

# Cationic Aryl Complexes of the Rare-Earth Metals

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Neutral rare-earth metal tri(aryl) complexes  $[\text{Ln}(\text{C}_6\text{H}_4\text{-}p\text{-R})_3(\text{THF})_2]$  ( $\text{Ln} = \text{Lu}, \text{Sc}; \text{R} = \text{H}, \text{Me}, \text{Et}$ ), synthesized by reacting anhydrous metal trichloride with 3 equiv of the corresponding aryllithium, react with 1 or 2 equiv of  $[\text{NR}'_3\text{H}][\text{BPh}_4]$  ( $\text{R}' = \text{Et}; \text{R}'_3 = \text{PhMe}_2$ ) to yield monocationic di(aryl) complexes  $[\text{Ln}(\text{C}_6\text{H}_4\text{-}p\text{-R})_2(\text{THF})_4]^+[\text{BPh}_4]^-$  and dicationic mono(aryl) complexes  $[\text{Ln}(\text{C}_6\text{H}_4\text{-}p\text{-R})(\text{THF})_5]^{2+}[\text{BPh}_4]^{-2}$ , respectively. Single-crystal X-ray diffraction studies of the mono- and dicationic compounds  $[\text{Sc}(\text{C}_6\text{H}_5)_2(\text{THF})_4]^+[\text{BPh}_4]^-$  and  $[\text{Lu}(\text{C}_6\text{H}_5)(\text{THF})_5]^{2+}[\text{BPh}_4]^{-2}$  show distorted octahedral coordination geometry around the metal center in the cation. Kinetic studies for the reaction of the dicationic complex  $[\text{Lu}(\text{C}_6\text{H}_4\text{-}p\text{-Me})(\text{THF})_5]^{2+}[\text{BPh}_4]^{-2}$  with pyridine suggest competition between C–H bond activation and insertion reactions.

## Introduction

Recent years have seen a steady increase in interest in cationic organometallic complexes of the rare-earth metals.<sup>1,2</sup> This interest has been prompted by the emergence of group 3 metal cations as key intermediates in homogeneous  $\alpha$ -olefin polymerization and other related catalytic reactions, previously described for the group 4 metal systems.<sup>3</sup> Significantly less is known about cationic aryl complexes of the rare-earth metals. A limited number of monocationic examples have been reported so far, all of them containing a perfluorinated aryl group.

Complexes containing divalent europium and ytterbium<sup>4</sup> or trivalent scandium<sup>5</sup> as the metal center were described. Neutral phenyl complexes of the rare-earth metals without ancillary ligands were already published 40 years ago,<sup>6</sup> followed by THF containing phenyl complexes,<sup>7,8</sup> other homoleptic aryl complexes,<sup>9</sup> and mixed aryl halide compounds.<sup>10</sup> A number of THF-containing aryl complexes of divalent rare-earth metals are also known.<sup>11</sup> We report here the first examples for both mono- and dicationic complexes of the trivalent rare-earth metals with non-fluorinated aryl ligands.

## Results and Discussion

**Di(aryl) Monocations.** Previously, neutral triphenyl complexes of the rare-earth metals  $[\text{Ln}(\text{C}_6\text{H}_5)_3(\text{THF})_n]$  ( $\text{Ln} = \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ ) were synthesized from the reaction of the metal with diphenyl mercury or triphenyl bismuth in THF.<sup>7</sup> In our

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(1) For reviews, see: (a) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339. (b) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404. (c) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114. (d) Deacon, G. B.; Evans, D. J.; Forsyth, C. M.; Junk, P. C. *Coord. Chem. Rev.* **2007**, *251*, 1699.

(2) For recent examples, see: (a) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454. (b) Bambirra, S.; Meetsma, A.; Hessen, B.; Bruins, A. P. *Organometallics* **2006**, *25*, 3486. (c) Ge, S.; Bambirra, S.; Meetsma, A.; Hessen, B. *Chem. Commun.* **2006**, 3320. (d) Evans, W.; Davis, B.; Champagne, T.; Ziller, J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 12678. (e) Evans, W. J.; Champagne, T. M.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 16178. (f) Evans, W. J.; Rego, D. B.; Ziller, J. W. *Inorg. Chem.* **2006**, *45*, 10790. (g) Luo, Y.; Hou, Z. *Organometallics* **2006**, *25*, 6162. (h) Kretschmer, W. P.; Meetsma, A.; Hessen, B.; Schmalz, T.; Qayyum, S.; Kempe, R. *Chem.-Eur. J.* **2006**, *12*, 8969. (i) Hitzbleck, J.; Beckerle, K.; Okuda, J.; Halbach, T.; Müllhaupt, R. *Macromol. Symp.* **2006**, *236*, 23. (j) Hitzbleck, J.; Okuda, J. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1947. (k) Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chim. Acta* **2006**, *359*, 4769. (l) Evans, W. J.; Champagne, T. M.; Ziller, J. W. *Organometallics* **2007**, *26*, 1204. (m) Marinescu, S. C.; Agapie, T.; Day, M. W.; Bercaw, J. E. *Organometallics* **2007**, *26*, 1178. (n) Wang, B.; Wang, D.; Cui, D.; Gao, W.; Tang, T.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 3167. (o) Lukešová, L.; Ward, B. D.; Bellemín-Lapponnaz, S.; Wadeplol, H.; Gade, L. H. *Dalton Trans.* **2007**, 920. (p) Bambirra, S.; van Leusen, D.; Tazelaar, C. G. J.; Meetsma, A.; Hessen, B. *Organometallics* **2007**, *26*, 1014. (q) Zhang, L.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. *Angew. Chem.* **2007**, *119*, 1941; *Angew. Chem., Int. Ed.* **2007**, *46*, 1909. (r) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. *J. Organomet. Chem.* **2007**, *692*, 806. (s) Hayes, P. G.; Piers, W. E.; Parvez, M. *Chem.-Eur. J.* **2007**, *13*, 2632. (t) Nakajima, Y.; Okuda, J. *Organometallics* **2007**, *26*, 1270. (u) Paolucci, G.; Zanella, A.; Bortoluzzi, M.; Sostero, S.; Longo, P.; Napoli, M. *J. Mol. Catal. A: Chem.* **2007**, *272*, 258. (v) Kramer, M. U.; Robert, D.; Nakajima, Y.; Englert, U.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2007**, 665. (w) Hitzbleck, J.; Okuda, J. *Organometallics* **2007**, *26*, 3227. (x) Conroy, K. D.; Hayes, P. G.; Piers, W. E.; Parvez, M. *Organometallics* **2007**, *26*, 4464. (y) Li, X.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2007**, 4137.

(3) (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Guram, A. N.; Jordan, R. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon: Oxford, New York, Tokyo, 1995; Vol. 4, p 589. (c) Resconi, L.; Chadwick, J.; Cavallo, L. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Eds.; Elsevier: Oxford, 2007; Vol. 4, p 1005. (4) Deacon, G. B.; Forsyth, C. M. *Chem.-Eur. J.* **2004**, *10*, 1798.

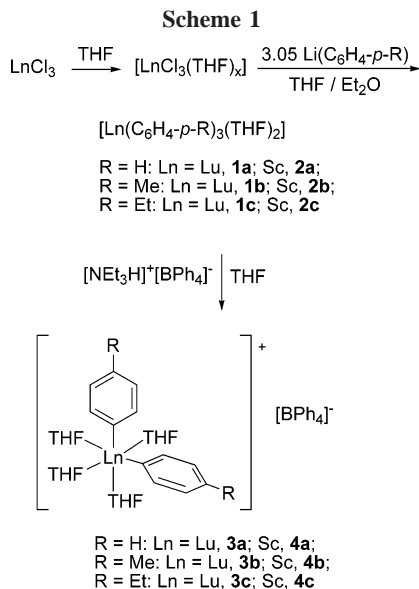
(5) Hayes, P. G.; Piers, W. E.; Parvez, M. *Organometallics* **2005**, *24*, 1173.

(6) (a) Hart, F. A.; Saran, M. S. *Chem. Commun.* **1968**, 1614. (b) Hart, F. A.; Massey, A. G.; Saran, M. S. *J. Organomet. Chem.* **1970**, *21*, 147.

(7) (a) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y. F.; Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1991**, *421*, 29. (b) Bochkarev, L. N.; Stepanitseva, T. A.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y. T. *Organometallics* **1995**, *14*, 2127. (c) Bochkarev, L. N.; Zheleznova, T. A.; Safronova, A. V.; Drozdov, M. S.; Zhil'tsov, S. F.; Zakharov, L. N.; Fukin, G. K.; Khorshev, S. Y. *Russ. Chem. Bull.* **1998**, *47*, 165. (d) Zheleznova, T. A.; Bochkarev, L. N.; Safronova, A. V.; Zhil'tsov, S. F. *Russ. J. Gen. Chem.* **1999**, *69*, 784. (e) Kirillov, E. N.; Fedorova, E. A.; Trifonov, A. A.; Bochkarev, M. N. *Appl. Organomet. Chem.* **2001**, *15*, 151. (f) Deacon, G. B.; Forsyth, C. M. *Organometallics* **2003**, *22*, 1349.

(8) Putzer, M. A.; Bartholomew, G. P. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1777.

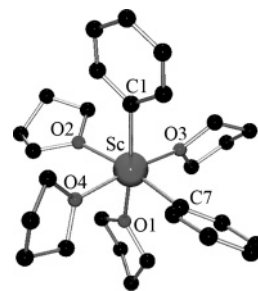
(9) (a) Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1225. (b) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068. (c) Wayda, A. L.; Atwood, J. J.; Hunter, W. E. *Organometallics* **1984**, *3*, 939. (d) Wayda, A. L.; Rogers, R. D. *Organometallics* **1985**, *4*, 1440. (e) Booij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79. (f) Ihara, E.; Adachi, Y.; Yasuda, H.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1998**, *569*, 147.



experience, salt metathesis using aryllithium reagents proved to be more reproducible than this transmetallation reaction. We isolated the neutral tri(aryl) complexes of the trivalent rare-earth elements  $[\text{Ln}(\text{C}_6\text{H}_4\text{-}p\text{-R})_3(\text{THF})_2]$  (Ln = Lu, R = H, **1a**; Me, **1b**; Et, **1c**; Ln = Sc, R = H, **2a**; Me, **2b**; Et, **2c**) in variable yields in a metathesis reaction of the anhydrous lutetium or scandium trichloride with slightly more than 3 equiv of the corresponding aryllithium, following a modification of a procedure previously reported for the synthesis of **2a** (Scheme 1).<sup>8</sup>

When these neutral lutetium complexes **1a–c** or scandium complexes **2a–c** were treated with 1 equiv of the Brønsted acid  $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$  in THF, the monocationic bis(aryl) complexes  $[\text{Ln}(\text{C}_6\text{H}_4\text{-}p\text{-R})_2(\text{THF})_4]^+[\text{BPh}_4]^-$  (Ln = Lu, R = H, **3a**; Me, **3b**; Et, **3c**; Ln = Sc, R = H, **4a**; Me, **4b**; Et, **4c**) were isolated as colorless microcrystals in yields of 50–66% for lutetium and 68–82% for scandium (Scheme 1).

Single crystals of the scandium complex  $[\text{Sc}(\text{C}_6\text{H}_5)_2(\text{THF})_4]^+[\text{BPh}_4]^-$  (**4a**) suitable for X-ray diffraction were obtained from a THF solution by slow evaporation of the solvent at room



**Figure 1.** Molecular structure of the cationic part of **4a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Sc–C1 2.298(2), Sc–C7 2.259(2), Sc–O1 2.2572(16), Sc–O2 2.2554(16), Sc–O3 2.1994(17), Sc–O4 2.1712(16); C1–Sc–O1 169.09(7), C7–Sc–O2 171.66(7), O3–Sc–O4 169.36(6).

temperature. Figure 1 shows the molecular structure of the cationic part of the compound displaying a slightly distorted octahedral coordination geometry with angles of 169.09(7)° (C1–Sc–O1), 171.66(7)° (C7–Sc–O2), and 169.36(6)° (O3–Sc–O4) along the respective axes and the two phenyl groups in a cis arrangement. No cation–anion interactions were observed in the solid state.

The Sc–C(aryl) distances of 2.259(2) and 2.298(2) Å in **4a** are in the range reported for other scandium aryl complexes (2.214(3)–2.266(4) Å),<sup>12</sup> but slightly longer than in the neutral triphenyl complex  $[\text{Sc}(\text{C}_6\text{H}_5)_3(\text{THF})_2]$  (2.240(3), 2.245(4), and 2.266(4) Å).<sup>8</sup> This counter-intuitive finding may be due to the increase of coordination number from five to six upon cationization (overriding the expected bond shortening) and/or due to some Sc–C bond shortening in the ground state of the neutral triphenyl complex. The distances between scandium and the oxygen atoms of the THF ligands range from 2.1712(16) to 2.2572(16) Å, being also comparable to those found in other organometallic scandium complexes with THF ligands.<sup>2w,8,12a,13</sup> Interestingly, the Sc–O separations trans to the phenyl groups are significantly longer than those in cis positions (2.2554(16) and 2.2572(16) versus 2.1712(16) and 2.1994(17) Å). Such a trans influence<sup>14</sup> could also be observed in other lanthanide

(10) (a) Hou, Z.; Mine, N.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1700. (b) Syutkina, O. P.; Rybakova, L. F.; Petrov, E. S.; Beletskaya, I. P. *J. Organomet. Chem.* **1985**, *280*, C67. (c) Lin, G.; Jin, Z.; Zhang, Y.; Chen, W. *J. Organomet. Chem.* **1990**, *396*, 307. (d) Boje, B.; Magull, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 703. (e) Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem.-Eur. J.* **1995**, *1*, 343. (f) Rabe, G. W.; Strissel, C. S.; Liable-Sands, L. M.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 3446. (g) Rabe, G. W.; Berube, C. D.; Yap, G. P. A. *Inorg. Chem.* **2001**, *40*, 2682. (h) Rabe, G. W.; Berube, C. D.; Yap, G. P. A. *Inorg. Chem.* **2001**, *40*, 4780. (i) Rabe, G. W.; Berube, C. D.; Yap, G. P. A.; Lam, K.-C.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1446. (j) Rabe, G. W.; Rhatigan, B.; Golen, J. A.; Rheingold, A. L. *Acta Crystallogr.* **2003**, *E59*, m99. (k) Rabe, G. W.; Zhang-Presse, M.; Riederer, F. A.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 7587. (l) Niemeyer, M. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1413.

(11) (a) Deacon, G. B.; Vince, D. G. *J. Organomet. Chem.* **1976**, *112*, C1. (b) Deacon, G. B.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1977**, *135*, 103. (c) Deacon, G. B.; Koplick, A. J.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1979**, *182*, 121. (d) Deacon, G. B.; Tuong, T. D. *J. Organomet. Chem.* **1981**, *205*, C4. (e) Deacon, G. B.; MacKinnon, P. I. *Tetrahedron Lett.* **1984**, *25*, 783. (f) Deacon, G. B.; Forsyth, C. M.; Newham, R. H. *Polyhedron* **1987**, *6*, 1143. (g) Heckmann, G.; Niemeyer, M. *J. Am. Chem. Soc.* **2000**, *122*, 4227. (h) Forsyth, C. M.; Deacon, G. B. *Organometallics* **2000**, *19*, 1205. (i) Niemeyer, M. *Acta Crystallogr.* **2001**, *E57*, m578. (j) Qi, G.; Nitto, Y.; Saiki, A.; Tomohiro, T.; Nakayama, Y. *Tetrahedron* **2003**, *59*, 10409. (k) Beaini, S.; Deacon, G. B.; Hilder, M.; Junk, P. C.; Turner, D. R. *Eur. J. Inorg. Chem.* **2006**, *17*, 3434.

(12) (a) Putzer, M. A.; Rogers, J. S.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 8112. (b) Fryzuk, M. D.; Giesbrecht, G. R.; Rettig, S. J. *Can. J. Chem.* **2000**, *78*, 1003. (c) Rabe, G. W.; Bérubé, C. D.; Yap, G. P. A.; Lam, K.-C.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1446. (d) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577.

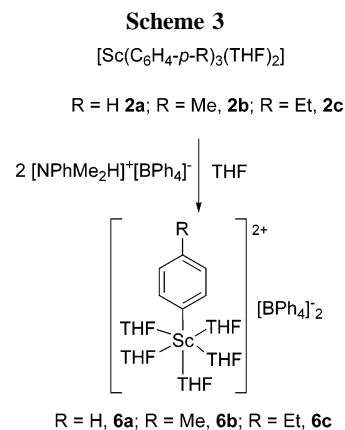
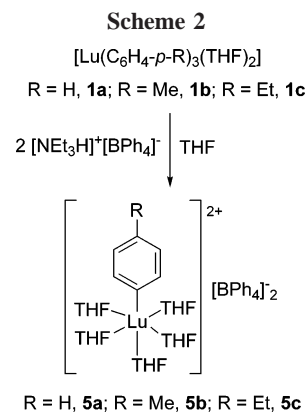
(13) (a) Burton, N. C.; Cloke, F. G. N.; Hitchcock, P. B.; de Lemos, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1462. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1993**, *12*, 2584. (c) Blackwell, J.; Lehr, C.; Sun, Y.; Piers, W. E.; Pearce-Batchilder, S. D.; Zaworotko, M. J.; Young, V. G., Jr. *Can. J. Chem.* **1997**, *75*, 702. (d) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947. (e) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533. (f) Ward, B. D.; Dubberley, S. R.; Maisse-François, A.; Gade, L. H.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4649. (g) Emslie, D. J. H.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 4226. (h) Lara-Sanchez, A.; Rodriguez, A.; Hughes, D. L.; Schormann, M.; Bochmann, M. *J. Organomet. Chem.* **2002**, *663*, 63. (i) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003**, *22*, 1212. (j) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182. (k) Luo, Y. J.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910. (l) Li, X. F.; Baldamus, J.; Hou, Z. *Angew. Chem.* **2005**, *117*, 984; *Angew. Chem., Int. Edit.* **2005**, *44*, 962. (m) Luo, Y.; Nishiura, M.; Hou, Z. *J. Organomet. Chem.* **2007**, *692*, 536.

(14) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707. (c) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5.

complexes,<sup>10f,15</sup> and in the monocationic bis(alkyl) complexes  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_4]^+[\text{Et}(\text{CH}_2\text{SiMe}_3)_4]^-$  (Et = Al,<sup>16</sup> Ga<sup>2v</sup>). In the hepta-coordinate monocationic dimethyl complex  $[\text{YMe}_2(\text{THF})_5]^+[\text{BPh}_4]^-$ , the two methyl groups were found to be trans to each other.<sup>17</sup> For the crystallographically characterized monocationic dibenzyl complex containing THF ligands,  $[\text{La}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{THF})_4]^+[\text{BPh}_4]^-$ , a trans influence could not be observed as this system shows more distortion from the octahedral coordination due to polyhapto bonding of the benzyl groups.<sup>2a</sup> The scandium center in the cation of **4a** is situated 0.1890(3) and 0.2324(4) Å away from the planes defined by the two phenyl groups. Usually the central atoms are located in the planes defined by the phenyl groups,<sup>7b,c,f,8,12b,21</sup> whereas some other crystallographically characterized phenyl complexes of the rare-earth metals show similar distances (0.1384(11) and 0.1475(15) Å for  $[\text{Sc}(\eta^6\text{-C}_5\text{H}_5\text{BPh})\text{Ph}_2(\text{THF})]$ ,<sup>12a</sup> 0.2293(17) and 0.2495(17) Å for two crystallographically independent molecules of  $[\text{Li}(\text{DME})_3]^+[\text{Nd}(\eta^5\text{-C}_5\text{H}_5)_3\text{Ph}]^-$ ,<sup>18</sup> 0.3928(3) Å for  $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ph}(\text{THF})]$ ,<sup>19</sup> and 0.1703(2) Å for  $[\text{Yb}\{\text{PhP}(\text{CH}_2\text{-SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}\}\text{Ph}]$ <sup>20</sup>).

All signals of the monocationic compounds are unambiguously assignable in the <sup>1</sup>H and <sup>13</sup>C NMR spectra with the exception of the ipso carbon atoms of the aryl groups in the scandium complexes, which are not observed due to quadrupolar relaxation ( $I = 7/2$  for <sup>45</sup>Sc). The cation-independent resonance of  $\delta = -6.6$  ppm in the <sup>11</sup>B NMR spectrum is indicative of a non-coordinating anion.

**Aryl Dications.** One of the most remarkable aspects of the organometallic chemistry of the cationic rare-earth metal complexes is the availability of dicationic mono(alkyl) complexes.<sup>1a,b,16</sup> Analogously to the synthesis of dicationic mono(alkyl) complexes,<sup>2a,16,17,22</sup> the isolation of mono(aryl) dication was successfully accomplished by the reaction of the neutral triphenyl complex with 2 equiv of an appropriate Brønsted acid in THF. Thus, the reaction of 2 equiv of the ammonium salt  $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$  with the neutral lutetium complexes **1a–c** in THF resulted in the precipitation of the dicationic mono(aryl) complexes of the rare-earth metals  $[\text{Lu}(\text{C}_6\text{H}_4\text{-}p\text{-R})(\text{THF})_5]^{2+}[\text{BPh}_4]^-_2$  (R = H, **5a**; Me, **5b**; Et, **5c**) as colorless microcrystals in yields of 41–66% (Scheme 2).



The same reaction carried out with the analogous scandium complexes **2a–c** gave only a mixture of the monocationic complexes **4a–c** and unreacted  $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ . However, the use of 2 equiv of the more acidic anilinium salt  $[\text{NPhMe}_2\text{H}]^+[\text{BPh}_4]^-$  allowed for the isolation of the dicationic scandium complexes  $[\text{Sc}(\text{C}_6\text{H}_4\text{-}p\text{-R})(\text{THF})_5]^{2+}[\text{BPh}_4]^-_2$  (R = H, **6a**; Me, **6b**; Et, **6c**) as colorless microcrystals in yields of 36–67% (Scheme 3). The requirement for a stronger acid to protonolyze a scandium–aryl bond as compared to the lutetium–aryl bond can be ascribed to the difference of the basicity between scandium and lutetium.

Single crystals of  $[\text{Lu}(\text{C}_6\text{H}_5)(\text{THF})_5]^{2+}[\text{BPh}_4]^-_2$  (**5a**) could be obtained from a supersaturated THF solution at room temperature. As for the monocationic compound **4a**, no cation–anion interactions could be observed for **5a** in the crystal; two free THF molecules were retained in the crystal lattice. Figure 2 shows the molecular structure of the cationic part of **5a**. The coordination geometry around the metal center can be described as a slightly distorted octahedron with angles of 176.7(3)° (C1–Lu–O3), 175.7(3)° (O2–Lu–O5), and 176.3(2)° (O1–Lu–O4) along the respective axes.

The Lu–C(aryl) distance of 2.303(7) Å is shorter than those previously reported for other lutetium aryl complexes (2.32–(3)–2.877(9) Å).<sup>10e,23</sup> Likewise, the distances between lutetium and the oxygen donors of the THF ligands (2.207(8)–2.320(8) Å) are among the shortest found for organometallic lutetium compounds with THF ligands (2.268(3)–2.455(2) Å).<sup>13m,23b,d,24</sup> This effect arises probably from the increased positive charge in the dication. Analogously to the monocationic scandium complex **4a**, in the crystal structure of **5a** a significantly longer Lu–O distance of 2.320(8) Å to the THF molecule coordinated trans to the phenyl group as compared to those in cis position (2.207(8)–2.249(6) Å) could be observed. The related dicationic mono(alkyl) complexes  $[\text{YMe}(\text{THF})_6]^{2+}[\text{BPh}_4]^-_2$ ,<sup>16</sup>  $[\text{HoMe}(\text{THF})_6]^{2+}[\text{BPh}_4]^-_2$ ,<sup>17</sup> and  $[\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Me})(\text{THF})_6]^{2+}$

(15) (a) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanchisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523. (b) Geissinger, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1995**, 621, 2043. (c) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, 34, 3215. (d) Freedman, D.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, 37, 4162. (e) Aspinall, H. C.; Cunningham, S. A.; Maestro, P.; Macaudire, P. *Inorg. Chem.* **1998**, 37, 5396. (f) Kornienko, A.; Melman, J. H.; Hall, G.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2002**, 41, 121. (g) Domingos, A.; Elsegood, M. R. J.; Hillier, A. C.; Lin, G.; Liu, S. Y.; Lopes, I.; Marques, N.; Maunder, G. H.; McDonald, R.; Sella, A.; Steed, J. W.; Takats, J. *Inorg. Chem.* **2002**, 41, 6761. (h) Deacon, G. B.; Feng, T.; Junk, P. C.; Skelton, B. W.; White, A. H. *Z. Anorg. Allg. Chem.* **2006**, 632, 1986.

(16) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem.* **2003**, 115, 5229; *Angew. Chem., Int. Ed.* **2003**, 42, 5075.

(17) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Angew. Chem.* **2005**, 117, 7640; *Angew. Chem., Int. Ed.* **2005**, 44, 7473.

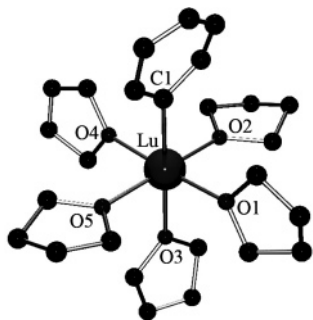
(18) Gao, H.; Shen, Q.; Hu, J.; Jin, S.; Lin, Y. *J. Organomet. Chem.* **1992**, 427, 141.

(19) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, 4, 112.

(20) Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, 20, 1387.

(21) Lin, G.; Jin, Z.; Zhang, Y.; Chen, W. *J. Organomet. Chem.* **1990**, 396, 307.

(22) (a) Ward, B. D.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem.* **2005**, 117, 1696; *Angew. Chem., Int. Ed.* **2005**, 44, 1668. (b) Tredget, B. D.; Bonnet, F.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3301. (c) Elvidge, B. R.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2005**, 44, 6777. (d) Arndt, S.; Elvidge, B. R.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, 25, 793.



**Figure 2.** Molecular structure of the cationic part of **5a**·2THF. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Lu–C1 2.303(7), Lu–O1 2.239(6), Lu–O2 2.207(8), Lu–O3 2.320(8), Lu–O4 2.249(6), Lu–O5 2.237(7); C1–Lu–O3 176.7(3), O2–Lu–O5 175.7(3), O1–Lu–O4 176.3(2).

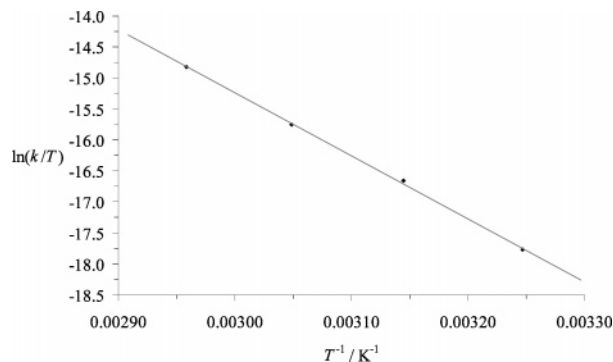
[BPh<sub>4</sub>]<sup>−2a</sup> showed a higher coordination number of seven at the metal center and no such trans influence. Moreover, in the structurally similar cationic parts of [Yb(C<sub>6</sub>F<sub>5</sub>)(THF)<sub>5</sub>]<sup>+</sup>[Yb(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]<sup>−</sup> and [Yb(C<sub>6</sub>F<sub>5</sub>)(THF)<sub>5</sub>]<sup>+</sup>[BPh<sub>4</sub>]<sup>−</sup>, no such trans influence could be observed either.<sup>4</sup> A difference in the trans influence of phenyl and perfluorinated phenyl ligand was also reported for the trigonal bipyramidal coordinated germatrane compounds [(C<sub>6</sub>X<sub>5</sub>)Ge{(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N}] (X = H, F).<sup>25</sup> As for the monocationic complex **4a**, the metal center in **5a** is located outside of the plane defined by the phenyl group; here, the distance is 0.6928(3) Å.

These dicationic complexes were found to be insoluble in THF. Thus, NMR spectra were recorded in pyridine-*d*<sub>5</sub>, as their reactivity toward pyridine is quite low at room temperature. For all compounds, the same resonance of  $\delta = -5.8$  ppm in the

(23) (a) Cotton, S. A.; Welch, A. J.; Hursthouse, M. B.; Hart, F. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1225. (b) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194. (c) Wayda, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1984**, *3*, 939. (d) Wayda, A. L.; Rogers, R. D. *Organometallics* **1985**, *4*, 1440. (e) Protchenko, A. V.; Almazova, O. G.; Zakharov, L. N.; Fukin, G. K.; Struchkov, Y. T.; Bochkarev, M. N. *J. Organomet. Chem.* **1997**, 536–537, 457. (f) Deacon, G. B.; Feng, T.; Forsyth, C. M.; Gitlits, A.; Hockless, D. C. R.; Shen, Q.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 961. (g) Rabe, G. W.; Zhang-Presse, M.; Riederer, F. A.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L. *Acta Crystallogr.* **2004**, E60, m1389. (h) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 6393.

(24) (a) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292. (b) Schumann, H.; Genthe, W.; Bruncks, N. *Angew. Chem.* **1981**, *93*, 126; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 119. (c) Roitershtein, D. M.; Ellern, A. M.; Antipin, M. Y.; Rybakova, L. F.; Struchkov, Y. T.; Petrov, E. S. *Mendeleev Commun.* **1992**, 118. (d) Schumann, H.; Meese-Marktscheffel, J. A.; Dietrich, A.; Pickardt, J. *J. Organomet. Chem.* **1992**, 433, 241. (e) Schumann, H.; Keitsch, M. R.; Winterfeld, J.; Mühle, S.; Molander, G. A. *J. Organomet. Chem.* **1998**, 559, 181. (f) Arndt, S.; Spaniol, T. P.; Okuda, J. *Chem. Commun.* **2002**, 896. (g) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allg. Chem.* **2002**, 628, 2422. (h) Arndt, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 775. (i) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184. (j) Tardif, O.; Nishiura, M.; Hou, Z. *Organometallics* **2003**, *22*, 1171. (k) Tardif, O.; Nishiura, M.; Hou, Z. *Tetrahedron* **2003**, *59*, 10525. (l) Cameron, T. M.; Gordon, J. C.; Scott, B. L. *Organometallics* **2004**, *23*, 2995. (m) Rufanov, K. A.; Freckmann, D. M. M.; Kroth, H. J.; Schutte, S.; Schumann, H. *Z. Naturforsch., B: Chem. Sci.* **2005**, *60*, 533. (n) Schumann, H.; Freckmann, D. M. M.; Schutte, S.; Dechert, S.; Hummert, M. *Z. Anorg. Allg. Chem.* **2007**, 633, 888. (o) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 2747. (p) Miao, W.; Li, S.; Cui, D.; Huang, B. *J. Organomet. Chem.* **2007**, 692, 3823. (q) Liu, B.; Yang, Y.; Cui, D.; Tang, T.; Chen, X.; Jing, X. *Dalton Trans.* **2007**, 4252.

(25) (a) Lukevics, E.; Ignatovich, L.; Belyakov, S. *J. Organomet. Chem.* **1999**, 588, 222. (b) Kulyshyev, R. G.; Prakash, G. K. S.; Olah, G. A.; Faller, J. W.; Parr, J. *Organometallics* **2004**, *23*, 3184.



**Figure 3.** Eyring plot for the reaction of **5a** with pyridine-*d*<sub>5</sub>.

<sup>11</sup>B NMR spectra arising from the tetraphenylborate anions could be observed. This indicates that ion separation is retained in solution. Similar to the observations made for the monocationic complexes, all of the resonances in the <sup>1</sup>H and <sup>13</sup>C NMR spectra were detected except for that corresponding to the ipso carbon atom at the scandium center.

**Reaction with Pyridine.** Many C–H bond activation processes proceed via  $\sigma$ -bond metathesis using complexes of metals with an f<sup>x</sup>d<sup>0</sup> electron configuration.<sup>26,27</sup> As could be shown previously for dicationic alkyl complexes of the rare-earth metals, they easily react with pyridine by C–H bond activation to yield  $\eta^2$ -(C,N)-pyridyl complexes.<sup>22c,d,28</sup> Because of the large number of signals in the aromatic region, the dicationic lutetium complex **5b** with the *p*-methyl-substituted aryl group was used for kinetic measurements as the sharp resonance of the methyl group could be easily observed. For the determination of the activation parameters, four separate runs at 35, 45, 55, and 65 °C were performed by monitoring <sup>1</sup>H NMR spectra of a solution of **5b** in pyridine-*d*<sub>5</sub>. The decrease of the signal intensity attributed to the *p*-methyl group of the dicationic complex **5b** was found to follow pseudo-first-order kinetics, and the half-lives at the respective temperatures were determined to be as follows:  $\tau_{1/2}$  (35 °C) = 1962 min,  $\tau_{1/2}$  (45 °C) = 625 min,  $\tau_{1/2}$  (55 °C) = 243 min, and  $\tau_{1/2}$  (65 °C) = 93 min. The activation parameters were calculated by means of an Eyring plot to be  $\Delta S^\ddagger = -70 \pm 4$  J K<sup>−1</sup> mol<sup>−1</sup> and  $\Delta H^\ddagger = 85 \pm 5$  kJ mol<sup>−1</sup> (Figure 3).

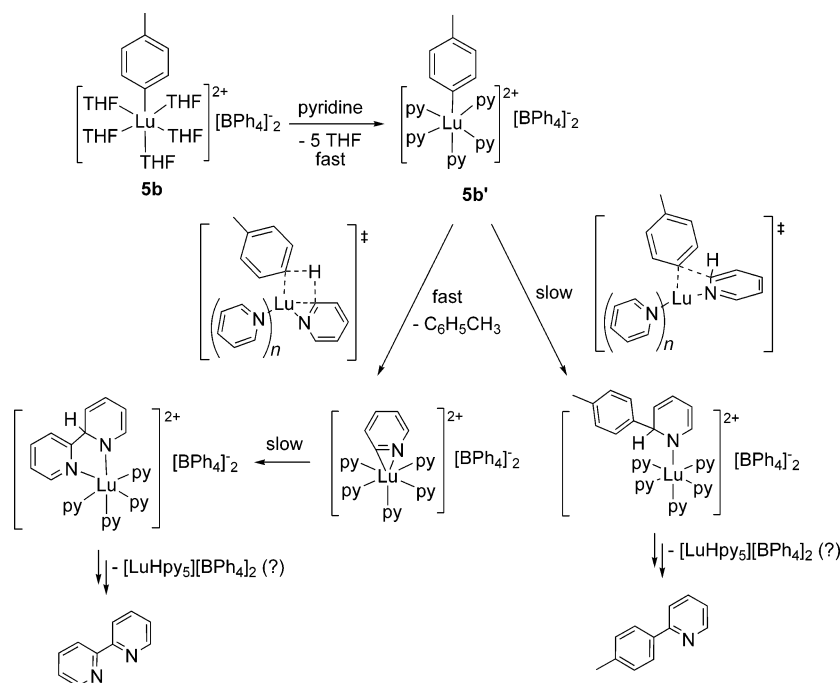
In the <sup>1</sup>H NMR spectrum of the reaction of **5b** with pyridine-*d*<sub>5</sub>, the formation of toluene deuterated in the para position (*p*-CH<sub>3</sub>–C<sub>6</sub>H<sub>4</sub>–D, singlet at  $\delta = 2.21$  ppm for *p*-CH<sub>3</sub>) was observed as well as the formation of 2-*p*-tolyl-pyridine-*d*<sub>4</sub> (two doublets at  $\delta = 7.16$  and 8.21 ppm with <sup>3</sup>J<sub>HH</sub> = 8.0 Hz). When **5b** was stirred at 50 °C for 5 days in pyridine and worked up, the examination of the volatile organic products via GC/MS confirmed the formation of 2-*p*-tolyl-pyridine (*R*<sub>t</sub> = 9.54 min,

(26) For C–H bond activation by lanthanide complexes, see: (a) Watson, P. G. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (b) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (c) Gossage, R. A.; van Koten, G. *Top. Organomet. Chem.* **1999**, *3*, 9. (d) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (e) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(27) For C–H bond activation by actinide complexes, see: (a) Boaretto, R.; Roussel, P.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P. *Chem. Commun.* **1999**, 1701. (b) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Chem. Commun.* **2002**, 30. (c) Pool, J. A.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 1338. (d) Pool, J. A.; Scott, B. L.; Kiplinger, J. L. *J. Alloys Compd.* **2006**, *418*, 178.

(28) For the formation of a neutral  $\eta^2$ -(C,N)-pyridyl complex from the reaction of [Lu( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>](THF)] with pyridine and its crystal structure, see: Jantunen, K. C.; Scott, B. L.; Gordon, J. C.; Kiplinger, J. L. *Organometallics* **2007**, *26*, 2777.

Scheme 4



$M^+$ : 169.0).<sup>29</sup> Additionally, the formation of 2,2'-bipyridyl could be detected ( $R_t = 7.76$  min,  $M^+$ : 156.0).<sup>30</sup> A possible explanation for the formation of these products is shown in Scheme 4.

In the first step, the THF ligands are rapidly replaced by pyridine. When the dicationic complex **5b** was dissolved in pyridine and immediately precipitated upon addition of pentane, only the resonances of the THF-free complex  $[\text{Lu}(\text{C}_6\text{H}_4\text{-}p\text{-Me})(\text{py})_5]^{2+}[\text{BPh}_4]_2^-$  (**5b'**) could be observed in the  $^1\text{H}$  NMR spectra in pyridine- $d_5$ . The  $^1\text{H}$  NMR data for **5b'** are identical to those arising from **5b** in pyridine- $d_5$ , except for the absence of free THF. For neutral cyclopentadienyl-containing complexes, such a greater affinity of lanthanide centers for the nitrogen donors of pyridine over oxygen donors of other Lewis bases has already been noted.<sup>31</sup> After the initial Lewis base exchange, two reaction pathways are conceivable: the first one leading via C–H bond activation of pyridine and loss of toluene to the formation of a  $\eta^2$ -(C,N)-pyridyl lutetium complex. This might react further with a second molecule of pyridine under insertion into the Lu–C bond, which leads after hydrolysis to the observed 2,2'-

bipyridyl.<sup>32</sup> Such reactions have been reported earlier for neutral yttrium alkyl and hydride complexes with two benzamidinato<sup>33</sup> or pentamethylcyclopentadienyl ligands.<sup>34</sup> The involvement of radicals in this reaction cannot be excluded, but seems to be quite unlikely as the reaction of either 2- or 3-pyridyl radicals with an excess of pyridine should lead almost exclusively to the formation of 2,3'-bipyridyl.<sup>29e</sup> In a reaction competing with the C–H bond activation of pyridine, the aryl group attacks a pyridine ligand as a nucleophile, resulting upon hydride elimination (to give formally a dicationic hydride complex  $[\text{LuHpy}_5]^{2+}[\text{BPh}_4]_2^-$ ) in the formation of 2-*p*-tolyl-pyridine. The two transition states must be energetically different, as a product ratio of 3:2 is observed. Such a competition between C–H bond activation and insertion of pyridine for organometallic rare-earth metal compounds was also found for reactions of pyridine and neutral yttrium complexes with two benzamidinato ligands.<sup>33</sup> In comparison with the results previously obtained for the C–H bond activation of pyridine with the dicationic methyl complex  $[\text{LuMe}(\text{THF})_6]^{2+}[\text{BPh}_4]_2^-$  ( $\tau_{1/2}$  (35 °C)  $\approx$  8 d),<sup>22d</sup> the dicationic aryl complex **5b** reacts significantly faster ( $\tau_{1/2}$  (35 °C) = 1962 min). This agrees well with studies of metallocene derivatives  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2\text{R}]$  (R = Me, Ph).<sup>26d,35</sup> Despite the higher relative bond dissociation energy of the Sc–C bond for the phenyl complex as compared to that of the methyl complex, the aryl compounds were found to react faster. As an explanation for this, the initial formation of a  $\pi$  complex was proposed.<sup>35</sup>

## Conclusion

We have shown that cationic aryl complexes of scandium and lutetium are accessible in a manner analogous to that of

(29) (a) Terent'ev, P. B.; Khmel'nitskii, R. A.; Kost, A. N. *Zh. Org. Khim.* **1971**, 7, 1777; *J. Org. Chem. USSR* **1971**, 7, 1843. (b) Terashima, M.; Seki, K.; Yoshida, C.; Ohkura, K.; Kanaoka, Y. *Chem. Pharm. Bull.* **1985**, 33, 1009. (c) Inada, K.; Miyaura, N. *Tetrahedron* **2000**, 56, 8661. (d) Heller, B.; Sundermann, B.; Buschmann, H.; Drexler, H. J.; You, J.; Holzgrabe, U.; Heller, E.; Oehme, G. *J. Org. Chem.* **2002**, 67, 4414. (e) Núñez, A.; Sánchez, A.; Burgos, C.; Alvarez-Builla, J. *Tetrahedron* **2004**, 60, 6217. (f) Wang, L.; Zhang, Y.; Liu, L.; Wang, Y. *J. Org. Chem.* **2006**, 71, 1284.

(30) (a) Brown, E. V.; Ahmad, I. *Phytochemistry* **1972**, 2, 3485. (b) Gillard, R. D.; Hill, R. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1217. (c) Keats, N. G.; Summers, L. A. *J. Heterocycl. Chem.* **1976**, 13, 369. (d) Hassanaly, P.; Vernin, G.; Dou, H. J. M.; Metzger, J. *Bull. Soc. Chim. Fr.* **1976**, 461. (e) Luanratana, O.; Griffin, W. J. *Phytochemistry* **1982**, 21, 449. (f) Crank, G.; Gately, G. E.; Makin, M. I. H. *Aust. J. Chem.* **1984**, 37, 2499.

(31) (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, 106, 1291. (b) Clark, D. L.; Gordon, J. C.; Scott, B. L.; Watkin, J. G. *Polyhedron* **1999**, 18, 1389. (c) Li, J. S.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2002**, 628, 45. (d) Giesbrecht, G. R.; Clark, D. L.; Gordon, J. C.; Scott, B. L. *Appl. Organomet. Chem.* **2003**, 17, 473.

(32) From the reaction mixture of  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_4]^+[\text{BPh}_4]^-$  with pyridine, a crystallographically characterized dicationic complex that contains a bipyridyl ligand,  $[\text{Y}\{\eta^2\text{-(C,N)-C}_5\text{H}_4\text{N}\}(\text{bpy})(\text{py})\text{-}fac\text{-(THF)}_3]^{2+}[\text{BPh}_4]_2^-$ , was isolated in low yield: Nakajima, Y.; Spaniol, T. P.; Okuda, J., unpublished results.

(33) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, 15, 2291.

(34) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, 13, 3881.

(35) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, 7, 1409.

the still growing number of cationic alkyl complexes of the rare-earth metals. Whereas the number of previous reports on monocationic aryl complexes is very limited, the first examples of dicationic derivatives have been synthesized and characterized. In the solid state, both crystallographically characterized mono- and dicationic complexes adopt a slightly distorted octahedral coordination geometry, in which a significant trans influence of the aryl ligands is observed. The dicationic aryl complexes activate pyridine. In contrast to the C–H bond activation found for related methyl dication, evidence has been found that the C–H bond activation competes with insertion of pyridine into the aryl complexes.

## Experimental Section

**General Procedures.** All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glove box techniques. Diethyl ether, THF, and toluene were distilled from sodium benzophenone ketyl. Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous rare-earth metal trichlorides (Strem or Aldrich) were used as received. [Sc(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(THF)<sub>2</sub>] (**2a**)<sup>7</sup> and the lithium aryls<sup>36</sup> were prepared by literature procedures. NMR spectra were recorded on a Varian Mercury 200 BB (<sup>1</sup>H, 200.0 MHz), Varian Unity 500 (<sup>1</sup>H, 499.6 MHz; <sup>13</sup>C, 125.6 MHz; <sup>11</sup>B, 160.3 MHz), or Bruker DRX 400 spectrometer (<sup>1</sup>H, 400.1 MHz; <sup>13</sup>C, 100.6 MHz; <sup>11</sup>B, 128.4 MHz) at 25 °C, unless otherwise stated. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally using the residual solvent resonances and are reported relative to tetramethylsilane. <sup>11</sup>B NMR spectra were referenced externally to a 1 M solution of NaBH<sub>4</sub> in D<sub>2</sub>O. Elemental analyses were performed by the Microanalytical Laboratory of the Institute of Organic Chemistry at the RWTH Aachen University. In many cases, the results were not satisfactory and the best values from repeated runs were given. Moreover, the results were inconsistent from run to run and therefore irreproducible. In the context of organometallic rare-earth metal compounds, this difficulty was also observed by other groups and may be ascribed to the formation of inert carbides.<sup>37</sup> Metal analysis was performed by complexometric titration.<sup>38</sup> The GC/MS(EI) experiments were run on a Varian VF-5ms spectrometer.

[Lu(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(THF)<sub>2</sub>] (**1a**). LuCl<sub>3</sub> (0.844 g, 3.00 mmol) was suspended in THF (10 mL) and stirred at 40 °C overnight. After addition of Et<sub>2</sub>O (10 mL) to the suspension, a solution of Li(C<sub>6</sub>H<sub>5</sub>) (0.769 g, 9.15 mmol) in Et<sub>2</sub>O (25 mL) was added dropwise at 0 °C. After the mixture was stirred for 2.5 h at this temperature, all volatiles were removed in vacuo and the residue was extracted with toluene (2 × 40 mL) at 0 °C. After removal of the solvent in vacuo, recrystallization from THF (40 mL) afforded **1a** (0.482 g, 24%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.10 (br s, 8H, β-THF), 3.54 (br s, 8H, α-THF), 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 6H, LuC<sub>6</sub>H<sub>5</sub>-4), 7.59 (d, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 6H, LuC<sub>6</sub>H<sub>5</sub>-3), 8.18 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 3H, LuC<sub>6</sub>H<sub>5</sub>-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 25.3 (β-THF), 69.2 (α-THF), 126.8 (LuC<sub>6</sub>H<sub>5</sub>-4), 127.4 (LuC<sub>6</sub>H<sub>5</sub>-3), 136.3 (LuC<sub>6</sub>H<sub>5</sub>-2), 198.7 (LuC<sub>6</sub>H<sub>5</sub>-1). Anal. Calcd for C<sub>26</sub>H<sub>31</sub>LuO<sub>2</sub> (550.50): C, 56.73; H, 5.68; Lu, 31.78. Found: C, 56.75; H, 6.44; Lu, 31.56.

[Lu(C<sub>6</sub>H<sub>4</sub>-*p*-Me)<sub>3</sub>(THF)<sub>2</sub>] (**1b**). LuCl<sub>3</sub> (0.844 g, 3.00 mmol) was suspended in THF (10 mL) and stirred at 40 °C overnight. After addition of Et<sub>2</sub>O (10 mL) to the suspension, a solution of Li(C<sub>6</sub>H<sub>4</sub>-*p*-Me) (0.897 g, 9.15 mmol) in Et<sub>2</sub>O (25 mL) was added dropwise at 0 °C. After the mixture was stirred for 2.5 h at this temperature,

all volatiles were removed in vacuo and the residue was extracted with toluene (2 × 40 mL) at 0 °C. After removal of the solvent in vacuo, recrystallization from THF (20 mL) afforded **1b** (1.14 g, 64%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.22 (br s, 8H, β-THF), 2.40 (s, 9H, CH<sub>3</sub>), 3.57 (br s, 8H, α-THF), 7.46 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 6H, LuC<sub>6</sub>H<sub>4</sub>-3), 8.17 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 6H, LuC<sub>6</sub>H<sub>4</sub>-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 21.8 (CH<sub>3</sub>), 25.4 (β-THF), 68.8 (α-THF), 128.1 (LuC<sub>6</sub>H<sub>4</sub>-4), 135.3 (LuC<sub>6</sub>H<sub>4</sub>-3), 136.6 (LuC<sub>6</sub>H<sub>4</sub>-2), 195.2 (LuC<sub>6</sub>H<sub>4</sub>-1). Anal. Calcd for C<sub>29</sub>H<sub>37</sub>LuO<sub>2</sub> (592.58): C, 58.78; H, 6.29; Lu, 29.53. Found: C, 53.76; H, 5.65; Lu, 29.21.

[Lu(C<sub>6</sub>H<sub>4</sub>-*p*-Et)<sub>3</sub>(THF)<sub>2</sub>] (**1c**). LuCl<sub>3</sub> (0.844 g, 3.00 mmol) was suspended in THF (10 mL) and stirred at 40 °C overnight. After addition of Et<sub>2</sub>O (10 mL) to the suspension, a solution of Li(C<sub>6</sub>H<sub>4</sub>-*p*-Et) (1.03 g, 9.15 mmol) in Et<sub>2</sub>O (25 mL) was added dropwise at 0 °C. After the mixture was stirred for 2.5 h at this temperature, all volatiles were removed in vacuo and the residue was extracted with toluene (2 × 40 mL) at 0 °C. After removal of the solvent in vacuo, recrystallization from THF (20 mL) afforded **1c** (0.782 g, 41%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.08 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 1.34 (br s, 8H, β-THF), 2.71 (quartet, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 3.54 (br s, 8H, α-THF), 7.48 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H, LuC<sub>6</sub>H<sub>4</sub>-3), 8.21 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H, LuC<sub>6</sub>H<sub>4</sub>-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 16.4 (CH<sub>2</sub>CH<sub>3</sub>), 25.7 (β-THF), 29.7 (CH<sub>2</sub>CH<sub>3</sub>), 67.8 (br, α-THF), 126.6 (LuC<sub>6</sub>H<sub>4</sub>-4), 134.4 (LuC<sub>6</sub>H<sub>4</sub>-3), 140.1 (LuC<sub>6</sub>H<sub>4</sub>-2), 194.2 (LuC<sub>6</sub>H<sub>4</sub>-1). Anal. Calcd for C<sub>32</sub>H<sub>43</sub>LuO<sub>2</sub> (634.66): C, 60.56; H, 6.83; Lu, 27.57. Found: C, 59.91; H, 7.04; Lu, 27.46.

[Sc(C<sub>6</sub>H<sub>4</sub>-*p*-Me)<sub>3</sub>(THF)<sub>2</sub>] (**2b**). ScCl<sub>3</sub> (0.454 g, 3.00 mmol) was suspended in THF (10 mL) and stirred at 40 °C overnight. After addition of Et<sub>2</sub>O (10 mL) to the suspension, a solution of Li(C<sub>6</sub>H<sub>4</sub>-*p*-Me) (0.897 g, 9.15 mmol) in Et<sub>2</sub>O (25 mL) was added dropwise at 0 °C. After the mixture was stirred for 2.5 h at this temperature, all volatiles were removed in vacuo and the residue was extracted with toluene (2 × 40 mL) at 0 °C. After removal of the solvent in vacuo, recrystallization twice from THF (70 mL each) afforded **2b** (1.10 g, 79%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.18 (br s, 8H, β-THF), 2.38 (s, 9H, CH<sub>3</sub>), 3.64 (br s, 8H, α-THF), 7.34 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, ScC<sub>6</sub>H<sub>4</sub>-3), 8.14 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, ScC<sub>6</sub>H<sub>4</sub>-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 21.9 (CH<sub>3</sub>), 25.3 (β-THF), 70 (br, α-THF), 127.8 (ScC<sub>6</sub>H<sub>4</sub>-4), 134.7 (ScC<sub>6</sub>H<sub>4</sub>-3), 135.3 (ScC<sub>6</sub>H<sub>4</sub>-2), resonance for ScC<sub>6</sub>H<sub>4</sub>-1 not detected. Anal. Calcd for C<sub>29</sub>H<sub>37</sub>O<sub>2</sub>Sc (462.57): C, 75.30; H, 8.06; Sc, 9.72. Found: C, 74.92; H, 7.62; Sc, 9.89.

[Sc(C<sub>6</sub>H<sub>4</sub>-*p*-Et)<sub>3</sub>(THF)<sub>2</sub>] (**2c**). ScCl<sub>3</sub> (0.454 g, 3.00 mmol) was suspended in THF (10 mL) and stirred at 40 °C overnight. After addition of Et<sub>2</sub>O (10 mL) to the suspension, a solution of Li(C<sub>6</sub>H<sub>4</sub>-*p*-Et) (1.03 g, 9.15 mmol) in Et<sub>2</sub>O (25 mL) was added dropwise at 0 °C. After the mixture was stirred for 2.5 h at this temperature, all volatiles were removed in vacuo and the residue was extracted with toluene (2 × 40 mL) at 0 °C. After removal of the solvent in vacuo, recrystallization twice from THF (40 mL each) afforded **2c** (0.760 g, 50%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.91 (br s, 8H, β-THF), 1.29 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 2.69 (quartet, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 3.68 (br s, 8H, α-THF), 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, ScC<sub>6</sub>H<sub>4</sub>-3), 8.18 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, ScC<sub>6</sub>H<sub>4</sub>-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 16.4 (CH<sub>2</sub>CH<sub>3</sub>), 24.8 (β-THF), 29.7 (CH<sub>2</sub>CH<sub>3</sub>), 71 (br, α-THF), 126.6 (ScC<sub>6</sub>H<sub>4</sub>-4), 134.7 (ScC<sub>6</sub>H<sub>4</sub>-3), 142.0 (ScC<sub>6</sub>H<sub>4</sub>-2), signal for ScC<sub>6</sub>H<sub>4</sub>-1 not detected. Anal. Calcd for C<sub>32</sub>H<sub>43</sub>O<sub>2</sub>Sc (504.65): C, 76.16; H, 8.59; Sc, 8.91. Found: C, 75.27; H, 8.20; Sc, 9.10.

[Lu(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(THF)<sub>4</sub>]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (**3a**). A solution of [NEt<sub>3</sub>H]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (0.102 g, 0.242 mmol) in THF (5 mL) was added dropwise at 0 °C to a solution of **1a** (0.133 g, 0.242 mmol) in THF (10 mL) and stirred at this temperature for 30 min. Evaporation of all volatiles in vacuo and washing the colorless residue with pentane (3 × 10 mL) afforded **3a** (0.119 g, 52%) as a colorless powder. <sup>1</sup>H NMR

(36) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.

(37) (a) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (b) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197.

(38) Das, B.; Shome, S. C. *Anal. Chim. Acta* **1971**, *56*, 483.



**Table 1.** Experimental Data for the Crystal Structure Determination of the Complexes **4a** and **5a**·2THF

	<b>4a</b>	<b>5a</b> ·2THF
empirical formula	C <sub>52</sub> H <sub>62</sub> BO <sub>4</sub> Sc	C <sub>82</sub> H <sub>101</sub> B <sub>2</sub> LuO <sub>7</sub>
$M_r$	806.79	1395.22
cryst size/mm	0.22 × 0.34 × 0.62	0.09 × 0.17 × 0.31
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
$a/\text{Å}$	10.110(2)	12.3689(15)
$b/\text{Å}$	26.266(5)	13.8132(16)
$c/\text{Å}$	16.681(3)	41.361(5)
$\beta/\text{deg}$	94.084(4)	
$V/\text{Å}^3$	4418.3(15)	7066.7(15)
$Z$	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.213	1.311
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.211	1.452
$F(000)$	1728	2920
$T/\text{K}$	110(2)	130
$\theta$ range/deg	1.45–28.34	0.98–25.00
no. of rflns collected	58 078	40 836
no. of rflns obsd [ $I > 2\sigma(I)$ ]	9869	8186
no. of indep rflns ( $R_{\text{int}}$ )	10 894 (0.0490)	12 426 (0.0917)
no. of data/restraints/params	10 894/0/523	12 426/0/399
GOF	1.221	1.019
final $R$ indices $R_1$ , $wR_2^b$ (obsd data)	0.0744, 0.1793	0.0692, 0.1450
final $R$ indices $R_1$ , $wR_2$ (all data)	0.0827, 0.1847	0.1024, 0.1555
largest $e$ (max), $e$ (min)/ $e \text{ Å}^{-3}$	0.502 and -0.896	0.892 and -1.918

<sup>a</sup>  $R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2(F) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .

LuO<sub>5</sub> (1265.10): C, 71.21; H, 6.93; Lu, 13.83. Found: C, 69.67; H, 6.76; Lu, 13.81.

**[Lu(C<sub>6</sub>H<sub>4</sub>-p-Me)(C<sub>5</sub>H<sub>5</sub>N)<sub>5</sub>]<sup>2+</sup>[BPh<sub>4</sub>]<sup>-2</sup> (**5b'**)**. Complex **5b** (0.070 g, 0.0552 mmol) was dissolved in pyridine (1.5 mL) and stirred for 1 min. Pentane (10 mL) was added to the colorless solution to give an oily deposit. Further washings with pentane (3 × 10 mL) gave 54.0 mg (41.5 μmol, 75%) of **20b'** as a slightly yellow powder after drying in vacuo. <sup>1</sup>H NMR (400.1 MHz, pyridine-*d*<sub>5</sub>): δ 2.38 (s, 3H, CH<sub>3</sub>), 7.07 (m, 2H + 8H, LuC<sub>6</sub>H<sub>4</sub>-3 + BPh-4), 7.23 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 16H, BPh-3), 7.31 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, LuC<sub>6</sub>H<sub>4</sub>-2), 8.02 (m, 16H, BPh-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, pyridine-*d*<sub>5</sub>): δ 21.5 (CH<sub>3</sub>), 122.4 (BPh-4), 126.2 (quartet, <sup>3</sup>J<sub>BC</sub> = 3.2 Hz, BPh-3), 129.0 (LuC<sub>6</sub>H<sub>4</sub>-4), 137.0 (LuC<sub>6</sub>H<sub>4</sub>-3), 137.1 (BPh-2), 139.9 (LuC<sub>6</sub>H<sub>4</sub>-2), 165.0 (q, <sup>1</sup>J<sub>BC</sub> = 49.4 Hz, BPh-1), 188.7 (LuC<sub>6</sub>H<sub>4</sub>-1). <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, pyridine-*d*<sub>5</sub>): δ -5.8.

**Reaction of 5b with Pyridine.** Complex **5b** (0.0350 g, 27.7 μmol) was dissolved in pyridine (2 mL) and stirred at 50 °C for 5 days. After addition of one drop H<sub>2</sub>O, filtration on silica gel, and washing with pyridine (10 mL), the volume of the solution was slowly reduced by evaporation of the solvent to approximately 2 mL. The resulting yellow solution was analyzed via GC/MS(EI), and two products could be detected: 2,2'-bipyridyl,  $R_t = 7.76$  min, MS  $m/z$  (rel. int.), 156.0 (M<sup>+</sup>, 100), 129.0 (17), 127.9 (20), 77.9 (16); and 2-*p*-tolyl-pyridine,  $R_t = 9.54$  min, MS  $m/z$  (rel. int.), 169.0 (M<sup>+</sup>, 100), 154.0 (6), 83.4 (11).

**Kinetic Measurements of the Reaction of 5b with Pyridine-*d*<sub>5</sub>.** Complex **5b** (0.0250 g, 20.0 μmol) was dissolved in pyridine-*d*<sub>5</sub> (0.5 mL). In four separate experiments, the sample was heated in the NMR spectrometer to 35, 45, 55, and 65 °C, respectively. <sup>1</sup>H NMR spectra were recorded at regular intervals (35 °C, every 30 min for 14 h; 45 °C, every 15 min for 14.25 h; 55 °C, every 15 min for 7.5 h; 65 °C, every 15 min for 4.5 h) using short delay ( $d_1 = 0.2$  s) and acquisition ( $nt = 2$ ) times. The rate constants were determined by plotting  $\ln(I_0/I)$  against  $t$  ( $I =$  integral of the Lu-(C<sub>6</sub>H<sub>4</sub>-*p*-Me) group). The Ph-2 group of the tetraphenylborate anion was used as an internal standard for the integration by which the extent of the conversion of **5b** was calculated.

**[Lu(C<sub>6</sub>H<sub>4</sub>-*p*-Et)(THF)<sub>5</sub>]<sup>2+</sup>[BPh<sub>4</sub>]<sup>-2</sup> (**5c**)**. To a mixture of **1c** (0.200 g, 0.315 mmol) and [NEt<sub>3</sub>H]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (0.266 g, 0.630 mmol)

was added THF (20 mL) at -78 °C. After the stirred mixture was allowed to slowly warm to room temperature overnight, the supernatant was decanted and the colorless precipitate was washed with THF (3 × 20 mL). All volatiles were removed under reduced pressure to yield **5c** (0.228 g, 57%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, pyridine-*d*<sub>5</sub>): δ 1.25 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.60 (m, 20H, β-THF), 2.68 (quartet, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 3.63 (m, 20H, α-THF), 7.07 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 8H, BPh-4), 7.23 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 16H, BPh-3), 7.34 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, LuC<sub>6</sub>H<sub>4</sub>-3), 8.02 (m, 16 + 2H, BPh-2 + LuC<sub>6</sub>H<sub>4</sub>-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, pyridine-*d*<sub>5</sub>): δ 22.5 (CH<sub>2</sub>CH<sub>3</sub>), 25.8 (br, β-THF), 29.1 (CH<sub>2</sub>CH<sub>3</sub>), 67.8 (br, α-THF), 122.4 (BPh-4), 126.2 (quartet, <sup>3</sup>J<sub>BC</sub> = 3.2 Hz, BPh-3), 127.8 (LuC<sub>6</sub>H<sub>4</sub>-4), 135.2 (LuC<sub>6</sub>H<sub>4</sub>-3), 137.1 (BPh-2), 139.9 (LuC<sub>6</sub>H<sub>4</sub>-2), 165.0 (quartet, <sup>1</sup>J<sub>BC</sub> = 49.4 Hz, BPh-1), 189.1 (LuC<sub>6</sub>H<sub>4</sub>-1). <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, pyridine-*d*<sub>5</sub>): δ -5.8. Anal. Calcd for C<sub>76</sub>H<sub>89</sub>B<sub>2</sub>LuO<sub>5</sub> (1279.13): C, 71.36; H, 7.01; Lu, 13.68. Found: C, 69.28; H, 7.19; Lu, 13.81.

**[Sc(C<sub>6</sub>H<sub>5</sub>)(THF)<sub>5</sub>]<sup>2+</sup>[BPh<sub>4</sub>]<sup>-2</sup> (**6a**)**. To a mixture of **2a** (0.200 g, 0.476 mmol) and [NPhMe<sub>2</sub>H]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (0.420 g, 0.951 mmol) was added THF (20 mL) at -78 °C. After the stirred mixture was allowed to slowly warm to room temperature overnight, the supernatant was decanted and the colorless precipitate was washed with THF (3 × 20 mL). All volatiles were removed under reduced pressure to yield **6a** (0.356 g, 67%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, pyridine-*d*<sub>5</sub>): δ 1.60 (br, 20H, β-THF), 3.63 (br, 20H, α-THF), 7.06 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 8H, BPh-4), 7.22 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 16H, BPh-3), 7.31–7.38 (m, 1H + 2H, ScC<sub>6</sub>H<sub>5</sub>-4 + ScC<sub>6</sub>H<sub>5</sub>-3), 7.49 (dd, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, <sup>3</sup>J<sub>HH</sub> = 1.3 Hz, 2H, ScC<sub>6</sub>H<sub>5</sub>-2), 8.00 (m, 16H, BPh-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, pyridine-*d*<sub>5</sub>): δ 26.3 (β-THF), 68.3 (α-THF), 122.9 (BPh-4), 126.7 (quartet, <sup>3</sup>J<sub>BC</sub> = 2.6 Hz, BPh-3), 128.4 (ScC<sub>6</sub>H<sub>5</sub>-4), 135.7 (ScC<sub>6</sub>H<sub>5</sub>-3), 137.6 (BPh-2), 137.1 (ScC<sub>6</sub>H<sub>5</sub>-2), 165.4 (quartet, <sup>1</sup>J<sub>BC</sub> = 49.4 Hz, BPh-1), signal for ScC<sub>6</sub>H<sub>5</sub>-1 not detected. <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, pyridine-*d*<sub>5</sub>): δ -5.8. Anal. Calcd for C<sub>74</sub>H<sub>85</sub>B<sub>2</sub>O<sub>5</sub>Sc (1121.06): C, 79.28; H, 7.64; Sc, 4.01. Found: C, 75.96; H, 7.27; Sc, 4.07.

**[Sc(C<sub>6</sub>H<sub>4</sub>-*p*-Me)(THF)<sub>5</sub>]<sup>2+</sup>[BPh<sub>4</sub>]<sup>-2</sup> (**6b**)**. To a mixture of **2b** (0.200 g, 0.423 mmol) and [NPhMe<sub>2</sub>H]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (0.382 g, 0.865 mmol) was added THF (20 mL) at -78 °C. After the stirred mixture was allowed to slowly warm to room temperature overnight, the supernatant was decanted and the colorless precipitate was washed with THF (3 × 20 mL). All volatiles were removed under reduced pressure to yield **6b** (0.172 g, 36%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, pyridine-*d*<sub>5</sub>): δ 1.60 (m, 20H, β-THF), 2.28 (s, 3H, CH<sub>3</sub>), 3.64 (m, 20H, α-THF), 7.04 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2H, ScC<sub>6</sub>H<sub>4</sub>-3), 7.07 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 8H, BPh-4), 7.24 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 16H, BPh-3), 7.30 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2H, ScC<sub>6</sub>H<sub>4</sub>-2), 8.02 (m, 16H, BPh-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, pyridine-*d*<sub>5</sub>): δ 21.5 (CH<sub>3</sub>), 25.8 (br, β-THF), 67.8 (br, α-THF), 122.4 (BPh-4), 126.2 (quartet, <sup>3</sup>J<sub>BC</sub> = 3.2 Hz, BPh-3), 128.3 (ScC<sub>6</sub>H<sub>4</sub>-4), 136.8 (ScC<sub>6</sub>H<sub>4</sub>-3), 137.2 (BPh-2), 138.6 (ScC<sub>6</sub>H<sub>4</sub>-2), 165.0 (quartet, <sup>1</sup>J<sub>BC</sub> = 49.4 Hz, BPh-1), resonance ScC<sub>6</sub>H<sub>4</sub>-1 not detected. <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, pyridine-*d*<sub>5</sub>): δ -5.8. Anal. Calcd for C<sub>75</sub>H<sub>87</sub>B<sub>2</sub>O<sub>5</sub>Sc (1135.09): C, 79.36; H, 7.73; Sc, 3.96. Found: C, 77.33; H, 7.77; Sc, 3.88.

**[Sc(C<sub>6</sub>H<sub>4</sub>-*p*-Et)(THF)<sub>5</sub>]<sup>2+</sup>[BPh<sub>4</sub>]<sup>-2</sup> (**6c**)**. To a mixture of **2c** (0.200 g, 0.396 mmol) and [NPhMe<sub>2</sub>H]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (0.350 g, 0.793 mmol) was added THF (20 mL) at -78 °C. After the stirred mixture was allowed to slowly warm to room temperature overnight, the supernatant was decanted and the colorless precipitate was washed with THF (3 × 20 mL). All volatiles were removed under reduced pressure to yield **6c** (0.304 g, 67%) as a colorless powder. <sup>1</sup>H NMR (400.1 MHz, pyridine-*d*<sub>5</sub>): δ 1.17 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.63 (m, 20H, β-THF), 2.58 (quartet, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 3.63 (m, 20H, α-THF), 7.06 (m, 8H + 2H, BPh-4 + ScC<sub>6</sub>H<sub>4</sub>-3), 7.22 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 16H, BPh-3), 7.33 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, ScC<sub>6</sub>H<sub>4</sub>-2), 8.00 (m, 16H, BPh-2). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, pyridine-*d*<sub>5</sub>): δ 15.7 (CH<sub>2</sub>CH<sub>3</sub>), 25.8 (br, β-THF), 29.1 (CH<sub>2</sub>CH<sub>3</sub>),



67.8 (br,  $\alpha$ -THF), 122.4 (BPh-4), 126.2 (quartet,  $^3J_{BC} = 3.2$  Hz, BPh-3), 127.1 (ScC<sub>6</sub>H<sub>4</sub>-4), 136.9 (ScC<sub>6</sub>H<sub>4</sub>-3), 137.1 (BPh-2), 144.9 (ScC<sub>6</sub>H<sub>4</sub>-2), 165.0 (quartet,  $^1J_{BC} = 49.4$  Hz, BPh-1), signal for ScC<sub>6</sub>H<sub>4</sub>-1 not detected.  $^{11}\text{B}\{^1\text{H}\}$  NMR (128.4 MHz, pyridine-*d*<sub>5</sub>):  $\delta$  -5.8. Anal. Calcd for C<sub>76</sub>H<sub>89</sub>B<sub>2</sub>O<sub>5</sub>Sc (1149.12): C, 79.44; H, 7.81; Sc, 3.91. Found: C, 78.91; H, 7.89; Sc, 4.17.

**X-ray Crystal Structure Determination.** Crystallographic data for **4a** and **5a**·2THF are summarized in Table 1. X-ray diffraction data were collected on a Bruker CCD area-detector with Mo K $\alpha$  radiation (graphite monochromator,  $\lambda = 0.71073$  Å) using  $\omega$  scans. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT.<sup>39</sup> The structures were solved by direct methods using the SHELXS-97 program<sup>40</sup> and refined against  $F^2$  using all reflections with the SHELXL-97 software.<sup>41</sup> The hydrogen atoms were placed in calculated positions. Relevant crystallographic

(39) Siemens, ASTRO, SAINT, and SADABS. Data Collection and Processing Software for the SMART System; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996.

(40) Sheldrick, G. M. *SHELXS-97, A program for automatic solution of crystal structures*; University of Göttingen: Göttingen, Germany, 1997, Release 97-2.

(41) Sheldrick, G. M. *SHELXL-97, A program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997, Release 97-2.

data for **4a** and **5a** are summarized in Table 1. Pronounced disorder in the conformationally soft THF rings of **5a**·2THF, both in the peripheric atoms of the metal coordinated moieties and in the solvent THF, resulted in less well-defined electron density maxima. To obtain a sufficiently simple model without major artifacts in displacement parameters, most atoms were treated as isotropic in refinement. While the disorder limits the accuracy, the results are adequate to describe the overall geometry. An alternative, much more complicated model with refinement of the disordered atoms at separate split positions did not improve the model.

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**Supporting Information Available:** CIF files giving full crystallographic data, and ORTEP plots for **4a** and **5a**·2THF and time-conversion and Arrhenius plots for the reaction of **5b** with pyridine-*d*<sub>5</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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