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

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Bis(trimethylsilyl)benzamidine: 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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Permethyltrocene 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)benzamidine ligand, earlier employed by Roesky,³ Dehnicke⁴ and Edlmann,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)benzamidine)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 ($^1J_{Y-C} = 30$ Hz, $^1J_{C-H} = 88$ 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 $Cp^*_2YCH(SiMe_3)_2$ ($^1J_{C-H} = 84$ Hz),⁹ the small coupling constant for the α -carbon resonance ($^1J_{C-H} = 88$ 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 ($^1J_{Y-H} = 27.6$ 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 $HC\equiv CR$ ($R = t\text{-Bu, Ph}$) gives a slow but selective reaction affording the head-to-tail coupled product $H_2C=C(R)C\equiv CR$ ($R = t\text{-Bu, Ph}$).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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(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 ($R = t\text{-Bu}$, GC pure; $R = Ph$, >95%; $R = SiMe_3$, GC pure).

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(16) Crystal data for **4**: $(C_{28}H_{32}N_4Si_4Y)_2$, 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, $d_{\text{calc}} = 1.206$ g cm^{−3}, and $Z = 8$. Data were collected on an Enraf–Nonius CAD-4F diffractometer at 130 K with Mo K α ($\lambda = 0.71073$ 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)-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

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)-C(29) bond lengths and the Y(3)-C(29)-C(30) (98.4(5)°) and Y(3)-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. $\nu(C\equiv C)$ ($Cp_2UC\equiv CH$) 2062 cm^{-1}),²⁰ the $^1J_{C-H}$ coupling constant for $YC\equiv CH$ of 218 Hz in the ^{13}C NMR spectrum, and the Y(3)-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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