



Lutetium gets a crown: Synthesis, structure and reaction chemistry of the separated ion pair complex, [Li(12-crown-4)₂][(C₅Me₅)₂LuMe₂]

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This article is dedicated to Professor
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ABSTRACT

Reaction of (C₅Me₅)₂Lu(Me)(μ-Me)Li(THF)₃ (**2**) with excess 12-crown-4 affords the new separated ion pair complex, [Li(12-crown-4)₂][(C₅Me₅)₂LuMe₂] (**3**), in excellent yield. This complex reacts with 2,6-diisopropylaniline and phenylacetylene to give the methyl amide complex [Li(12-crown-4)₂][(C₅Me₅)₂Lu(Me)(NH-2,6-ⁱPr₂C₆H₃)] (**4**) and the bis(acetylide) complex [Li(12-crown-4)₂][(C₅Me₅)₂Lu(C≡C-Ph)₂] (**5**), respectively. Attempts to promote methane loss from complexes **3** and **4** to generate a lutetium methylenide or imido complex, respectively, were unsuccessful. The ability of the bis(acetylide) complex **5** to act as a π-tweezer complex was also explored. Reaction between [Li(12-crown-4)₂][(C₅Me₅)₂Lu(C≡C-Ph)₂] (**5**) and CuSPh gave only intractable lutetium products and the copper(I) species [Li(12-crown-4)₂][Cu(C≡C-Ph)₂] (**8**). The new lutetium complexes have been characterized by elemental analysis and NMR spectroscopy. Finally, the X-ray crystal structures of (C₅Me₅)₂Lu(Me)(μ-Me)Li(THF)₃ (**2**), [Li(12-crown-4)₂][(C₅Me₅)₂LuMe₂] (**3**), [Li(12-crown-4)₂][(C₅Me₅)₂Lu(Me)(NH-2,6-ⁱPr₂C₆H₃)] (**4**), [Li(12-crown-4)₂][(C₅Me₅)₂Lu(C≡C-Ph)₂] (**5**), and [Li(12-crown-4)₂][Cu(C≡C-Ph)₂] (**8**) are also reported.

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1. Introduction

Molecules containing multiply bonded functional groups such as alkylidene (=CR₂), imido (=NR), phosphinidene (=PR), and oxo (=O) are known for most of the main-group [1–3], actinide [4–10], and transition metals [11,12], representing a cornerstone of modern coordination and organometallic chemistry. Many of these complexes have been shown to undergo a wide range of reactivity, including ring-opening polymerization, cycloaddition, metathesis and C–H bond activation chemistry [11–15]. Consequently, they have found many useful applications in areas of catalysis and materials.

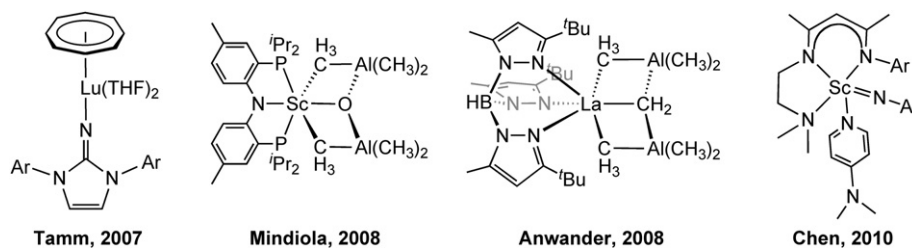
By contrast, this area of chemistry is far less developed for the lanthanide metals [16,17], with capping and bridging imido [18–21], oxo [22], alkylidene [23,24] and phosphinidene [25,26] ligands being more common. It has been suggested that the difficulty in accessing terminal moieties is due to a mismatch in orbital energies between the electropositive lanthanide metal ion and the electro-negative ligand, which frustrates the formation of the metal-ligand

multiple bond [16]. However, recently Tamm and co-workers demonstrated that imidazolin-2-iminato ligands could be used to prepare the first examples of mononuclear lanthanide imido complexes (ImN^{Dipp})MCl₂(THF)₃ and (C₈H₈)M(ImN^{Dipp})(THF)₂ (where M = Gd, Lu; ImN^{Dipp} = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imide) (Scheme 1) [27,28].

Greater progress has been made with related group 3 chemistry [29,30]. The Mindiola group has used Lewis acids to stabilize the scandium methylenide and oxo complexes, (PNP)Sc(μ₃-CH₂)(μ₂-CH₃)₂[Al(CH₃)₂]₂ and (PNP)Sc(μ₃-O)(μ₂-CH₃)₂[Al(CH₃)₂]₂ (where PNP = bis[2-(diisopropylphosphino)-4-methylphenyl]amido) (Scheme 1) [17,31]. In a contemporary report, Andwander and co-workers reported a similar Lewis acid stabilized methylenide complex of lanthanum, (Tp*)La(μ₃-CH₂)(μ₂-CH₃)₂[Al(CH₃)₂]₂ (where Tp* = 3,5-^tBu,CH₃-(hydrotrispyrazolyl)borate) (Scheme 1) [32]. Recently, Chen and co-workers successfully employed a β-diketiminato-based tridentate ligand to synthesize the first scandium terminal imido complex, (L)Sc(=NAr)(DMAP) (where L = (Ar)NC(Me)CHC(Me)N(CH₂CH₂NMe₂); Ar = 2,6-ⁱPr₂C₆H₃; DMAP = 4-dimethylaminopyridine) (Scheme 1) [33].

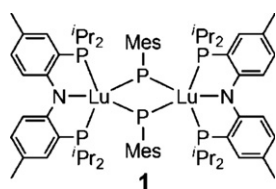
We have been interested in the synthesis and chemistry of lanthanide complexes containing multiply bonded functional groups. Toward this goal, we reported the preparation of a variety of

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Scheme 1. Selected examples of lanthanide and group 3 complexes featuring terminal and Lewis acid stabilized imido, oxo and methylene functional groups.

alkyl, amide and mixed-ligand lutetium complexes supported by non-Cp, multidentate ligand sets such as neutral 4,4'-di-*tert*-butyl-2,2'-bipyridine (^tBu₂bpy) [34] and 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine (^tBu₃tpy) [35], monoanionic bis[2-(diisopropylphosphino)-4-methylphenyl]amido (PNP) [25], and the modified terpyridine 4,4',4''-tri-*tert*-butyl-2'-trimethylsilylmethyl-2,2':6',2''-terpyridyl [^tBu₃(2'-Me₃SiCH₂)tpy] [36]. From these studies, we showed that the lutetium μ₂-phosphinidene complex **1** could be supported with a PNP framework [25].



As an extension of our ongoing studies, we examined the chemistry of the [(C₅Me₅)₂LuMe₂]⁻ fragment and its ability to support multiply bonded functional groups. Although this classic lanthanide system exists as the “ate” complexes (C₅Me₅)₂Lu(μ-Me)₂Li(THF)₂ and (C₅Me₅)₂Lu(μ-Me)₂Li(tmeda) with bridging metal groups, it shares structural and chemical similarities with known bis(cyclopentadienyl) transition-metal bis(alkyl) complexes [37]. For example, (C₅Me₅)₂Lu(μ-Me)₂Li(THF)₂ features a tetrahedral bent-metallocene geometry around the lutetium metal center and participates in protonolysis chemistry with alcohols and thiols to yield alkoxide and thiolate complexes [38,39]. The bent-metallocene platform is known to support numerous actinide and transition metal multiple bonds; however, (C₅Me₅)₂Lu(μ-Me)₂Li(THF)₂ exists as a contact-ion pair complex with bridging methyl groups. To enhance the reactivity of the lutetium methyl groups we prepared the solvent separated ion-pair complex, [Li(12-crown-4)₂][(C₅Me₅)₂LuMe₂]. Herein, we describe the preparation, characterization, and chemistry of this new lutetium system and our attempts to use this system for the stabilization of multiply bonded functional groups.

2. Experimental

2.1. General synthetic procedures

Reactions and manipulations were performed at ambient temperatures in a Vacuum Atmospheres (MO 40-2 Dri-train) recirculating nitrogen atmosphere drybox or using standard Schlenk techniques. Glassware was dried overnight at 150 °C before use. NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer at ambient temperature. Chemical shifts for ¹H NMR spectra were referenced to solvent impurities calibrated against external SiMe₄. Mass spectrometric (MS) analyses were performed at the University of California, Berkeley Mass Spectrometry Facility,

using a VG Prospec (EI) mass spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility.

2.2. Materials

Except where otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), alumina (Aldrich, Brockman I), and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous and dried over KH for 24 h, passed through a column of activated alumina, and stored over activated 4 Å molecular sieves under N₂ prior to use. Benzene-*d*₆ (Aldrich) was purified by storage over activated 4 Å molecular sieves under N₂ prior to use. THF-*d*₈ (CIL) was dried over a Na mirror under N₂ prior to use.

2.3. Synthesis of Na(C₅Me₅)

This is a similar procedure to that reported for K(C₅Me₄Et) [40] and K(C₅Me₅) [41]: A 125-mL side-arm flask equipped with a magnetic stir bar was charged with Na[N(SiMe₃)₂] (12.7 g, 69.3 mmol) and Et₂O (60 mL). The resulting slurry was stirred at room temperature. To this stirring suspension was added C₅Me₅H (10.3 g, 75.6 mmol) dropwise by pipette over 10 min. The solution became increasingly cloudy, and the white suspension was stirred for 15 h at room temperature. The reaction mixture was filtered through a medium-porosity fritted filter to collect an off-white powder, which was washed with Et₂O (2 x 5 mL), pentane (2 x 10 mL), and dried under reduced pressure to give Na(C₅Me₅) as an off-white powder (9.52 g, 60.2 mmol, 87%). ¹H NMR (THF-*d*₈, 298 K): δ 1.97 (s, 15H, C₅Me₅).

2.4. Synthesis of (C₅Me₅)₂Lu(Me)(μ-Me)Li(THF)₃ (**2**)

This is a slight modification to a literature procedure [38]. A 125-mL side-arm flask was charged with a stir bar, Na(C₅Me₅) (2.50 g, 15.8 mmol) and THF (25 mL). To this colorless solution was added portionwise LuCl₃ (2.22 g, 7.89 mmol). THF (25 mL) was added and the cloudy reaction mixture was stirred for two days at room temperature. Next, methyl lithium was added using a syringe (12.5 mL, 1.6M/Et₂O, 20.0 mmol), and the reaction mixture was allowed to stir for 15 h at room temperature. The volatiles were then removed under reduced pressure. The residue was dissolved in Et₂O (300 mL) and filtered through a Celite-padded coarse porosity fritted filter. The filtrate was collected and the volume was reduced to 40 mL, and placed in a -35 °C freezer to afford **2** as a colorless crystalline solid. The Et₂O was decanted from the crystalline solid, the solid was washed with Et₂O, and dried under reduced pressure (3.18 g, 4.55 mmol, 58%). ¹H NMR (THF-*d*₈, 298 K): δ 3.62 (s, 12H, THF-CH₂), 1.83 (s, 12H, THF-CH₂), 1.80 (s, 30H, C₅Me₅), -1.88 (s, 6H, CH₃).

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