents of the TMT system LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ were found to satisfactorily dimetallate **1** in methylcyclohexane under reflux conditions (101 °C) for 3.5 hours. This transformation produced **4** (Scheme 4) in near quantitative yield as evidenced from ^1H and ^{13}C NMR spectra, with total absence of either **1** or **3** in the product mixtures (Figure S17 and S18). As discussed above, approximately 2.2 molar equivalents of “LiTMP/ $i\text{Bu}_2\text{AlTMP}/\text{THF}$ ” would be enough to compensate the loss of the metallating reagent by reaction with THF, but by adding a slight excess of metallating reagent (3 equiv.) full conversion of **1** to **4** was accomplished.

Longer reaction times than 3.5 h under reflux conditions in methylcyclohexane gave complicated NMR spectra, probably due to degradation of **4** at high temperatures, while shorter reaction times gave lower *in situ* conversions for the

transformation of **1** to **4** with varying amounts of **3** seen in the reaction mixtures. When **1** was reacted with "LiTMP/*i*Bu₂AlTMP/THF" in a 1:3 molar ratio in hexane (instead of methylcyclohexane) under reflux conditions (bp 68 °C) the transformation of **1** to **4** was incomplete and **3** is also detected in solution (Figure S19). It seems that **4** is only efficiently obtained at temperatures in excess of that possible with boiling *n*-hexane (68 °C) and short periods of time (3.5 h) are needed to ensure near quantitative conversions.



Scheme 4. Metallation of [(η^5 -C₅H₅)Sc(η^8 -C₈H₈)] (**1**) with conversion by NMR spectroscopy.

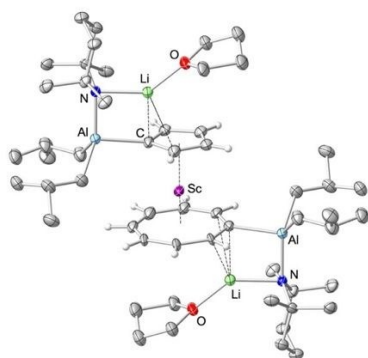


Figure 2. Molecular structure of [(THF·Li(μ -TMP)Al(*i*Bu)₂)₂]₂{ μ -[(η^5 -C₅H₄)Sc(η^8 -C₈H₇)]₂} (**4**) displaying its atom connectivity. Hydrogen atoms, except on the {(C₅H₄)Sc(C₈H₇)} unit, and all disordered components are omitted for clarity. Displacement ellipsoids are displayed at 30% probability. The dashed lines illustrate Li...C and Sc...centroid interactions.

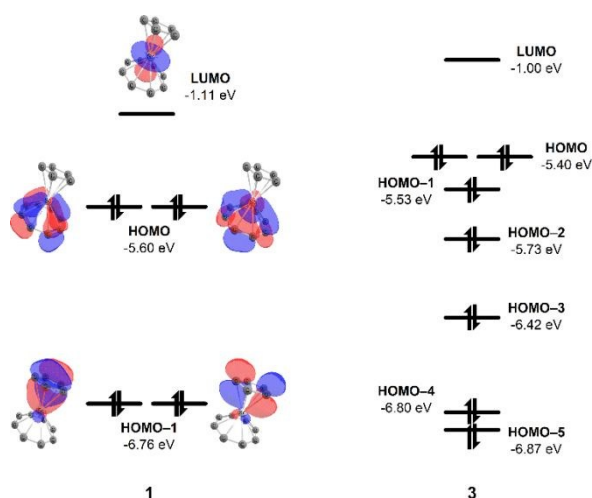


Figure 3. Frontier molecular orbitals of **1** (left) and **3** (right) at the B3LYP/6-311++G** level of theory. Orbital energies are in eV.

Hydrogen atoms are omitted for clarity. Surface isovalue: ± 0.04 [e a₀⁻³]^{1/2}.

The dimetallated sandwich complex **4** was isolated as orange crystals in a modest yield of 43%. Complex **4** exhibited high solubility in hydrocarbons at ambient temperature, which hindered its isolation in high yields. While **4** was crystallographically characterized (Figure 2), heavy disorder of the entire molecular structure prevents a discussion of the metric parameters. In addition, **4** was fully characterized in solution by ¹H, ¹³C and ⁷Li NMR spectroscopy (Figure S9-16, spectroscopic assignments were performed, in some cases, via ¹³C{¹H}-DEPT135, ¹H,¹H-COSY, ¹H,¹³C-HMQC and ¹H,¹³C-HMBC experiments). Furthermore, the aggregation state of **4** in [D₈]THF solution (for comparison with **3**) was studied by ¹H DOSY NMR spectroscopy (Figure S24). Akin to **3** and within an accepted experimental error for MW_{DOSY} determinations (< 10%), the ¹H DOSY NMR spectra were in agreement with the retention of the solid-state structure of **4** in [D₈]THF solution. Satisfactory elemental analyses were also obtained for **4**.

The next challenge was to find a method of cleanly cleaving the carbon-aluminium bonds in the metallated systems. So far, attempts to react **3** and **4** with various stoichiometric quantities of electrophiles such as D₂O, I₂, TMSCl and MeOTf, failed. These quenches generally resulted in intractable reaction mixtures as determined by mass spectrometry and NMR spectroscopy. In case of the silylation, the expected reaction products have been reported elsewhere¹¹ and were thus easily identified using NMR spectroscopy. The reaction of **3** with iodine yielded very small amounts of a compound that sublimates at 130 °C, together with the reprotonated [(η^5 -C₅H₅)Sc(η^8 -C₈H₈)]₂, but shows ¹H NMR signals consistent with a monosubstituted sandwich complex (Figure S21). Additional sequestration of Li⁺, by adding 12-crown-4, TMEDA or PMDTA during the quenching protocols also led to complicated reaction mixtures.

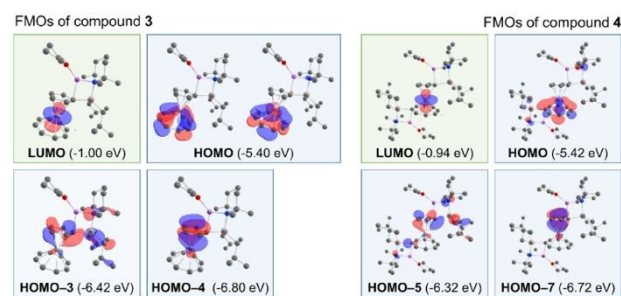


Figure 4. Frontier molecular orbitals of metallated species **3** (left) and **4** (right) at the B3LYP/6-311++G** level of theory. Orbital energies are in eV. Hydrogen atoms are omitted for clarity. Surface isovalue: ± 0.04 [e a₀⁻³]^{1/2}.

In an attempt to provide an explanation for the inconclusive quenching results we performed DFT calculations on the parent sandwich complex **1** (Figure 3, left, Figure S25) and both metallated congeners **3** and **4** (Figure 4, Figure S26). While the LUMO of the sandwich complex **1** comprises the metal-dz² orbital, the HOMO is composed of two degenerate orbitals of

purely Sc-COT π -bonding character. The metalation of **1** with the Li/Al bimetallic system leads to very similar electronic situations in both the mono- and dimetallated species **3** and **4** (Figure 4). The HOMOs experience a destabilisation, with their basic shape remaining unchanged. The lower-lying molecular orbitals show spreading of electron density throughout the Al/Li periphery, with significant electron density on the ring carbon atom present only in the HOMO-4 of compound **3** or the HOMO-7 of compound **4**, respectively. That the ring carbon atom is not present in the high-lying orbitals goes some way towards explaining the poor nucleophilic reactivity of **3** and **4**.

In conclusion, facile selective metallation of the previously obstinate heteroleptic scandium sandwich compound **1** has been realized using a *trans*-metal-trapping approach. Depending on the reaction conditions, monometallation can be achieved selectively at the cyclopentadienide ring ligand, while dimetallation yields a 1,1'-substituted product. Due to the challenges encountered during studies of the reactivity of the metallated complexes, the electronic structure of the parent complex was investigated for the first time, in addition to its metallated derivatives, revealing the non-nucleophilic character of the ring-carbon atom. The success of this TMT method provides hope for further metallation chemistry of *d*- and *f*-block sandwich complexes with inert C-H bonds, which will open up new synthetic possibilities in metallocene chemistry.

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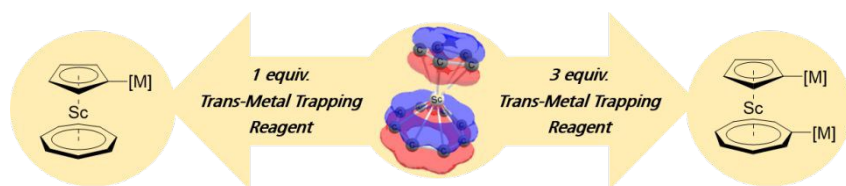
Conflicts of interest

There are no conflicts to declare.

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While lithium alkyls and lithium amides do not metallate the scandium compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Sc}(\eta^8\text{-C}_8\text{H}_8)]$, a synergistic lithium-aluminium base-trap partnership cannot resist taking a bite with one C-H bond selectively cleaved from both Cp and COT rings.