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The First Isolation and Structural Characterization of a Lanthanoid−Imine Azametallacyclopropane Complex, [Yb(η^2-Ph$_2$CNPh)(hmpa)$_3$]

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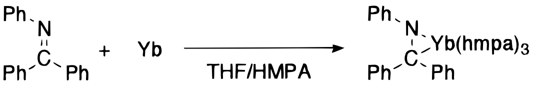
Summary: A dianionic lanthanoid(II)−imine azametallacyclopropane complex, [Yb(η^2-Ph$_2$CNPh)(hmpa)$_3$] (hmpa = hexamethylphosphoramide), has been directly synthesized by the reaction of ytterbium metal with N-(diphenylmethylidene)aniline in THF/HMPA and structurally characterized by X-ray analysis.

Although *in situ* reactions[1,2] and structures of several azametallacyclopropane complexes, formed *via* ligand−metal exchange followed by a loss of the β-hydrogen of the amide moiety,[3] migration of the alkyl groups to the (iminoacyl)metals,[4] and reduction of a low-valent complex with phosphaazaallene,[5] have been documented, no structural information regarding azametallacyclopropane complexes generated by the direct reaction of imines with metallic reductants has been obtained because of their instability and complicated coordination states. In addition, azametallacyclopropane complexes of lanthanoids have not been characterized or isolated. We have demonstrated that cationic imine carbons of *C*,*C*-diaryl imines become anionic on treatment with lanthanoids such as ytterbium metal and that α-amino acids can be obtained by the reaction of ytterbium triaryl imine complexes formed *in situ* with carbon dioxide.[6] Herein we report that we have succeeded in isolating and structurally characterizing the first dianionic ytterbium(II)−imine complex, [Yb(η^2-Ph$_2$CNPh)(hmpa)$_3$] (hmpa = hexamethylphosphoramide).

An extremely air- and moisture-sensitive ytterbium-imine complex, [Yb(η^2-Ph$_2$CNPh)(hmpa)$_3$] (**1**) could be conveniently prepared in 44.5% yield as red-black needles by the reaction of metallic ytterbium with *N*-(diphenylmethylidene)aniline in THF/HMPA (eq 1).[7,8]



(1)

1 (44.5%)

Treatment of **1** with D$_2$O afforded Ph$_2$CDNDPh, Ph$_2$CD$_2$, and PhND$_2$ in 49, 43, and 43% yields, respectively. This result shows that the cationic imine carbon of free Ph$_2$C═NPh certainly becomes anionic by the reduction with ytterbium metal. Ph$_2$CD$_2$ and PhND$_2$ would be formed by further reductive C−N bond fission of Ph$_2$CDNDPh with divalent ytterbium. In addition, all observed signals of the phenyl groups and the imine carbons of **1** are shifted upfield in the ^{1}H (δ 5.52−6.95

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(7) Procedure for the synthesis of **1** is as follows. To a mixture of metallic ytterbium (346 mg, 2.0 mmol, activated by 2 μL of CH$_3$I), THF (8 mL), and HMPA (2 mL) in a Schlenk tube under argon was added Ph$_2$C═NPh (514 mg, 2.0 mmol), and the mixture was stirred at room temperature for 4 h to give a red-black suspension. The suspension was moved into another Schlenk tube to remove the unreacted ytterbium metal. A red-black solution was obtained by heating the suspension under reflux, which was allowed to stand at room temperature to precipitate red-black needles. The complex **1** (860 mg, 0.889 mmol, 44.5%) was isolated by removing the solvent followed by drying the needles *in vacuo*.

(8) Reaction of Ph$_2$C═NPh with ytterbium in the absence of HMPA at room temperature for 48 h afforded violet powders, which gave Ph$_2$CHNHPh in quantitative yield after the treatment with H$_2$O. However, crystallization of this complex was unsuccessful. We have tried but not succeeded in isolating ytterbium−Ph$_2$C═NPh complexes containing other ligands such as 1,3-dimethyl-2-imidazolidinone and pyridine.

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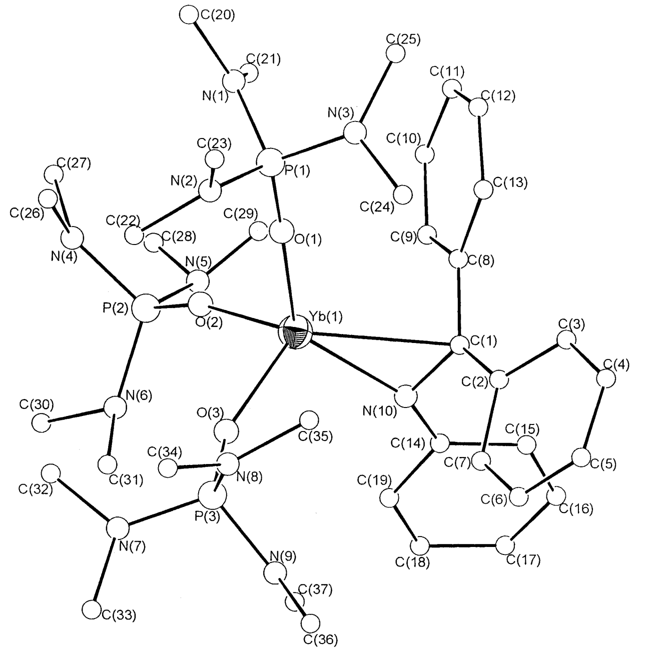

Figure 1. ORTEP drawing of **1**. Selected bond lengths (Å) and angles (deg): Yb(1)−C(1), 2.679(18); Yb(1)−N(10), 2.318(15); C(1)−N(10), 1.43(3); Yb(1)−O(1), 2.320(14); Yb(1)−O(2), 2.275(12); Yb(1)−O(3), 2.298(12); Yb(1)−C(1)−N(10), 59.9(9); Yb(1)−N(10)−C(1), 87.8(10); C(1)−Yb(1)−N(10), 32.3(5); C(2)−C(1)−C(8), 125.6(15); C(2)−C(1)−N(10), 118.2(15); C(8)−C(1)−N(10), 115.3(14); C(1)−N(10)−C(14), 117.5(15); O(1)−Yb−O(2), 107.1(5); O(2)−Yb−O(3), 99.7(5); O(3)−Yb−O(1), 95.6(5); C(1)−Yb−O(1), 102.7(6); C(1)−Yb−O(2), 128.2(6); C(1)−Yb−O(3), 118.6(5).

ppm) and ^{13}C NMR spectra (δ 94.2−143.4 and 162.0 ppm) and appear without broadening, indicating that two electrons are transferred from ytterbium to the imine, increasing the electron density of the phenyl ring, and that ytterbium becomes divalent.[9] It should be noted that signals of the five protons and six carbons of the *N*-phenyl group were independently observed, respectively, whereas those of the *C*-phenyl groups were detected as three and four equivalent signals. These results suggest that only on the nitrogen atom has the rotation of the aromatic ring ceased even in the solution state.

Figure 1 shows the structure and bond lengths and angles of **1** obtained by the X-ray crystallographic study.[10] The complex is monomeric and five-coordinate. Although the complex seems to possess a tetrahedral pyramid-like structure composed of three HMPA ligands and the imine π-ligand, the imine should be dianionic and ytterbium should be divalent from the NMR spectroscopy and D_2O quenching of **1**, as mentioned above. The sum of the angles formed by N(10), C(2), and C(8) around C(1) is over 359°, which is larger than that of the ytterbium−benzophenone complex [Yb(Ph$_2$CO)(hpma)$_2$]$_2$,[11] suggesting that C(1) is still sp^2-hybridized. The sp^2 character of C(1) is consistent with the Yb−C(1)−N(10) angle (87.8(10)°), which is nearly orthogonal to the C(1)−N(10) bond and considerably larger than in the zirconametallacyclopropane complex Cp$_2$Zr(PhCHNPh)(thf) (64.1(3)°).[3b] The C(1)−N(10) bond distance of the imine moiety in the complex **1** (1.43(3) Å) can be considered as a C−N single bond[12] and is longer than that of the zirconium azametallacyclopropane complex Cp$_2$Zr(PhCHNPh)(thf) (1.375(7) Å)[3b] and almost the same as in the azatitanacyclopropane complex Ti(OAr)$_2$(^{t}BuNCCH$_2$Ph)(Py-4Ph) (1.421(7) Å; Ar = 2,6-di-*tert*-butylphenyl).[4b] The C(1)−Yb−N(10) angle (32.3(5)°) is smaller than those of Cp$_2$Zr(PhCHNPh)(thf) (37.5(7) Å),[3b] Cp$_2$Zr(PhCHNTMS)(thf) (37.6(3)°),[3c] and Ti(OAr)$_2$(^{t}BuNCCH$_2$Ph)(Py-4Ph) (40.6(2)°),[4b] The Yb−C(1) bond distance (2.679(18) Å) is larger than that of [Yb(Ph$_2$CO)(hmpa)$_2$]$_2$ (2.59(5) Å).[11] Three Yb−O(hmpa) bonds (2.320(14), 2.275(12), and 2.298(12) Å, respectively) are almost as long as those for divalent ytterbium complexes having a low coordination number such as [Yb(Ph$_2$CO)(hmpa)$_2$]$_2$ (2.28(3) Å)[11] and Yb(OAr′)$_2$(hmpa)$_2$ (2.298(7) Å; Ar = 2,6-di-*tert*-butyl-4-methylphenyl)[11b] and slightly shorter than that of YbI$_2$(hmpa)$_4$(thf)$_2$ (2.357(6) Å),[13] which has a high coordination number.

With respect to the chemical properties of **1**, the complex is found to be more basic and less nucleophilic than the Yb−diaryl ketone[11,14] and −diaryl thioketone[15] dianion complexes. The reaction of **1** with acetone resulted in the quantitative formation of Ph$_2$CHNHPh due to the abstraction of the acidic hydrogen in the substrate (Scheme 1),[16] whereas nucleophilic addition of the anionic carbonyl carbons to those electrophiles occurred to give Ph$_2$C(XH)C(OH)Me$_2$ (X = O, 60%; X = S, 72%) in the reaction of [Yb(Ph$_2$CO)(hmpa)$_2$]$_2$[11a,14] or the ytterbium−thiobenzophenone dianion complex.[15] The reaction with isopropyl isocyanate followed by treatment with H_2O afforded 2,2-diphenyl-*N*-isopropyl-2-(phenylamino)acetamide as the sole product in 94%

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[9] For **1**: ^{1}H NMR (THF-d_8/HMPA) δ 5.52 (t, J = 6.8 Hz, 1 H, *p*-PhN), 5.58 (t, J = 7.7 Hz, 2 H, *p*-PhC), 5.82 (d, J = 6.8 Hz, 1 H, *o*-PhN), 6.30 (t, J = 6.8 Hz, 1 H, *m*-PhN), 6.35 (d, J = 6.8 Hz, 1 H, *o*-PhN), 6.42 (t, J = 7.7 Hz, 4 H, *m*-PhC), 6.56 (t, J = 6.8 Hz, 1 H, *m*-PhN), 6.95 (d, J = 7.7 Hz, 4 H, *o*-PhC); ^{13}C NMR (THF-d_8/HMPA) δ 94.2 (*ipso*-PhN), 105.1 (*p*-PhN), 107.3 (*p*-PhC), 112.8 (*o*-PhN), 116.3 (*o*-PhC), 117.9 (*m*-PhN), 127.4 (*m*-PhN), 128.6 (*m*-PhC), 128.9 (*o*-PhN), 143.4 (*ipso*-PhC), 162.0 (CN). Anal. Calcd for $C_{37}H_{69}N_{10}O_3P_3Yb$: C, 45.91; H, 7.18; N, 14.47. Found: C, 45.58; H, 7.20; N, 14.31.

[10] Crystal data for **1**: $C_{37}H_{69}N_{10}O_3P_3Yb$, fw = 967.99, monoclinic, space group $P2_1/n$ (No. 14), a = 20.747(7) Å, b = 21.077(6) Å, c = 11.712(5) Å, β = 101.28(3)°, V = 5022(3) Å^3, Z = 4, D_{calcd} = 1.28 g cm^{-3}, μ(Mo Kα) = 19.892 cm^{-1}, R = 0.0740 (R_w = 0.1118) for 6546 unique data with $F_o > 3\sigma(I)$ and 487 variables. Crystals were sealed in thin-walled glass capillaries under N_2. Data were collected on a Mac Science MXC3K diffractometer (20 °C, Mo Kα radiation, graphite monochromator, λ = 0.710 69 Å, $\omega-2\theta$ scan, $2° \le \theta \le 27.5°$) and were corrected for absorption effects. Structures were solved by direct methods using SIR92 in the CRYSTAN-GM software package. Refinements were performed anisotropically by the block-diagonal least-squares method.

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(12) C−N single-bond length 1.45 Å and C−N double-bond length 1.27 Å; Burkr-Laing, M.; Laing, M. *Acta Crystallogr.* **1976**, *32B*, 3216.

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(16) Reaction of **1** with $(CD_3)_2CO$ followed by treatment with H_2O afforded Ph$_2$CDNHPh in quantitative yield and 94% deuterium incorporation.

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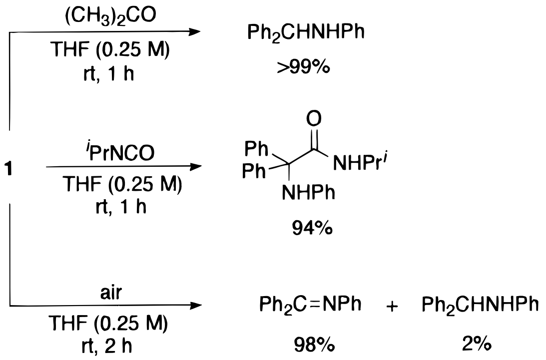
Scheme 1



yield. Aerobic oxidation of **1** in THF regenerated the C=N double bond to produce $Ph_2C{=}NPh$ (98%), similar to the oxidation of $[Yb(Ph_2CO)(hmpa)_2]_2$.[11a] It is interesting that a catalytic amount of **1** (5 mol %) causes the isomerization of 1-hexyne to 2-hexyne (95%), and neither formation of other unsaturated hydrocarbons such as 1,2- and 2,4-hexadiene[17] nor addition of the imine carbanion to the alkyne was observed.[1,3]

In summary, we have demonstrated the structure and the chemical properties of the first lanthanoid–imine azametallacycle complex which can be directly synthesized from a free imine and metallic ytterbium. The significant information obtained about this complex should be of assistance in exploring the chemistry of lanthanoid-heterocarbonyl dianionic complexes and in the construction of novel catalytic pathways. Further studies on the synthetic application of lanthanoid–imine complexes are currently underway.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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