4f-*ansa*-Metallocenes−Dinuclear Complexes where the *ansa*-Dicyclopentadienyl Ligands Simultaneously Act in a Chelating and Bridging Mode − Crystal Structure of $(LY)_2(\mu\text{-}L)$ [L = 2,6-Pyridinediylbis(methylcyclopentadienyl)]

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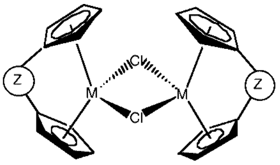
Keywords: Yttrium / Praseodymium / Dinuclear *ansa*-lanthanocenes / Metallocenes

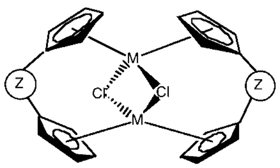
The reaction between $[L^NYX]_2$ [X = Cl, OTf; L^N = 2,6-pyridinediylbis(methylcyclopentadienyl] and $L'Na_2$ [L' = L^N = 2,6-pyridinediylbis(methylcyclopentadienyl; L^{Si} = dimethylsilanediylbis(cylopentadienyl); L^O = 2,5-furanediylbis(methylcyclopentadienyl)] in a 2:1 molar ratio affords dinuclear complexes of formula $(LY)_2(\mu\text{-}L')$, in which the *ansa*-bis(cyclopentadienyl) ligands simultaneously act both in a chelating and bridging mode. The X-ray crystal structure of $(L^NY)_2(\mu\text{-}L^N)$, determined at 193 K shows an arrangement close to trigonal planar of the centroids C_g of the three Cp ligands around the Y atoms. The reactivity of the $(L^NLn)_2(\mu\text{-}L')$ species containing different bridging *ansa*-bis(cyclopentadienyl) groups with an additional free donor atom was tested to verify the possibility of coordination of a third lanthanide ion. The rearrangement reactions that occur, finally leading to the formation of the only $[L^NLnX]_2$ species, are likely to depend on the presence of the further coordinating atom in the ligand bridging the two metal ions.

Introduction

ansa-Bis(cyclopentadienyl) ligands usually bind to early d-transition,[1] lanthanoid,[2] and actinide[3] metal ions exclusively as metal-chelating ligands (isomeric species **I**). However, the *ansa*-bis(cyclopentadienyl) ligands in dimeric *ansa*-lanthanocene complexes can, in principle, behave both in a chelating and bridging mode with formation of the isomeric species **I** and **II**, respectively. Some examples of dimeric complexes in which each *ansa*-bis(cyclopentadienyl) ligand bridges the two metal ions (**II**) are known both in complexes of d-[4,5] and f-elements.[6–10] To date, no example of completely characterized dinuclear complexes containing the *ansa*-bis(cyclopentadienyl) ligands simultaneously acting in the two binding modes have been reported.



Isomer I



Isomer II

Recently, we have observed that the disodium salt of 2,6-bis(cyclopentadienylmethyl)pyridine (L^NNa_2) affords Pr^{III} or U^{IV} complexes of the type $[(L^NPr)_2(\mu\text{-}L^N)]$[11] and $[(L^NUCl)_2(\mu\text{-}L^N)]$,[12] respectively, where the ligand simultaneously acts both in a chelating and bridging mode. The $[(L^NPr)_2(\mu\text{-}L^N)]$ complex firstly obtained[11] as a by-product in the synthesis of the complex $[L^NPrCl]_2$ was successively prepared in moderate yield (60–70%) by reaction of L^NNa_2 and $PrCl_3$ in a 3:2 molar ratio. Here we report an improved synthesis of $[(L^NPr)_2(\mu\text{-}L^N)]$ together with the synthesis and characterization of some $(L^NY)_2(\mu\text{-}L^N)$, $(L^NY)_2(\mu\text{-}L^{Si})$, and $(L^NY)_2(\mu\text{-}L^O)$ dinuclear complexes [L^N = 2,6-$(C_5H_4CH_2)_2$-C_5H_3N; L^{Si} = $Me_2Si(C_5H_4)_2$; L^O = 2,5-$(C_5H_4CH_2)_2$-C_4H_2O]. The presence of the additional free donor atom in the bridging ligand in the complexes $(L^NY)_2(\mu\text{-}L^N)$ and $(L^NY)_2(\mu\text{-}L^O)$, prompted us to investigate the possibility of coordinating a third metal ion, thus obtaining homo- and heterotrinuclear species.

Results and Discussion

Synthesis and Characterization of $[(L^NLn)_2(\mu\text{-}L^N)]$ (Ln = Y, Pr) and $[(L^NY)_2(\mu\text{-}L')]$ (L' = L^{Si}, L^O)

In a previous work dealing with the synthesis of the complex $[L^NPrCl]_2$, we observed[11] the presence of an impurity which, on the basis of analytical and ^1H NMR spectroscopic data, was defined as $[L^NPr]_2[\mu\text{-}L^N]$. As a confirmation, the same compound was obtained by reaction of L^NNa_2 and $PrCl_3$ in a 3:2 molar ratio. This complex was also prepared by reaction of $[L^NPrCl]_2$ and L^NNa_2 in a 2:1 molar ratio. However, the workup of the reaction mixture was difficult and any attempt to purify the complex to obtain crystals suitable for X-ray analysis was unsuccessful, mainly due to the very similar solubilities of the reagents

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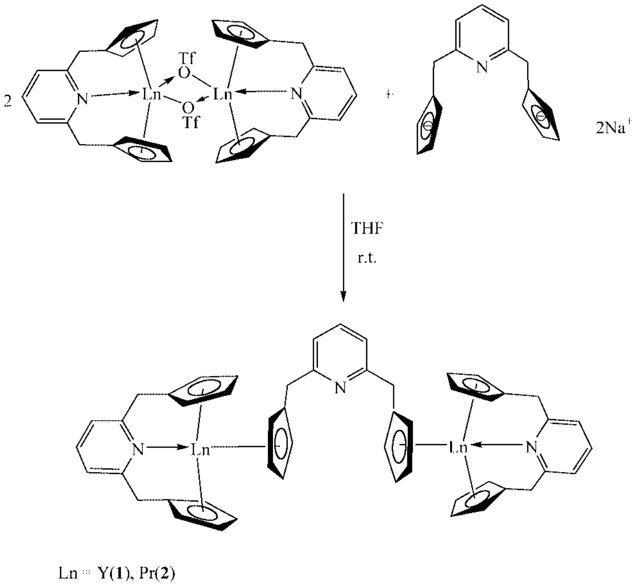
and the product. By using as starting materials the *ansa*-lanthanocene triflates, $[L^NLnOSO_2CF_3]_2$ (Ln = Y, Pr), more soluble and reactive species than the analogous chlorides $[L^NLnCl]_2$, the yields of the resulting $[L^NLn]_2[\mu\text{-}L^N]$ complexes are very high, thus making the workup and purification of the reaction products easier (Scheme 1).



Scheme 1.

The NMR (^{1}H and ^{13}C) characterization of the diamagnetic complex $[L^NY]_2[\mu\text{-}L^N]$ (**1**) was simple and clearly indicative of its structure in solution (Figure 1).

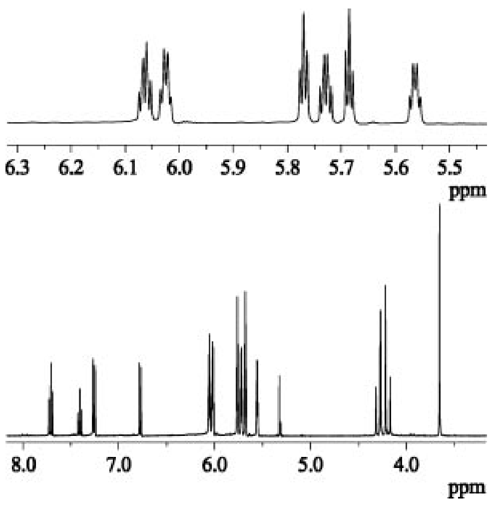


Figure 1. ^{1}H NMR of $[L^NY]_2[\mu\text{-}L^N]$ (**1**) ([D$_2$]dichloromethane, 400 MHz) (bottom) and its expanded part in the range δ = 6.3–5.5 ppm (top).

As reported in Figure 1, the ^{1}H NMR spectrum of **1** shows, in addition to a signal pattern similar to that observed in the ^{1}H NMR spectrum of the complex $[L^NYOSO_2CF_3]_2$ where the ligands act exclusively in a chelating mode,[2c] an additional rather simple pattern of signals readily assignable to the ligand acting in the bridging mode, with an intensity halved with respect to the signals of the two chelating ligands. In fact, the AB systems at δ = 6.06, 6.03, 5.73, 5.56 ppm correspond to the C_5H_4 protons of the chelating ligands, as the rigidity due to the additional coordination of the pyridine nitrogen atoms typical of these chelate systems makes the four C_5H_4 protons non-equivalent. On the contrary, in the case of the ligand bridging the two yttrium ions, the absence of evidence of substantial N→Y coordination makes the two pyridine-bonded C_5H_4 units virtually equivalent so that the two $\alpha\text{-}C_5H_4$ and the two $\beta\text{-}C_5H_4$ protons give rise to two pseudo-triplets at δ = 5.77 and 5.69 ppm (A_2B_2 system), respectively. More diagnostic of the different rigidity of the two types of ligand L^N of **1** (i.e. in the chelating and bridging modes) are the resonances of the relative methylene groups. In fact in the case of the chelating ligands the two methylene protons are diastereotopic and give rise to an AB system centered at δ = 4.25 ppm, while in the ligand bridging the two yttrium ions free rotation makes all the methylene protons equivalent (singlet at δ = 3.66 ppm).

In the case of the paramagnetic complex $[L^NPr]_2[\mu\text{-}L^N]$ (Ln = Pr: **2**) the previously proposed structure[11] similar to that of the yttrium complex **1** could again be deduced from its ^{1}H NMR spectrum.

Crystal Structure of 1·CH$_2$Cl$_2$

The results of a single-crystal X-ray analysis of **1** (Figure 2) confirms the presence of discrete $[Y_2L^N{}_3]$ molecules, involving two chelating and one bridging ligand L^N. Somewhat surprisingly, the $\mu\text{-}L^N$ ligand displays a conformation with *anti*-oriented C_5H_4 rings rendering the two (*chel*-L^N) Y fragments non-equivalent. Interestingly, the N2–Y2–N3 angle is not far from 180°, suggesting some weak N2→Y2 interaction, in spite of a rather long N2–Y2 distance of 3.39 Å. Another reason for the unsymmetrical conformation of $\mu\text{-}L^N$ could be the formation of more favorable crystal packing. Within both (*chel*- L^N)Y fragments N–Y distances of 2.528(3) Å (N1–Y1) and 2.571(3) Å (N3–Y2), respectively, were found, which are in excellent agreement with data reported for $[YL^N(\mu\text{-OTf})]_2$ [2.506(4) Å[2i]], $[YL^N(\mu\text{-OH})]_2$ [2.621(3) Å[2j]], and $[YL^{ind}N(SiHMe_2)_2]$ [2.511(2) Å; L^{ind} carries two indenyl units instead of two C_5H_4 rings[20]]. Thus, substantial N→Y interaction must be assumed to take place within each (*chel*-L^N)Y fragment of **1**, as confirmed by the NMR spectrum of dissolved **1** (vide supra).

Each Y ion formally adopts a coordination number of 10, owing to three $\eta^5\text{-}C_5H_4$ rings and one N atom. The arrangement of the centers C_g of the three C_5H_4 ligands around the Y atoms is close to trigonal-planar symmetry (Table 1). There is no significant difference in the distances Y–C_g between the chelating and the bridging C_5H_4 ligands. The N-atoms are on the top of the pyramids with the $Y(C_5H_4)_3$ base plane. A packing diagram is shown in Figure 3. The dichloromethane molecules are positioned in gaps between five complex molecules. According to the criteria of Takahashi et al.,[22] a CH–π interaction can be dis-

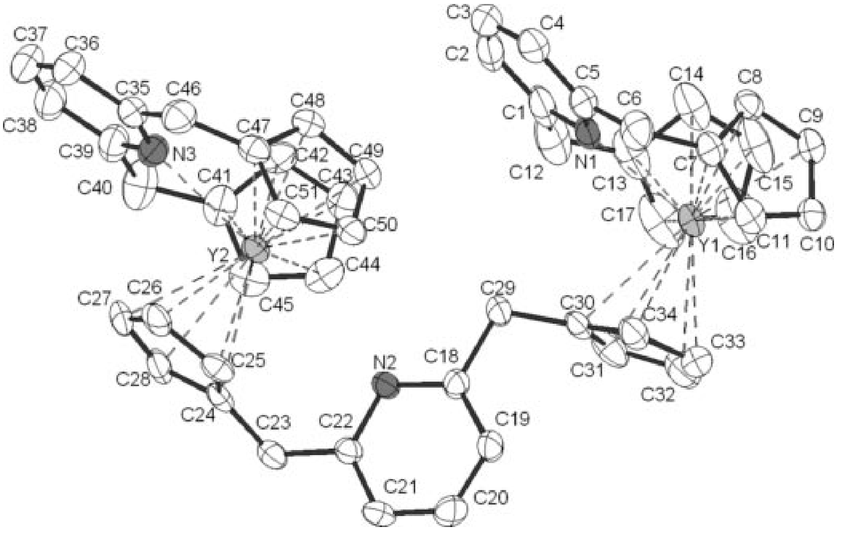


Figure 2. Perspective drawing of the molecular structure of $(L^NY)_2(\mu\text{-}L^N)$ (**1**). Displacement ellipsoids at the 50% probability level.[21]

cussed in relation to one of these neighbors. The distance of H60A (from CH_2Cl_2) to the best plane of ring 6 (C47–C51) is only 2.39 Å, with shortest contacts of 2.44 Å and 2.60 Å to C49 and C48, respectively (Figure 3), and angles C60–H60A–C49 of 142° and C60–H60A–C48 of 139°.

Table 1. Selected bond lengths [Å] and angles [°] including ring centroids (C_g) of **1**·CH_2Cl_2.

Bond lengths	
Y1–C_g2	2.428(2)
Y1–C_g3	2.465(2)
Y2–C_g4	2.454(2)
Y2–C_g5	2.442(2)
Y2–C_g6	2.430(2)
Y1–N1	2.528(3)
Y2–N3	2.571(3)
Bond angles	
C_g1–Y1–C_g2	119.25(8)
C_g1–Y1–C_g3	118.37(7)
C_g2–Y1–C_g3	119.98(8)
N1–Y1–C_g1	90.65(8)
N1–Y1–C_g2	90.50(1)
N1–Y1–C_g3	104.30(1)
C_g5–Y2–C_g6	121.41(7)
C_g4–Y2–C_g6	117.56(6)
C_g4–Y2–C_g5	120.91(6)
N3–Y2–C_g4	95.16(8)
N3–Y2–C_g5	88.78(9)
N3–Y2–C_g6	89.63(8)
Center definitions:	
C_g1: C7–C11	C_g2: C13–C17
C_g3: C30–C34	C_g4: C24–C28
C_g5: C41–C44	C_g6: C47–C51

To verify if there is a possibility that one additional *ansa*-bis(cyclopentadienyl) unit bridging two chelated $[L^NLnOSO_2CF_3]_2$ units could be extended to other *ansa*-bis(cyclopentadienyl) ligands, containing an, in principle additional, coordinating atom in the side chain, the two new yttrium species $[L^NY]_2[\mu\text{-}L^{Si}]$ (**3**) and $[L^NY]_2[\mu\text{-}L^O]$ (**4**) were prepared [L^{Si} = dimethylsilanediylbis(cyclopentadienyl), L^O = 2,5-furanediylbis(methylcyclopentadienyl)] by reaction of $[L^NYOSO_2CF_3]_2$ with $L^{Si}Li_2$ and L^ONa_2 in a 1:1 molar ratio (Scheme 2).

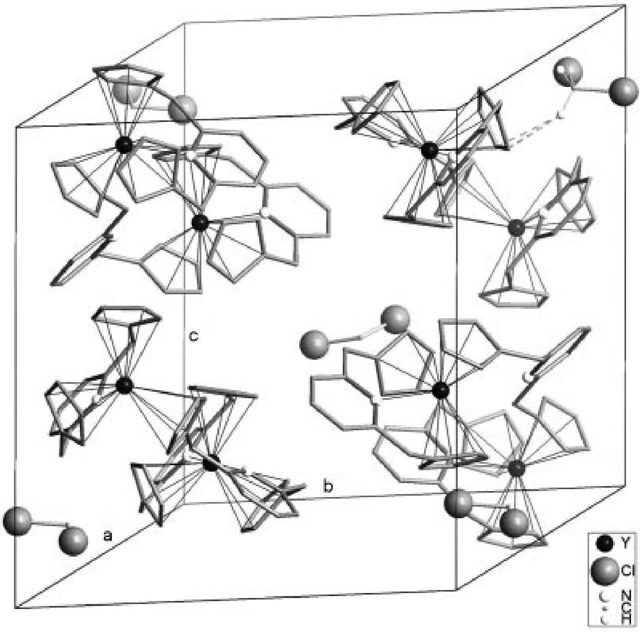
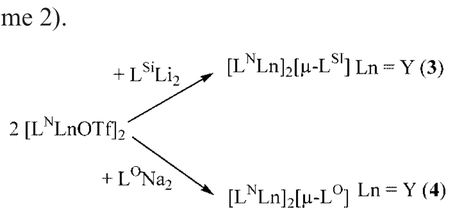


Figure 3. Packing diagram of **1**·CH_2Cl_2. Hydrogen atoms omitted. Possible CH–π interaction marked with dashed lines (H60A···C48, C49) for the upper right CH_2Cl_2 molecule only.



Scheme 2.

The ^1H NMR spectrum of **3** suggests a greater flexibility of the two L^NY systems derived from the presence of a broad singlet at $\delta = 4.23$ ppm instead of the AB system (due to the diastereotopic methylene protons) observed in the case of **1**. The cyclopentadienyl protons of the L^N unities are still non-equivalent giving rise to four pseudoquadruplets centered at $\delta = 6.23$, 6.18, 6.07, and 5.83 ppm, while the signals of the α- and β-cyclopentadienyl protons of the bridging ligand L^{Si} appear at $\delta = 6.17$ and 6.05 ppm, respectively.

The ^{1}H NMR spectrum of species **4** suggests either a higher or lower rigidity with respect to species **3** and **1**, as shown by the AB pattern at $\delta = 4.26$ ppm for the diastereotopic methylene protons of the two L^N units, while the methylene protons of the L^O unit give rise to a singlet at $\delta = 3.40$ ppm. The cyclopentadienyl protons of the chelated L^N units originate four pseudoquadruplets at $\delta =$ 6.00–5.85 (m), 5.67 (q), 5.64–5.58 (m), and 5.43 (q) ppm, partially superimposed with the triplets of the α- and β-cyclopentadienyl protons of the bridging L^O unity.

Reactivity Tests of $[LY]_2[M\text{-}L]$ Complexes

By considering the presence of an uncoordinated pyridine nitrogen atom in the bridging ligand of **1**, and with the aim to verify the possibility of access to homo- and heterotrinuclear complexes by coordination of a third metal ion into the bridging unity, the dinuclear yttrium complex **1** was treated with an equimolar amount of $Y(OTf)_3$. Not quite unexpectedly, the only isolated product was the complex $[L^NYOTf]_2$.

$$[L^NY]_2[\mu\text{-}L^N] + Y(OTf)_3 \rightarrow 3/2\ [L^NYOTf]_2$$

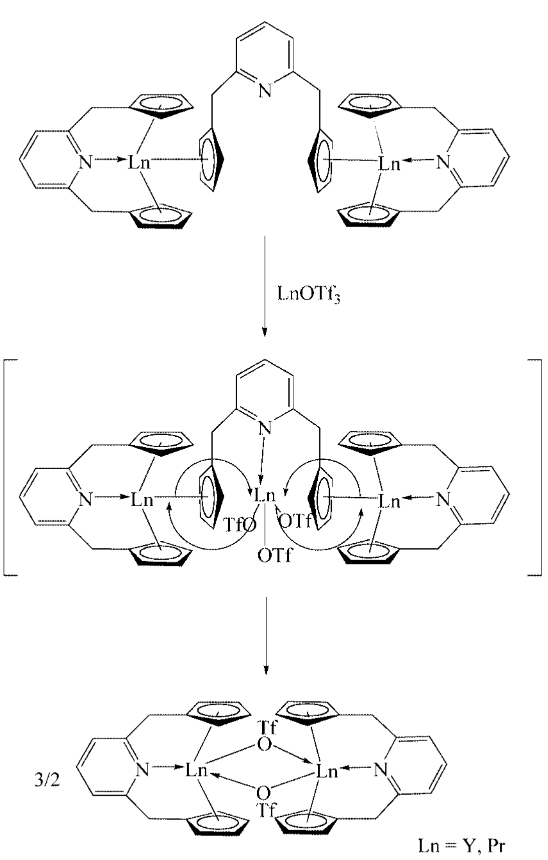
The same behavior was observed by treating the complex $[L^NPr]_2[\mu\text{-}L^N]$ with $Pr(OTf)_3$ in a 1:1 molar ratio and under the same experimental conditions. Also in this case, the ^{1}H NMR spectrum of the final product is consistent with the formulation of $[L^NPrOTf]_2$.

One possible explanation could imply a preliminary coordination of the third lanthanide ion by the free pyridine nitrogen atom, followed by a rapid intramolecular rearrangement through redistribution of the ligands as shown in Scheme 3.

On the basis of the proposed reaction pathway, the driving force could be the presence of the coordinating pyridine nitrogen atom of the bridging ligand unity. As a consequence, this type of intramolecular rearrangement must be absent in complexes of the type $[L^NLn]_2[\mu\text{-}L']$ where the bridging unit does not contain further coordinating atoms.

Accordingly, by treating $[L^NY]_2[\mu\text{-}L^{Si}]$ (**3**) with $Y(OTf)_3$ under the same experimental conditions as for complex **1**, no change of the initial ^{1}H NMR spectrum was observed even after 36 h of reaction at room temperature.

To confirm that the coordination step of the third metal ion by the coordinating atom of the bridging ligand into the molecule plays a fundamental role in allowing the intramolecular rearrangement, the same reaction was carried out with the complex $[L^NY]_2[\mu\text{-}L^O]$ (**4**) and, as expected, the rearrangement took place and dinuclear $[L^NYOTf]_2$ was isolated (Figure 4). From the mother liquor a mixture of other hardly separable complexes, probably containing the species $[L^OYOTf]_2$ and $[L^NY(\mu\text{-}OTf)(\mu\text{-}OTf)YL^O]$ was recovered.



Scheme 3.

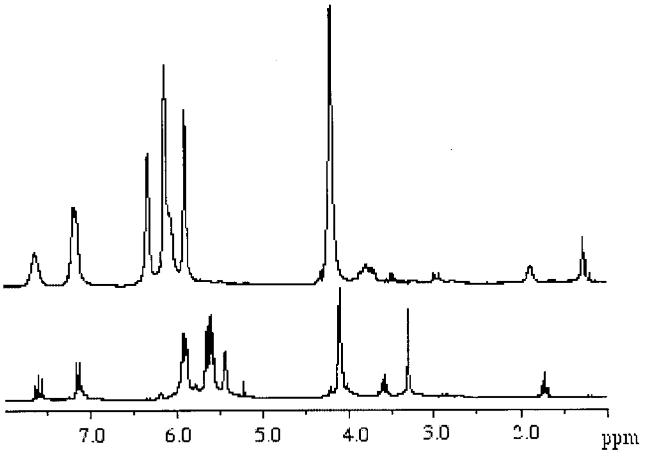


Figure 4. ^{1}H NMR spectra of $[L^NY]_2[\mu\text{-}L^O]$ (bottom) and of the reaction mixture $[L^NY]_2[\mu\text{-}L^O] + Y(OTf)_3$ (top).

Conclusions

ansa-Lanthanocene complexes of the type L^NLnX (X = OTf, Cl) react in a 2:1 molar ratio with *ansa*-bis(cyclopentadienyl) ligands with, or devoid of, an additional coordinating atom in the chain bridging the two cyclopentadienyl rings to give dinuclear species containing the *ansa*-bis(cyclopentadienyl) ligands simultaneously acting in a chelating and bridging mode. In the case of the species $[L^{N}Ln]_2[\mu\text{-}L']$ (Ln = Y, Pr), where the bridging ligand L′ contains an additional coordinating atom, any attempt to introduce a third Ln^{III} ion to form homo- or heterotrinuclear complexes failed due to an intramolecular ligand redistribution reaction affording $L^{N}LnX$ species.

Experimental Section

General Procedures: All manipulations were carried out under purified nitrogen in a glove-box apparatus (MBraun G200). The commercially available solvents, tetrahydrofuran, toluene, *n*-hexane, and diethyl ether, were firstly distilled from $LiAlH_4$ and then from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from CaH_2. Deuterated $[D_8]$toluene was dried with Na/K alloy and collected by thaw cycles. CD_2Cl_2 and $CDCl_3$ were dried with CaD_2 and collected by taw cycles. Yttrium and praseodymium trifluoromethanesulfonates were prepared according to literature methods.[13] *n*BuLi (Aldrich) in THF and pentane or *n*-hexane solutions were titrated before use. The disodium salt of the ligands ($L^{N}Na_2$,[14] $L^{Si}Na_2$,[15] $L^{O}Na_2$[16]) and the complexes $[L^{N}LnOTf]_2$[17] were prepared as reported in the literature. NMR spectra were recorded with a Bruker AC 200 or a Varian Unity 400 spectrometer. Chemical shifts (ppm) for ^1H and ^{13}C spectra were internally referenced to the residual undeuterated solvent resonances and related to tetramethylsilane (δ = 0 ppm).

$[(L^{N}Y)_2(\mu\text{-}L^{N})]$ (1): To a solution of $[L^{N}YOTf]_2$ (0.942 g, 1.0 mmol) in THF (20 mL) a solution of $L^{N}Na_2$ (0.139 g, 0.5 mmol) in THF (20 mL) was slowly added at room temperature under magnetic stirring, and the mixture reacted at room temperature overnight. After removal of the solvent and volatiles under vacuum, the solid residue was added to dichloromethane (50 mL) and the insoluble sodium triflate filtered off. The volume of the resulting yellow solution was then reduced to 20 mL under vacuum and the solution left to crystallize at –20 °C to give pale yellow crystals (0.799 g, 91.1% yield). $C_{51}H_{45}N_3Y_2$ (877.75): calcd. C 69.79, H 5.17, N 4.79; found C 69.65, H 5.25, N 4.65. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.72 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, Py^a-4), 7.41(t, $^3J_{H,H}$ = 7.6 Hz, 1 H, Py^b-4), 7.26 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, Py^a-3,5), 6.70 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Py^b-3,5), 6.06 (AB system, δ_A = 6.07, δ_B = 6.06, J_{AB} = 3.0 Hz, 4 H, Cp^a), 6.03 (AB system, δ_A = 6.03, δ_B = 6.02, J_{AB} = 2.4 Hz, 4 H, Cp^a), 5.77 (A_2B_2 system, J_{AB} = 2.6 Hz, 4 H, Cp^b), 5.73 (AB system, δ_A = 5.74, δ_B = 5.72, J_{AB} = 3.0 Hz, 4 H, Cp^a), 5.69 (A_2B_2 system, J_{AB} = 2.6 Hz, 4 H, Cp^b), 5.56 (AB system, δ_A = 5.57, δ_B = 5.56, J_{AB} = 2.4 Hz, 4 H, Cp^a), 4.25 (AB system, δ_A = 4.29, δ_B = 4.21, J_{AB} = 18.5 Hz, 8 H, CH_2^a), 3.66 (s, 4 H, CH_2^b) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 166.33, 162.12, 136.66 (C9), 136.99 (C26), 123.29, 122.35 (C8), 121.40, 120.10 (C25), 119.34 (C4), 114.11 (C2), 112.63 (C18), 109.23 (C19), 108.03 (C1), 103.27 (C3), 38.90 (C23), 37.65 (C6) ppm.

$[(L^{N}Pr)_2(\mu\text{-}L^{N})]$ (2): The compound was prepared in a manner analogous to that for **1** from $[L^{N}PrOTf]_2$ (1.047 g, 2 mmol) and $L^{N}Na_2$ (0.279, 1 mmol) in a 2:1 molar ratio. Dark green crystals of **2** were obtained (0.863 g, 88% yield). $C_{51}H_{45}N_3Pr_2$ (981.76): calcd. C 62.39, H 4.62, N 4.28; found C 62.50, H 4.55, N 4.50.

$[(L^{N}Y)_2(\mu\text{-}L^{Si})]$ (3): To a solution of $[L^{N}YOTf]_2$ (0.942 g, 1.0 mmol) in THF (20 mL) a solution of $L^{Si}Li_2$ (0.100 g, 0.5 mmol) in THF (20 mL) was slowly added at room temperature under magnetic stirring, and the mixture reacted at room temperature overnight. After removal of the solvent and volatiles under vacuum, the solid residue was added to dichloromethane (50 mL) and the insoluble lithium triflate filtered off. The volume of the resulting yellow solution was reduced to 20 mL under vacuum and the solution left to crystallize at –20 °C to give pale yellow crystals (0.706 g, 85% yield). $C_{46}H_{44}N_2SiY_2$ (830.77): calcd. C 66.50, H 5.34, N 3.37; found C 66.60, H 5.40, N 3.50. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.69 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, Py-4), 7.21 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, Py-3,5), 6.23 (AB system, J_{AB} = 3.0 Hz, 4 H, Cp^a), 6.18 (m, 8 H, Cp^a + Cp^b), 6.07 (AB system, J_{AB} = 3.0 Hz, 4 H, Cp), 6.05 (A_2B_2 system, J_{AB} = 2.6 Hz, 4 H, Cp^b), 5.83 (AB system, J_{AB} = 3.0 Hz, 4 H, Cp^a), 4.23 (br. s, 4 H, CH_2^a), –0.18 (s, 6 H, CH_3) ppm.

$[(L^{N}Y)_2(\mu\text{-}L^{O})]$ (4): To a solution of $[L^{N}YOTf]_2$ (0.942 g, 1.0 mmol) in THF (20 mL) a solution of $L^{O}Na_2$ (0.134 g, 0.5 mmol) in THF (20 mL) was slowly added at room temperature under magnetic stirring, and the mixture reacted at room temperature overnight. After removal of the solvent and volatiles under vacuum, the solid residue was added to dichloromethane (30 mL) and the sodium triflate filtered off. The volume was reduced to 20 mL under vacuum and the yellow solution left to crystallize at –20 °C giving yellow-orange crystals (0.719 g, 83% yield). $C_{50}H_{44}N_2OY_2$ (866.72): calcd. C 69.29, H 5.12, N 3.23; found C 69.35, H 5.20, N 3.30. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.68 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, Py-4), 7.24 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, Py-3,5), 6.12–5.92(m, 8 H, Cp^b), 5.75 (AB system, J_{AB} = 2.6 Hz, 4 H, Cp^a), 5.72–5.69 (m, 8 H, Cp^a + Fur), 5.68 (AB system, J_{AB} = 3.0 Hz, 4 H, Cp^a), 5.55 (AB system, J_{AB} = 2.6 Hz, 4 H, Cp^a), 4.21 (A_2B_2, J_{AB} = 18.5 Hz, 8 H, CH_2^a), 3.40 (s, CH_2^b) ppm.

X-ray Crystal Structure Determination: A single crystal was mounted under inert oil in a glass capillary and investigated at 193 K with an IPDS image plate system. The data were corrected for Lorentz and polarization effects, and a numerical absorption correction based on indexed faces was applied. The structure was solved by direct methods (SHELXS-97)[18] and difference Fourier syntheses in space group $P21/c$ and refined against all F^2 data using the SHELXL-97 program.[19] All hydrogen atoms were kept riding on calculated positions (C–H 0.95 Å) with isotropic displacement factors taken as 1.2 times the U_{eq} value of the corresponding C atom. All heavier atoms were refined with anisotropic displacement parameters. No disorder was observed for the CH_2Cl_2 solvent molecule. Details of the experimental and crystal data are summarized in Table 2. CCDC-261469 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reactivity Test of $[(L^{N}Y)_2(\mu\text{-}L^{N})]$ (1) with $Y(OTf)_3$: To a solution of $[(L^{N}Y)_2(\mu\text{-}L^{N})]$ (**1**) (0.439 g, 0.5 mmol) in THF (20 mL) a solution of $Y(OTf)_3$ (0.268 g, 0.5 mmol) in the same solvent (15 mL) was added at room temperature under vigorous magnetic stirring, and the mixture reacted overnight at room temperature. After solvent removal under vacuum, the solid residue was completely dissolved in dichloromethane (20 mL). By slow evaporation of the solvent, pale yellow microcrystals of $[L^{N}YOTf]_2$ were obtained (0.629 g, 89% yield) as confirmed by elemental analysis, NMR spectroscopic data, and comparison with an authentic sample.

Reactivity Test of $[(L^{N}Pr)_2(\mu\text{-}L^{N})]$ (2) with $Pr(OTf)_3$: To a deep green solution of $[(L^{N}Pr)_2(\mu\text{-}L^{N})]$ (**2**) (0.491 g, 0.5 mmol) in THF (20 mL) a solution of $Pr(OTf)_3$ (0.294 g, 0.5 mmol) in the same solvent (15 mL) was added at room temperature under vigorous magnetic stirring, and the resulting green reaction mixture reacted

Table 2. Crystal and data collection parameters for $Y_2L_3{\cdot}CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$).

Empirical formula	$C_{52}H_{47}Cl_2N_3Y_2$
Formula mass [g/mol]	962.65
Color, habit	yellow-brown, column
Column crystal size [mm]	$0.60 \times 0.23 \times 0.14$
Crystal system	monoclinic
Space group	$P21/c$ (no. 14)
a [Å]	16.949(1)
b [Å]	15.997(1)
c [Å]	16.442(1)
β [°]	108.121(5)
Volume [Å^3]	4236.8(3)
Z	4
Calcd. density [Mg/m^3]	1.509
Temperature [K]	193(2)
λ (Mo-K_α) [Å]	0.71073
Absorption coefficient [mm^{-1}]	2.893
$F(000)$	1968
2θ range [°]	5.54–60.72
Reflections: total, unique, $>4\sigma(F)$	44912, 11702, 6145
No. of parameters	532
Final R index [$F > 4\sigma(F)$]	0.0474
wR_2 (all reflections)	0.1100
Goodness-of-fit on F^2	0.824
Residual electrondensity [e/Å^3]	0.67, –0.86

overnight at room temperature. The solvent was removed under vacuum and the solid residue completely dissolved in dichloromethane (20 mL). By slow evaporation of the solvent, green microcrystals of $[L^NPrOTf]_2$ were separated (0.465 g, 89% yield) as confirmed by elemental analysis, NMR spectroscopic data, and comparison with an authentic sample.

Reactivity Test of $[(L^NY)_2(\mu\text{-}L^{Si})]$ (3) with $Y(OTf)_3$: To a solution of $[(L^NY)_2(\mu\text{-}L^{Si})]$ (**3**) (0.415 g, 0.5 mmol) in THF (20 mL) a solution of $Y(OTf)_3$ (0.268 g, 0.5 mmol) in the same solvent (15 mL) was added at room temperature under magnetic stirring, and the mixture reacted overnight at room temperature. The solvent was removed under vacuum and the solid residue was added to dichloromethane (20 mL) where it was partially soluble. The solid residue was filtered off and characterized by elemental analysis as unreacted $Y(OTf)_3$. By addition of *n*-hexane to the solution, pale yellow microcrystals of $[(L^NY)_2(\mu\text{-}L^{Si})]$ separated.

Reactivity Test of $[(L^NLn)_2(\mu\text{-}L^O)]$ (4) with $Ln(OTf)_3$: To a solution of $[(L^NY)_2(\mu\text{-}L^O)]$ (**4**) (0.433 g, 0.5 mmol) in THF (20 mL) a solution of $Y(OTf)_3$ (0.268 g, 0.5 mmol) in the same solvent (15 mL) was added at room temperature under vigorous magnetic stirring, and the mixture reacted overnight at room temperature. The solvent was removed under vacuum and the solid residue was dissolved in dichloromethane (20 mL). The solvent was then removed under vacuum at room temperature to give, as the main product, pale yellow microcrystals of $[L^NYOTf]_2$ (0.193 g, 41% yield), as confirmed by elemental analysis and NMR spectroscopic data. From the mother liquor a mixture of compounds hardly separable was recovered.

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