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Communications

Synthesis and Catalytic Properties of Phenylene-Bridged Binuclear Organolanthanide Complexes

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Summary: Using base-free $Ln[N(SiHMe_2)_2]_3$ *complexes as highly effective protodeamination reagents, the binuclear lanthanide complexes p-bis{*η^5*-(2,3,4,5-tetramethylcyclopentadienyl)*$Ln[N(SiHMe_2)_2]_2$*}phenylene [p-*Ln_2*] (Ln = Y, La, Lu) and m-bis{*η^5*-(2,3,4,5-tetramethylcyclopentadienyl)La-*$[N(SiHMe_2)_2]_2$*}phenylene [m-*La_2*] were synthesized from the corresponding phenylene-linked tetramethylcyclopentadienes. The resulting products serve as new types of multicenter homogeneous 4f catalysts. Reactivity studies reveal that these binuclear organolanthanide complexes efficiently catalyze the intramolecular hydroamination/cyclization of aminoalkenes, aminoalkynes, and aminodienes, with turnover frequencies as high as 10* h^{-1} *at 60 °C.*

Introduction

The catalytic addition of an N−H bond across C−C unsaturation is a highly desirable, atom-economical transformation for the synthesis of nitrogen-containing molecules,[1] and organolanthanide complexes are known to be efficient catalysts for such inter- and intramolecular hydroamination processes.[1e] A large number of heterocyclic structures, including diastereomerically pure natural products, have been synthesized via regioselective organolanthanide-catalyzed hydroamination and tandem C−N/C−C bond formation processes.[2,3] The success achieved thus far in the structural tailoring of organolanthanide

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(1) For recent hydroamination reviews, see: (a) Widenhoefer, R. A.; Han, X. *Eur. J. Org. Chem.* **2006**, *20*, 4555–4563. (b) Odom, A. L. *Dalton Trans.* **2005**, 225–233. (c) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367–391. (d) Hultzsch, K. C.; Gribkov, D. V.; Hampel, F. *J. Organomet. Chem.* **2005**, *690*, 4441–4452. (e) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673–686. (f) Doye, S. *Synlett* **2004**, 1653–1672. (g) Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708–2710. (h) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104–114. (i) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, *6*, 935–946. (j) Seayad, J.; Tillack, A.; Hartung, C. G.; Beller, M. *Adv. Synth. Catal.* **2002**, *344*, 795–813.

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(3) For additional examples of group 3- and lanthanide-catalyzed hydroamination, see: (a) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem.−Eur. J.* **2007**, *13*, 3606–3616. (b) Riegert, D.; Collin, J.; Daran, J.-C.; Fillebeen, T.; Schulz, E.; Lyubov, D.; Fukin, G.; Trifonov, A. *Eur. J. Inorg. Chem.* **2007**, *8*, 1159–1168. (c) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. *Dalton Trans.* **2006**, 1157–1161. (d) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759. (e) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197–2202. (f) Kim, J. Y.; Livinghouse, T. *Org. Lett.* **2005**, *7*, 4391–4393. (g) Molander, G. A.; Hasegawa, H. *Heterocycles* **2004**, *64*, 467–474. (h) Lauterwasser, F.; Hayes, P. G.; Bräse, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234–2237. (i) O'Shaughnessy, P. N.; Gillespie, K. M.; Knight, P. D.; Munslow, I. J.; Scott, P. *Dalton Trans.* **2004**, 2251–2256.

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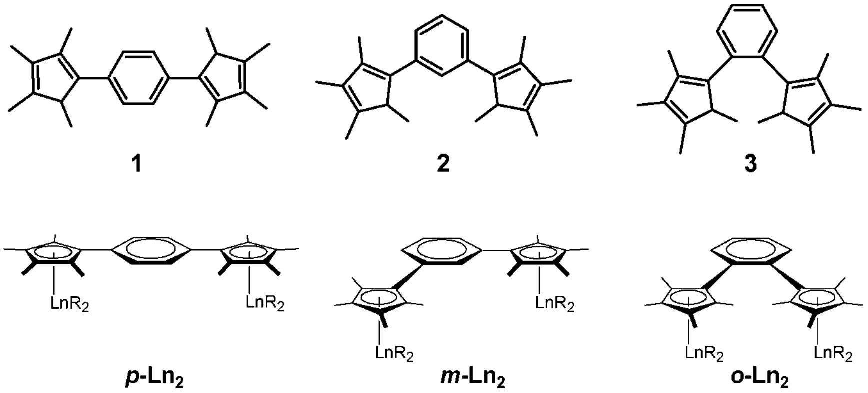
Chart 1. Bis(tetramethylcyclopentadienyl)phenylene Ligands and Their Respective Binuclear Ln Complexes



catalysts for activity/selectivity optimization prompts a continuing effort to develop new strategies for manipulating reactivity and exploring new hydroamination pathways.

Enzymes achieve unique catalytic activity and selectivity characteristics as a consequence of achieving high local reagent concentrations and conformationally advantaged spatial relationships.[4] Similarly, multinuclear metal complexes offer the possibility of unique and more selective catalytic transformations by facilitating cooperative effects between active sites.[5] This approach suggests the interesting and attractive possibility of joining catalytically-active lanthanide centers via a multinuclear ligand scaffold. Herein we report preliminary results on the synthesis and catalytic hydroamination characteristics of a new class of phenylene-bridged binuclear tetramethylcyclopentadienyl organolanthanide catalysts.

In this study, a planar phenylene unit is envisioned as a bridging element to modulate the distance between lanthanide active centers via substitution at *ortho*, *meta*, or *para* positions (Chart 1). The *p*-phenylene-bridged ligand **1**, developed by Manriquez,[6] was synthesized as described in the literature.[7] An analogous procedure is used to prepare *m*-bis(2,3,4,5-tetramethylcyclopentadienyl)phenylene, **2**. Stepwise addition of 2,3,4,5-tetramethylcyclopent-2-en-1-one to an ether solution of the corresponding *meta*-substituted aryllithium reagent, followed by reaction with aqueous *p*-toluenesulfonic acid, affords the *m*-phenylene-bridged ligand precursor, which was characterized by standard analytical techniques (see Supporting Information for details). Protodeaminative reaction of **1** with 2 equiv of $\mathrm{Y[N(SiHMe_2)_2]_3(THF)_2}$[8] in refluxing toluene for 4 weeks affords binuclear complex **4** in 19% yield (Scheme 1, eq i). The sluggish reaction rate and low yield are attributable to steric saturation incurred by the basic THF ligands.[9]

To overcome the limitations of THF-coordinated/deactivated lanthanide reagents, the solvent-free tris(disilylamido) reagent $\mathrm{La[N(SiHMe_2)_2]_3}$ (**5**) was prepared. As anticipated from pK_a differences between the parent disilylamines (25.8, $\mathrm{HN(TMS)_2}$;[10a] 22.6, $\mathrm{HN(SiHMe_2)_2}$[10b]), the desired transamination proceeds readily in hydrocarbon media to form complex **5** and $\mathrm{HN(TMS)_2}$ (eq 1).

$$\mathrm{La[N(TMS)_2]_3 + 3\ HN(SiHMe_2)_2 \xrightarrow{pentane} \underset{\mathbf{5}}{La[N(SiHMe_2)_2]_3} + 3\ HN(TMS)_2} \qquad (1)$$

X-ray diffraction analysis reveals that complex **5** crystallizes as a C_1-symmetric dimer (Figure 1).[11] The molecular structure features average La–N bond distances of 2.377(9) Å (terminal) and 2.654(35) Å (bridging), which lie in the expected range. For comparison, the terminal La–N bond lengths in $\mathrm{La[N(SiHMe_2)_2]_3(THF)_2}$ are somewhat larger, ranging from 2.395(5) to 2.416(5) Å.[8] As in the $\mathrm{Y^{3+}}$ analogue,[11] complex **5** exhibits pronounced Si–H β-agostic interactions with the $\mathrm{La^{3+}}$ center. Each of the terminal silylamide ligands is tilted to allow one close La···H–Si contact with minimum La···Si and La···H distances of 3.191(2) and 2.56(6) Å, respectively. Each bridging ligand exhibits β-diagostic interactions and is aligned in such a way that the two Si–H units of one ligand form close contacts with both $\mathrm{La^{3+}}$ centers. The IR spectrum of **5** supports the presence of both noninteracting ($\nu_{\text{Si-H}}$ = 2092, 2060 cm^{-1}) and interacting ($\nu_{\text{Si-H}}$ = 2023, 1920 cm^{-1}) ^{29}Si–H units.[12] Furthermore, the smaller Si–H coupling in **5** ($^1J_{\text{SiH}}$ = 154 Hz) versus $\mathrm{HN(SiHMe_2)_2}$ ($^1J_{\text{SiH}}$ = 170 Hz)[8] in the ^{1}H NMR spectrum also supports the presence of Si–H β-agostic interactions.[13]

Solvent-free $\mathrm{Ln[N(SiHMe_2)_2]_3}$ complexes are excellent organolanthanide precursors, and binuclear complex **7** is readily obtained in 66% yield after 2 days from the room-temperature reaction of **1** with 2 equiv of $\mathrm{La[N(SiHMe_2)_2]_3}$ (Scheme 1, eq ii). ^{1}H NMR *in situ* experiments indicate that the reaction proceeds in quantitative yield and in >95% purity, with the yield-limiting step being crystallization of the extremely lipophilic product. The Si–H β-agostic interac-

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(4) See, for example: (a) Bauer-Siebenlist, B.; Dechert, S.; Meyer, F. *Chem.–Eur. J.* **2005**, *11*, 5343–5352. (b) Collman, J. P.; Boulatov, R.; Sunderland, C. J.; Fu, L. *Chem. Rev.* **2004**, *104*, 561–588. (c) Voo, J. K.; Riordan, C. G.; Zahkarov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 4422–4423. (d) Bruice, T. C. *Acc. Chem. Res.* **2002**, *35*, 139–148.

(5) For examples of multinuclear catalysis, see: (a) Li, H.; Marks, T. J. *PNAS* **2006**, *103*, 15295–15302. (b) Feng, G.; Natale, D.; Prabaharan, R.; Mareque-Rivas, J. C.; Williams, N. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 7056–7059. (c) Noh, S. K.; Jung, W.; Oh, H.; Lee, Y. R.; Lyoo, W. S. *J. Organomet. Chem.* **2006**, 5000–5006. (d) Martin, M.; Sola, E.; Tejero, S.; Lopez, J. A.; Oro, L. A. *Chem.–Eur. J.* **2006**, *12*, 4057–4068. (e) Trost, B. M.; Jaratjaroonphong, J.; Reutrakul, V. *J. Am. Chem. Soc.* **2006**, *128*, 2778–2779. (f) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421–431. (g) Molenveld, P.; Engbersen, J. F. J.; Reinhoudt, D. N. *Chem. Soc. Rev.* **2000**, *29*, 75.

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(8) Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M *J. Chem. Soc., Dalton Trans.* **1998**, 847–858.

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(11) The Y analogue, prepared via a different methodology, is isostructural: Dietrich, H. M.; Meermann, C.; Törnroos, K. W.; Anwander, R. *Organometallics* **2006**, *25*, 4316–4321.

Scheme 1. Syntheses of Phenylene-Bridged Binuclear Lanthanide Complexes

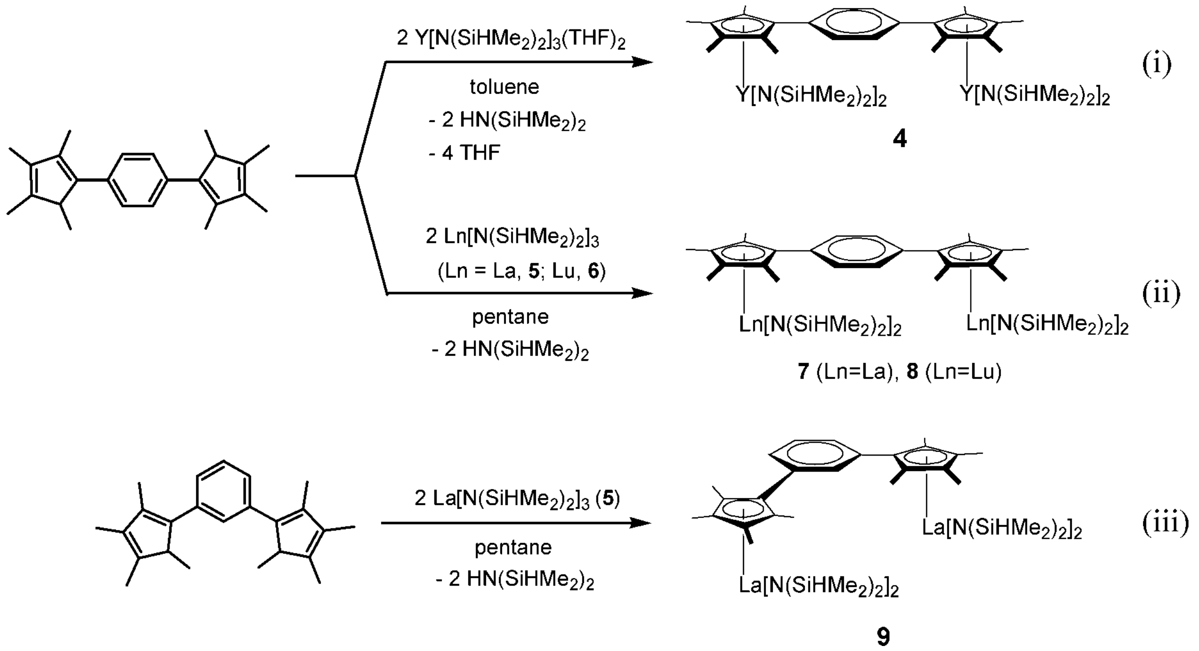

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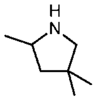
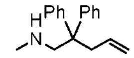
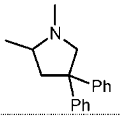
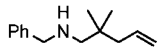
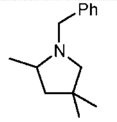
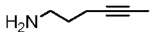
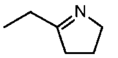
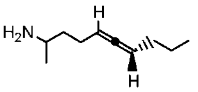
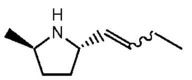
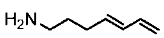
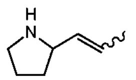
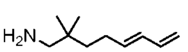
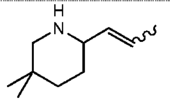
Table 1. Summary of Hydroamination/Cyclization Processes with Binuclear Organolanthanide Catalysts

Entry	Substrate	Product[a]		Precatalyst	N_t, hr^{-1} (°C)[b]
1.				*p*-Y_2 (**4**)	0.3 (25)
2.				*p*-La_2 (**7**)	0.4 (25)
3.				*p*-La_2 (**7**)	2 (60)
4.				*m*-La_2 (**9**)	0.7 (25)
5.				$La[N(SiHMe_2)_2]_3$ (**5**)	3 (25)
6.				$Cp'_2LaCH(TMS)_2$	95 (25)[c]
7.				*p*-La_2 (**7**)	No rxn (25)
8.				*p*-La_2 (**7**)	1 (60)
9.				*p*-La_2 (**7**)	No rxn (60)
10.				*p*-La_2 (**7**)	1 (120)
11.				*p*-La_2 (**7**)	0.4 (25)
12.				$Cp'_2SmCH(TMS)_2$	96 (25)[d]
13.			(E:Z = 44:56)	*p*-La_2 (**7**)	0.8 (25)
14			(E:Z = 42:58)	*m*-La_2 (**9**)	0.3 (25)
15.			(E:Z = 45:55)	$Cp'_2LaCH(TMS)_2$	(25)[e]
16.			(E:Z = 33:67)	$Cp'_2SmCH(TMS)_2$	>630 (25)[e]
17.			(E:Z = 41:59)	*p*-La_2 (**7**)	0.07 (25)
18.			(E:Z = 43:57)	*p*-La_2 (**7**)	~10 (60)
19.			(E:Z = 38:62)	*m*-La_2 (**9**)	0.02 (25)
20.			(E:Z = 27:73)	*m*-La_2 (**9**)	0.9 (60)
21.			(E:Z = 84:16)	$Cp'_2LaCH(TMS)_2$	40 (25)[f]
22.			(E:Z = 60:40)	*p*-La_2 (**7**)	0.03 (25)
23.			(E:Z = 57:43)	*p*-La_2 (**7**)	10 (60)
24.			(E:Z = 93:7)	$Cp'_2LaCH(TMS)_2$	21 (25)[f]

[a] Yields >95% determined by ^1H NMR spectroscopy. [b]Turnover frequencies measured in C_6D_6 with 3–5 mol % precatalyst (normalized to number of Ln centers). [c]Ref 2m. [d]Ref 2j. [e]Ref 2g. [f]Ref 2d.

tions with the La^{3+} center remain intact in **7**, as evidenced by the low ν_{Si-H} IR frequencies (1995, 1874 cm^{-1}) and the diminished $^{29}Si-H$ coupling ($^1J_{SiH}$ = 144 Hz) in the ^1H NMR spectrum. Unlike the mononuclear analogue $Cp'La[N(SiHMe_2)_2]_2$,[14] complex **7** does not show signs of disproportionation in solution, even when heated to 90 °C in C_6D_6.

Similarly to the La^{3+} analogue, $Lu[N(SiHMe_2)_2]_3$ (**6**) can be generated from $Lu[N(TMS)_2]_3$ transamination with $HN(SiHMe_2)_2$. Although reagent **6** was not scrupulously purified, reaction of the crude compound with ligand reagent **1** in

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(12) Weidlein, J.; Muller, U.; Dehnicke, K. Vibration Frequencies; Thieme: Stuttgart, New York, 1986;Bd. 1.

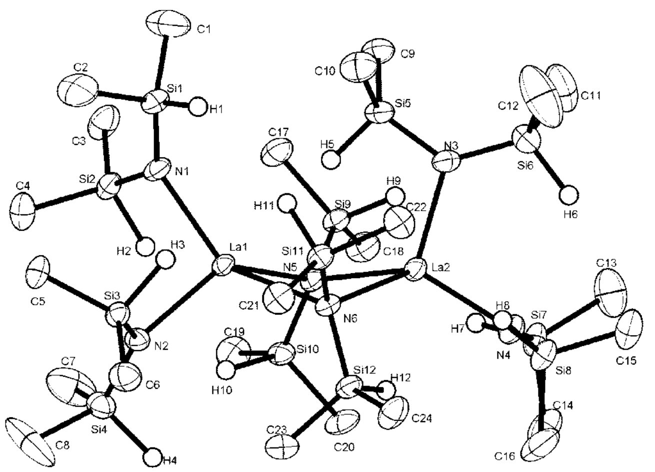

Figure 1. Crystal structure of complex **5**. All hydrogen atoms except those directly attached to Si are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): La1−N1, 2.381(5); La1−N2, 2.386(4); La1−N5, 2.695(4); La1−N6, 2.670(4); La2−N3, 2.375(5); La2−N4, 2.366(5); La2−N5, 2.629(5); La2−N6, 2.622(5); La1···Si2, 3.234(2); La1···Si3, 3.191(2); La1···Si10, 3.306(2); La1···Si11, 3.430(2); La2···Si5, 3.335(2); La2···Si8, 3.295(2); La2···Si9, 3.295(2); La2···Si12, 3.336(2); La1···H2, 2.56(6); La1···H3, 2.61(6); La1···H10, 2.62(6); La1···H11, 2.94(8); La2···H5, 2.85(8); La2···H8, 2.76(8); La2···H9, 2.61(6); La2···H12, 2.62(6); La1−N5−La2, 95.4(1); La1−N6−La2, 96.1(1); N1−La1−N2, 97.2(2); N1−La1−N5, 114.4(2); N1−La1−N6, 138.5(2); N2−La1−N5, 126.2(2); N2−La1−N6, 105.9(2); N5−La1−N6, 78.6(1).

refluxing toluene for 3 days affords binuclear Lu complex **8** (eq ii). Heating is necessary in this reaction, presumably owing to the combination of decreased access to the smaller Lu^{3+} ion and competing impurities in the crude Lu[N(SiHMe$_2$)$_2$]$_3$ mixture. As with the La analogue **7**, Si−H *β*-agostic interactions are evident in complex **8** from the diminished ^{29}Si−H coupling ($^1J_{\mathrm{SiH}}$ = 149 Hz) in the ^{1}H NMR. Reaction of 2 equiv of La[N(SiHMe$_2$)$_2$]$_3$ (**5**) with the *m*-phenylene-bridged ligand reagent **2** yields binuclear complex **9** (eq iii), which similarly displays evidence for such Si−H *β*-agostic interactions ($^1J_{\mathrm{SiH}}$ = 144 Hz).

In regard to catalytic properties, binuclear complexes **4**, **7**, and **9**, as well as homoleptic complex **5**, exhibit significant activity for aminoalkene, aminoalkyne, and aminodiene intramolecular hydroamination/cyclization (Table 1). All conversions proceed with zero-order dependence on substrate concentration, and *in situ* ^{1}H NMR spectroscopy reveals that the Ln^{3+} centers remain bound to their respective cyclopentadienyl ligands throughout catalytic turnover. Conversions of 4-alkenylamines proceed as with mononuclear lanthanocene catalysts[2m] to yield exocyclic products (Table 1, entries 1–10). Binuclear La^{3+} complexes **7** and **9** mediate these processes with slightly increased turnover frequencies (0.4, 0.7 h^{-1}, respectively; Table 1, entries 2 and 4) versus binuclear Y^{3+} complex **4** (0.3 h^{-1}; Table 1, entry 1), presumably reflecting the increased steric openness of the larger La^{3+} ion. Homoleptic complex **5**, which lacks phenylenecyclopentadienyl ligand steric crowding, effects the most rapid conversion (3 h^{-1}; Table 1, entry 5), although with lower efficiency than the corresponding lanthanocene[2m] (95 h^{-1}; Table 1, entry 6). As expected, increased reaction temperatures result in increased turnover frequencies (Table 1, entry 3). Owing to the increased steric hindrance, heating is required for efficient turnover of secondary amine substrates (Table 1, entries 7–10). The reaction of 4-pentynylamine also produces the same exocyclic product as mononuclear catalysts,[2j] albeit with somewhat decreased efficiency (Table 1, entries 11 and 12).

Reactions of a 4,5-dienylamine (Table 1, entries 13 and 14) parallel trends observed with Cp′$_2$Ln catalysts[2g] (Table 1 entries 15 and 16), exclusively generating the *trans*-pyrrolidine product with a slight *Z* isomer preference. However, the approximately equal *E* and *Z* isomer yields produced by the binuclear catalysts in conjugated aminodiene conversions (Table 1, entries 17–20, 22, and 23) stand in marked contrast to the strong *E* preference exhibited by Cp′$_2$LaCH(TMS)$_2$[2d] (Table 1, entries 21 and 24). Interestingly, binuclear complex **9** shows a stronger *Z* isomer preference than complex **7**. Unlike the reactions with terminal aminoalkenes (Table 1, entries 2 and 4), *para*-substituted binuclear complex **7** exhibits more rapid aminoallene hydroamination/cyclization (0.8 h^{-1}; Table 1, entry 13) than the *meta*-substituted complex **9** (0.3 h^{-1}; Table 1, entry 14). Similarly, the reactions with aminodiene substrates also proceed more rapidly with **7** (0.07 h^{-1}; Table 1, entry 17) than with **9** (0.02 h^{-1}; Table 1, entry 19). These lesser rates for **9** are likely a result of hindered approaches for *internal* alkene units caused by the closer substituents at the *meta* position.

In summary, the binuclear single-ring organolanthanide complexes described here efficiently mediate aminoalkene, aminoalkyne, and aminodiene intramolecular hydroamination/cyclization. Reactivity and/or selectivity enhancements indicative of unambiguous cooperativity effects are not pronounced in this system. Studies further exploring the reactivity and selectivity of such multinuclear catalysts are in progress.

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Supporting Information Available: Detailed synthetic procedures and characterization data for all new compounds. Crystallographic data for complex **5** is available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Mononuclear complex Cp′La[N(SiHMe$_2$)$_2$]$_2$ is quantitatively formed by the stoichiometric reaction between La[N(SiHMe$_2$)$_2$]$_3$ and Cp′H within 1 h. Disproportionation of Cp′La[N(SiHMe$_2$)$_2$]$_2$ is observed in C$_6$D$_6$ at room temperature. Unpublished results.