# **ORGANOMETALLICS**

# Yttrium Anilido Hydride: Synthesis, Structure, and Reactivity

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## Supporting Information

**ABSTRACT:** The synthesis, structure, and reactivity of the yttrium anilido hydride  $[LY(NH(DIPP))(\mu-H)]_2$  (3; L =  $[MeC(N(DIPP))CHC(Me)(NCH_2CH_2NMe_2)]^-$ , DIPP =  $2,6^{-j}Pr_2C_6H_3)$ ) are reported. The protonolysis reaction of the yttrium dialkyl  $[LY(CH_2SiMe_3)_2]$  (1) with 1 equiv of 2,6-diiso-propylaniline gave the yttrium anilido alkyl  $[LY(NH(DIPP))-(CH_2SiMe_3)]$  (2), and a subsequent  $\sigma$ -bond metathesis reaction of 2 with 1 equiv of PhSiH<sub>3</sub> offered the yttrium anilido hydride 3. The structure of 3 was characterized by X-ray crystallography, which showed that the complex is a  $\mu$ -H dimer. 3 shows high reactivity toward a variety of unsaturated substrates, including imine, azobenzene, carbodiimide, isocyanide, ketone, and Mo- $(CO)_{6}$ , giving some structurally intriguing products.



# ■ INTRODUCTION

Rare-earth-metal hydrides have attracted intense interest due to their fascinating structural features and high reactivity.<sup>1</sup> The most widely investigated rare-earth-metal hydrides are those bearing Cp-type ligands.<sup>1a-c,2</sup> To further explore the chemistry of the rare-earth-metal complexes, ancillary ligands other than Cp and Cp derivatives recently have been introduced.<sup>1d,e,3</sup> To date, most of the reported rare-earth-metal hydrides have been those supported by one dianionic ancillary ligand (LLnH), two of the same monoanionic ancillary ligands (L<sub>2</sub>LnH), or one monoanionic ancillary ligand for the dihydrides (LLnH<sub>2</sub>). Examples of heteroleptic rare-earth-metal hydrides are very rare.<sup>4</sup> Rare-earthmetal hydrides containing mixed monoanionic ancillary ligands are of interest, as they have powerful electronic and steric tuning capability as well as rich structural features. The  $\beta$ -diketiminato rare-earth-metal complexes have attracted growing attention in the past decade.<sup>5</sup> We have developed  $\beta$ -diketiminato-based tridentate ligands,<sup>5d</sup> and these ligands have exhibited excellent effects on stabilizing a series of rare-earth-metal dialkyl complexes and a scandium terminal imido complex.<sup>5d,6</sup> The steric and electronic features of these ligands give them an advantage in preventing ligand redistribution reactions. Recently, on the basis of one of these ligands, we synthesized an yttrium anilido hydride. The complex shows high reactivity toward a variety of unsaturated substrates. Herein, we report these results.

# RESULTS AND DISCUSSION

Synthesis and Crystal Structure of Yttrium Anilido Hydride (3). The yttrium dialkyl 1 was synthesized as we previously reported.<sup>5d</sup> The protonolysis reaction of 1 with 1 equiv of 2, 6-diisopropylaniline in hexane gave the yttrium anilido alkyl **2** as a pale yellow solid in 58% isolated yield (Scheme 1). **2** is soluble in toluene and benzene and slightly soluble in hexane. The complex was characterized by NMR spectroscopy and elemental analysis. The reaction of **2** with 1 equiv of PhSiH<sub>3</sub> in toluene gave the desired yttrium anilido hydride **3** as colorless crystals in 69% isolated yield (Scheme 1). **3** is sparingly soluble in toluene and benzene and nearly insoluble in hexane. In the <sup>1</sup>H NMR spectrum of **3**, the Y–H signal is overlapped with the aromatic H signals.

Single crystals of 3 were grown from a toluene solution and characterized by X-ray crystallography (Figure 1). 3 is a dimer with a 2-fold screw axis, and two yttrium centers (Y1 and Y1A) are linked by two bridging hydrido ligands (H5 and H6). The yttrium center adopts a distorted-octahedral geometry with three nitrogen atoms of the tridentate ligand [MeC(N(DIPP)CHC(Me)(NCH<sub>2</sub>CH<sub>2</sub>- $NMe_2$ ]<sup>-</sup> (L; DIPP = 2,6-'Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and a hydrido ligand forming the equatorial plane and a nitrogen atom of the anilido ligand and a hydrido ligand occupying the axial positions. The  $\beta$ -diketiminato backbone of L is bonded to the yttrium center at Y-N separations of 2.388(3) and 2.353(3) Å; the Y-N bond of the pendant arm (2.502(3) Å) is longer than those of the backbone because the pendant arm acts as a neutral donor while the backbone is an anionic donor. The C–N and C–C bond lengths of the  $\beta$ -diketiminato backbone are between those of typical single and double bonds, and the N1, C2, C3, C4 and N2 atoms are coplanar, indicating that there is a delocalized electronic structure. The anilido ligand is coordinated with a Y-N bond distance of 2.234(3) Å

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#### Scheme 1





Figure 1. Molecular structure of 3 with ellipsoids set at the 30% probability level. Isopropyl groups of DIPP, hydrogen atoms (except hydrides and anilide hydrogen atoms), and toluene molecules in the lattice have been omitted for clarity. Selected bond lengths (Å) and angles (deg):  $Y1 \cdots Y1A = 3.748(8)$ , Y1-H5 = 2.16(3), Y1-H6 = 2.13(3), Y1-N1 = 2.388(3), Y1-N2 = 2.353(3), Y1-N3 = 2.502(3), Y1-N4 = 2.234(3), C1-C2 = 1.518(5), C2-C3 = 1.394(5), C3-C4 = 1.398(6), C4-C5 = 1.519(5), C2-N1 = 1.333(4), C4-N2 = 1.333(5); H5-Y1-H6 = 58.1(19), Y1-H5-Y1A = 120.8(3), Y1-H6-Y1A = 122.7(3), H5-Y1-N4 = 142.4(12), H6-Y1-N4 = 87.3(13), Y1-N4-C33 = 157.0(2), N1-C2-C3 = 125.0(3), C2-C3-C4 = 130.9(3), C3-C4-N2 = 125.4(3).

and a Y–N–C angle of 157.0(2)°. The distances from Y1 to H5 and H6 of the hydrido ligands are 2.16(3) and 2.13(3) Å, respectively, falling in the range of 2.00–2.30 Å observed for Y–H bonds in other reported dimeric yttrium  $\mu$ -hydrido complexes.<sup>1b,d</sup> The Y1–H5–Y1A, Y1–H6–Y1A, and H5–Y1–H6 angles are 120.8(3), 122.7(3), and 58.1(19)°, respectively, and the Y1, H5, H6, and Y1A atoms are coplanar. The Y···Y distance (3.748(8) Å) is longer than those in the complexes [Y(MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>-(thf)( $\mu$ -H)]<sub>2</sub> (3.66(1) Å),<sup>7</sup> [Y{(Me<sub>3</sub>Si)<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>}<sub>2</sub>( $\mu$ -H)]<sub>2</sub> (3.6825(5) Å),<sup>8</sup> and [Me<sub>2</sub>Si{NC(Ph)N(2,6<sup>-i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}<sub>2</sub>Y-( $\mu$ -H)]<sub>2</sub> (3.4661(5) Å)<sup>3e</sup> and close to that in the complex [Y( $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SiMe<sub>2</sub>NCMe<sub>3</sub>)(thf)( $\mu$ -H)]<sub>2</sub> (3.7085(8) Å).<sup>9</sup> Scheme 2



**Reactivity of 3 toward Unsaturated Substrates.** The reaction of 3 with a substrate containing a C=N bond was initially studied. <sup>1</sup>H NMR spectral monitoring of the reaction of 3 with 2 equiv of *N*-benzylidene-2,6-dimethylaniline in C<sub>6</sub>D<sub>6</sub> showed that 3 was almost completely converted into the new complex 4 at room temperature in 8 h. A subsequent scaled-up reaction in toluene provided 4 as pale yellow crystals in 64% isolated yield. 4 was characterized by NMR spectroscopy and elemental analysis, which revealed that the complex is an yttrium amido anilide (Scheme 2). The <sup>1</sup>H NMR spectrum of the complex in C<sub>6</sub>D<sub>6</sub> features two doublets at 4.67 and 4.58 ppm for two diastereotopic hydrogen atoms of  $-NCH_2Ar-$  in the amido ligand, and each doublet has an integration value of 1 and a <sup>2</sup>J<sub>H-H</sub> coupling constant of 13.6 Hz. Therefore, the reaction of 3 with *N*-benzylidene-2,6-dimethylaniline selectively gave the addition reaction product,



**Figure 2.** Molecular structure of 4 with ellipsoids set at the 30% probability level. Isopropyl groups of DIPP and hydrogen atoms (except methylene hydrogen atoms on C34 and anilide hydrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y-N1 = 2.362(2), Y-N2 = 2.360(2), Y-N3 = 2.529(2), Y-N4 = 2.257(2), Y-N5 = 2.213(2), N5-C34 = 1.473(3), C1-C2 = 1.514(3), C2-C3 = 1.405(3), C3-C4 = 1.407(3), C4-C5 = 1.505(3), N1-C2 = 1.338(3), N2-C4 = 1.322(3); N4-Y-N5 = 116.6(1), Y-N5-C34 = 114.9(2), Y-N5-C41 = 132.2(2), N1-C2-C3 = 124.6(2), C2-C3-C4 = 128.5(2), C3-C4-N2 = 122.8(2).

and deprotonation at the ortho H of the substrate's phenyl ring was not observed.<sup>10</sup> 4 is soluble in toluene and benzene and sparingly soluble in hexane. Single crystals of 4 were grown from a hexane solution and characterized by X-ray crystallography (Figure 2). 4 is a monomer, in which the yttrium center is fivecoordinate. The geometry of the yttrium center can be described as a distorted square pyramid with a nitrogen atom of the amido ligand taking the apical position. The tridentate ligand (L) coordinates to the yttrium center via N1, N2, and N3 atoms with Y–N bond lengths of 2.362(2), 2.360(2), and 2.529(2) Å, respectively. The yttrium center sits above the N1-C2-C3-C4–N2 plane of L with a much longer C<sub>3</sub>N<sub>2</sub> plane–Y distance (1.34 Å) in comparison to that in 3 (0.56 Å). However, the distances from the yttrium center to the C2, C3, and C4 atoms are longer than 3.20 Å, indicating that the  $\beta$ -diketiminato backbone of L still acts as a two- $\sigma$ -electron donor. In 4, the Y–N<sub>amido</sub> bond length is 2.213(2) Å, the  $Y-N_{anilido}$  bond length is 2.257(2) Å, and the  $N_{anilido}$ -Y- $N_{amido}$  angle is 116.6(1)°. The N5-C34 bond length, 1.473(3) Å, is consistent with a single bond.

The reaction of 3 with azobenzene, which has an N=N bond, in toluene at room temperature gave the yttrium anilido hydrazide 5 as an off-white crystalline solid in 74% isolated yield (Scheme 2). 5 is sparingly soluble in toluene and benzene and nearly insoluble in hexane. The complex was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. Although there are many examples of the reactions of rareearth-metal complexes with azobenzene, most are about the reduction of azobenzene by divalent rare-earth-metal complexes.<sup>1</sup> Reports on the reactions of rare-earth-metal hydrides with azobenzene are very scarce; the only precedent is that of  $[(C_5Me_5)_2Sm(\mu-H)]_2$  with azobenzene, giving the samarium hydrazide  $[(C_5Me_5)_2Sm(PhNNHPh)(thf)]^{12}$  X-ray crystallography showed that 5 is a monomer with a six-coordinate yttrium center, and the hydrazido ligand [PhNHNPh]<sup>-</sup> serves as a bidentate ligand (Figure 3). The N5–N6 distance of the hydrazido ligand, 1.441(2) Å, is similar to that in  $[(C_5Me_5)_2Sm(PhNNHPh)(thf)]$ 



**Figure 3.** Molecular structure of **5** with ellipsoids set at the 30% probability level. Isopropyl groups of DIPP and hydrogen atoms (except hydrazide hydrogen atom and anilide hydrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y-N1 = 2.353(2), Y-N2 = 2.375(2), Y-N3 = 2.493(2), Y-N4 = 2.228(2), Y-N5 = 2.245(2), Y-N6 = 2.517(2), N5-N6 = 1.441(2), C1-C2 = 1.516(3), C2-C3 = 1.398(3), C3-C4 = 1.403(3), C4-C5 = 1.518(3), C2-N1 = 1.329(2), C4-N2 = 1.329(3); N5-N6-Y = 62.30(8), N6-N5-Y = 83.08(9), N5-Y-N6 = 34.62(5), N4-Y-N5 = 113.1(1), N4-Y-N6 = 88.7(1), N1-C2-C3 = 123.8(2), C2-C3-C4 = 128.9(2), C3-C4-N2 = 124.8(2).



**Figure 4.** Molecular structure of **6** with ellipsoids set at the 30% probability level. Isopropyl groups of DIPP, hydrogen atoms (except amidinate hydrogen atoms and anilide hydrogen atoms), and the hexane molecules in the lattice have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y-N1 = 2.371(3), Y-N2 = 2.372(3), Y-N3 = 2.511(3), Y-N4 = 2.254(3), Y-N5 = 2.369(3), Y-N6 = 2.428(3), N5-C34 = 1.331(5), C34-N6 = 1.309(5), C1-C2 = 1.502(5), C2-C3 = 1.405(5), C3-C4 = 1.408(5), C4-C5 = 1.510(5), C2-N1 = 1.334(4), C4-N2 = 1.339(5); N5-C34-N6 = 119.4(3), C34-N5-Y = 92.6(2), C34-N6-Y = 90.5(2), N5-Y-N6 = 56.7(1), N4-Y-N5 = 96.9(1), N4-Y-N6 = 150.0(1), N1-C2-C3 = 125.6(3), C2-C3-C4 = 132.6(4), C3-C4-N2 = 125.6(3).

(1.443(7) Å),<sup>12</sup> falling within the single-bond range. The Y–N5 bond is significantly shorter than the Y–N6 bond, 2.245(2) Å vs 2.517(2) Å, indicating different donating properties between N5 and N6 atoms: the former acts as an anionic donor, while the



**Figure 5.** Molecular structure of 7 with ellipsoids set at the 30% probability level. Isopropyl groups of DIPP and hydrogen atoms (except formimidoyl hydrogen atom and anilide hydrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y-N1 = 2.365(4), Y-N2 = 2.373(4), Y-N3 = 2.510(4), Y-N4 = 2.240(4), Y-N5 = 2.326(4), Y-C34 = 2.374(5), C34-N5 = 1.258(7), C1-C2 = 1.519(7), C2-C3 = 1.410(7), C3-C4 = 1.387(7), C4-C5 = 1.506(7), C2-N1 = 1.328(6), C4-N2 = 1.333(7); N5-C34-Y = 72.4(3), C34-N5-Y = 76.6(3), N5-Y-C34 = 31.0(2), N4-Y-N5 = 93.0(2), N4-Y-C34 = 119.5(2), N1-C2-C3 = 124.9(5), C2-C3-C4 = 129.4(5), C3-C4-N2 = 125.8(4).

latter is a neutral donor. The H6 atom bound to the N6 atom was located from the Fourier map, and no interaction between the H6 atom and the yttrium center was observed.

3 has both hydrido and anilido ligands, and the addition of a rare-earth-metal-nitrogen bond to the N=C=N bond of the carbodiimide is known.<sup>13</sup> Therefore, the reaction of 3 with 4 equiv of N,N'-diisopropylcarbodiimide was carried out. Monitoring of the reaction in  $C_6D_6$  by <sup>1</sup>H NMR spectroscopy revealed that 3 was almost completely converted into the yttrium amidinato anilide 6 along with 2 equiv of unreacted  $N_{,N'}$ -diisopropylcarbodiimide at room temperature in 5 min. No further transformation was observed, even when the reaction time was extended to 24 h. The reaction was scaled up in toluene, and 6 was isolated as a pale yellow solid in 84% yield (Scheme 2). The complex is soluble in toluene and benzene and nearly insoluble in hexane. In the <sup>1</sup>H NMR spectrum of 6, the -NCHN- signal of the amidinato ligand appears as a doublet at 8.03 ppm with a unique  $J_{Y-H}$  coupling constant of 3.0 Hz. The X-ray diffraction analysis reveals that 6 is a monomer with a six-coordinate yttrium center (Figure 4). The amidinato ligand coordinates to the yttrium center through two nitrogen atoms with Y-N bond lengths of 2.369(3) and 2.428(3) Å, respectively. The amidinato ligand displays a delocalized electronic framework. For example, the N5-C34 (1.331(5) Å) and C34-N6 (1.309(5) Å) bonds are intermediate between those of typical single and double bonds, and the N5, N6, C34, C35, and C38 atoms are coplanar.

Reactions of **3** with substrates containing other carbon—nitrogen unsaturated bonds were also studied. The reaction of **3** with 2 equiv of *tert*-butyl isocyanide in C<sub>6</sub>D<sub>6</sub> was monitored by <sup>1</sup>H NMR spectroscopy. **3** was completely converted into the new complex 7 in 15 min at room temperature. A subsequent scaledup reaction in toluene provided 7 as a yellow crystalline solid in 96% isolated yield. 7 was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, confirming that 7 is an yttrium  $\eta^2$ -*N-tert*-butylformimidoyl anilide (Scheme 2). 7 exists as a monomer, while the reactions of  $[(C_5H_4R)_2Ln(\mu-H)-$ (THF)  $]_{2}$  (R = H, Me; Ln = Y, Er) with *tert*-butyl isocyanide gave the  $\eta^2$ -N-tert-butylformimidoyl-bridged dimers [(C<sub>5</sub>H<sub>4</sub>R)Ln- $(\mu, \eta^2$ -HC=NCMe<sub>3</sub>)]<sub>2</sub>.<sup>14</sup> In the <sup>1</sup>H NMR spectrum of 7, the signal for the formimidoyl hydrogen appears at 10.89 ppm as a doublet with a  $J_{Y-H}$  coupling constant of 1.8 Hz. X-ray crystallography showed that the formimidoyl ligand coordinates to the yttrium center through carbon and nitrogen atoms with Y-C34 and Y–N5 bond lengths of 2.374(5) and 2.326(4) Å, respectively, and the N5-C34 (1.258(7) Å) bond reveals sp<sup>2</sup>-carbon-nitrogen double-bond character (Figure 5).<sup>15</sup> It is noteworthy that the Y– C34 bond in 7 is significantly shorter than those in the  $[(C_5H_5)Y_{-}]$  $(\mu_{\eta}\eta^{2}-HC=NCMe_{3})]_{2}$  dimer (2.545(5) and 2.561(5) Å).<sup>14a</sup> <sup>1</sup>H NMR spectral monitoring of the reaction of 3 with 2 equiv of benzonitrile in C6D6 showed that 3 was almost completely converted into a new complex in 40 min at room temperature, and the complex that formed slowly decomposed into a complicated mixture. A subsequent scaled-up reaction in toluene provided an orange oil. Efforts to obtain pure product by recrystallization of the orange oil have been unsuccessful so far.

To investigate the reactivity of 3 toward substrates containing a C=O double bond, benzophenone was chosen as the substrate. The reaction of 3 with 2 equiv of benzophenone in toluene at room temperature gave the yttrium alkyloxo anilide 8 as a pale yellow crystalline solid in 92% isolated yield (Scheme 2). 8 was characterized by NMR spectroscopy and elemental analysis. The <sup>1</sup>H NMR spectrum of 8 shows a characteristic singlet around 5.00 ppm for the methine proton of the alkyloxo ligand  $[OCHPh_2]^-$ , which results from the addition of the Y-H bond of 3 to the C=O double bond of benzophenone.<sup>16</sup> The anilide proton of the  $[NH(DIPP)]^-$  ligand displays a broad peak at 4.68 ppm. The reaction of 3 with CO<sub>2</sub> (1.0 atm) at room temperature was also studied. <sup>1</sup>H NMR spectral monitoring showed that the reaction gave a complicated mixture, and no precipitate formed as the reaction proceeded.

Reduction of coordinated carbon monoxide in transitionmetal carbonyls by metal hydrides has attracted intense interest and has been extensively studied.  $^{17-19}$  The reaction of rareearth-metal hydrides with transition-metal carbonyls, in contrast, has been far less studied. To the best of our knowledge, there have been only two reports: one of [Cp\*2ScH(thf)] with  $[Cp_2W(CO)]$  or  $[CpCo(CO)_2]^{20}$  and the other of  $[\{Cp'Y (\mu-H)_{2}_{4}(thf)$  (Cp' =  $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>) with [Cp\*M(CO)<sub>2</sub>(NO)] (M = Mo, W),  $[Cp^*Re(CO)_3]$ , or  $[Cp^*M(CO)_2]$  (M = Rh, Ir).<sup>21</sup> The reaction of 3 with 2 equiv of  $Mo(CO)_6$  in  $C_6D_6$  was monitored by <sup>1</sup>H NMR spectroscopy, showing that 3 was almost completely converted into the new complex 9 at room temperature in 20 min. A subsequent scaled-up reaction in toluene provided 9 as pale yellow crystals in 80% isolated yield. 9 was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, confirming that 9 is a yttrium molybdenum oxycarbene (Scheme 2). The complex is soluble in toluene and benzene and nearly insoluble in hexane. The oxycarbene ligand [HCO]<sup>-</sup> of the complex shows a singlet at 13.13 ppm in the <sup>1</sup>H NMR spectrum and a doublet at 358.1 ppm with a  $^{2}J_{Y-C}$ coupling constant of 20.6 Hz in the <sup>13</sup>C NMR spectrum. 9 is stable at room temperature in the solid state but slowly decomposed into a complicated mixture in a  $C_6D_6$  solution. In 9, the yttrium center and molybdenum center are bridged by a  $\mu$ -oxycarbene ligand, which coordinates to the yttrium center through an oxygen atom with a Y–O bond length of 2.172(4) Å and to the molybdenum center through a carbon atom with a



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**Figure 6.** Molecular structure of **9** with ellipsoids set at the 30% probability level. Isopropyl groups of DIPP and hydrogen atoms (except oxycarbene hydrogen atom and anilide hydrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y-O1 = 2.172(4), MO-C34 = 2.136(6), C34-O1 = 1.248(7), Y-N1 = 2.279(4), Y-N2 = 2.330(4), Y-N3 = 2.446(5), Y-N4 = 2.186(4), MO-C35 = 2.008(9), MO-C36 = 2.038(7), MO-C37 = 2.046(11), MO-C38 = 1.995(9), MO-C39 = 1.999(8), C1-C2 = 1.509(8), C2-C3 = 1.388(8), C3-C4 = 1.405(9), C4-C5 = 1.490(8), N1-C2 = 1.333(6), N2-C4 = 1.323(7); Y-O1-C34 = 152.7(4), O1-C34-MO = 131.5(5), N4-Y-O1 = 99.0(2), C34-MO-C35 = 87.8(2), C34-MO-C36 = 174.8(3), C34-MO-C37 = 90.0(3), C34-MO-C38 = 81.6(3), C34-MO-C39 = 87.7(3), N1-C2-C3 = 123.4(5), C2-C3-C4 = 128.8(5), C3-C4-N2 = 124.0(5).

Mo-C bond length of 2.136(6) Å (Figure 6). The Y-O bond is slightly longer than those reported for the yttrium phenoxide derivatives  $(2.02-2.15 \text{ Å})^{22}$  and is shorter than Y–O bonds in the yttrium ketone complexes  $[Cp_2^*Y(Cl)(O=CPh_2)](2.312(2) Å)^{23}$ and  $[L'_2Y(OCHPh_2)(O=CPh_2)]$  (L' is a salicylaldiminato ligand) (2.444(2) Å).<sup>22f</sup> The Mo-C bond is close to that in  $[L''(CO)_3 \text{Mo}^0 =$ C(OMe)Ph] (2.136(4) Å) (L" is a bidentate phosphite ligand)<sup>24</sup> and shorter than  $Mo-C_{carbene}$  bonds in Mo(0) N-heterocyclic carbene complexes (2.23-2.33 Å).<sup>25</sup> The C-O bond of the  $\mu$ -oxycarbene ligand, 1.248(7) Å, is close to that in the scandium cobalt oxycarbene  $[Cp_{2}^{*}Sc-O(H_{3}C)C=Co(CO)Cp]$  (1.268(4) Å)<sup>20</sup> and significantly shorter than that in an oligonuclear yttrium molybdenum oxycarbene (1.423(10) Å).<sup>21</sup> This C–O bond is much shorter than the typical  $C(sp^2)$ –O single bond  $(1.35 \text{ Å})^{26}$ and close to a typical  $C(sp^2)=O$  double bond (1.21 Å) and that in the molybdenum formyl complex Cp\*Mo(CO)<sub>2</sub>(PMe<sub>3</sub>)CHO (1.212(7) Å).<sup>27</sup> The Mo-C34-O1 and Y-O1-C34 angles are 131.5(5) and 152.7(4)°, respectively, and the Mo, C34, O1, and Y atoms are coplanar. On the basis of these structural features, 9 is best described as two resonance forms, A and B (Scheme 3). The Mo-Y separation (5.26 Å) is rather long, indicating that there is no metal-metal interaction. The Mo-C bonds for the carbonyl ligands range from 1.995(9) to 2.046(11) Å.

In summary, the yttrium anilido hydride **3** was synthesized by using a  $\beta$ -diketiminato-based tridentate ligand (L = [MeC(N-(DIPP))CHC(Me)(NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sup>-</sup>, DIPP = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)) as an ancillary ligand. X-ray crystallography showed that **3** is a dimer with two yttrium centers linked by two bridging hydrido ligands. The addition of the Y–H bond of **3** across C=N, N=N, N=C=N, NC, and C=O bonds of *N*-benzylidene-2,6-dimethylaniline, azobenzene, *N*,*N*<sup>'</sup>-diisopropylcarbodiimide, *tert*-butyl



isocyanide, and benzophenone gave the yttrium amido anilide 4, yttrium anilido hydrazide 5, yttrium amidinato anilide 6, yttrium  $\eta^2$ -N-*tert*-butylformimidoyl anilide 7, and yttrium alkyloxo anilide 8, respectively. The addition of the Y–H bond of 3 to one coordinated carbon monoxide of Mo(CO)<sub>6</sub> provided the heterobimetallic yttrium molybdenum oxycarbene 9, where the oxycarbene ligand coordinates to the yttrium center through an oxygen atom and to the molybdenum center through a carbon atom. During the reactions of 3 with the studied unsaturated substrates, the Y–N<sub>anilide</sub> bond of the complex remained intact. Further studies will strive to prepare rare-earth-metal phosphido, arylthio, and aryloxo hydrides, which are based on the mono-anionic tridentate nitrogen ligand L.

#### EXPERIMENTAL SECTION

General Procedures. All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogenfilled glovebox. Toluene, hexane, and C<sub>6</sub>D<sub>6</sub> were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. 2,6-Diisopropylaniline, phenylsilane, N-benzylidene-2,6-dimethylaniline, N,N'-diisopropylcarbodiimide, and tert-butyl isocyanide were dried over activated 4 Å molecular sieves, distilled under vacuum, degassed three times by freeze-thaw-vacuum, and stored in the glovebox. Molybdenum hexacarbonyl, azobenzene, and benzophenone were purchased from Aldrich and used without further purification. The yttrium dialkyl 1 was synthesized as we previously reported.<sup>5d 1</sup>H and <sup>13</sup>C spectra were recorded on a Varian Mercury 300 MHz spectrometer and a Varian 400 MHz spectrometer at 300 or 400 MHz and at 75 or 100 MHz, respectively. All chemical shifts are reported in  $\delta$  units with reference to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts. Elemental analysis was performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry.

[LY(NH(2,6-'Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))(CH<sub>2</sub>SiMe<sub>3</sub>)] (2). A solution of 2,6-diisopropylaniline (254 mg, 1.43 mmol; in 1 mL of hexane) was added to 1 (848 mg, 1.43 mmol) in 5 mL of hexane at room temperature. After the mixture stood at room temperature for 30 min, all volatiles were removed under vacuum. The residue was washed with cold hexane  $(1 \text{ mL} \times 3)$  and dried under vacuum to afford 2 as a pale yellow solid (568 mg, 58% yield). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 25 °C):  $\delta$  (ppm)  $7.15 - 7.11 \text{ (m, 5H, ArH)}, 6.84 \text{ (t, }^{3}J_{H-H} = 7.6 \text{ Hz}, 1H, ArH), 4.91 \text{ (s, 1H,}$ MeC(N)CH, 4.45 (s, br, 1H, YNHAr), 3.30 (sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 1H, ArCHMe<sub>2</sub>), 3.23 (sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 1H, ArCHMe<sub>2</sub>), 2.84–2.79 (m, 4H, ArCHMe<sub>2</sub> and NCH<sub>2</sub>), 2.37 (m, 1H, NCH<sub>2</sub>), 2.11 (s, 3H, NCH<sub>3</sub>), 1.90 (m, 1H, NCH<sub>2</sub>), 1.83 (s, 3H, NCH<sub>3</sub>), 1.70 (s, 3H, H<sub>3</sub>CC(N)), 1.63 (s, 3H,  $H_3CC(N)$ ), 1.41 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 3H, ArCHMe<sub>2</sub>), 1.38 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 6H, ArCHMe<sub>2</sub>), 1.32 (d,  ${}^{3}J_{H-H} = 6.4$  Hz, 6H, Ar CHMe<sub>2</sub>), 1.26 (d,  ${}^{3}J_{H-H}$  = 6.8 Hz, 3H, ArCHMe<sub>2</sub>), 1.14 (d,  ${}^{3}J_{H-H}$  = 7.2 Hz, 3H, ArCHMe<sub>2</sub>), 1.08 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 3H, ArCHMe<sub>2</sub>), 0.20 (s, 9H, YCH<sub>2</sub>SiMe<sub>3</sub>), -0.70 (dd,  ${}^{2}J_{H-H} = 11.2$  Hz,  ${}^{2}J_{Y-H} = 3.6$  Hz, 1H, YCH<sub>2</sub>SiMe<sub>3</sub>), -0.78 (dd,  ${}^{2}J_{H-H} = 11.2$  Hz,  ${}^{2}J_{Y-H} = 3.6$  Hz, 1H, YCH<sub>2</sub>SiMe<sub>3</sub>).  ${}^{13}$ C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  (ppm) 166.9, 166.4 (imine C), 152.0, 144.4, 143.3, 143.2, 133.1, 126.2, 124.6, 124.4, 123.0, 115.3 (ArC), 98.5 (MeC(N)CH), 58.1, 47.5, 45.6, 44.5 (NMe2 and NCH<sub>2</sub>), 34.0 (d,  ${}^{1}J_{Y-C}$  = 45.5 Hz, YCH<sub>2</sub>SiMe<sub>3</sub>), 30.1, 29.0, 28.0,

25.1, 25.0, 24.9, 24.6, 24.5, 24.4, 24.3, 24.2, 23.3 ( $Ar^{i}Pr$  and MeC), 4.3 ( $CH_{2}SiMe_{3}$ ). Anal. Calcd for  $C_{37}H_{63}N_{4}SiY$ : C, 65.26; H, 9.33; N, 8.23. Found: C, 65.14; H, 9.12; N, 8.43.

[LY(NH(2,6-'Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))(*µ*-H)]<sub>2</sub> (3). A solution of PhSiH<sub>3</sub> (79 mg, 0.731 mmol; in 1 mL of toluene) was added to 2 (500 mg, 0.734 mmol) in 2 mL of toluene at -35 °C. After the mixture stood at -35 °C for 18 h, the reaction solution was concentrated to approximately 0.5 mL and cooled to -35 °C to afford 3 as colorless crystals (300 mg, 69% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  (ppm) 7.24 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 1H, ArH), 7.17 (m, 1H, ArH), 7.08-6.99 (m, 4H, ArH and YH), 6.88 (t,  ${}^{3}J_{H-H} = 7.6$  Hz, 1H, ArH), 5.11 (br s, 1H, YNHAr), 4.79 (s, 1H, MeC(N)CH), 3.47–3.36 (m, 2H, ArCHMe<sub>2</sub>), 3.26 (sept,  ${}^{3}J_{H-H} = 6.8$ Hz, 1H, ArCHMe<sub>2</sub>), 3.16 (sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 1H, ArCHMe<sub>2</sub>), 3.03 (m, 1H, NCH<sub>2</sub>), 2.91 (m, 1H, NCH<sub>2</sub>), 2.08 (s, 3H, NMe<sub>2</sub>), 1.88 (s, 3H, NMe<sub>2</sub>), 1.76 (s, 3H, MeC), 1.72 (m, 1H, NCH<sub>2</sub>), 1.61 (s, 3H, MeC), 1.54  $(d, {}^{3}J_{H-H} = 6.8 \text{ Hz}, 3H, \text{ArCHM}e_{2}), 1.53 (m, 1H, \text{NCH}_{2}), 1.49 (d,$  ${}^{3}J_{H-H}$  = 6.4 Hz, 3H, ArCHMe<sub>2</sub>), 1.39 (d,  ${}^{3}J_{H-H}$  = 6.8 Hz, 3H, ArCHMe<sub>2</sub>), 1.31 (d,  ${}^{3}J_{H-H}$  = 6.4 Hz, 3H, ArCHMe<sub>2</sub>), 1.20 (d,  ${}^{3}J_{H-H}$ = 6.8 Hz, 3H, ArCHM $e_2$ ), 1.16 (d,  ${}^{3}J_{H-H}$  = 6.4 Hz, 3H, ArCHM $e_2$ ), 1.06  $(d, {}^{3}J_{H-H} = 6.4 \text{ Hz}, 3H, \text{ ArCHMe}_{2}), 0.87 (d, {}^{3}J_{H-H} = 6.0 \text{ Hz}, 3H,$ ArCHMe<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 167.1, 165.9 (imine C), 152.2, 146.1, 145.9, 144.3, 135.0, 132.2, 125.9, 125.4, 124.5, 123.4, 122.7, 114.9 (ArC), 98.3 (MeC(N)CH), 57.8, 48.3, 47.8, 46.9 (NCH<sub>2</sub> and NMe<sub>2</sub>), 30.3, 28.3, 28.0, 27.4, 27.2, 27.0, 26.0, 25.7, 25.4, 24.7, 24.4, 24.2, 23.7, 23.5 (Ar<sup>i</sup>Pr and MeC). Anal. Calcd for C<sub>66</sub>H<sub>106</sub>N<sub>8</sub>Y<sub>2</sub>: C, 66.65; H, 8.98; N, 9.42. Found: C, 66.55; H, 8.90; N, 9.57.

[LY(NH(2,6-'Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))(N(CH<sub>2</sub>Ph)(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))] (4). A solution of N-benzylidene-2,6-dimethylaniline (35 mg, 0.167 mmol; in 1 mL of toluene) was added to 3 (100 mg, 0.084 mmol) in 2 mL of toluene at room temperature. After the mixture stood at room temperature for 12 h, the volatiles were removed under vacuum to give a yellow oil. The yellow oil was extracted with 2 mL of hexane. After standing at room temperature for several minutes, 4 precipitated from the hexane solution as pale yellow crystals (87 mg, 64% yield). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 25 °C):  $\delta$  (ppm) 7.10 (d,  ${}^{3}J_{H-H}$  = 7.2 Hz, 2H, ArH), 7.08–6.98 (m, 8H, ArH), 6.88–6.85 (m, 3H, ArH), 6.80 (t,  ${}^{3}J_{H-H} = 7.8$  Hz, 1H, ArH), 4.97 (s, 1H, MeC(N)CH), 4.67 (d,  ${}^{2}J_{H-H} = 13.6$  Hz, 1H, one H of PhCH<sub>2</sub>N AB system), 4.58 (d,  ${}^{2}J_{H-H}$  = 13.6 Hz, 1H, one H of PhCH<sub>2</sub>N AB system), 4.32 (br s, 1H, Y–NHAr), 3.61 (sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 1H, ArCHMe<sub>2</sub>), 3.14 (sept,  ${}^{3}J_{H-H}$  = 7.2 Hz, 1H, ArCHMe<sub>2</sub>), 3.00 (m, 1H, NCH<sub>2</sub>), 2.85-2.78 (m, 3H, two H of ArCHMe<sub>2</sub> and 1H of NCH<sub>2</sub>), 2.61 (m, 1H, NCH<sub>2</sub>), 2.29 (s, 6H, NMe<sub>2</sub>), 1.86 (br s, 3H, ArMe), 1.79 (br s, 3H, ArMe), 1.70 (m, 1H, NCH2), 1.67 (s, 3H, MeC), 1.65 (s, 3H, MeC), 1.47 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 3H, ArCHMe<sub>2</sub>), 1.27–1.22 (m, 12H, ArCHMe<sub>2</sub>), 1.10 (d,  ${}^{3}J_{H-H}$  = 6.8 Hz, 9H, ArCHMe<sub>2</sub>).  ${}^{13}$ C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 167.0, 166.2 (imine C), 152.4, 151.8, 151.7, 146.8, 143.2, 143.1, 134.3, 134.1, 129.2, 128.9, 127.6, 126.2, 126.1, 124.9, 124.4, 123.1, 121.4, 115.5 (ArC), 99.8 (MeC(N)CH), 58.3, 53.8, 47.2, 45.6, 43.7 (NCH<sub>2</sub>, NMe<sub>2</sub>, and NCH<sub>2</sub>Ph), 29.7, 29.4, 27.7, 25.8, 25.5, 25.1, 24.9, 24.8, 24.7, 24.3, 23.1, 20.8 (Ar<sup>i</sup>Pr, MeC, and ArMe). Anal. Calcd for C<sub>48</sub>H<sub>68</sub>N<sub>5</sub>Y: C, 71.71; H, 8.52; N, 8.71. Found: C, 72.11; H, 8.80; N, 8.91.

**[LY(NH(2,6-'Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))**( $\eta^2$ (*N,N*')-PhNHNPh)] (5). A solution of azobenzene (31 mg, 0.170 mmol in 1 mL of toluene) was added to 3 (100 mg, 0.084 mmol) in 2 mL of toluene at room temperature. After the mixture stood at room temperature for 3.5 days, the volatiles were removed under vacuum to give an off-white solid with green oil. The crude product was washed with hexane (1 mL × 4) and dried under vacuum to afford 5 as an off-white crystalline solid (98 mg, 74% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 7.27 (d, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 1H, ArH), 7.14–7.03 (m, 8H, ArH), 6.86–6.77 (m, 4H, ArH), 6.63 (t, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 1H, ArH), 6.56–6.53 (br d, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 2H, ArH), 4.89 (s, 1H, MeC(N)CH), 4.11 (br s, 1H, YNHAr or PhNNH(Ph)), 3.97 (br s, 1H, YNHAr or PhNNH(Ph)), 3.43 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 1H, ArCHMe<sub>2</sub>), 3.31 (m, 1H, NCH<sub>2</sub>), 3.17 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.3 Hz, 1H,

ArCHMe<sub>2</sub>), 3.02 (m, 1H, NCH<sub>2</sub>), 2.90–2.68 (m, 2H, ArCHMe<sub>2</sub> and NCH<sub>2</sub>), 2.36 (s, 3H, NMe<sub>2</sub>), 1.99–1.84 (br m, 1H, NCH<sub>2</sub> or ArCHMe<sub>2</sub>), 1.78 (s, 3H, NMe<sub>2</sub>), 1.77 (s, 3H, MeC), 1.78–1.72 (br m, 1H, NCH<sub>2</sub>), 1.69 (s, 3H, MeC), 1.60–1.42 (br m, 3H, ArCHMe<sub>2</sub>), 1.40–1.20 (br m, 3H, ArCHMe<sub>2</sub>), 1.22 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 3H, ArCHMe<sub>2</sub>), 1.14 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 3H, ArCHMe<sub>2</sub>), 1.15–0.90 (br m, 6H, ArCHMe<sub>2</sub>), 0.90 (d, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 3H, ArCHMe<sub>2</sub>), 0.68 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 3H, ArCHMe<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  (ppm) 167.9, 166.4 (imine C), 154.8, 152.0, 151.9, 148.9, 145.3, 142.7, 129.5, 125.6, 125.0, 124.0, 123.0, 122.4, 115.7, 114.8, 114.2 (ArC), 98.6 (MeC(N)CH), 57.9, 48.2, 48.1, 43.9 (NCH<sub>2</sub> and NMe<sub>2</sub>), 32.0, 29.6, 27.6, 27.4, 26.7, 25.5, 25.4, 25.1, 24.8, 24.7, 24.5, 24.3, 23.9, 22.2 (Ar<sup>i</sup>Pr and MeC). Anal. Calcd for C<sub>45</sub>H<sub>63</sub>N<sub>6</sub>Y: C, 69.57; H, 8.17; N, 10.82. Found: C, 69.58; H, 8.29; N, 10.75.

 $[LY(NH(2,6-Pr_2-C_6H_3))(\eta^2(N,N')-PrNCHN^Pr)]$  (6). N,N'-Diisopropylcarbodiimide (34 mg, 0.269 mmol) was added to 3 (80 mg, 0.067 mmol) in 1 mL of toluene at room temperature. After the mixture stood at room temperature for 30 min, the volatiles were removed under vacuum to give a yellow oil. The yellow oil was added to 0.5 mL of hexane, and 6 precipitated from the solution as a pale yellow crystalline solid (86 mg, 84% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 8.03 (d,  ${}^{3}J_{Y-H}$  = 3.0 Hz, 1H, NCHN), 7.22 (d,  ${}^{3}J_{H-H}$  = 7.5 Hz, 2H, ArH), 7.13-7.09 (m, 3H, ArH),  $6.86 \text{ (t, }^{3}J_{H-H} = 7.8 \text{ Hz}$ , 1H, ArH), 4.71(s, 1H, MeC(N)CH), 4.29 (br s, 1H, YNHAr), 3.50 (sept,  ${}^{3}J_{H-H} = 6.3$ Hz, 1H, CHMe<sub>2</sub>), 3.45-3.25 (m, 4H, NCH<sub>2</sub> and CHMe<sub>2</sub>), 3.24-2.95 (m, 4H, NCH<sub>2</sub> and CHMe<sub>2</sub>), 2.21 (br s, 3H, NMe<sub>2</sub>), 2.00 (br s, 3H, NMe<sub>2</sub>), 1.76 (s, 3H, MeC), 1.63 (m, 1H, NCH<sub>2</sub>), 1.60 (s, 3H, MeC), 1.47  $(d, {}^{3}J_{H-H} = 6.9 \text{ Hz}, 6H, CHMe_{2}), 1.37 (d, {}^{3}J_{H-H} = 6.6 \text{ Hz}, CHMe_{2}),$ 1.30–1.25 (m, 4H, CH<sub>2</sub> of hexane), 1.21 (d,  ${}^{3}J_{H-H}$  = 7.2 Hz, 3H, CHMe<sub>2</sub>), 1.16 (d,  ${}^{3}J_{H-H}$  = 6.6 Hz, 3H, CHMe<sub>2</sub>), 1.13 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 3H, CHMe<sub>2</sub>), 1.10 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 3H, CHMe<sub>2</sub>), 1.07 (d,  ${}^{3}J_{H-H}$ = 6.3 Hz, 6H, CHMe<sub>2</sub>), 0.89 (t,  ${}^{3}J_{H-H}$  = 6.6 Hz, 3H, CH<sub>3</sub> of hexane), 0.83 (br, 6H, CHMe<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 169.7 (d,  ${}^{2}J_{Y-C}$  = 2.6 Hz, NCHN), 166.9, 166.2 (imine C), 153.0, 152.9, 145.1, 144.6, 143.5, 133.6, 125.8, 125.3, 123.5, 123.3, 114.4 (ArC), 97.0 (MeC(N)CH), 58.0, 52.9, 48.9, 46.0 (NCH<sub>2</sub> and NMe<sub>2</sub>), 31.9, 29.1, 27.6, 27.4, 26.1, 25.5, 25.3, 25.2, 25.0, 24.9, 23.9, 23.0 (<sup>i</sup>Pr, MeC and CH<sub>2</sub> of hexane), 14.3 (CH<sub>3</sub> of hexane). Anal. Calcd for C<sub>40</sub>H<sub>67</sub>N<sub>6</sub>Y·0.5 C<sub>6</sub>H<sub>14</sub>: C, 67.60; H, 9.76; N, 11.00. Found: C, 68.18; H, 9.44; N, 10.88.

 $[LY(NH(2,6-Pr_2-C_6H_3))(\eta^2(N,C)-(H)CN^tBu)]$  (7). A solution of 3 (100 mg, 0.084 mmol in 2 mL of toluene) was added to tert-butyl isocyanide (14.0 mg, 0.168 mmol) in 0.5 mL of toluene at room temperature. After the mixture stood at room temperature for 10 min, the volatiles were removed under vacuum to give 7 as a pale yellow crystalline solid (110 mg, 96% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  (ppm) 10.89 (d, <sup>2</sup> $J_{Y-H}$  = 2.1 Hz, 1H, <sup>t</sup>BuNCH), 7.20 (d,  ${}^{3}J_{H-H}$  = 7.2 Hz, 2H, ArH), 7.12–6.98 (m, 3H, ArH), 6.83 (t,  ${}^{3}J_{H-H}$  = 7.2 Hz, 1H, ArH), 4.95 (br s, 1H, YNHAr), 4.86 (s, 1H, MeC(N)CH), 3.43 (sept,  ${}^{3}J_{H-H}$  = 6.9 Hz, 2H, ArCHMe<sub>2</sub>), 3.05–2.87 (m, 5H, NCH<sub>2</sub> and ArCHMe2), 1.80 (s, 3H, NMe2), 1.78 (s, 3H, NMe2), 1.75 (s, 3H, MeC), 1.62 (s, 3H, MeC), 1.43 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 6H, ArCHMe<sub>2</sub>), 1.38 (d,  ${}^{3}J_{H-H} = 7.2$  Hz, 3H, ArCHMe<sub>2</sub>), 1.36 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 6H, ArCHMe<sub>2</sub>), 1.22 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 3H, ArCHMe<sub>2</sub>), 1.13 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 3H, ArCHMe<sub>2</sub>), 1.08 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 3H, ArCHMe<sub>2</sub>), 1.00 (s, 9H, <sup>t</sup>BuNCH). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 245.2 (d,  ${}^{1}J_{Y-C} = 24.9$  Hz,  ${}^{t}BuNCH$ ), 167.1, 165.6 (imine C), 153.0, 152.9, 144.6, 144.1, 143.3, 133.0, 125.6, 124.3, 124.1, 123.1, 123.0, 114.0 (ArC), 98.1 (MeC(N)CH), 59.6, 58.3, 48.1, 47.6, 44.3 (NCH<sub>2</sub>, NMe<sub>2</sub>, and CMe<sub>3</sub>), 29.9, 29.6, 28.6, 27.7, 25.4, 25.3, 25.2, 24.7, 24.5, 24.3, 23.6, 23.4 (Ar<sup>*i*</sup>*Pr*, *MeC*, and *CMe*<sub>3</sub>). Anal. Calcd for C<sub>38</sub>H<sub>62</sub>N<sub>5</sub>Y: C, 67.33; H, 9.22; N, 10.33. Found: C, 67.68; H, 9.28; N, 10.32.

[LY(NH(2,6-'Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))(OCHPh<sub>2</sub>)] (8). The title compound was prepared by the procedure described for 7, but with 3 (80 mg, 0.067 mmol) and benzophenone (24.5 mg, 0.134 mmol), and the reaction

Table 1.	Crystallographic	Data and I	Refinement	Details for	3-7 and 9
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	$3 \cdot 2(toluene)$	4	5	<b>6</b> •0.5(hexane)	7	9
formula	$C_{80}H_{122}N_8Y_2$	C <sub>48</sub> H <sub>68</sub> N <sub>5</sub> Y	C45H63N6Y	$C_{43}H_{74}N_{6}Y$	C <sub>38</sub> H <sub>62</sub> N <sub>5</sub> Y	C <sub>39</sub> H <sub>53</sub> MoN <sub>4</sub> O <sub>6</sub> Y
fw	1373.68	803.98	776.92	763.99	677.84	858.70
color	colorless	yellow	colorless	pale yellow	pale yellow	orange
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	C2/c	$P2_1/n$	$P2_1/n$	$P\overline{1}$	$P2_{1}/c$	$P2_1/n$
<i>a,</i> Å	21.552(4)	13.580(1)	11.094(7)	11.955(1)	12.916(3)	14.276(4)
<i>b,</i> Å	18.772(4)	15.711(1)	19.042(1)	12.368(1)	14.940(3)	20.640(5)
<i>c,</i> Å	19.399(4)	21.773(2)	20.950(1)	14.907(1)	20.858(5)	14.382(4)
$\alpha$ , deg	90.00	90.00	90.00	86.963(1)	90.00	90.00
$\beta$ , deg	92.502(2)	107.742(1)	103.220(1)	81.089(1)	107.507(3)	94.245(4)
γ, deg	90.00	90.00	90.00	78.696(2)	90.00	90.00
V, Å <sup>3</sup>	7841(3)	4424.5(6)	4308.3(4)	2134.8(3)	3838.8(1)	4225.9(2)
Z	4	4	4	2	4	4
$D_{\text{calcd}}$ mg/mm <sup>3</sup>	1.164	1.207	1.198	1.189	1.173	1.350
F(000)	2944	1720	1656	826	1456	1776
heta range, deg	1.44-26.00	1.58 - 27.00	1.46-26.00	1.38-27.00	1.65-26.00	1.73-27.00
no. of rflns collected	28 055	31 721	32 275	15 311	19 726	28 884
no. of unique rflns	7661	9638	8440	9145	7527	9174
no. of obsd rflns	5692	7284	7415	7492	5013	5830
no. of params	412	501	489	468	428	470
final R, $R_w$ ( $I > 2\sigma(I)$ )	0.0579, 0.1465	0.0389, 0.0997	0.0282, 0.0776	0.0490, 0.1470	0.0714, 0.1798	0.0687, 0.1686
goodness of fit on $F^2$	1.081	1.090	1.017	1.064	1.040	1.011
$\Delta  ho_{ m max,\ min}$ e Å $^{-3}$	0.927, -1.039	0.559, -0.621	0.754, -0.467	0.751, -0.669	1.725, -1.351	1.555, -0.831

time was 30 min. 8 was obtained as a pale yellow crystalline solid (95.2 mg, 92% yield). <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  (ppm) 7.40–7.37 (m, 4H, ArH), 7.32–7.06 (m, 11H, ArH), 6.89 (t,  ${}^{3}J_{H-H} = 7.8$  Hz, 1H, ArH), 5.21 (s, 1H, OCHPh<sub>2</sub> or MeC(N)CH), 4.96 (s, 1H, OCHPh<sub>2</sub> or MeC(N)CH), 4.68 (br s, 1H, YNHAr), 3.42 (sept,  ${}^{3}J_{H-H} = 6.6$  Hz, 1H, ArCHMe<sub>2</sub>), 3.10–2.78 (m, 5H, ArCHMe<sub>2</sub> and NCH<sub>2</sub>), 2.33 (m, 1H, ArCHMe<sub>2</sub> or NCH<sub>2</sub>), 2.17 (m, 1H, ArCHMe<sub>2</sub> or NCH<sub>2</sub>), 2.13 (s, 3H, NMe<sub>2</sub>), 2.01 (s, 3H, NMe<sub>2</sub>), 1.77 (s, 3H, MeC), 1.68 (s, 3H, MeC), 1.47 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 6H, ArCHMe<sub>2</sub>), 1.38 (d,  ${}^{3}J_{H-H}$  = 6.6 Hz, 6H, ArCHMe<sub>2</sub>), 1.18–1.10 (m, 9H, ArCHMe<sub>2</sub>), 1.05 (d,  ${}^{3}J_{H-H} = 6.3$  Hz, 3H, ArCHMe<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 167.4, 166.1 (imine C), 152.2, 152.1, 150.0, 149.9, 144.5, 143.2, 142.6, 132.8, 128.2, 127.0, 126.6, 126.2, 126.1, 125.6, 124.6, 124.2, 122.8, 114.7 (ArC), 98.5 (MeC(N)CH), 81.3 (d,  ${}^{2}J_{Y-C}$  = 4.4 Hz, OCHPh<sub>2</sub>), 57.9, 47.6, 44.8, 44.7 (NCH2 and NMe2), 30.2, 28.4, 28.3, 25.5, 24.6, 24.3, 24.2, 24.1, 24.0, 23.7, 23.5 (Ar<sup>i</sup>Pr and MeC). Anal. Calcd for C<sub>46</sub>H<sub>63</sub>N<sub>4</sub>OY: C, 71.11; H, 8.17; N, 7.21. Found: C, 70.70; H, 8.16; N, 7.02.

[LY(NH(2,6-'Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>))(*µ*-OCH)Mo(CO)<sub>5</sub>] (9). A solution of 3 (100 mg, 0.084 mmol; in 2 mL of toluene) was added to molybdenum hexacarbonyl (44 mg, 0.167 mmol) in 1 mL of toluene at -35 °C. After the addition, the solution was warmed to room temperature. After the mixture stood at room temperature for 30 min, the volatiles were removed under vacuum to give a yellow viscous oil. The yellow oil was added to 1 mL of hexane, and 9 precipitated from the solution as a yellow crystalline solid (115 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ (ppm) 13.13 (s, 1H, CHO), 7.20–7.18 (m, 3H, ArH), 7.07  $(dd, {}^{3}J_{H-H} = 7.6 \text{ Hz}, {}^{4}J_{H-H} = 1.2 \text{ Hz}, 1\text{H}, \text{Ar}H), 7.02 (dd, {}^{3}J_{H-H} = 7.2 \text{ Hz})$ Hz,  ${}^{4}J_{H-H} = 1.6$  Hz, 1H, ArH), 6.90 (t,  ${}^{3}J_{H-H} = 7.6$  Hz, 1H, ArH), 5.07 (br s, 1H, YNHAr), 4.93 (s, 1H, MeC(N)CH), 3.04–2.88 (m, 4H, NCH<sub>2</sub> and ArCHMe<sub>2</sub>), 2.73 (m, 1H, NCH<sub>2</sub>), 2.65-2.57 (m, 2H, ArCHMe2), 2.43 (s, 3H, NMe2), 2.06 (s, 3H, NMe2), 1.83 (m, 1H,  $NCH_2$ ), 1.68 (s, 3H, MeC), 1.51 (s, 3H, MeC), 1.43 (d,  ${}^{3}J_{H-H} = 6.4$  Hz, 6H, ArCHMe<sub>2</sub>), 1.33 (d,  ${}^{3}J_{H-H}$  = 6.8 Hz, 6H, ArCHMe<sub>2</sub>), 0.99 (d,  ${}^{3}J_{H-H}$ = 7.2 Hz, 3H, ArCHM $e_2$ ), 0.98 (d,  ${}^{3}J_{H-H}$  = 6.8 Hz, 3H, ArCHM $e_2$ ), 0.96 (d,  ${}^{3}J_{H-H} = 6.4$  Hz, 3H, ArCHMe<sub>2</sub>), 0.95 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 3H, ArCHMe<sub>2</sub>).  ${}^{13}$ C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  (ppm) 358.1 (d,  ${}^{2}J_{Y-C} = 20.6$  Hz, MoC(H)OY), 216.8, 208.5 (Mo(CO)<sub>5</sub>), 168.1, 166.6, 151.0, 150.9, 143.4, 142.2, 140.2, 133.2, 126.9, 124.9, 124.7, 123.0, 116.5 (ArC), 99.5 (MeC(N)CH), 57.6, 47.3, 46.5, 42.2 (NCH<sub>2</sub> and NMe<sub>2</sub>), 31.3, 28.8, 28.0, 25.1, 24.5, 24.1, 23.8, 23.7, 23.5, 23.3 (Ar<sup>i</sup>Pr and MeC). Anal. Calcd for C<sub>39</sub>H<sub>53</sub>MoN<sub>4</sub>O<sub>6</sub>Y: C, 54.55; H, 6.22; N, 6.52. Found: C, 54.11; H, 6.27; N, 6.42.

**X-ray Crystallography.** Suitable single crystals of 3-7 and 9 were mounted under a nitrogen atmosphere on a glass fiber, and data collection was performed at 173(2) K (for 3) or 133(2) K (for 4-7and 9) on a Bruker APEX2 diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculations, except for the hydrogen atoms of Y–H in 3 and the anilide hydrogen atom H4 and the hydrazide hydrogen atom H6 in 5, which were located from the Fourier map. All calculations were carried out using the SHELXL-97 program. The software used is given in ref 28. Crystallographic data and refinement details for 3-7 and 9 are given in Table 1.

## ASSOCIATED CONTENT

**Supporting Information.** CIF files giving X-ray crystallographic data for 3–7 and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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