Organometallics **2007,** *26,* 5132−5135

The Azametallacyclopropane Ca(η^2-Ph$_2$CNPh)(hmpa)$_3$: A Calcium Alternative to a Versatile Ytterbium(II) Catalyst

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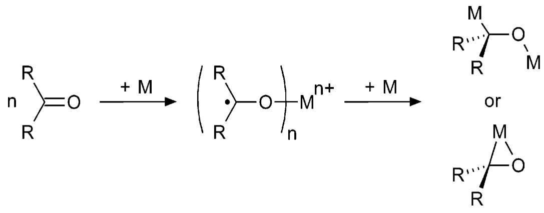
Received June 22, 2007

*Summary: The azametallacyclopropane complex Ca(η^2-Ph$_2$CNPh)(hmpa)$_3$ (**2-Ca**) can be conveniently obtained in crystalline purity via a one-pot procedure (yield 48%). The catalytic activities and selectivities of **2-Ca** and its Yb(II) analogue **2-Yb** have been found to be comparable in a variety of reactions; therefore, **2-Ca** could be a cheap substitute for the extensively studied Yb(II) catalyst.*

Since the pioneering work of Beckmann and Schlenk,[1] ketyl complexes of alkali and alkaline-earth metals, i.e., complexes obtained via the one-electron reduction of ketones, have been among the earliest well-defined complexes in organometallic chemistry. Also, the second reduction step, resulting in the dianion, was known already at that early stage (eq 1).



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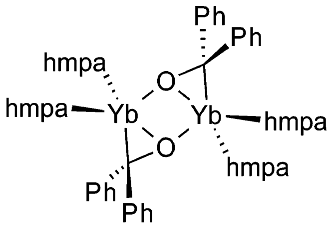
Some of the synthetically useful ketyl complexes that play a major role in organic redox chemistry have only recently been structurally characterized.[2] One of the few characterized metal compounds that include a dianionic benzophenone ligand is the Yb$^{\mathrm{II}}$ complex **1**, which crystallizes as a dimer.[3] Recently a convenient synthetic route (eq 2; hmpa = hexamethylphosphoramide) was also developed for its isolobal imine analogue **2-Yb**, a complex that has been fully characterized by crystal structure analysis.[4]



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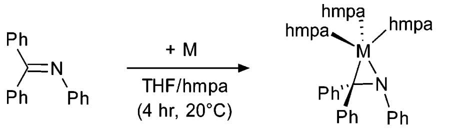

(2)

2-M

This particular Yb$^{\mathrm{II}}$ complex **2-Yb** has been applied as a versatile and easily accessible catalyst for an impressive number of catalytic conversions which recently have been reviewed:[5] alkyne isomerization,[6] dehydrogenative silylation of terminal alkynes[7] and amines,[8] hydrosilylation of imines[8] and olefins,[9] dehydrogenative polymerization of PhSiH$_3$,[5] and intermolecular hydrophosphination of alkynes.[10]

Our continuous interest in the similarities and differences in the chemistry of organometallic complexes of Ca^{2+} and Yb^{2+} [11] motivated us to explore the synthesis and structure of **2-Ca**. We are, however, especially interested in the catalytic activity of **2-Ca**. Successful catalytic application of the calcium analogue **2-Ca** not only would add substantially to the current research activity in the area of Ca-catalyzed reactions[12] but would also provide a much cheaper alternative to the well-explored Yb$^{\mathrm{II}}$ catalysts.

The extremely air and moisture sensitive azametallacyclopropane complex **2-Ca** was prepared analogously to **2-Yb**.[13] Addition of diphenylmethylene-*N*-phenylimine to a suspension of commercially available calcium metal chunks (99% purity) in a THF/hmpa mixture slowly gave a color change to red. This color deepened over time, and **2-Ca** deposited from solution. Slow crystallization from a hot THF/hmpa solution gave the product in the form of large shiny black (intensely dark red) needles in 48% yield. The crystals are extremely air-sensitive: even under paraffin oil rapid decolorization is observed. For

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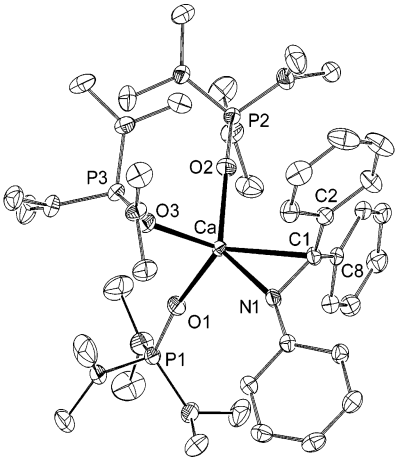
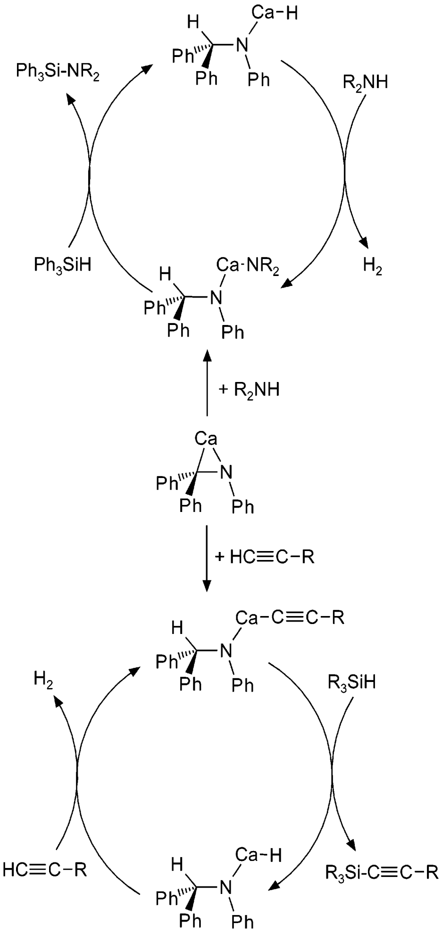


Figure 1. Crystal structure of **2-Ca** (30% probability). For clarity all hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg) (the values for **2-Yb**[4] are given in brackets): Ca−C1, 2.611(2) [2.679(2)]; Ca−N1, 2.281(1) [2.318(2)]; Ca−O1, 2.245(1) [2.275(1)]; Ca−O2, 2.245(1) [2.320(1)]; Ca−O1, 2.271(1) [2.298(1)]; C1−N1, 1.451(2) [1.43(3)]; Ca−C1−N1, 60.59(7) [59.9(9)]; Ca−N1−C1, 85.75(8) [87.8(1)].

general use in catalysis, isolation of complex **2-Ca** could be avoided by in situ preparation of the catalyst via a straightforward one-pot procedure (as has been done for **2-Yb**).

Complex **2-Ca** crystallizes isomorphously with **2-Yb** (Figure 1),[13] and although the bond distances to the somewhat smaller Ca^{2+} are slightly shorter,[14] their structures show the same characteristic features that would be expected for the dianionic ligand $Ph_2C^-{-}(Ph)N^-$. As for **2-Yb**, the sum of the C−C−C and C−C−N valence angles around C1 is 359.9(1)°, which indicates perfect sp^2 hybridization. The planar framework of the imine parent compound $Ph_2C{=}NPh$ has transformed into a structure in which the Ph−N vector is nearly perpendicular to the plane spanned by N1, C1, C2, and C8: the C(Ph)−N1−C1−C(2,8) torsion angles are 102.3(2) and −81.5(2)°. The C1−N1 bond distance of 1.451(2) Å in **2-Ca** can be considered as a single C−N bond.[15] The Ca−N1 bond distance of 2.281(1) Å compares well to the terminal Ca−N bond distance of 2.275(7) Å in $[((Me_3Si)_2N)_2Ca]_2$.[16] The Ca−C1 bond distance of 2.611(1) Å is in the range observed for the Ca−C σ bonds observed in dibenzylcalcium complexes (2.59−2.65 Å).[17]

Scheme 1



In this preliminary investigation on the catalytic activity of **2-Ca** we focused on the dehydrogenative silylation of amines and acetylenes: i.e., two reactions that have no precedence in Ca-mediated catalysis. We suggest catalytic cycles (Scheme 1) similar to those proposed for the Yb-mediated reactions. These routes would involve calcium acetylide and amide intermediates that are converted to an intermediate heteroleptic calcium hydride complex, for which we recently found experimental evidence.[18] For the catalyst **2-Yb** the substituent on nitrogen plays an important role in its catalytic activity through electronic and steric effects.[5] It is therefore likely that the remaining $Ph_2(H)C(Ph)N^-$ ligand acts as a spectator ligand and does not

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[13] The synthesis was performed analogously to that reported for **2-Yb**, with the difference that longer reaction times were used. To a mixture of metallic calcium pieces (99% purity, ca. 10−20 mesh, 160 mg, 4.0 mmol, activated by 8 μL of $Br_2C_2H_4$), THF (16 mL), and HMPA (4 mL) in a Schlenk tube was added diphenylmethylene-*N*-phenylimine (1028 mg, 4.0 mmol). Stirring this mixture at room temperature for 16 h gave a very dark red suspension. Heating this suspension gave a dark solution which could be decanted from unreacted metal. Slow cooling of this solution gave precipitation of **2-Ca** as a uniform crop of large, shiny, black (very dark red) needles. These were washed with pentane and dried in vacuo: yield 1604 mg, 1.92 mmol, 48%. See the Supporting Information for more information and analyses. Crystal data for **2-Ca**: data collection on a Siemens SMART diffractometer with APEXII area detector system at −70 °C (Mo Kα), formula $C_{37}H_{69}CaN_{10}O_3P_3$, M_r = 835.01, monoclinic, space group $P2_1/n$, a = 11.5977(4) Å, b = 20.7073(8) Å, c = 20.6254(7) Å, β = 101.527(2)°, V = 4853.4(3) Å^3, Z = 4, ρ_{calcd} = 1.143 Mg m^{-3}, $F(000)$ = 1800, μ(Mo Kα) = 0.270 mm^{-1}, 108 700 measured reflections, 9626 independent reflections (R_{int} = 0.036, θ_{max} = 26.1°) and 8429 observed reflections ($I > 2\sigma(I)$), R1 = 0.0440 for $I > 2\sigma(I)$, wR2 = 0.1134, GOF = 1.07 for all data, minimum/maximum residual electron density −0.35/+0.21 e Å^{-3}. Hydrogen atoms on aryl groups were observed in a difference Fourier map and refined isotropically; hydrogen atoms at hmpa ligands have been placed on calculated positions and were refined in a riding mode. Rotational disorder in one of the hmpa ligands has been solved with a disorder model. The structure was solved by direct methods (SHELXS-97)[13a] and was refined on F^2 (SHELXL-97).[13b] Geometry calculations and graphics were carried out with PLATON.[13c] A molecule of THF cocrystallized around the center of inversion and was completely disordered. This disorder was treated with the SQUEEZE procedure[13d] incorporated in PLATON. (a) Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution; Universität Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, Göttingen, Germany, 1997. (c) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2000. (d) van der Sluis, P. A.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

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[15] Due to strong $C^-{-}N^-$ repulsion, the C1−N1 bond in **2-Ca** is considerably longer than an average C(sp^2)−N(sp^2) single bond (1.355 Å) and compares better to an average C(sp^3)−N(sp^2) single bond (1.469 Å). Values taken from: Allen, F. A.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

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Table 1. Summary of Results for the Dehydrogenative Silylation of Amines with Ph_3SiH^a

entry	$(R^1)(R^2)NH$	cat.	amt of cat. (mol %)	*t* (h)	conversn (%)
	$(R^1)(R^2)NH + Ph_3SiH \rightarrow (R^1)(R^2)N-SiPh_3 + H_2$				
1	R^1 = pentyl, R^2 = H	**2-Ca**	3	0.5	>98
2[8]	R^1 = pentyl, R^2 = H	**2-Yb**	3	2	93
3	R^1 = pentyl, R^2 = H	**3**	5	0.5	95
4	R^1 = Bu, R^2 = Me	**2-Ca**	10	3	95
5[8]	R^1 = Bu, R^2 = Me	**2-Yb**	10	5	95
6	R^1 = $Et(Me)_2C$, R^2 = H	**2-Ca**	10	24	55
7[8]	R^1 = $Et(Me)_2C$, R^2 = H	**2-Yb**	10	192	81
8	R^1 = Ph, R^2 = H	**2-Ca**	10	20	69
9[8]	R^1 = Ph, R^2 = H	**2-Yb**	10	20	56
10	R^1 = Ph, R^2 = H	**3**	10	20	1
11	R^1 = Ph, R^2 = H	**3** + 3 hmpa	10	20	48

[a] All reactions were carried out in THF at 20 °C.

eliminate via protonation by acidic substrates or σ-bond metathesis with $PhSiH_3$.

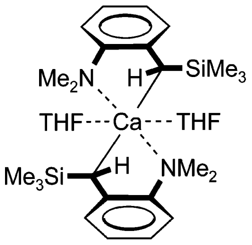
Dehydrogenative silylation of *n*-pentylamine with **2-Ca** is a clean and smooth reaction that proceeds at room temperature (Table 1, entry 1). This result is in line with the data for the Yb analogue reported by Takaki et al. (entry 2).[8] Also, the more sterically hindered secondary amine *N*-methyl-*n*-butylamine reacts well, and the results for the Ca-catalyzed and earlier reported Yb-catalyzed reactions are similar (entries 4 and 5). Primary amines with tertiary alkyl substituents react much more slowly (entry 6), as has been found earlier for the Yb-catalyzed reaction (entry 7). Also, both catalysts convert aniline more slowly than alkylamines (entries 8 and 9). Therefore, **2-Ca** is an effective catalyst for the dehydrogenative silylation of amines and the same trends that have been reported for catalyst **2-Yb** are observed.

In a second series of experiments we investigated the dehydrogenative silylation of 1-hexyne. Although alkynylsilanes can be obtained by stoichiometric reactions between metal alkynides and chlorosilanes, a halogen-free and metal-poor route is in some cases highly desired: e.g., in the syntheses of polyalkynylsilanes.[7,19]

The reaction of 1-hexyne with Ph_3SiH catalyzed by **2-Ca** shows, even with a 50% reduction in catalyst load, conversion very similar to that reported for **2-Yb**[7] (Table 2, entries 1 and 2). Use of the secondary silane $Ph(Me)SiH_2$ gave a mixture of mono- and dialkynated silanes (entry 5). The ratio of products observed in the Ca-mediated reaction is slightly different from that reported for the **2-Yb** catalyst (entry 6). The percentage of monoalkynated product can be increased by increasing the silane/alkyne ratio (entries 7 and 8), whereas the dialkynated product is favored at lower ratios (entries 9 and 10). Although control over product distribution is slightly better for the Yb-catalyzed reactions, essentially the same trends are observed for the analogue Ca catalyst.

The complex **2-Yb** is reportedly a selective catalyst for the remarkably clean isomerization of 1-alkynes to 2-alkynes without formation of the usual allene or butadiene byproducts: e.g., addition of 10 mol % **2-Yb** to neat 1-hexyne at 20 °C gave after 17 h 89% conversion to 2-hexyne.[6] Under the same conditions, we observed an equal isomerization process with the catalyst **2-Ca** (10 mol %), which gave at 20 °C after 17 h full conversion to 2-hexyne (>98%). This process presumably goes through a Ca−acetylide species that isomerizes via intermediate allenyl− and propargyl−calcium species. As 2-hexyne was not observed as a byproduct in the dehydrogenative silylation of 1-hexyne, the intermediate calcium hydride is likely the resting state in latter silylation.

In addition, we compared the catalytic properties of **2-Ca** with those of the dibenzylcalcium catalyst **3**, which we recently introduced for the catalytic hydrosilylation of alkenes.[12e]



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Although **3** showed similar catalytic behavior in the dehydrogenative silylation of pentylamine (Table 1, entry 3), we found essentially no activity for aniline (entry 10). Also, **3** is not catalytically active in the dehydrogenative silylation of 1-hexyne (Table 2, entry 3). As in these experiments no formation of precipitates was observed, the differences in catalytic behavior between **2-Ca** and **3** should be explained either by different catalytically active intermediates or by the effect of hmpa. Addition of 3 equiv of hmpa to **3** indeed gave conversion in the dehydrogenative silylation both of aniline (Table 1, entry 11) and of 1-hexyne (Table 2, entry 4). Thus, the polar solvent hmpa plays an essential role in these catalytic systems.

In summary we can conclude the following. (i) The synthesis and structure of **2-Ca** are essentially analogous to those for **2-Yb**. (ii) The calcium complex **2-Ca** is an effective catalyst in the dehydrogenative silylation of amines and alkynes, and its activities as well as selectivities are similar to those reported for **2-Yb**. It is anticipated that **2-Ca** can substitute for **2-Yb** also in more of its diverse catalytic applications. This not only widens the scope of organocalcium complexes in homogeneous catalysis but also indicates that **2-Ca** is an easily accessible and

Table 2. Summary of Results for the Dehydrogenative Silylation of Amines with Ph_3SiH^a

entry	substrate	cat.	amt of cat. (mol %)	*t* (h)	product(s)	conversn (%)
			$BuC{\equiv}CH + Ph_3SiH \rightarrow BuC{\equiv}CSiPh_3 + H_2$			
1	$BuC{\equiv}CH/Ph_3SiH$	**2-Ca**	5	17	$BuC{\equiv}CSiPh_3$	81
2[7]	$BuC{\equiv}CH/Ph_3SiH$	**2-Yb**	10	17	$BuC{\equiv}CSiPh_3$	82
3	$BuC{\equiv}CH/Ph_3SiH$	**3**	5	17	$BuC{\equiv}CSiPh_3$	1
4	$BuC{\equiv}CH/Ph_3SiH$	**3** + 3 hmpa	5	17	$BuC{\equiv}CSiPh_3$	49
			$a BuC{\equiv}CH + b Ph(Me)SiH_2 \rightarrow c BuC{\equiv}C-Si(H)PhMe + d (BuC{\equiv}C)_2Si(Me)Ph + H_2$			
5	a/b = 1/1	**2-Ca**	5	17	c/d = 53/47	>98
6[7]	a/b = 1/1	**2-Yb**	10	17	c/d = 64/36	>98
7	a/b = 1/2	**2-Ca**	5	17	c/d = 76/24	>98
8[7]	a/b = 1/2	**2-Yb**	10	17	c/d = 87/13	>98
9	a/b = 2/1	**2-Ca**	5	17	c/d = 26/74	>98
10[7]	a/b = 2/1	**2-Yb**	10	17	c/d = 10/90	>98

[a] All reactions were carried out in THF at 20 °C.

very cheap alternative for the well-studied catalyst **2-Yb** (1 mol Ca, 10 euros; 1 mol of Yb, 2637 euros).[20] (iii) Good agreement in the catalytic behavior of **2-Ca** and **2-Yb** is indirect proof for the Yb^{II} nature of the catalytically active species in **2-Yb**-catalyzed reactions and rules out the possibility of Yb^{III} in the mechanism. (iv) In addition, it is shown that polar (co)solvents play a major role in catalysis with highly polar calcium or ytterbium(II) complexes. Future research will focus on such solvent effects and the replacement of the toxic hmpa for alternative cosolvents.

Acknowledgment. Prof. Dr. R. Boese and D. Bläser (Universität Duisburg-Essen) are thanked for collection of the X-ray diffraction data.

Supporting Information Available: Text and a table giving experimental details of the synthesis of **2-Ca** and of all catalytic experiments and product analyses and a CIF file giving complete crystal data for **3-Ca**. This material is available free of charge via the Internet at http://pubs.acs.org.

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