

Bis(trimethylsilyl)benzamidinate: A Promising Spectator Ligand in Organoyttrium Chemistry. Synthesis and Reactivity of $\{[C_6H_5C(NSiMe_3)_2]_2Y-\mu-R\}_2$ ($R = H, C\equiv CH$) and X-ray Structure of $\{[C_6H_5C(NSiMe_3)_2]_2Y-\mu-C\equiv CH\}_2$

Robbert Duchateau, Cornelis T. van Wee, Auke Meetsma, and Jan H. Teuben*

Groningen Center for Catalysis and Synthesis
Department of Chemistry, University of Groningen
Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

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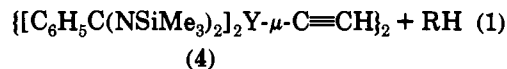
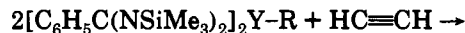
Permethylyttrocene alkyl and hydrido derivatives Cp^*_2Y-R ($Cp^* = \eta^5-C_5Me_5$; $R = H, CH(SiMe_3)_2$) are effective catalysts for a variety of reactions.¹ Previously we have found that Cp^*_2LnR ($Ln = Y, La, Ce$; $R = CH(SiMe_3)_2$) catalyzes, for instance, the oligomerization of terminal alkynes.^{1a,2} We were interested in exploring yttrium-based systems with an alternative coordination environment and comparing these with the known chemistry. We have chosen the bidentate *N,N'*-bis(trimethylsilyl)benzamidinate ligand, earlier employed by Roesky,³ Dehnicke⁴ and Edelmann,⁵ to develop new catalytic group 3 chemistry for C-C and C-H bond formation.

Here we describe the preparation of bis(*N,N'*-bis(trimethylsilyl)benzamidinate)yttrium hydride, $\{[C_6H_5C(NSiMe_3)_2]_2Y-\mu-H\}_2$, and its use as a precursor in the catalytic dimerization of terminal alkynes, together with the synthesis and crystal structure of the novel acetylide complex $\{[C_6H_5C(NSiMe_3)_2]_2Y-\mu-C\equiv CH\}_2$.

Multigram quantities of the chloride complex $[C_6H_5C(NSiMe_3)_2]_2YCl \cdot THF$ (**1**)^{7a} can be easily obtained by reaction of $Li[C_6H_5C(NSiMe_3)_2]_2$ with $YCl_3 \cdot THF_{3.5}$.^{7b} The chloride is an excellent precursor to new yttrium alkyl complexes.⁸ For instance, reaction of **1** with $LiCH(SiMe_3)_2$ afforded salt-free $[C_6H_5C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**2**).^{7b} The proton-coupled ¹³C NMR spectrum of **2** shows a double doublet from the methyne carbon at δ 43.5 (¹ $J_{Y-C} = 30$ Hz, ¹ $J_{C-H} = 88$ Hz), which is shifted significantly downfield from the C-H resonance in $Cp^*_2YCH(SiMe_3)_2$ (δ 25.2),⁹ suggesting a more electrophilic yttrium environment in **2**. Like in $Cp^*_2YCH(SiMe_3)_2$ (¹ $J_{C-H} = 84$ Hz),⁹ the small coupling constant for the α -carbon resonance (¹ $J_{C-H} = 88$ Hz) indicates an agostic interaction¹⁰ of the alkyl C-H bond with yttrium as is expected for an electronically very unsaturated

compound (14 electron system at maximum). Treatment of **2** with dihydrogen (3 atm, 40 °C) in benzene gives the very air-sensitive hydride $\{[C_6H_5C(NSiMe_3)_2]_2Y-\mu-H\}_2$ (**3**).^{7b} The ¹H NMR spectrum of **3** shows a triplet at 8.3 ppm (¹ $J_{Y-H} = 27.6$ Hz), which suggests a symmetric dimeric structure in solution.¹¹ None of the synthesized complexes (**1–3**) shows any disproportionation or decomposition after 24 h at 100 °C in benzene, demonstrating the high stability of this new class of yttrium compounds.

With **3** available, we were interested in examining the reactivity with terminal alkynes, and making comparisons with the bis-(permethylcyclopentadienyl) analogues of yttrium, lanthanum, and cerium. Treatment of **3** with an excess of $HC\equiv CR$ ($R = t-Bu, Ph$) gives a slow but selective reaction affording the head-to-tail coupled product $H_2C=C(R)C\equiv CR$ ($R = t-Bu, Ph$).¹² However, for $HC\equiv CSiMe_3$, a dramatic change in regioselectivity takes place and catalytic dimerization to exclusively the head-to-head coupled product *trans*- $R(H)C=C(H)C\equiv CR$ ($R = SiMe_3$) is observed.^{12,13} By contrast, the Cp^*_2LnR -catalyzed coupling of $HC\equiv CPh$ and $HC\equiv CSiMe_3$ gives either mixtures of head-to-tail and head-to-head isomers ($Ln = Y$) or formation of higher oligomers ($Ln = La, Ce$).² The mechanism for this reaction is believed to be the same as for the catalytic dimerization of terminal alkynes by Cp^*_2LnR ($Ln = Sc, Y, La, Ce$).^{1a,2,14} Unlike Cp^*_2ScMe ,¹⁵ **3** does not oligomerize ethyne. Treating **3** with an excess of ethyne resulted in the formation of an acetylide.^{7b} An X-ray structure determination revealed the compound to be $\{[C_6H_5C(NSiMe_3)_2]_2Y-\mu-C\equiv CH\}_2$ (**4**), a dimer with bridging ethynyl groups. **4** was also prepared by treatment of **2** with ethyne in benzene (eq 1).^{7b}



(4)

An ORTEP drawing of **4** is shown in Figure 1. The unit cell contains two crystallographically independent molecules, both obeying C_2 symmetry, that do not differ markedly in their structures.¹⁶ In one molecule, two identical $[C_6H_5C(NSiMe_3)_2]_2Y-C\equiv CH$ units are related to each other by a 2-fold axis perpendicular to the plane of the acetylide bridge. In the other molecule, the two yttrium atoms are on a special position along the 2-fold axis, with disordered acetylide fragments. Notable features of the nondisordered molecule will be discussed

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(7) (a) Both ¹H NMR and elemental analysis of **1** indicate that the compound contains 0.25 equiv of pentane in the crystal lattice, which is not further mentioned in the text. (b) All complexes were prepared on gram scale and extensively characterized (IR, ¹H NMR, ¹³C NMR, elemental analysis). Detailed information is provided in the supplementary material.

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(12) The reactions were followed by ¹H NMR at elevated temperatures (70–100 °C, average turnover number of 35 h⁻¹), and the products were characterized by GC/MS and ¹H NMR ($R = t-Bu$, GC pure; $R = Ph$, >95%; $R = SiMe_3$, GC pure).

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(16) Crystal data for **4**: $(C_{28}H_{47}N_4Si_4Y)_2$, space group $C2/c$ with $a = 27.088(2)$, $b = 27.102(2)$, and $c = 20.964(1)$ Å, $\beta = 113.40(1)^\circ$, $V = 14125(2)$ Å³, $d_{calc} = 1.206$ g cm⁻³, and $Z = 8$. Data were collected on an Enraf–Nonius CAD-4F diffractometer at 130 K with $Mo K\alpha$ ($\lambda = 0.71073$ Å). The structure was solved by Patterson methods and refined to $R(F) = 0.044$, $R_w(F) = 0.036$, for 7813 unique reflections with $I \geq 2.5 \sigma(I)$ and 1035 parameters.

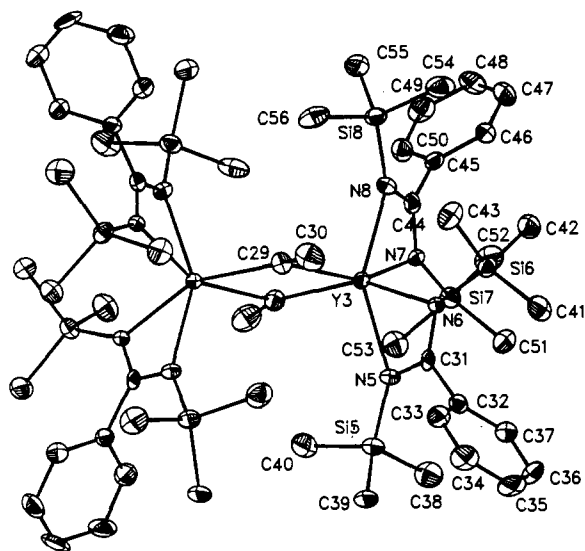


Figure 1. ORTEP drawing of $[(C_6H_5C(NSiMe_3)_2)_2Y-\mu-C\equiv CH]_2$ (**4**). Only one of the crystallographically independent molecules is shown with 50% probability ellipsoids.

here (Figure 1). **4** is formed by two distorted octahedral yttrium atoms, each coordinated by two chelating benzamidinate ligands and two bridging acetylides. Due to a *trans*-effect, the Y(3)-N(5) (2.395(4) Å) and Y(3)-N(8) (2.381(4) Å) bond lengths are longer than Y(3)-N(6) (2.345(4) Å) and Y(3)-N(7) (2.335(4) Å) (*trans* to the acetylide). The Y(3)-C(29) (2.556(5) Å) and Y(3)-a-C(29) (2.509(5) Å) bonds are longer than in $Cp^*_2Y(\mu-C\equiv CMe_3)_2Li\cdot THF$ (2.38(2) Å)^{17a} but very similar to the Y-C distances in $[Cp_2Y-\mu-Me]_2$ (2.553(1), 2.537(9) Å).^{17b} The Y-C bond lengths of **4** compare well with the Ln-C distances of some 4f element acetylide complexes, $[Cp'_2Ln-\mu-C\equiv CR]_2$ ($Cp' =$ substituted cyclopentadienyl, Ln = Sm, Er) when the differences

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in atomic radii are taken into account.¹⁸ A remarkable feature is that, in contrast to the Cp^*_2Ln (Ln = La, Ce,^{19a} and Sm^{19b}) systems, no coupling of acetylide fragments is observed. Both the Y(3)-C(29) and Y(3)-a-C(29) bond lengths and the Y(3)-C(29)-C(30) (98.4(5)°) and Y(3)-a-C(29)-C(30) (159.8(5)°) angles indicate that the bridge is clearly asymmetric with a strong interaction of the α -carbon atom, C(29), with both yttrium centers. The acetylide absorption ($\nu(C\equiv C)$ 1915 cm^{-1}) in the IR spectrum (cf. $\nu(C\equiv C)$ ($Cp_3UC\equiv CH$) 2062 cm^{-1}),²⁰ the $^1J_{C-H}$ coupling constant for $YC\equiv CH$ of 218 Hz in the ¹³C NMR spectrum, and the Y(3)-a-C(29)-C(30) angle of 159.8(5)° suggest η^2 interaction of the triple-bond π orbitals with Y(3).^{18a} Since π interaction of the acetylide is expected to result in elongation of the C \equiv C bond, the C(29)-C(30) bond length of 1.164(8) Å, shorter than that in free acetylene (1.21 Å), is very surprising.

These preliminary results show that the *N,N'*-bis(trimethylsilyl)benzamidinate acts as an inert spectator ligand in these complexes. The thermal stability and catalytic activity of **3** clearly demonstrate that a much more diverse chemistry is available to yttrium than that of cyclopentadienyl systems only. Indeed, exploratory experiments showed that the hydride $\{(C_6H_5C(NSiMe_3)_2)_2Y-\mu-H\}_2$ (**3**) also polymerizes ethene under mild conditions. These promising perspectives for catalytic C-H and C-C bond formation are currently under investigation.

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Supplementary Material Available: Full experimental details; spectroscopic and analytical data; ORTEP drawings; tables of crystal data, anisotropic thermal displacement parameter atomic coordinates, bond lengths, bond angles and torsion angles (33 pages); list of observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

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