# Catalytic Activity of an Encaged Verkade's Superbase in a Base-Catalyzed Diels−Alder Reaction

Bastien Chatelet,[†] Véronique Dufaud,[‡] Jean-Pierre Dutasta,[†] and Alexandre Martinez*,[†]

[†]Laboratoire de Chimie, École Normale Supérieure de Lyon, CNRS, UCBL, 46 allée d'Italie, F-69364 Lyon, France
[‡]Université de Lyon, Laboratoire de Chimie, Catalyse, Polymère, Procédés (C2P2), CNRS, Université Claude Bernard Lyon1, CPE Lyon, 43 Bd du 11 novembre 1918, F-69616 Villeurbanne cedex, France

**S** *Supporting Information*
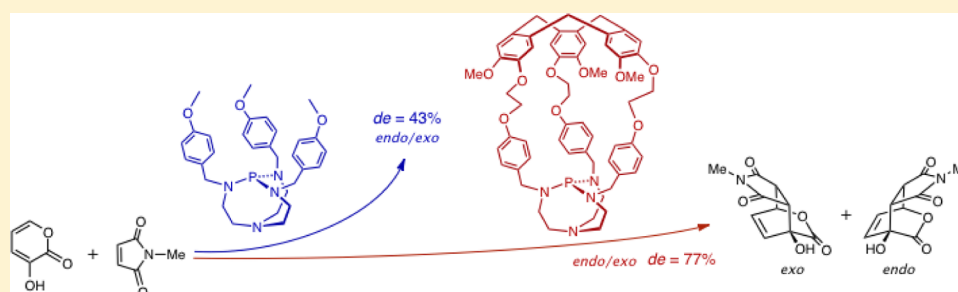
**ABSTRACT:** Organocatalysis in a confined space has been performed through encapsulation of a proazaphosphatrane superbase in a hemicryptophane host. The resulting catalyst displays good to high catalytic activity in the base-catalyzed Diels−Alder reactions investigated. A comparison with the model superbase, which lacks a cavity, shows much higher diastereomeric excess with the encaged proazaphosphatrane for the reaction of 3-hydroxy-2-pyrone with *N*-methylmaleimide. The use of an encaged superbase as organocatalyst is unprecedented and highlights how the confinement may impact the stereoselectivity.

## INTRODUCTION

Because of their high activity and selectivity, enzymes have been a source of inspiration for supramolecular catalysis.[1−13] The peculiar confined environment induced by the cavity around the substrate should provide a structural preorganization that can stabilize a transition state and ensure the desolvation of the guest molecule. The design of such nanoreactors appears very promising to develop new catalytic processes. Molecular capsules allowing encapsulation of a substrate in a restrained space have already been described as reaction vessels for chemical transformations.[3] The specific size, shape, and chemical environment of the confined nanospace induce new activities and selectivities by imposing specific orientation and conformation of the guest molecule. Nevertheless, there are only few examples of molecular containers dealing with the encapsulation of a reactive center (either organic or metallic) through the endohedral functionalization of the molecular host.[14,15]

Among the host structures presenting an endohedral functionalization, hemicryptophanes appear as good candidates.[16] For instance, the introduction of an oxidovanadium or a zinc metal center has led to highly active supramolecular catalysts for the oxidation of sulfide to sulfoxide or the hydrolysis of methyl *para*-nitrophenyl carbonate.[17−19] In particular, it was shown that both catalysts displayed higher rate constants than their related models without a cavity. The insertion of a Cu(II) ion in the hemicryptophane structure was

also described, and the resulting catalyst was applied in C−H oxidation reactions.[20]

Recently, we have reported the synthesis of the hemicryptophane-capped proazaphosphatrane **1** as a potential supramolecular organocatalyst (Figure 1).[21,22] Proazaphosphatranes, often named Verkade's superbases ($pK_a \approx 32$), belong to the class of nonionic strong bases combining phosphorus and nitrogen atoms[23,24] and are now broadly used as basic or nucleophilic catalysts in organic reactions, including transesterification, allylation, silylation, and elimination.[25−36] It was found that the confinement of the organocatalyst in a
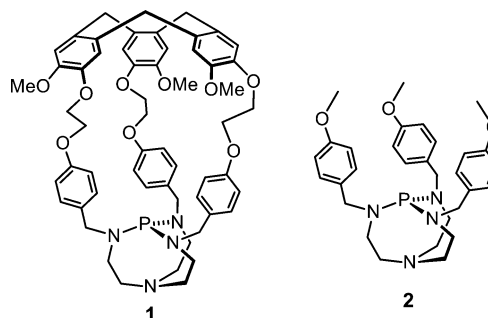


**Figure 1.** Supramolecular superbase **1** and the corresponding model **2**.

hemicryptophane structure affects the $pK_a$ values of the proazaphosphatranes. The increase or decrease of the superbasic character of the compounds, when compared to their open-faced model molecules, strongly depends on the hemicrytophane structure. Moreover, the encapsulation of the phosphorus moiety also dramatically impacts the rate of proton transfer. Because of this remarkable change in reactivity induced by the confinement of the active site, we decided to investigate further the catalytic activity of such supramolecular superbases. Herein, we report the first use of an encaged Verkade's superbase as a basic organocatalyst. Comparison with the model compound, which lacks a cavity, in a base-catalyzed Diels−Alder reaction showed that the confinement strongly improved the diastereoselectivity, favoring the *endo* adducts.

### ■ RESULTS AND DISCUSSION

The Diels−Alder reaction, which allows the simultaneous regio- and stereoselective formation of two carbon−carbon bonds, is one of the most powerful reactions in organic synthesis. A supramolecular approach based on molecular recognition using nanoreactors has been reported to improve very efficiently the rate and the selectivity of this reaction.[37−39] The design of systems capable of catalyzing cycloaddition between anthrone [9-(10*H*)-anthracetone] and dienophiles is of continuous interest since anthrone can act as a protecting group for a wide range of olefins.[40−42] Thus, the reactivity of the supramolecular (**1**) and model (**2**) proazaphosphatrane-based catalysts was first examined in the base-catalyzed Diels−Alder reaction of anthrone with two electron-deficient dienophiles, namely, *N*-methylmaleimide and dimethylfumarate (Scheme 1).

**Scheme 1. Diels−Alder Reaction of Anthrone with (a) *N*-Methylmaleimide and (b) Dimethylfumarate**
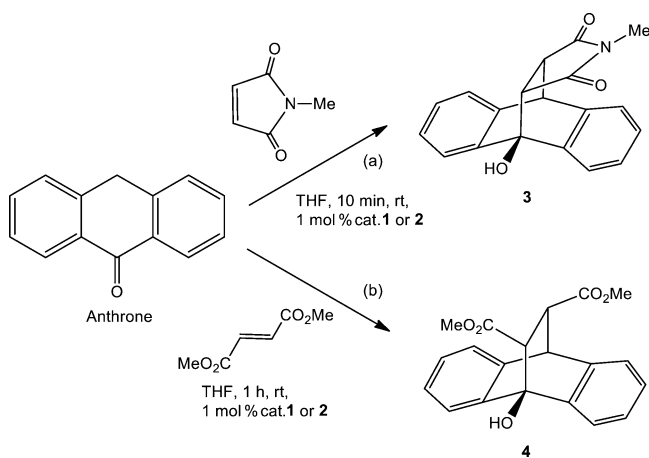


Reactions were carried out in THF at room temperature with an equimolar mixture of anthrone and the corresponding dienophile in the presence of 1 mol % of catalyst. Under these conditions, the cycloadducts **3** and **4** were the only products obtained (no Michael adduct was detected). Both compounds **1** and **2** are efficient catalysts, leading to high and comparable yields, much higher than those obtained with the triethylamine (NEt₃) reference catalyst (Table 1).

To compare more accurately the catalytic activity of **1** and **2**, the time course for the Diels−Alder reaction of anthrone with dimethylfumarate, in the presence of **1** or **2**, was followed by

**Table 1. Diels−Alder Reaction between Anthrone and *N*-Methylmaleimide or Dimethylfumarate in the Presence of Catalysts 1, 2, or NEt₃**

| catalyst | yields (%)[a] | |
| --- | --- | --- |
| | 3 | 4 |
| − | <1 | <1 |
| 1 | 95 | 100 |
| 2 | 100 | 95 |
| NEt₃ | 38 | 3 |

[a]Yields were determined from NMR spectra using 2,4-dibromomesitylene as internal reference.

NMR spectroscopy. The reaction between anthrone and the very reactive dienophile *N*-methylmaleimide was too fast to allow for accurate monitoring (the reaction was completed in less than 10 min). The results are shown in Figure 2. The rate
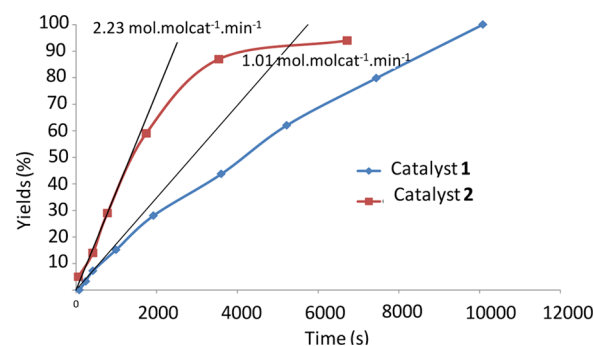


**Figure 2.** Time course of the Diels−Alder reaction between anthrone and dimethylfumarate catalyzed by **1** and **2** (THF, $T$ = 298 ± 1 K, 1 mol % of catalyst).

constant was found to be 2-fold lower with the supramolecular catalyst **1** than with the model **2** ($k(\mathbf{2})/k(\mathbf{1})$ = 2.2). Interestingly, the decrease in activity imposed by the confinement is much lower for this reaction than that previously observed for the rate of protonation of the proazaphosphatrane moiety in acetonitrile, which was found to be 100 times lower with the encapsulated species than with the model compound.[8] This constitutes a key point in the development of supramolecular catalysts based on encaged Verkade's superbases, since (i) a decrease of reactivity similar to that previously observed for the proton transfer would strongly limit the interest of such systems, and (ii) this supramolecular catalyst does not suffer from product inhibition,[43] highlighting the relevance of designing more efficient encaged catalysts, based on hemicryptophane structures.

Given the efficiency of our system for the cycloaddition of anthrone with dienophiles, we then investigated the Diels−Alder reaction of 3-hydroxy-2-pyrone with *N*-methylmaleimide and dimethylfumarate (Scheme 2). This reaction is known to be an attractive method to access a wide variety of functional cycloadducts that can be used as building blocks, after decarboxylation, for the synthesis of polyoxygenated natural products.[44,45] Moreover, this reaction leads to the formation of *endo* and *exo* diastereomeric products, allowing the study of the stereoselectivity of the reaction with respect to the confinement of the active site. The reactions were performed under the same conditions than those described above: 1:1 diene-to-dienophile molar ratio, room temperature, THF as solvent, and 1 mol % of catalyst. Two main conclusions can be drawn from Table 2.

**Scheme 2. Diels−Alder Reaction of 3-Hydroxy-2-pyrone with (a) *N*-Methylmaleimide and (b) Dimethylfumarate**
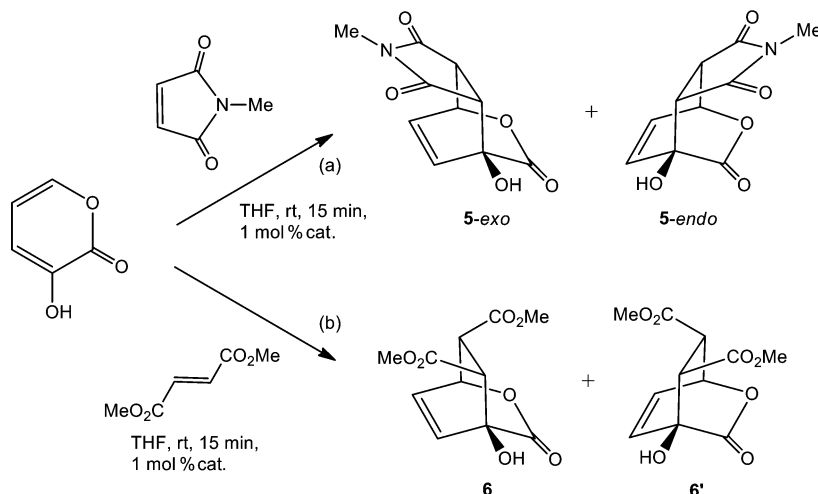


**Table 2. Diels−Alder Reaction between 3-Hydroxy-2-pyrone and *N*-Methylmaleimide or Dimethylfumarate with Catalysts 1 and 2**

| dienophile | catalyst | compound (%)[a] | de (%)[b] |
|---|---|---|---|
| dimethylfumarate | 2 | 6 (95) | 20 |
| dimethylfumarate | 1 | 6 (<1) | |
| *N*-methylmaleimide | 2 | 5 (99) | 43[c] |
| *N*-methylmaleimide | 1 | 5 (100) | 77[c] |

[a]Yields were determined from NMR spectra using 2,4-dibromomesitylene as internal reference. [b]Diastereomeric excesses were determined by NMR. [c]The major product is 5-*endo*.[48]

First, an important difference between the two catalysts is observed; the model **2** is able to perform this reaction efficiently with both substrates, and high yields are obtained in less than 10 min (99% and 95% yields for *N*-methylmaleimide and dimethylfumarate, respectively). In contrast, the supramolecular catalyst **1** displays a catalytic activity, which is substrate-dependent. A quantitative yield is achieved with *N*-methylmaleimide as dienophile, whereas no reaction occurs with dimethylfumarate. The confinement of the organocatalyst in a deep and narrow cavity combined with steric hindrance of the *trans*-dimethylfumarate could account for this result. This highlights that encaging the Verkade's superbase induces an improvement of its ability to carry out substrate-dependent reactions. Second, both catalysts display quantitative yields for the reaction between 3-hydroxy-2-pyrone and *N*-methylmaleimide, but a much higher diastereomeric excess is observed with the supramolecular catalyst than with the corresponding model (77% and 43%, respectively, both in favor of the **5**-*endo* product). This is in agreement with previous reports that suggest that a catalyst presenting a deep and narrow cavity should favor *endo* control of the reaction.[46,47] Moreover, large active sites allow various transition-state geometries, whereas a catalyst encaged in a tight space can limit them, thus favoring the more compact ones and leading to an overall improvement of the selectivity. This constitutes an important step in the development of encaged catalysts based on the hemicryptophane structure. Not only the yields and catalytic activities are only slightly altered by the confinement of the active site, but the encapsulation of the organocatalyst also improves the stereoselectivity of the Diels−Alder reaction. Furthermore, these results show that the space above the basic

phosphorus center strongly affects the substrate and stereoselectivity of the reaction, suggesting that a partial encapsulation of at least the activated diene occurs during the reaction. This is also supported by the low polarity and acidity of the solvent (THF): the deprotonation of the diene by the Verkade's superbase has to take place inside the cavity, giving a tight ion pair; then, the anionic diene reacts with the dienophile, this latter being probably not trapped inside the cavity.

## ■ CONCLUSION

In summary, we have reported on the unprecedented use of an encaged proazaphosphatrane superbase as an efficient organocatalyst in two base-catalyzed Diels−Alder reactions. High yields were obtained with both the model and the supramolecular catalysts. The catalytic activity in the confined space of the hemicryptophane cage remains very close to that of the uncapped proazaphosphatrane. Interestingly, the diastereoselectivity of the Diels−Alder reaction can be improved by encaging the catalytic species. This emphasizes the relevance of the hemicryptophane structure to design highly effective supramolecular catalysts, since, depending on the reaction and the catalytic site considered, such an encapsulation could enhance the reaction rate, the stability of the catalyst, or the selectivity.

## ■ EXPERIMENTAL SECTION

**Methods and Materials.** All manipulations were conducted at 298 K, under an inert atmosphere or vacuum conditions using Schlenk techniques, including the transfer of the catalysts to the reaction vessel. The solvents were dried using standard methods and stored over 4 Å activated molecular sieves. Anthrone, dimethylfumarate, *N*-methylmaleimide, and 3-hydroxy-2-pyrone were purchased from commercial suppliers. Compounds **1** and **2** were synthesized as previously reported.[21] The *endo* and *exo* isomers obtained in the Diels−Alder reactions of 3-hydroxy-2-pyrone with *N*-methylmaleimide were assigned according to the literature.[49]

**Cycloaddition of 3-Hydroxy-2-pyrone and *N*-Methylmaleimide.** In a 10 mL round-bottom flask, 3-hydroxy-2-pyrone (30 mg, 0.268 mmol), dibromomesitylene (as an internal standard), superbase catalyst (1 mol %), and THF (1 mL) were successively added. Then, *N*-methylmaleimide (30 mg, 0.270 mmol) was added, and the reaction was allowed to proceed. After 15 min of stirring, a solution of 4 M HCl in 1,4-dioxane (0.005 mL) was added in order to quench the reaction. Volatiles were reduced in vacuo, and the final solid residue was

dissolved in DMSO-$d6$ to allow the estimation of the reaction yield via NMR quantification. The $^1H$ NMR displays the characteristic signals for **5**-*endo* and **5**-*exo*: $^1H$ NMR of **5**-*endo* (250 MHz, DMSO-$d6$): 6.51 (br d, $J$ = 8.1 Hz, 1H), 6.42 (dd, $J$ = 4.8, 8.1 Hz, 1H), 5.59 (dt, $J$ = 1.8, 4.8 Hz, 1H), 3.95 (br s, 1H), 3.77 (dd, $J$ = 4.8, 8.1 Hz, 1H), 3.13 (d, $J$ = 8.1 Hz, 1H), 2.97 (s, 3H). $^1H$ NMR of **5**-*exo* (250 MHz, CDCl$_3$): 6.60−6.51 (m, 2H), 5.60−5.67 (m, 1H), 3.92 (br s, 1H), 3.27 (dd, $J$ = 2.2, 9.2 Hz, 1H), 3.20 (d, $J$ = 1 Hz, 9.2 Hz, 1H), 2.99 (s, 3H). The stereochemistry was assigned according to the literature.[48]

**Cycloaddition of 3-Hydroxy-2-pyrone and Dimethylfumarate.** In a 10 mL round-bottom flask, 3-hydroxy-2-pyrone (30 mg, 0.268 mmol), dibromomesitylene (as an internal standard), superbase catalyst (1 mol %), and THF (1 mL) were successively added. Then, dimethylfumarate (39 mg, 0.270 mmol) was added, and the reaction was allowed to proceed. After 15 min of stirring, a solution of 4 M HCl in 1,4-dioxane (0.005 mL) was added in order to quench the reaction. Volatiles were reduced in vacuo, and the final solid residue was dissolved in CDCl$_3$ to allow the estimation of the reaction yield via NMR quantification. The $^1H$ NMR displays the characteristic signals for **6**-*endo* and **6**-*exo*: $^1H$ NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) 6.54−6.52 (m, 1 H), 6.50−6.45 (m, 2H), 6.42−6.40 (m, 1H), 5.56−5.55 (m, 1H), 5.49−5.47 (m, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.60 (dd, 1H, $J$ = 5.9 Hz and $J$ = 3.7 Hz), 3.43 (d, 1H, $J$ = 4.7 Hz), 3.26 (d, 1H, $J$ = 5.9 Hz), 3.20 (dd, 1H, $J$ = 4.5 Hz and $J$ = 1.6 Hz).

**Cycloaddition of Anthrone and *N*-Methylmaleimide.** In a 10 mL round-bottom flask, anthrone (25 mg, 0.129 mmol), dibromomesitylene (as an internal standard), and superbase catalyst (1 mol %) were successively added. The round-bottom flask was put in an ice bath, and THF (1.2 mL) was added before stirring the whole mixture. Then, *N*-methyl maleimide (14.3 mg, 0.130 mmol) was added, and the reaction was allowed to proceed. After 10 min of stirring, a solution of 4 M HCl in 1,4-dioxane (0.005 mL) was added in order to quench the reaction. Volatiles were removed in vacuo, and the final solid residue was dissolved in CDCl$_3$ to allow the determination of the reaction yield via NMR quantification.

The $^1H$ NMR displays the characteristic signals for **3**: $^1H$ NMR (250 MHz, CDCl$_3$) $\delta$ (ppm) 7.47 (d, 1H, $J$ = 7.5 Hz), 7.68 (d, 1H, $J$ = 7.5 Hz), 7.36 (d, 1H, $J$ = 7.5 Hz), 7.21 (m, 5H), 4.71 (d, 1H, $J$ = 3.5 Hz), 4.48 (s, 1H), 3.31 (dd, 1H, $J$ = 8.5, 3.5 Hz), 2.50 (s, 3H).[42]

**Cycloaddition of Anthrone and Dimethylfumarate.** In a 10 mL round-bottom flask, anthrone (25 mg, 0.129 mmol), dibromomesitylene (as an internal standard), and superbase catalyst (1 mol %) were successively added, followed by THF (1 mL). Then, dimethylfumarate (18.6 mg, 0.129 mmol) was added, and the reaction was allowed to proceed. After 1 h, a solution of 4 M HCl in 1,4-dioxane (0.005 mL) was added in order to quench the reaction. Volatiles were removed in vacuo, and the final solid residue was dissolved in CDCl$_3$ to allow the estimation of the reaction yield via NMR quantification. The $^1H$ NMR displays the characteristic signals for **4**: $^1H$ NMR (250 MHz, CDCl$_3$) $\delta$ (ppm) 7.66 (d,1H, $J$ = 7.5 Hz), 7.53 (d, 1H, $J$ = 7.5 Hz), 7.32 (d, 1H, $J$ = 7.0 Hz), 7.21 (m, 3H), 7.13 (m, 2H), 5.30 (s, 1H), 4.67 (d,1H, $J$ = 3.0 Hz), 3.65 (s,3H), 3.58 (9, 3H), 3.46 (d, 1H, $J$ = 5.0 Hz), 3.42 (dd, 1H, $J$ = 5,3 Hz).[42]

The reaction was monitored by taking 0.1 mL aliquots from the reaction mixture. A few drops of a 4 M HCl solution in 1,4-dioxane were added to this sample in order to quench the reaction. Volatiles were removed in vacuo, and the final solid residue was dissolved in CDCl$_3$ to allow the estimation of the reaction yield via NMR quantification. The ratio of the rate constants is given by the ratio of the slopes at short times of the curves displayed in Figure 2.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

Determination of the yields, from $^1H$ NMR spectra, for the reactions of 3-hydroxy-2-pyrone with dimethylfumarate and of anthrone with *N*-methylmaleimide; $^1H$ NMR spectra recorded to monitor the catalytic reactions of 3-hydroxy-2-pyrone with dimethylfumarate in the presence of catalyst **1** or **2**; and $^1H$ NMR experiment for the assignment of the *endo* and *exo* isomers in the reaction of 3-hydroxy-2-pyrone with *N*-methylmaleimide. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: alexandre.martinez@ens-lyon.fr.

### Notes

The authors declare no competing financial interest.

## REFERENCES

(1) Rebek, J., Jr. *Acc. Chem. Res.* **2009**, *42*, 1660.
(2) Lehn, J.-M. *Rep. Prog. Phys.* **2004**, *67*, 245.
(3) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418.
(4) Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H. *Chem. Soc. Rev.* **2008**, *37*, 247.
(5) Feiters, M. C.; Rowan, A. E.; Nolte, R. J. M. *Chem. Soc. Rev.* **2000**, *29*, 375.
(6) Kirby, A. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 707.
(7) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349.
(8) Murakami, Y.; Kikuchi, J.; Hisaeda, Y.; Hayashida, O. *Chem. Rev.* **1996**, *96*, 721.
(9) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2010**, *50*, 114.
(10) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 11459.
(11) Smith, P. B.; Dye, J. L.; Cheney, J.; Lehn, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6044.
(12) Ciampolini, M.; Nardi, N.; Valtancoli, B.; Micheloni, M. *Coord. Chem. Rev.* **1992**, *120*, 223.
(13) Chambron, J.-C.; Meyer, M. *Chem. Soc. Rev.* **2009**, *38*, 1663.
(14) Shenoy, S. R.; Crisóstomo, F. R. P.; Iwasawa, T.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2008**, *130*, 5658.
(15) Harris, K.; Sun, Q.-F.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2013**, *135*, 12497.
(16) Canceill, J.; Collet, A.; Gabard, J.; Kotzyba-Hibert, F.; Lehn, J.-M. *Helv. Chim. Acta* **1982**, *65*, 1894.
(17) Martinez, A.; Dutasta, J.-P. *J. Catal.* **2009**, *267*, 188.
(18) Makita, Y.; Sugimoto, K.; Furuyosho, K.; Ikeda, K.; Jujiwara, S. I.; Shin-ike, T.; Ogawa, A. *Inorg. Chem.* **2010**, *49*, 7220.
(19) Makita, Y.; Ikeda, K.; Sugimoto, K.; Fujita, T.; Danno, T.; Bobuatong, K.; Ehara, M.; Jujiwara, S. I.; Ogawa, A. *J. Organomet. Chem.* **2012**, *706*, 26.
(20) Perraud, O.; Sorokin, A. B.; Dutasta, J.-P.; Martinez, A. *Chem. Commun.* **2013**, *49*, 1288.
(21) Dimitrov-Raytchev, P.; Martinez, A.; Gornitzka, H.; Dutasta, J.-P. *J. Am. Chem. Soc.* **2011**, *133*, 2157.
(22) Chatelet, B.; Gornitzka, H.; Dufaud, V.; Jeanneau, E.; Dutasta, J.-P.; Martinez, A. *J. Am. Chem. Soc.* **2013**, *135*, 18659.
(23) Schwesinger, R.; Hasenfratz, C.; Schlemper, H.; Walz, L.; Peters, E. M.; Peters, K.; Von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1361.
(24) Schwesinger, R.; Schlemper, H. *Angew. Chem.* **1987**, *99*, 1212.
(25) Lensink, S. K. X.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.
(26) Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 5431.
(27) Raders, M. R.; Verkade, J. G. *J. Org. Chem.* **2010**, *75*, 5308.
(28) For a review on Verkade's superbases, see: Kisanga, P. B.; Verkade, J. G. *Tetrahedron* **2001**, *57*, 467.
(29) Verkade, J. G.; Kisanga, P. *Tetrahedron* **2003**, *59*, 7819.
(30) Chintareddy, V. R.; Wadhwa, K.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 8118.

(31) Wadhwa, K.; Chintareddy, V. R.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 6681.

(32) Wadhwa, K.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 5683.

(33) Wadhwa, K.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 4368.

(34) Urgaonkar, S.; Verkade, J. G. *Org. Lett.* **2005**, *7*, 3319.

(35) Su, W.; McLeod, D.; Verkade, J. G. *J. Org. Chem.* **2003**, *68*, 9499.

(36) Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem.* **2010**, *75*, 7166.

(37) Murase, T.; Horiuchi, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 2866.

(38) Nishioka, Y.; Yamagushi, T.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 7000.

(39) Ikemoto, K.; Inokuma, Y.; Fujita, M. *J. Am. Chem. Soc.* **2011**, *133*, 16806.

(40) Harrison, R.; Rickborn, B. *Org. Lett.* **2002**, *4*, 1711.

(41) Koerner, M.; Rickborn, B. *J. Org. Chem.* **1989**, *54*, 9.

(42) Koerner, M.; Rickborn, B. *J. Org. Chem.* **1990**, *55*, 2662.

(43) Sanders, J. K. M. *Chem.—Eur. J.* **1998**, *4*, 1378.

(44) Cano, P.; Echavarren, A.; Prados, P. *J. Org. Chem.* **1983**, *48*, 5373.

(45) Corey, E. J.; Kozikowski, A. P. *Tetrahedron Lett.* **1975**, *28*, 2389.

(46) Hatano, M.; Ishihara, K. *Chem. Commun.* **2012**, *48*, 4273.

(47) Hatano, M.; Mizuno, T.; Izumiseki, A.; Usami, R.; Asai, T.; Akarura, M.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 12189.

(48) Okamura, H.; Iwagawa, T.; Nakatani, M. *Tetrahedron Lett.* **1995**, *36*, 5939.