

# Potassium Yttrium Ate Complexes: Synergistic Effect Enabled Reversible H<sub>2</sub> Activation and Catalytic Hydrogenation

Dan-Dan Zhai, Hui-Zhen Du, Xiang-Yu Zhang, Yu-Feng Liu, and Bing-Tao Guan\*®

State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

**Supporting Information** 

**ABSTRACT:** A potassium yttrium benzyl ate complex was generated simply by mixing an yttrium amide and potassium benzyl. The benzyl ate complex could undergo peripheral deprotonation to produce a cyclometalated complex or hydrogenation to give a hydride ate complex. The latter hydride ate complex features a  $(KH)_2$  structure protected by two yttrium amide complexes. The synergistic effect between potassium hydride and the amide ligand enables the complex to deprotonate a methyl C–H bond. The combination of intramolecular deprotonation of the hydride ate complex and



hydrogenation of the cyclometalated complex constitutes a reversible  $H_2$  activation process. Using this process involving formal addition and elimination of  $H_2$ , we accomplished the catalytic hydrogenation of alkenes, alkynes, and imines.

**KEYWORDS:** potassium hydride, ate complex, synergistic effect, reversible H<sub>2</sub> activation, hydrogenation

Reversible activation of  $H_2$  is crucial both for energy storage and for catalytic hydrogenation reactions, which are among the most fundamental transformations in organic synthesis; various metal-mediated  $H_2$  activation processes have been reported.<sup>1</sup> Activation of  $H_2$  with late-transition-metal catalysts, either heterogeneous or homogeneous, occurs via a redox process at the metal center (Scheme 1, eq 1).<sup>2</sup> Over the past couple of decades, metal–ligand cooperation in pincer complexes of late-transition metals has emerged as a powerful alternative  $H_2$  activation strategy to the redox process (Scheme

## Scheme 1. Metal-Mediated H<sub>2</sub> Activation

M: late-transition metals

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$$M \xrightarrow{H} H \xrightarrow{\text{oxidative addition}} M \xrightarrow{H} (eq 1)$$

$$(eq 1)$$

$$(X \xrightarrow{H} \text{metal-ligand cooperation} (X \xrightarrow{H} (eq 2))$$

widativa addition

M: early-transition metals or s-block metals

$$\begin{array}{ccc} & C & H & \sigma \text{-bond metathesis} & (-C-H) \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

This work:



1, eq 2).<sup>3</sup> In contrast, alkyl early transition-metal catalysts prefer to undergo  $\sigma$ -bond metathesis reaction<sup>4</sup> between the M-C bond and H<sub>2</sub>, proceeding via a four-centered transition state and giving an alkane and a metal hydride complex (Scheme 1, eq 3).<sup>4-6</sup> Metal hydride complexes, which are important intermediates and catalyst precursors, have been extensively studied over the past several decades, because of their versatile structures and reactivities.7 Some hydride complexes are reactive enough to undergo intramolecular C-H bond activation of their own ligands to give "tuck-in" cyclometalated complexes and liberate H<sub>2</sub>.<sup>8</sup> The combination of internal deprotonation of a hydride complex and hydrogenation of the cyclometalated complex constitutes a process for reversible activation of  $H_2$ , which provide a  $H_2$  activation approach involving early transition metals and even s-block metals.<sup>9</sup> In 1979, Andersen and co-workers reported  $\gamma$ metalation reactions of actinide hydride complexes HAn[N- $(SiMe_3)_2]_3$  (An = Th and U) in which  $H_2$  is reversibly activated via  $\gamma$ -deprotonation of one of the silylamide ligands and subsequent hydrogenation of a four-membered metallocycle.<sup>9a,b</sup> The research groups of Evans, Teuben, Chirik, and Sutton reported the reversible addition and release of H<sub>2</sub> from metallocene hydrides of samarium, yttrium, cerium, and zirconium.<sup>9c-g</sup> Okuda recently achieved a reversible H<sub>2</sub> release and capture by using a cationic lutetium polyhydride complex;<sup>9h</sup> specifically, a C-H bond of one of the methyl groups of the neutral Me<sub>4</sub>TACD ligand of the complex is

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activated. Despite these achievements, this reversible  $H_2$  activation process remains underdeveloped in catalytic transformations.

Because of the strong coordination ability of the hydride anion, hydride complexes of early transition metals and s-block metals usually prefer to form dimers or clusters via bridging coordination of the hydrides to the metals.<sup>7,10</sup> In contrast to the well-developed homometallic hydride complexes, heterometallic hydride complexes have rarely been explored, because of the shortage of available synthetic methods. Several groups have synthesized hydride complexes containing M1-H-M2 moieties (where  $M^1 = Ti$ , Zr, Ln, or Al and  $M^2 = Li$ , Na, or K).<sup>11</sup> However, the reactivity of these heterometallic hydride complexes remains mostly unknown. Herein, we report the synthesis and reactions of a potassium yttrium hydride ate complex featuring a protected  $(KH)_2$  unit. The synergistic effect of the potassium yttrium ate complexes can achieve a reversible H<sub>2</sub> activation and affect the hydrogenation of olefins, alkynes, and imines (Scheme 1, eq 4).

Because anionic rare-earth species form readily as byproducts in alkyl lanthanide synthesis, we began our study by combining an yttrium amide compound with KBn. When KBn, which is insoluble in benzene, was mixed with a  $C_6D_6$  solution of  $Y[N(SiMe_3)_2]_3$ , an orange solution formed rapidly (see Scheme 2). In-situ NMR spectroscopy revealed a doublet at  $\delta$ 





2.22 (I = 4.0 Hz, 2H) in <sup>1</sup>H NMR spectrum and doublet for a secondary carbon atom at  $\delta$  54.2 (J = 33.3 Hz) in the <sup>13</sup>C NMR spectrum, suggesting the generation of an ate complex with a newly formed Y-benzyl bond.<sup>12</sup> As shown in Figure 1 (left), X-ray diffraction (XRD) analysis indicated that the complex (A) is composed of contact ion pairs consisting of  ${\rm YBn}[{\rm N}({\rm SiMe}_3)_2]_3$ <sup>-</sup> and  $[{\rm K}({\rm THF})]^+$ . The potassium cation also coordinates with another molecular unit via an  $\eta^3$   $\pi$ interaction and an agostic interaction, which extends the structure supramolecularly (see the Supporting Information). In its solid state, complex A was stable for months in a glovebox at -35 °C. However, in benzene solution, the complex slowly underwent peripheral deprotonation reactions to produce cyclometalated complex B.<sup>13</sup> XRD analysis of a single crystal of B revealed a four-membered Y-N-Si-C ring similar to that described by Niemeyer (Figure 1, right).<sup>13b</sup>

Upon treatment with  $H_2$ , both benzyl ate complex A and cyclometalated complex B smoothly underwent hydrogenation to produce hydride complex C. X-ray analysis revealed that the hydride atom coordinates not only with the Y atom but also with two K atoms, forming a dimer held together by the interactions between the K and hydride atoms (Figure 2). The



Figure 1. Solid-state structures of potassium yttrium benzyl ate complex A (left) and cyclometalated complex B (right) with thermal ellipsoids set at 50% probability. H atoms (except H19, H19', H13A, and H13B) are omitted for clarity. Selected bond lengths for A: Y1–C19, 2.529(7) Å; K1–C19, 3.238(7) Å; K1–C20, 3.101(7) Å; K1–C21, 3.334(8) Å; K1–H19, 2.799(2) Å. Selected bond angle for A: Y1–C19–K1, 154.169(3)°. Selected bond lengths for B: Y1–C13, 2.452(3) Å; K1–C13, 2.998(3) Å; K1–H13A, 2.814(3) Å; K1–H13B, 2.839(3) Å. Selected bond angle for B: Y1–C13–K1, 177.035(1)°.



Figure 2. Solid-state structure of potassium yttrium hydride ate complex C,  $\{KHY[N(SiMe_3)_2]_3\}_2$ , with thermal ellipsoids set at 50% probability. H atoms (except Ha, Hb, H4, H6, H12, H14, H16, and H18) are omitted for clarity. Selected bond lengths: Y1-Ha, 2.034(2) Å; K1-Ha, 2.728(2) Å; K1-Hb, 2.643(2) Å; K1-H4, 2.661(4) Å; K1-H6, 2.823(4) Å; K1-H12, 2.781(4) Å; K1-H14, 3.104(4) Å; K1-H16, 2.679(3) Å; K1-H18, 2.842(4) Å; K1-N3, 3.029(1) Å. Selected bond angles: Y1-Ha-K1, 148.89(7)°; Ha-K1-Hb, 76.38(5)°; K1-Ha-K1', 103.62(5)°.

core of the dimeric hydride ate complex features a  $(KH)_2$  parallelogram structure. Remarkably, there were no coordinating solvent molecules; only a N atom and two hydride atoms were bonded directly to the K atom. The lack of solvent molecules may be attributable to six agostic interactions with the nearby methyl groups, meeting with the high coordination requirement of the K<sup>+</sup> cation.<sup>14</sup> Formally speaking, we synthesized a hydrocarbon-soluble  $(KH)_2$  unit protected by two yttrium amide complexes via Y–H and K–N coordinative interactions.<sup>15</sup> It is important to note that hydride ate complex C smoothly underwent intramolecular C–H bond activation upon heating to afford cyclometalated complex B with release of two H<sub>2</sub> molecules. Thus, by deprotonation of hydride ate complex C and hydrogenation of deprotonated complex B, we achieved a reversible H<sub>2</sub> activation process.

Given the reversible  $H_2$  activation ability of potassium yttrium ate complexes, we explored their applications for catalytic hydrogenation. After preliminary condition optimization, we achieved complete hydrogenation of 1-octene with 5 mol % of hydride ate complex C as a catalyst in 3 h at 80 °C under a 6 bar  $H_2$  pressure in  $C_6D_6$  (Table 1, entry 1). Complete hydrogenation of 1-octene could also be achieved by using benzyl ate complex A (prepared either in advance or in situ from the yttrium amide and KBn) as the catalyst (Table 1, entries 2 and 3). Control reactions that were conducted with

Table 1. Effects of Hydrogenation Reaction Parameters

C <sub>6</sub> l	H <sub>13</sub> + H <sub>2</sub> $\frac{\{\text{KHY}[\text{N}(\text{SiMe}_3)_2]_3\}_2 (\text{C}, 5 \text{ mol }\%)}{C_6 D_6, 80 \text{ °C}, 3 \text{ h}}$	H H C <sub>6</sub> H <sub>13</sub> 2a
entry	variation from standard conditions <sup>a</sup>	conversion <sup>b</sup> (%)
1	none	99
2	complex A (10 mol %) as catalyst	99
3	KBn + Y[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (10 mol %) as catalyst	99
4	$Y[N(SiMe_3)_2]_3$ (10 mol %) as catalyst	<5
5	KBn (10 mol%) as catalyst	<5
6	KN(SiMe <sub>3</sub> ) <sub>2</sub> (10 mol %) as catalyst	<5
7	KH (10 mol%) as catalyst	<5
8	NaBn + Y[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (10 mol %) as catalyst	70
9 <sup>c</sup>	LiBn' + Y[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (10 mol %) as catalyst	72
10	THF (0.5 mL) as additive	17
11	18-crown-6 (20 mol %) as additive	16
12 <sup>d</sup>	$\{KHY[N(SiMe_3)_2]_3\}_2$ (C, 0.5 mol%), 6 h	99
<sup>a</sup> Standard conditions: 1-octene 1a (0.3 mmol), C (5 mol%), H <sub>2</sub> (6		

"Standard conditions: 1-octene 1a (0.3 mmol), C (S mol%),  $H_2$  (6 bar), 80 °C,  $C_6D_6$  (0.5 mL), 3 h. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>LiBn' = LiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o. <sup>d</sup>1-Octene (1a) (3.0 mmol).

the yttrium amide, KBn, KN(SiMe<sub>3</sub>)<sub>2</sub>, or KH as a catalyst failed to give any of the desired hydrogenation product, suggesting the synergistic effect between KH and yttrium amide plays a crucial role for the catalytic hydrogenation (Table 1, entries 4–7). Combinations of the yttrium amide with LiBn' and with NaBn also catalyzed the hydrogenation, but with lower conversions (Table 1, entries 8 and 9). The addition of THF or 18-crown-6 drastically decreased the conversion (Table 1, entries 10 and 11), probably because coordination of these compounds with the K<sup>+</sup> cation destroyed the hydride ate structure and prevented the synergistic effect. The hydrogenation could actually be achieved, even at a much lower catalyst loading (0.5 mol %), when the reaction time was prolonged to 6 h (Table 1, entry 12).

We then explored the catalytic activity of the potassium yttrium hydride ate complex for the hydrogenation of a variety of alkenes, alkynes, and imines (see Table 2). Trimethylsilylethene, 1,5-hexadiene, and 1,9-decadiene smoothly gave the corresponding alkanes (2b-2d) in high conversions. Interestingly, the reaction of 1,5-hexadiene gave methylcyclopentane (28% yield) as an intramolecular cyclization byproduct, in addition to hexane. The hydrogenation reactions of alkenes with more sterically bulky alkyl substituents were relatively slow, requiring a longer reaction time to achieve complete conversion, they nevertheless afforded the desired alkanes (2e and 2f). Complete conversion of a disubstituted ethene (2,5dimethyl-1,5-hexadiene) to 2g required a reaction temperature of 100 °C. Norbornene smoothly underwent the catalytic hydrogenation under the standard conditions to afford 2h, whereas the hydrogenation of cyclohexene required much harsher conditions to afford 2i. The reaction of styrene resulted in the formation of oligomers, but disubstituted styrenes cleanly afforded catalytic hydrogenation products 2j, 2k, and 2l. 3-Hexyne was also a suitable substrate, undergoing selective semihydrogenation to afford (Z)-3-hexene (2m) in 81% yield (see the Supporting Information). Finally, we found that several imines also underwent hydrogenation to provide the corresponding amines (2n-2q) under the increased H<sub>2</sub> pressure conditions.



<sup>\*</sup>Conditions: 1 (0.3 mmol), C (5 mol %), H<sub>2</sub> (6 bar), 80 °C, C<sub>6</sub>D<sub>6</sub> (0.5 mL). Conversions were determined by <sup>1</sup>H NMR spectroscopy. <sup>a</sup>Methylcyclopentane also formed (in 28% yield). <sup>b</sup>100 °C. °H<sub>2</sub> (12 bar). <sup>d</sup>Z/E = 11:1 (determined by inverse gated decoupled spectroscopy), along with 11% 2-hexene (Z/E = 2.5:1). °H<sub>2</sub> (10 bar).

#### **Scheme 3. Control Experiments**



To gain insight into the mechanism of this catalytic hydrogenation reaction, we performed the hydrogenation of complex **B** with  $H_2$  and  $D_2$  under identical conditions at room temperature (Scheme 3, eqs 5 and 6). We found that the reaction of **B** with  $H_2$  was twice as fast as its reaction with  $D_2$ . A similar kinetic isotope effect (1.9) was also measured for the **B**-catalyzed hydrogenation of 1,1-diphenylethylene (1j) with  $H_2$  and  $D_2$ , (Scheme 3, eqs 7 and 8). For the reaction between **C** and  $D_2$ , we observed the emergence of a signal for a deuterated methyl group (see the Supporting Information). However, the reaction of 1j with  $D_2$  gave 2j-d with a lower deuterium content than expected (Scheme 3, eq 8). This result suggests that an H-D exchange reaction between  $D_2$  and the C-H of the methyl group occurred both in the hydrogenation of complex **B** and in the catalytic hydrogenation of the alkene.

To investigate product formation in more detail, we allowed 1j to react with hydride ate complex C (Scheme 3, eq 9). After heating at 80 °C for 3 h, the hydrogenated product 2j was obtained in 84% yield, and C was completely transformed to complex B. Notably, the hydrogenation reaction even occurred in the absence of H<sub>2</sub>; that is, hydride ate complex C, in effect, released the H<sub>2</sub>, which added across the double bond of the alkene. Based on the above-described observations, we propose the reaction mechanism shown in Scheme 4 for alkene 1j.

Scheme 4. A Possible Mechanism



Coordination of the unsaturated bond of the alkene to dimeric potassium yttrium hydride ate complex C results in deaggregation of the dimeric complex and a hydride insertion reaction to give an alkyl ate intermediate D. Subsequent peripheral deprotonation of a methyl group by the alkyl anion gives the hydrogenation product and four-membered ring complex B, which then undergoes a formal  $H_2$  addition reaction to regenerate hydride ate complex C, completing the catalytic cycle.

In conclusion, we prepared a potassium yttrium benzyl ate complex A that can undergo peripheral deprotonation of the methyl group to afford four-membered cyclometalated complex B. The subsequent hydrogenation of B with H<sub>2</sub> provides dimeric potassium yttrium hydride ate complex C, which features a formal (KH)<sub>2</sub> structure protected by two yttrium amides. For the synergistic effect between the potassium hydride and the amide ligand, complexes B and C exist in equilibrium and can be interconverted by reversible formal addition or elimination of a molecule of H<sub>2</sub>. Using this process, we accomplished the catalytic hydrogenation of alkenes, alkyne, and imines. Considering the ready availability and good activity of the catalyst, this reaction constitutes a practical approach to H<sub>2</sub> activation and catalytic hydrogenation reactions. Exploration of applications of the potassium yttrium ate complex and a search for additional ate complex systems are underway in our laboratory.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02899.

Experimental details, <sup>1</sup>H, <sup>13</sup>C NMR and other characterization data, single-crystal X-ray analysis (PDF) Crystallographic data for Complex A (CIF) Crystallographic data for Complex B (CIF) Crystallographic data for Complex C (CIF)

# AUTHOR INFORMATION

# **Corresponding Author**

\*E-mail: guan@nankai.edu.cn.

#### ORCID 0

Bing-Tao Guan: 0000-0003-0686-4945

# Notes

The authors declare no competing financial interest.

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### DEDICATION

Dedicated to the 100th anniversary of Nankai University.

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