New Syntheses of $Cp^*_2Th(Ph)_2$ and $Cp^*_2Th(Me)(aryl)$ Derivatives

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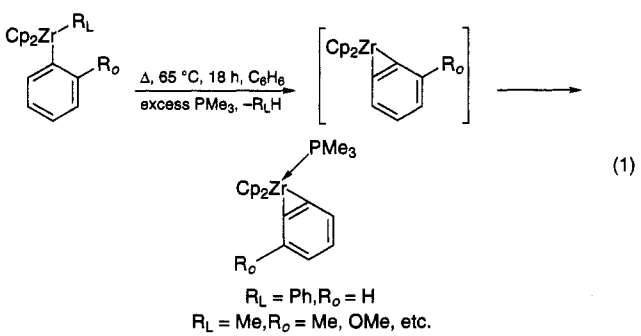
The complex $Cp^*_2ThPh_2$ (**1**) is known to be a useful precursor in elimination reactions to yield transient benzyne adduct. This complex may be prepared in improved yield from the reaction of PhMgBr with $Cp^*_2ThCl_2$ in the presence of *p*-dioxane. Ortho-substituted precursors $Cp^*_2Th(Me)(o\text{-}MeOC_6H_4)$ (**2**), $Cp^*_2Th(Me)(o\text{-}MeC_6H_4)$ (**3**), and $Cp^*_2Th(Me)(2,5\text{-}Me_2C_6H_3)$ (**4**) are reported for the first time, having been prepared in one-pot procedures using a similar method. The respective intermediate monohalide complexes have also been prepared at room temperature. The tolyl and xylyl derivatives exist as pairs of rotamers in solution, demonstrating the significant steric constraints imposed on this type of complex by ortho substituents. Halide exchange is observed in the preparation of the aryl–halide complexes when arylmagnesium bromides are employed. The extent of this exchange is influenced by the addition of *p*-dioxane to reaction mixtures.

Introduction

Organometallic complexes of the group 4 metals exhibit considerable utility in organic synthesis and are important reagents in such varied reactions as the hydrometalation,[1] olefin polymerization,[2] and reductive coupling[3] of unsaturated substrates. The bis(cyclopentadienyl)zirconium systems $Cp_2Zr(C_6H_5)_2$ and $Cp_2Zr(CH_3)(Ar)$ (Cp = η^5-cyclopentadienyl; Ar = *o*-tolyl, *o*-anisyl, 2-naphthyl (for example)) have been employed as general precursors to zirconocene aryne complexes by means of thermally induced intramolecular C–H activation reactions.[4,5] Thermally stable adducts of the benzyne complexes may be obtained by conducting these eliminations in the presence of a stabilizing Lewis base such as trimethylphosphine (eq 1). The resultant adducts are isolable and are useful as reagents for subsequent organic transformations.[6]



(1)

Tetravalent early actinide (i.e. Th and U) complexes often display chemistry similar to that of the Group 4 metals.[7] The large ionic radius and electropositive nature of the heavy elements, however, enable elimination reactions, proceeding by way of intramolecular C–H or N–H activation, to occur more readily than analogous reactions in the d transition series.[8–10] It has previously been reported that solutions of the complexes $Cp^*_2An(C_6H_5)_2$ (Cp^* = η^5-pentamethylcyclopentadienyl; An = Th, U) eliminate benzene at or above room temperature. The formation of benzyne intermediates in this system has been postulated from deuterium labeling experiments, and in the case of uranium, a uranaindene complex was prepared from the insertion of diphenylacetylene into one of the two U–C bonds of the transient Cp^*_2U(benzyne) species (Scheme 1).[8b]

As part of a study of the generation and reactivity of actinide benzyne complexes,[11] we have developed a

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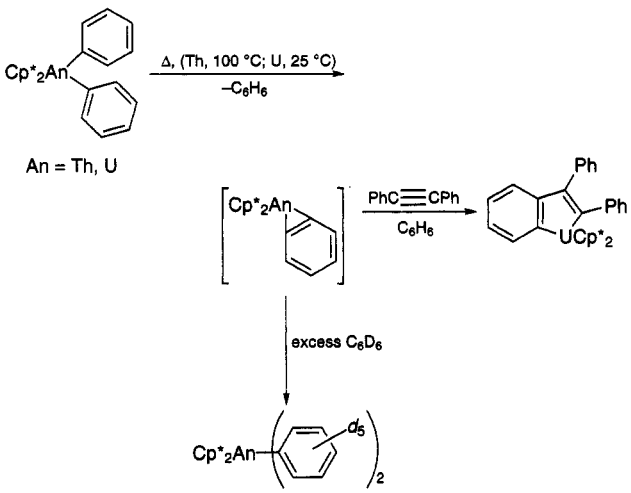
Scheme 1



general synthetic route to a series of alkyl–aryl complexes of thorium. To the best of our knowledge, there are no previous reports of mixed alkyl–aryl complexes. Such complexes could prove to be suitable precursors to benzyne species, in analogy with group 4 chemistry. A modified procedure provides a simple, high-yield route to the diphenyl complex $Cp^*_2ThPh_2$ (**1**).

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of helium in a Vacuum Atmospheres Co. drybox. Nuclear magnetic resonance (NMR) spectra were recorded on an IBM (Bruker) AF 250-MHz spectrometer. NMR chemical shifts were determined in benzene-d_6 and are internally referenced to the solvent (^1H, δ 7.15; ^{13}C, δ 128.0). Elemental analyses were performed in our laboratory using a Perkin-Elmer 2400 CHN analyzer.[12] Solvents were distilled from sodium/benzophenone ketyl (*p*-dioxane, hexane, diethyl ether, and toluene). Benzene-d_6 was vacuum-transferred, after drying over calcium hydride. $Cp^*_2ThCl_2$ was prepared according to the published procedure.[8b] Stock solutions of *o*-anisylmagnesium bromide and (2-(*p*-xylyl))magnesium bromide were prepared, using standard Schlenk techniques, from the respective aryl bromides and magnesium in THF. The concentrations of prepared Grignard reagents were determined after titration with *sec*-butyl alcohol, in toluene, using 1,10-phenanthroline as the indicator.[13] Methylmagnesium chloride (3.0 M in THF, d = 1.013 g/mL), phenylmagnesium bromide (3.1 M in Et_2O, d = 0.939 g/mL), and *o*-tolylmagnesium chloride (1.0 M in THF, d = 0.956 g/mL) solutions, 2-bromoanisole, and 2-bromo-*p*-xylene were purchased from Aldrich and used as received. The purity of isolated powders was determined by integration of methyl resonances in the product ^1H NMR spectrum of a weighed sample against a known quantity of hexamethylbenzene internal standard.

$Cp^*_2Th(C_6H_5)_2$ (1). Phenylmagnesium bromide (1.48 g, 4.89 mmol) was added to a stirred solution of $Cp^*_2ThCl_2$ (1.03 g, 1.80 mmol) in toluene (20 mL) at room temperature, resulting in the formation of a yellow suspension. After 40 min of stirring, *p*-dioxane (0.435 g, 4.94 mmol) was added to the reaction mixture, giving rise to an immediate precipitation of solids and the formation of a thick cream-colored suspension. Stirring was continued for 2 h, during which time the suspension turned yellow. The volatiles were removed under reduced pressure to yield a cream-colored product powder. The solid was extracted with toluene (4 × 15 mL) and filtered through Celite to remove insoluble salts. Toluene was removed under reduced pressure to yield **1** as an off-white powder. Isolated solid: 970 mg (82%; estimated purity 97% **1**; yield of **1** 80%). The identity of the product was confirmed by comparison of the ^1H NMR spectrum with that in the literature.[8b] Recrystallization of the product from toluene or hexane affords **1** as colorless crystals. Alternate reactions were carried out using diphenylmagnesium (generated *in situ* by the addition of *p*-dioxane to phenylmagnesium bromide) as the alkylating agent. These did not yield significantly different results.

Representative Procedure for the Preparation of Aryl–Halide Complexes $Cp^*_2Th(o\text{-}Ar)X$ (X = Br and/or Cl): $Cp^*_2Th(o\text{-}MeOC_6H_4)X$ (5; X = Br, Cl). The solvent was removed from a solution of *o*-anisylmagnesium bromide (0.5 mL, 0.96 M in THF, 0.48 mmol) under reduced pressure. The resultant oily residue was dissolved in toluene (10 mL) at room temperature. Solid $Cp^*_2ThCl_2$ (222 mg, 0.39 mmol) was then added to the stirred solution. Shortly after addition, a white precipitate formed. The reaction mixture was stirred for 75 min before being taken to dryness *in vacuo*. The residue was extracted with toluene (15 mL) and the solution filtered to remove magnesium salts. Compound **5** was isolated as a white powder after removal of the solvent. Isolated solid: 280 mg (107%; purity 81% **5**; yield of **5** 228 mg (87%); Br:Cl ratio 2.62:1). The mixture of halides may be recrystallized from ether. ^1H NMR (250 MHz, C_6D_6): $Cp^*_2Th(o\text{-}MeOC_6H_4)Cl$, δ 1.95 (s, 30H), 3.64 (s, 3H); $Cp^*_2Th(o\text{-}MeOC_6H_4)Br$, δ 1.97 (s, 30H), 3.70 (s, 3H); unassigned aromatic protons, δ 6.38 (m, 2 × 1H), 7.03 (m, 2 × 1H), 7.17 (m, 2 × 1H), 7.78 (m, 2 × 1H). ^{13}C NMR (62.9 MHz, C_6D_6): $Cp^*_2Th(o\text{-}MeOC_6H_4)Cl$, δ 11.6, 53.9, 107.1, 123.5, 125.0, 127.1, 138.2, 166.3, 196.6; $Cp^*_2Th(o\text{-}MeOC_6H_4)Br$, δ 12.0, 55.0, 107.5, 123.4, 125.4, 127.2, 138.1, 166.6, 195.8.

$Cp^*_2Th(2,5\text{-}Me_2C_6H_3)X$ (7; X = Br, Cl). Reagents: (2-(*p*-xylyl))magnesium bromide solution (0.50 mL, 1.16 M in THF, 0.58 mmol), toluene solvent (10 mL), $Cp^*_2ThCl_2$ (332 mg, 0.58 mmol), toluene extractant (15 mL). Isolated solid: 340 mg (88%; purity 84% **7**; yield of **7** 285 mg (74%); Br:Cl ratio 1.44:1). The product may be recrystallized as a mixture, from ether or hexane. ^1H NMR (250 MHz, C_6D_6): $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)Cl$ major rotamer, δ 1.95 (s, 30H), 2.29 (s, 3H), 2.53 (s, 3H); $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)Cl$ minor rotamer, δ 1.92 (s, 30H), 2.31 (s, 3H), 2.62 (s, 3H); $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)Br$ major rotamer, δ 1.96 (s, 30H), 2.32 (s, 3H), 2.54 (s, 3H); $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)Br$ minor rotamer, δ 1.94 (s, 30H), 2.30 (s, 3H), 2.65 (s, 3H); unassigned aromatic protons, δ 6.09 (s), 6.19 (s), 6.83 (m), 7.18 (m), 7.59 (s), 7.69 (s). ^{13}C NMR (62.9 MHz, C_6D_6): $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)Cl$ major rotamer, δ 11.6, 21.8, 26.2, 126.2, 224.5; $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)Cl$ minor rotamer, δ 11.7, 21.4, 25.6, 126.6, 214.8; unassigned aromatic carbons of both chloride rotamers, δ 123.8, 128.3, 129.2, 130.1, 130.3, 131.2, 132.1, 132.5, 133.4, 141.7, 142.8.

$Cp^*_2Th(o\text{-}MeC_6H_4)Cl$ (6). Reagents: *o*-tolylmagnesium chloride (411 mg, 0.39 mmol), toluene solvent (10 mL), $Cp^*_2Cl_2$ (250 mg, 0.44 mmol), toluene extractant (15 mL). Isolated solid: 270 mg (98%; estimated purity 76% **6**; yield of **6** 205 mg (75%)). Analytically pure **6** was obtained with recrystallization from toluene/hexane (~1:1). ^1H NMR (250 MHz, C_6D_6): major rotamer, δ 1.93 (s, 30H), 2.52 (s, 3H); minor rotamer, δ 1.92 (s, 30H), 2.62 (s, 3H); unassigned aromatic protons, δ 6.58 (d, J = 6.6 Hz, 1H (minor rotamer)), 6.99–7.08 (m, 2 × 1H), 7.21–7.31 (m, 2 × 1H), 7.73 (d, J = 6.7 Hz, 1H (major)). ^{13}C NMR (62.9 MHz, C_6D_6): major rotamer, δ 11.6, 26.7, 126.3, 224.8; minor rotamer, δ 11.7, 26.0, 126.7, 216.1; unassigned aromatic carbons of both rotamers, δ 122.4, 123.3, 123.8, 128.2, 129.3, 131.1, 131.5, 132.2, 144.9, 145.5. Anal. Calcd for $C_{27}H_{37}ClTh$: C, 51.55; H, 5.93. Found: C, 51.41; H, 5.76.

Representative Procedure for One-Pot Preparation of the Methyl–Aryl Complexes $Cp^*_2Th(Me)(o\text{-}Ar)$: Cp^*_2-

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(12) Satisfactory elemental analyses were obtained for compounds **2**–**5**; however, consistent analyses could not be obtained for halide mixtures **6** and **7**.

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Th(Me)(*o*-MeOC$_6$H$_4$) (2). *o*-Anisylmagnesium bromide (0.5 mL, 0.96 M in THF, 0.48 mmol) and $Cp^*_2ThCl_2$ (225 mg, 0.39 mmol) were reacted together, in toluene (10 mL), exactly as in the preparation of **5**. The reaction mixture was stirred for 75 min before being taken to dryness *in vacuo*. The residue was extracted with toluene (15 mL) and the solution filtered to remove magnesium salts.

Methylmagnesium chloride solution (126 mg, 0.37 mmol) was then added to the stirred solution of $Cp^*_2Th(o\text{-}MeOC_6H_4)X$ (**5**; X = Br, Cl). *p*-Dioxane (90 mg, 1.02 mmol) was added to the clear reaction solution, initiating the precipitation of a white solid. The resulting suspension was stirred for a further 45 min, and the solvents were removed *in vacuo*. The solid was extracted with toluene (15 mL) and the solution filtered. Toluene was then removed under reduced pressure, to yield the crude product as a white powder. Isolated solid: 240 mg (98%; purity 87% **2**; yield of **2** 210 mg (86%)). Analytically pure **2** may be obtained with recrystallization from ether or toluene. ^{1}H NMR (250 MHz, C_6D_6): δ −0.10 (s, 3H), 1.91 (s, 30H), 3.30 (s, 3H), 6.35 (d, J = 8.0 Hz, 1H), 7.05 (dt, J^1 = 1.7 Hz, J^2 = 7.7 Hz, 1H), 7.20 (t, J = 6.9 Hz, 1H), 7.75 (dd, J^1 = 1.6 Hz, J^2 = 6.6 Hz, 1H). ^{13}C NMR (62.9 MHz, C_6D_6): δ 11.4, 52.0, 68.4, 106.9, 122.2, 123.3, 126.8, 138.4, 170.0, 198.4. Anal. Calcd for $C_{28}H_{40}OTh$: C, 53.84; H, 6.45. Found: C, 54.23; H, 5.77.

$Cp^*_2Th(Me)(o\text{-}MeC_6H_4)$ (3). Reagents: *o*-tolylmagnesium chloride (1000 mg, 0.96 mmol), toluene solvent (20 mL), $Cp^*_2ThCl_2$ (606 mg, 1.06 mmol), toluene extractant/solvent (25 mL), MeMgCl solution (337 mg, 1.00 mmol), *p*-dioxane (238 mg, 2.70 mmol), toluene extractant (25 mL). Isolated solid: 586 mg (91%; purity 73% **3**; yield of **3** 427 mg (66%)). Recrystallization of **3** was achieved from hexane, at −40 °C. ^{1}H NMR (250 MHz, C_6D_6): δ 0.51 (s, 3H), 1.87 (s, 30H), 2.56 (s, 3H), 7.05 (m, 2H), 7.24 (d, J = 7.4 Hz, 1H), 7.38 (t, J = 6.9 Hz, 1H). ^{13}C NMR (62.9 MHz, C_6D_6): δ 11.4, 52.0, 68.4, 106.9, 122.2, 123.2, 126.8, 138.4, 170.0, 198.4. Anal. Calcd for $C_{28}H_{40}Th$: C, 55.25; H, 6.62. Found: C, 54.32; H, 6.39.

$Cp^*_2Th(Me)(2,5\text{-}Me_2C_6H_3)$ (4). Reagents: 2-(*p*-xylyl)magnesium bromide solution (1.6 mL, 0.36 M in THF, 0.58 mmol), toluene solvent (10 mL), $Cp^*_2ThCl_2$ (336 mg, 0.59 mmol), toluene extractant/solvent (15 mL), MeMgCl solution (176 mg, 0.52 mmol), *p*-dioxane (125 mg, 1.42 mmol), toluene extractant (15 mL). Isolated yield: 381 mg (104%; purity 77% **4**; overall yield of **4** 292 mg (80%)). Analytically pure **4** was obtained with recrystallization from hexane, at −40 °C. ^{1}H NMR (250 MHz, C_6D_6): δ 0.55 (s, 3H), 1.88 (s, 30H), 2.30 (s, 3H), 2.56 (s, 3H), 6.87 (m, 2H), 7.21 (d, J = 7.3 Hz, 1H). ^{13}C NMR (62.9 MHz, C_6D_6): δ 11.3, 22.1, 25.9, 56.5, 118.8, 123.2, 129.7, 131.7, 141.6, 221.5. Anal. Calcd for $C_{29}H_{42}Th$: C, 55.94; H, 6.80. Found: C, 55.31; H, 6.51.

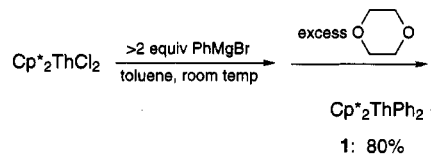
Results and Discussion

Extensive studies of the ligand metathesis chemistry of $Cp^*_2ThCl_2$ have been conducted by Marks and coworkers.[8a,b] These investigations have demonstrated the utility of alkyllithium reagents in the preparation of the dialkyl derivatives $Cp^*_2ThR_2$ (e.g. R = Me, CH_2CMe_3, CH_2SiMe_3, CH_2Ph, Ph). Yields realized using this synthetic route are, however, only moderate. For example, the reaction of $Cp^*_2ThCl_2$ with phenyllithium (Et_2O, −78 °C, 5 h) is reported to produce the diphenyl complex $Cp^*_2Th(C_6H_5)_2$ (**1**) in 32−40% yield.[8b]

In order to prepare sufficient quantities of this and related complexes needed for our investigation of actinide benzyne complexes, we sought to improve upon this method by developing a high-yield route to both the diphenyl complex and its monoalkyl−monoaryl analogues **2**−**4**. We have found that the use of Grignard reagents as the alkylating agents provides a convenient and reliable means for the preparation of **1**. Grignard reagents have frequently been used in the preparation of group 4 metallocene alkyl−halide and some homoleptic dialkyl complexes, although reported preparations of mixed dialkyl derivatives most commonly employ organolithium reagents in the second step.[14] Magnesium reagents have similarly been employed in organoactinide chemistry, both in the preparation of $Cp^*_2AnCl_2$ (An = Th, U) from the tetrachlorides $AnCl_4$[8b] and in the further alkylation of $Cp^*_2AnCl_2$ to generate the dialkyls $Cp^*_2An(\eta^4\text{-}C_4H_6)$[15] and $Cp^*_2Th(CH_2CH_2CH_3)_2$.[8b]

A rapid reaction takes place upon addition of phenylmagnesium bromide solution to a toluene solution of $Cp^*_2ThCl_2$ at room temperature. Within minutes after the Grignard addition, the starting dichloride is no longer detectable in the ^{1}H NMR spectrum of the reaction mixture. The reaction product is not solely the diphenyl complex, however, but rather a mixture of **1** and the intermediate phenyl−halide complex.[8b] Complete conversion to form the diphenyl complex does not occur when extended reaction times, elevated reaction temperatures, or an excess of Grignard reagent is used.

The addition of *p*-dioxane to the reaction mixture is key in the preparation of pure **1**. The room temperature reaction between $Cp^*_2ThCl_2$ (1 equiv), PhMgBr (≥2 equiv), and *p*-dioxane (≥2 equiv) provides a convenient preparation of $Cp^*_2ThPh_2$ in greater than 80% isolated yield (eq 2). A comparison of the ^{1}H NMR spectrum of



$Cp^*_2ThPh_2$ + $MgXY(C_4H_8O_2)_{1,2}$ (2)

1: 80% X,Y = Br, Cl

the product with that described in the literature illustrates the high degree of conversion achieved, even after only a short reaction time. Side products comprise only a small fraction of the reaction product (≤5%).

In the absence of dioxane, incomplete alkylation is likely due to back reaction between the product diphenyl thorium complex and solubilized magnesium salts. Electropositive metal complexes are known to participate in Schlenk-type equilibria with magnesium halides; halide exchange and the formation of complex mixed-metal halide complexes is well documented.[16] Halogen exchange reactions mediated by Grignard reagents have also been observed in group 4 chemistry.[17]

Addition of *p*-dioxane permits removal of precipitated $MgX_2(dioxane)_x$ adducts from solution[18] and eliminates

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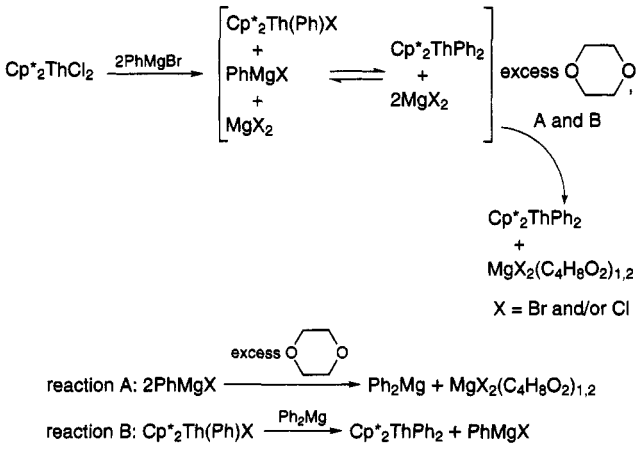
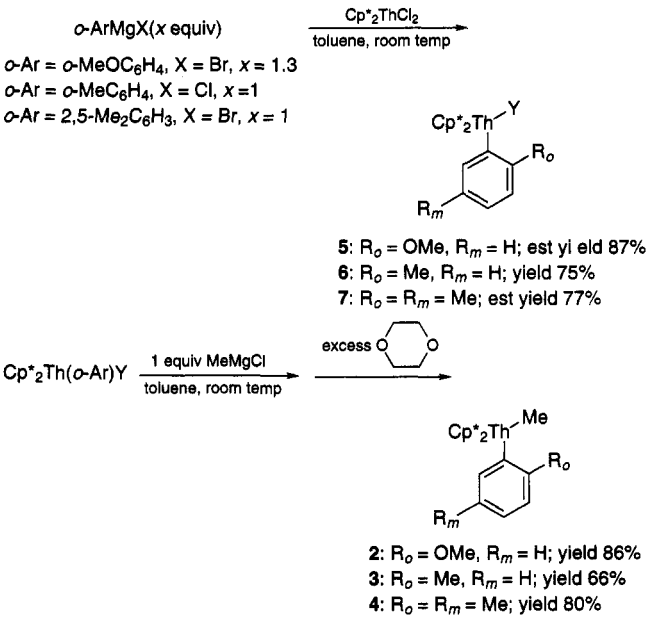
Scheme 2



Scheme 3



the possibility of back-reaction, driving the equilibrium toward the formation of **1** (Scheme 2).

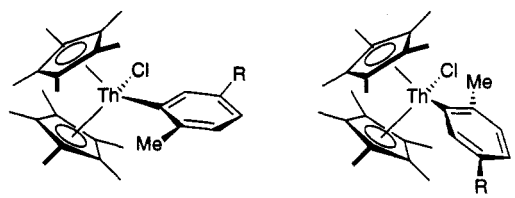
This simple methodology has been extended to the stepwise double alkylation of $Cp^*_2ThCl_2$, providing a direct route to the methyl-aryl complexes $Cp^*_2Th(Me)(o\text{-}Ar)$ (o-Ar = o-$MeOC_6H_4$ (**2**), o-MeC_6H_4 (**3**), 2, 5-$Me_2C_6H_3$ (**4**)). The preparation of **2**–**4** has been successful both with and without isolation of the respective aryl-halide intermediates, **5**-**7**.

Unlike the preparation of **1**, the syntheses of the methyl-substituted aryl complexes **3** and **4** are adversely affected by the use of an excess of Grignard reagent, resulting in reduced product purity. However, a similar effect is not observed in the preparation of the o-anisyl derivative **2**, and an excess of Grignard reagent is generally employed to achieve the best possible conversion.

In the procedures to prepare **2**–**4** from the respective aryl halides, p-dioxane is again added to the reaction mixtures. Experiments with the o-anisyl halide system have indicated that, in the absence of the complexing agent, conversion to the methyl–aryl species is limited; significant quantities of unreacted **5** are observed in the ^1H NMR spectrum of the reaction mixture.

The presence of THF (THF = tetrahydrofuran) in the preparations of **6** and **7** also results in the formation of significantly less pure products (the preparation of the o-anisyl derivative **5** is again less sensitive to variations in reaction conditions). The cleanest products are generally obtained upon removal of the THF solvent from the Grignard reagent prior to reaction with $Cp^*_2ThCl_2$. When the reaction is carried out in the presence of THF, ^1H NMR spectra of the crude reaction mixtures of **3** and **4** clearly indicate the presence of significant quantities of coordinated THF. The introduction of impurities in both cases is likely due to the presence of solubilized magnesium species, whether in the free state or in association with the thorium complex. THF adducts of both magnesium halides[19] and bis(alkyl)-magnesium species[20] are known to exist and may be carried through in the isolation of the thorium complexes. The tolerance of the o-anisyl system to variation in stoichiometry may be due to intra- or intermolecular magnesium–oxygen interactions which affect the solubility characteristics of the dialkyl species and/or inhibit THF coordination.[19a]

The complexes **6** and **7** exist as pairs of rotamers (**I** and **II**). The o-methyl substituent of the aryl group in



I **II**

R = H, Me

each is sufficiently bulky to inhibit free rotation about the metal–aryl bond. Variable-temperature ^1H NMR experiments performed on **6** and **7** have verified this phenomenon, since the rotameric pairs are observed to coalesce at elevated temperatures (~85–100 °C). This hindered rotation is not unexpected, judging from reports of similar barriers to rotation for the complexes $Cp^*_2U(C_6H_5)_2$[8b] and related bis(pentamethylcyclopentadienyl)actinide systems.[8b,9,21] Rotamers are not, however, observed for **5**. The possibility of free rotation in the o-anisyl system exists, although it is far more likely that the molecule is observed in one conformation only, due to being constrained by a significant intramolecular thorium–oxygen interaction.[22]

The situation for complex **7** is further complicated in that the alkylation of $Cp^*_2ThCl_2$ by (2-(p-xylyl))magnesium bromide results in the formation of a mixture of two pairs of aryl–halide rotamers, i.e $Cp^*_2Th(2,5\text{-}Me_2C_6H_3)X$ (X = Br, Cl). Mixtures of the chloride and bromide derivatives are generated in alkylations to prepare both **5** and **7** as the result of the halide-exchange equilibrium between the actinide metal center

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and solvated magnesium species. The bromide derivative appears to be favored, with product ratios ranging from near parity to almost 2:1 (Br:Cl), depending on both the aryl substituent and exact reaction stoichiometries. We have been able to successfully distinguish between the two halide derivatives $Cp^*_2Th(o\text{-}Ar)X$ (o-Ar = o-$MeOC_6H_4$, 2,5-$Me_2C_6H_3$; X = Br, Cl) by selectively enhancing the chloride component of the halide mixtures. The room temperature reaction between $Cp^*_2Th(o\text{-}Ar)X$ and an excess of $MgCl_2(THF)_2$[20] in toluene greatly increases the $Cp^*_2Th(o\text{-}Ar)Cl$ fraction. The observed halide ratios in the mixed species **5** and **7** may also be perturbed by the addition of p-dioxane. The presence of a large excess of p-dioxane results in the formation of product mixtures comprised of at least 90% chloride. The use of arylmagnesium chloride reagents in alkylation, as in the preparation of **6**, assures the formation of only one halide product.

Reaction of the aryl–halide complexes with MeMgCl in toluene results in the preparation of the methyl–aryl complexes $Cp^*_2Th(Me)(o\text{-}Ar)$ (o-Ar = o-$MeOC_6H_4$ (**2**), o-MeC_6H_4 (**3**), 2,5-$Me_2C_6H_3$ (**4**)). The dimethyl compound $Cp^*_2ThMe_2$ is a common side product in the methylation of the aryl–halide species and results by way of displacement of the aryl substituent from the starting $Cp^*_2Th(o\text{-}Ar)X$ (X = Br, Cl) and/or product $Cp^*_2Th(Me)(o\text{-}Ar)$. $Cp^*_2ThMeCl$ has also been observed to form.[21] Any further reductions in the purity of the products from the preparation of **2**–**7** are seemingly due to unreacted starting materials and solvated magnesium species.

Steric congestion about the actinide center may be responsible for the failure to observe the ortho-substituted diaryl complexes, even in the presence of excess aryl Grignard. Spectroscopic investigations of $Cp^*_2U(C_6H_5)_2$ suggest that the phenyl rings are required to be juxtaposed in a canted manner.[8b] Ortho-substitution of these aryl ligands would be expected to exacerbate steric constraints within the tight framework. Although the group 4 analog di-o-tolylzirconocene is known to exist transiently, this complex contains a less bulky bis(cyclopentadienyl) (Cp_2) ligand set and decomposes readily, even at low temperatures.[5a]

Conclusions

A simple Grignard alkylation strategy has been employed to prepare the known complex **1** and the previously unreported complexes **2**–**7**. All of the reported alkylation reactions occur readily in noncoordinating solvents at room temperature and provide the desired products in moderate to high yields. Similarly, the alkyl–aryl systems **2**–**4** have been prepared in good yield by a one-pot method from $Cp^*_2ThCl_2$. Methylation of the intermediate aryl–halide complexes **5**–**7** is readily achieved, but attempts to prepare the bis-o-substituted aryl derivatives have proven unsuccessful. Formation of these complexes is doubtless prevented by unfavorable steric interactions.

In the absence of o-substituted diaryl complexes analogous to the diphenyl complex, preliminary studies have demonstrated the utility of complexes **2**–**4** as suitable alternate precursors in the preparation of substituted benzyne complexes. Studies of the thermolysis of these species have provided insight into the mechanism of formation and reactivity of the thorium benzyne species.[22] Further, the unsubstituted diphenyl complex **1**, a known benzyne precursor, has been the subject of a comparison study of actinide and group 4 benzyne reactivity.[11] In all cases, it has proven unnecessary to further purify these materials to ensure successful reactivity.

These procedures for the preparation of **1**–**7** demonstrate the facile nature of metathesis reactions between actinide halides and Grignard reagents. Using this methodology, second alkylations of the metal center proceed readily. Magnesium-mediated alkyl and halide redistribution equilibria have been observed; these can result in "over-methylation" to yield $Cp^*_2ThMe_2$ in the preparation of **2**–**4** or in halide exchange equilibria in the preparation of the aryl halide precursors **5** and **7**.

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