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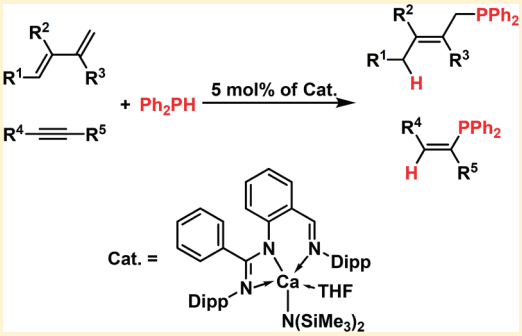
Synthesis of Calcium and Ytterbium Complexes Supported by a Tridentate Imino-Amidinate Ligand and Their Application in the Intermolecular Hydrophosphination of Alkenes and Alkynes

Hongfan Hu and Chunming Cui*

State Key Laboratory and Institute of Element-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Supporting Information

ABSTRACT: Well-defined calcium and ytterbium complexes [{2-NC(Ph)-NArC_6H_4CHNAr}M{N($SiMe_3$)$_2$}(THF)] (M = Ca, Yb; Ar = 2,6-*i*Pr$_2$$C_6H_3$) have been synthesized and characterized. They catalyze the intermolecular hydrophosphination of alkenes, dienes, and alkynes with high activity and selectivity under mild conditions. Highly selective 1,4-additions (94−100%) for the conjugated dienes examined have been observed with both catalysts. The calcium complex exclusively catalyzes anti addition to alkynes, including terminal alkynes, while the ytterbium, in most cases, catalyzes syn addition. The calcium catalyst could promote hydrophosphination of hindered alkenes such as stilbene under relatively mild conditions.



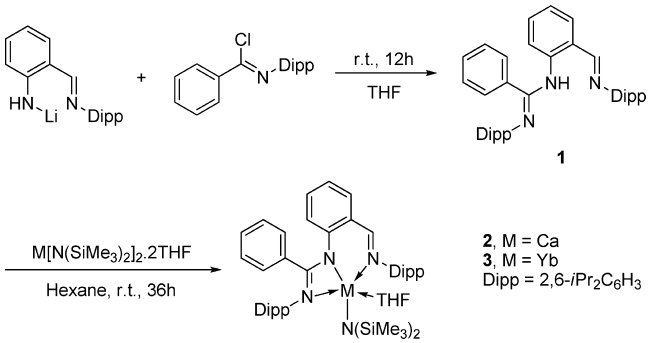
Since calcium is a cheap and environmentally benign element, the development of calcium-based homogeneous catalytic systems has received considerable attention in the past few years.[1] For example, they have been successfully used as polymerization,[2] hydroamination,[3] and hydrosilylation[4] catalysts. In 2007, Hill and co-workers reported that the hydrophosphination of unhindered activated alkenes and diphenylacetylene with diphenylphosphine was catalyzed by 10−20 mol % of the *β*-diketiminato complex [{HC(C(Me)$_2$N-2,6-*i*Pr$_2$$C_6H_3$)$_2$}Ca{N(SiMe$_3$)$_2$}(THF)] (**A**).[5] However, their attempts to catalyze hydrophosphination reactions with the homoleptic calcium amide [Ca{N(SiMe$_3$)$_2$}(THF)$_2$] met with very limited success. Subsequently, Westerhausen and co-workers reported that the calcium diphosphide complex [Ca(PPh$_2$)$_2$(THF)$_4$] catalyzes the intermolecular hydrophosphination of phenyl-substituted alkynes and butadiynes.[6] Intermolecular hydrophosphination of alkynes and olefins catalyzed by late-transition-metal complexes[7] and rare-earth-metal complexes[8] has also been reported.

Amidinate and *β*-diketiminato ligands have been extensively used as supporting ligands for the synthesis of rare-earth metal complexes and alkaline-earth-metal complexes.[1,9] In order to tune the catalytic performance and reaction patterns of the complexes of these highly electropositive metals, we have designed a new type of tridentate amidinate ligand featuring an imine arm with the expectation of stabilizing large ionic radii metal complexes. Herein we report on the synthesis, characterization, and catalytic hydrophosphination reactions of the well-defined calcium complex [{2-NC(Ph)NArC_6H_4CHNAr}Ca{N(SiMe$_3$)$_2$}(THF)] (**2**; Ar = 2,6-*i*Pr$_2$$C_6H_3$) with a modified tridentate amidinate ligand. The catalyst is highly efficient, with selectivity distinct from that of the reported calcium catalyst supported by a *β*-diketiminato ligand. In addition, the corresponding ytterbium complex has also been prepared for comparison.

RESULTS AND DISCUSSION

The ligand [2-{NHC(Ph)NAr}C_6H_4CHNAr] (**1**, Ar = 2,6-*i*Pr$_2$$C_6H_3$; Scheme 1) was synthesized by a salt metathesis reaction of [2-{CHNAr}C_6H_4NHLi] with [ArNC(Ph)Cl] (Ar = 2,6-*i*Pr$_2$$C_6H_3$) in good yield and was fully characterized by standard analytical and spectroscopic techniques. The calcium complex **2** was obtained as a light yellow solid in 78% yield by the silylamine elimination reaction of the calcium diamide [Ca{N(SiMe$_3$)$_2$}(THF)$_2$] with **1**. The corresponding ytterbium complex [{2-NC(Ph)NArC_6H_4CHNAr}Yb{N(SiMe$_3$)$_2$}(THF)] (**3**, Ar = 2,6-*i*Pr$_2$$C_6H_3$) was prepared similarly and obtained as dark green blocks in ca. 71% yield. Complexes **2** and **3** have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis.

Scheme 1. Synthesis of 2 and 3



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Single crystals of **2** suitable for X-ray single-crystal analysis were obtained from *n*-hexane at 25 °C, and the structure is shown in Figure 1 along with selected bond parameters.

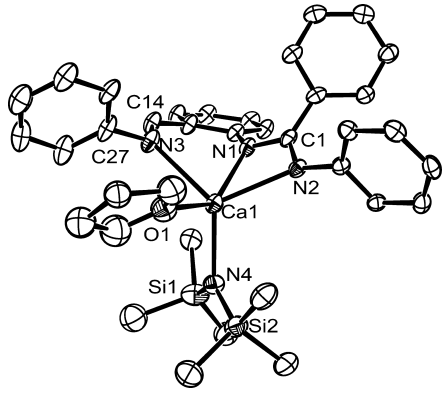
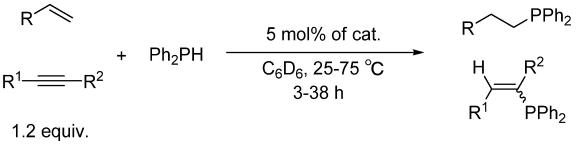


Figure 1. Ortep drawing of **2** with 30% probability ellipsoids. Hydrogen atoms and isopropyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ca1−N1 = 2.335(4), Ca1−N2 = 2.519(4), Ca1−N3 = 2.652(4), Ca1−N4 = 2.306(4), Ca1−C1 = 2.888(4), Ca1−O1 = 2.400(4); N1−Ca1−N2 = 54.84(11), N1−Ca1−N3 = 69.29(12), N1−C1−N2 = 112.9(4), N4−Ca1−O1 = 96.14(14).

Complex **2** is monomeric in the solid state with a five-coordinate calcium center. Most of the bond distances and angles are as expected, but there are exceptions. Unlike most amidinate metal complexes with two almost equal M−N bond lengths,[9a,c] the Ca1−N2 bond distance (2.519(4) Å) is noticeably longer than the Ca1−N1 distance (2.335(4) Å), indicating a relatively low degree of electron delocalization over the N1−C1−N2 amidinate backbone. The long Ca1−N3 bond length (2.652(4) Å) is indicative of a dative bond. Complexes **2** and **3** proved to be thermally robust, as no decomposition and ligand distribution were observed even in solution at 160 °C, indicating the unusual stabilizing effects of the tridentate ligand.

Although a few calcium catalysts for the hydrophosphination of alkynes and alkenes have been reported, the scope of the substrates and selectivity are not satisfactory.[5a,6] Since catalytic performances are largely related to the ligand sets, compounds **2** and **3** with the new tridentate ligand have been employed as catalysts for the intermolecular hydrophosphination of alkenes and alkynes (Scheme 2). The hydrophosphination reactions of

Scheme 2. Catalysis of Intermolecular Hydrophosphination



1,3-conjugated dienes, alkynes and sterically hindered olefins have been examined. The results for these catalytic reactions are given in Table 1. The catalysts are not active for unactivated substrates such as 1-hexene, norbornene, and 4-hexyne but showed a moderate activity for activated alkenes/alkynes. The hydrophosphination products are exclusively consistent with anti-Markovnikov rules, and 2,1-insertions have been observed as a result of the stabilizing effect of the aryl/alkyl group to the highly electropositive calcium center of the four-membered-ring intermediate that has been previously proposed for activated alkene/alkynes.[3a] Both steric and electronic factors of the substrate affect the catalytic activity: more hindered alkenes are less active, and electron-donating groups on the substrates lower the activity (entries 2, 6, and 7). These observations are in accordance with those for calcium-catalyzed intermolecular hydroamination reactions.[10] For every substrate, the loading of the catalyst and reaction temperatures have been optimized; only the lowest loadings and optimized temperatures are given in Table 1.

The calcium complex **2** shows a significantly higher activity than the reported $[\{HC(C(Me)_2N\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2\}Ca\{N(SiMe_3)_2\}(THF)]$ (**A**) (entries 1, 3, and 8). For example, the hydrophosphination of styrene with only 2 mmol % of **2** is complete (100% conversion) in 3 h at 25 °C, while the same reaction employing 10 mmol % of the β-diketiminato complex as catalyst occurred at 75 °C with only 95% conversion in 20 h. Interestingly, **2** can catalyze the hydrophosphination reactions of bulky substrates such as α-methylstyrene and *cis*-stilbene (entries 6 and 7). In contrast, the reported β-diketiminato complex is inactive for these substrates. **2** also catalyzes the hydrophosphination of the terminal alkynes PhCCH and PyCCH (entries 9 and 13). It is well-known that terminal alkynes tend to undergo σ-bond metathesis and subsequent dimerization in the presence of this type of catalyst.[11] To the best of our knowledge, this is the first calcium-mediated intermolecular hydrophosphination reaction of terminal alkynes.

The regioselectivity of **2** is somewhat different from the reported β-diketiminato complex. The hydrophosphination of isoprene catalyzed by the latter mainly results in the 1,2-addition product, while the same reaction catalyzed by **2** predominately gives the 1,4-addition product (entry 3). Similarly, other 1,3-dienes catalyzed by **2** also yield 1,4-addition products with high selectivity (entries 4 and 5). Different stereoselectivities for the hydrophosphination of alkynes have also been observed with **2** and the β-diketiminato complex. With the β-diketiminato complex as catalyst, a syn addition of diphenylphosphine to alkynes is favorable, which leads to *E* isomers (entry 8), while reactions mediated by **2** mainly lead to anti addition products and *Z* isomers are preferable (entries 8−13). All these observations reveal the impact of the ligand geometry on catalytic performance. It is noted that 1,4-hydrophosphination of 1,3-dienes has been rarely reported with early-transition-metal catalysts.[12,8a]

The same reactions have also been examined with the ytterbium complex **3** as catalyst. It can be concluded that **3** has activity comparable to that of **2** for almost all of the substrates. For the hydrophosphination of 1,3-dienes, **2** and **3** show extremely similar regioselectivities and catalyze 1,4-addition to the dienes (entries 3−5). However, differences emerge in the hydrophosphination of alkynes. Unlike the anti addition fashion catalyzed by **2**, the reactions catalyzed by **3** are somewhat substrate dependent but, in most cases, lead to syn addition products to form *E* isomers (entries 9−12).

The reaction of **2** with the same amount of diphenylphosphine has been investigated at room temperature on an NMR scale (Scheme 3). After 2 h, a singlet at 0.09 ppm in the ^{1}H NMR spectra indicates the protonolysis of $HN(SiMe_3)_2$ from **2**. A new peak at −21.1 ppm in the ^{31}P NMR spectrum may be attributed to the formation of a calcium phosphide complex. Both of these peaks can be observed in all of the catalytic reactions on the NMR scale, suggesting the formation of a reactive calcium phosphide intermediate. However, the stoichiometric reaction cannot achieve a complete transformation to the corresponding phosphide, even at 80 °C. Increasing the amount of diphenylphosphine to 5 equiv also led to a mixture of **2** and the corresponding calcium phosphide. Attempts to isolate the putative intermediate have been unsuccessful to date.

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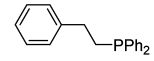
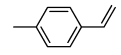
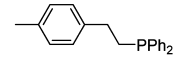
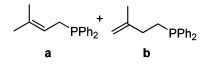
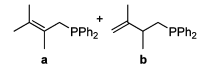
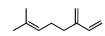
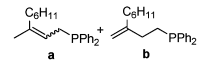
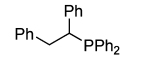
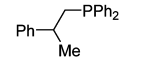
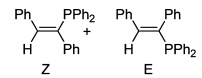
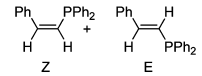
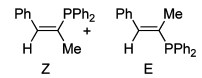
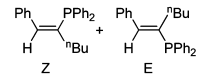
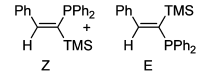
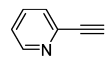
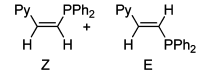
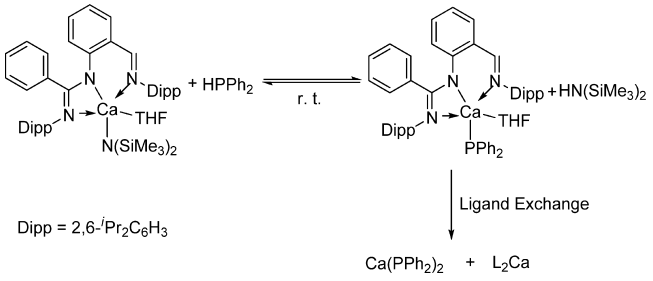
Table 1. Intermolecular Hydrophosphination of Alkenes and Alkynes

Entry	Substrate	Product	Catalyst[b]	T / °C	t / h	Conv./ %[a]	Regio-selectivity
			A[d]	75	20	95[h]	-
1			**2**[c]	25	3	100	-
			3[c]	25	2	100	-
2			**2**	25	3	99	-
			A[d]	25	24	95[h]	a : b = 21 : 79
3			**2**[c]	25	2	100	a : b = 95 : 5
			3[c]	25	1.5	100	a : b = 100 : 0
4			**2**	60	24	86	a : b = 100 : 0
			3	25	24	90	a : b = 100 : 0
5			**2**	25	8	100	a : b = 94 : 6[f]
			3	25	1.5	100	a : b = 97 : 3[g]
6			**2**	60	18	72	-
7			**2**	60	24	85	-
			A[e]	75	13	94[h]	Z : E = 2 : 98
8			**2**	25	10	99	Z : E = 86 : 14
			3	60	7	100	Z : E = 55 : 45
9			**2**	75	38	78	Z : E = 76 : 24
			3	75	38	91	Z : E = 10 : 90
10			**2**	60	5	99	Z : E = 91 : 9
			3	25	3	100	Z : E = 16 : 84
11			**2**	60	3	100	Z : E = 93 : 7
			3	25	2	100	Z : E = 7 : 93
12			**2**	75	3	0	-
			3	60	28	95[i]	Z : E = 6 : 94
13			**2**	25	2	100	Z : E = 69 : 31
			3	25	5	96	Z : E = 69 : 31

[a]On the basis of the consumption of phosphine from integration of signals in the ^{1}H and ^{31}P NMR. [b]5 mol % of catalyst used. [c]2 mol % of catalyst used. [d]10 mol % of catalyst used. [e]20 mol % of catalyst used. [f]*Z*:*E* ratio 20:80. [g]*Z*:*E* ratio 22:78. [h]Data taken from ref 5a. [i]10% of Markovnikov addition product.

Scheme 3. Stoichiometric Reaction between 2 and $HPPh_2$



■ CONCLUSION

Well-defined calcium and ytterbium complexes supported by a tridentate amidinate-based ligand have been synthesized and characterized. They are efficient catalysts for the intermolecular hydrophosphination of alkenes and alkynes. The complexes show high activity and regioselectivity distinct from that of the reported *β*-diketiminato calcium complex. Efforts to tune the ligand system for the development of highly active calcium catalysts with high selectivity are currently in progress.

■ EXPERIMENTAL SECTION

All manipulations of air-sensitive materials were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. All the liquid alkenes and alkynes were dried over CaH_2, freshly distilled, and freeze−thaw degassed prior to use. The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers.

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NMR-Scale Catalytic Reactions. In a glovebox, diphenylphosphine (43 μL, 0.25 mmol) was added to a solution of the catalyst (0.012 mmol, 5 mol %) in C_6D_6 and the alkene/alkyne (0.3 mmol, 1.2 equiv) was added either as a solid or a solution in the same solvent. The solution was then loaded into a Young tap NMR tube. The reaction was monitored by ^1H and ^{31}P spectroscopy.

LCaN(SiMe$_3$)$_2$·THF (2). A solution of **1** (1.63 g, 3 mmol) in 30 mL of hexane was added to a solution of Ca[N(SiMe$_3$)$_2$]$_2$·2THF (1.52 g, 3 mmol) in the same solvent. The mixture was stirred for 36 h at room temperature and then filtered. The filtrate was concentrated, and recrystallization at −40 °C yielded the product as light yellow crystals (1.90 g, 78%). Mp: 151−154 °C. ^1H NMR (C_6D_6, 400 MHz): δ 0.24 (s, 18H), 0.97 (d, 6H, 6.4 Hz), 1.10 (m, 4H), 1.27 (m, 6H), 1.31 (d, 12H, 6.4 Hz), 3.26 (sept, 2H, 6.8 Hz), 3.35 (m, 4H), 3.50 (sept, 2H, 6.8 Hz), 6.21 (d, 1H, 8.4 Hz), 6.44 (t, 1H, 7.2 Hz), 6.66 (t, 1H, 8.4 Hz), 6.81 (m, 3H), 6.97 (d, 1H, 7.6 Hz), 7.08 (m, 8H), 8.06 (s, 1H). ^{13}C NMR (C_6D_6, 100 MHz): 6.1 (SiMe$_3$), 24.0, 25.0, 25.5, 28.4 (CHMe$_2$), 29.0, 68.9 (THF), 117.6, 123.6, 123.9, 124.0, 124.1, 124.4, 126.0, 128.2, 128.5, 130.3, 132.2, 134.5, 135.7, 139.7, 141.3, 144.7, 150.7, 151.8 (ArC), 169.2, 171.8 (C═N). IR (KBr, cm^{-1}): 3689, 3646, 3372, 3061, 2960, 2868, 1916, 1800, 1621, 1576, 1456, 1316, 1249, 1213, 1128, 1058, 932, 842, 697, 617, 531, 419. Anal. Calcd for $C_{48}H_{70}CaN_4OSi_2$ (815.34): C, 70.71; H, 8.65; N, 6.87. Found: C, 70.16; H, 8.14; N, 6.33.

LYbN(SiMe$_3$)$_2$·THF (3). LYbN(SiMe$_3$)$_2$·THF was synthesized by a method similar to that described for complex **2**. The product was obtained as dark brown crystals (0.67 g, 71%). Mp: 160−163 °C. ^1H NMR (C_6D_6, 400 MHz): δ 0.30 (s, 18H), 0.98 (d, 6H, 5.2 Hz), 1.17 (d, 6H, 6.0 Hz), 1.23 (m, 4H), 1.29 (d, 6H, 6.4 Hz), 1.35 (d, 6H, 5.6 Hz), 3.19 (br, 4H), 3.37 (sept, 2H, 6.4 Hz), 3.56 (sept, 2H, 5.6 Hz), 6.24 (d, 1H, 8.4 Hz), 6.44 (t, 1H, 7.2 Hz), 6.72 (t, 1H, 7.6 Hz), 6.81 (m, 3H), 7.07 (m, 9H), 8.21 (s, 1H). ^{13}C NMR (C_6D_6, 100 MHz): 6.0 (SiMe$_3$), 24.1, 25.4, 25.7, 28.2 (CHMe$_2$), 28.8, 68.8 (THF), 118.1, 123.7, 124.1, 124.3, 125.0, 126.0, 128.0, 128.2, 128.6, 130.0, 132.3, 134.8, 135.8, 139.9, 141.6, 144.7, 150.2, 151.0 (ArC), 168.3, 170.8 (C═N). IR (KBr, cm^{-1}): 3645, 3060, 3025, 2960, 2868, 1917, 1620, 1534, 1440, 1402, 1362, 1317, 1248, 1214, 1162, 1128, 1044, 932, 898, 842, 754, 696, 619, 531, 468, 415. Anal. Calcd for $C_{48}H_{70}YbN_4OSi_2$ (948.31): C, 60.79; H, 7.44; N, 5.91. Found: C, 60.51; H, 7.18; N, 5.63.

X-ray Structural Determination. The X-ray data were collected on a Rigaku Saturn CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 113 K. The structure was solved by direct methods (SHELXS-97)[13] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a riding model (SHELXL-97).[14] Crystal data for **2**: $C_{48}H_{70}CaN_4OSi_2$, fw = 815.34, hexagonal, space group $R\bar{3}$, a = 50.829(8) Å, c = 11.144(2) Å, V = 24934(7) Å^3, Z = 18, ρ_{calcd} = 0.977 g cm^{-3}, 69 723 reflections, 9754 unique reflections(R_{int} = 0.0793), R1 = 0.1050 ($I > 2\sigma(I)$), wR2 = 0.2716 (all data).

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and CIF files giving experimental details for the synthesis and characterization of the compounds in this paper and crystal structure data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cmcui@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

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