New Coordinatively Unsaturated Lutetium Mono- and Bis(alkyl) Complexes with a Bis(*ortho*)-Chelating Aryldiamine Ligand—Crystal Structures of $[LuCl_2\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(\mu\text{-}Li(thf)_2)]_2$ and $[Lu(\mu\text{-}Cl)\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(CH_2SiMe_3)]_2$

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Abstract: New complexes of lutetium and yttrium containing the monoanionic, terdentate ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ (NCN) have been synthesized by substitution reactions starting from MCl_3 (M = Lu, Y). Reaction of MCl_3 (M = Y, Lu) with one equivalent of (NCN)Li affords the ate complexes $[(NCN)MCl_2(\mu\text{-}Cl)(\mu\text{-}Li(thf)_2)]_2$ (M = Lu (**1a**), Y (**1b**)) in which the terdentate ligand is bound in *mer* fashion and all three chloride atoms are retained in the product. Crystals of **1a** are monoclinic (space group $P2_1/n$, $a = 10.4559(4)$, $b = 21.6150(9)$, $c = 12.1700(7)$ Å, $\beta = 105.294(4)°$, $Z = 2$, final $R = 0.039$ for 3695 observed reflections $[I > 2.5\sigma(I)]$). Attempted substitution of chloride in the yttrium complex **1b** by $Me_3SiCH_2^-$ leads to decomposition. However, reaction of **1a** with Me_3SiCH_2Li gives the monoalkyl complex $[(NCN)Lu(\mu\text{-}Cl)(CH_2SiMe_3)]_2$ (**2**, 30% yield), in which the terdentate ligand is bound in a pseudo-facial manner. Crystals of **2** are triclinic (space group $P\bar{1}$, $a = 9.8575(7)$, $b = 10.0171(7)$, $c = 11.1460(14)$ Å, $\alpha = 75.096(8)$, $\beta = 78.092(8)$, $\gamma = 77.474(6)°$, $Z = 1$, final $R_1 = 0.11$ for 1361 reflections $[I > 2\sigma(I)]$). Substitution of the chloride ions in **2** by $Me_3SiCH_2^-$ is possible and affords quantitatively the bisalkyl complex $[(NCN)Lu(CH_2SiMe_3)_2]$ (**3**). The lutetium complexes **2** and **3** are formally coordinatively unsaturated complexes, which are moisture-sensitive and thermally stable for several weeks when dissolved in aromatic solvents. However, they decompose rapidly in aliphatic solvents such as hexane, and a decomposition route involving the formation of carbene species is proposed.

Keywords
ate complexes · intramolecular coordination · lutetium complexes · organometallic compounds · yttrium complexes

Introduction

In Group 3 and lanthanide chemistry the aryldiamine ligand 2,6-bis[(dimethylamino)methyl]benzenide ($[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ = NCN) may be considered as a replacement for the commonly used cyclopentadienyl ligand as regards both the number of coordination sites it can occupy and the number of bonding electrons it can provide.[1–7] Apart from the terdentate bonding mode,[1,4b,5–7] it can also engage in bidentate C,N-bonding[1j,2] and monodentate C-bonding modes[3] and act as a bridging ligand between two metal centers[1f,4] (see Fig. 1). Moreover, its coordinating properties may be fine-tuned through variation of substituents on the *ortho* aminomethyl groups or in the phenyl ring.[8] Recently, the anchoring on polysiloxane polymers[9a] and dendrimers[9b] of active catalysts based on this ligand has been realised through the use of suitable *para* substituents.

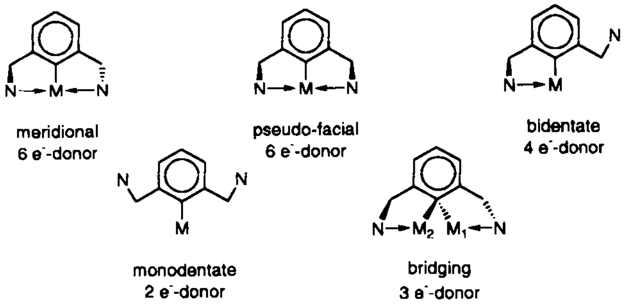

Fig. 1. Bonding modes previously reported for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ (NCN): meridional: Ga [1j], In [1f], Si [1g], Sn^{II} [1h], Sn^{IV} [1i], Sb [1k], Ta [4b], Ni^{II} [1c], Ni^{III} [1e], Pd [1a], Pt [1b,d]; pseudo-facial: Ti [7], Ta [5], Ru [6]; bidentate: Ga [1j], Ta [2d], Rh^I [2a], Ir^I [2b,c], Ir^{III} [2c]; monodentate: Ni [3a], Pt [3b]; bridging: $M_1 = M_2$: Li [4c], Cu [4a,d], Ga [1f]; $M_1 \neq M_2$: Ta/Zn [4b].

We have applied this ligand to the preparation of coordinatively unsaturated Group 3 and lanthanide complexes that

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might be used to activate aromatic halides towards nucleophilic substitution. In addition, the special chelating properties of NCN might allow us to prepare salt- and solvent-free lanthanide bisalkyl complexes, which are difficult to prepare with cyclopentadienyl-type ligands.[10] Such bisalkyl lanthanide complexes are of special interest because they contain two reactive metal–carbon bonds.

Until five years ago stabilization of Group 3 and lanthanide metal complexes by intramolecular coordination had only been reported for some complexes containing the *ortho*-chelating C,N ligand $[2\text{-}(Me_2NCH_2)C_6H_4]^-$.[11–14] Very recently, a number of reports have appeared on the successful use of alkyl,[15] η^5-cyclopentadienyl,[16] and η^1-ferrocenyl ligands with intramolecularly coordinating amino or ether substituents.[17]

We report here the first results of our study into the synthesis and structural aspects of lutetium and yttrium complexes containing the bis(*ortho*)-chelating aryldiamine ligand NCN. We show that our approach can lead to unique species, which provide a starting point for the synthesis of salt- and solvent-free monoligand-supported alkyl complexes, where the monoligand is the aryldiamine NCN rather than the commonly encountered cyclopentadienyl-type ligand.[10]

Results

Syntheses of monoligand (aryldiamine) metal chlorides: The 1:1 molar reaction of (NCN)Li with a suspension of MCl_3 (M = Lu, Y) in tetrahydrofuran (THF) resulted in the rapid dissolution of the metal chloride. The complex from the resulting solution, which analyzed as $[(NCN)MCl_3\cdot Li(thf)_2]$ (M = Lu (**1a**), Y (**1b**)), could be isolated as a white powder in 80% (**1a**) or quantitative (**1b**) yield. The lutetium complex was often contaminated with traces of the parent aryldiamine $1,3\text{-}(Me_2NCH_2)_2C_6H_4$, formed during the synthesis, which proved difficult to remove. Attempts to isolate lanthanum complexes of NCN, following the same procedure, were not successful.

Complexes **1a** and **1b** afforded temperature-dependent NMR data. In order to gain insight into the coordination geometry around the metal center in these unique species, the molecular structure of **1a** in the solid state was obtained by an X-ray structure determination (Fig. 2 and Tables 1 and 2).

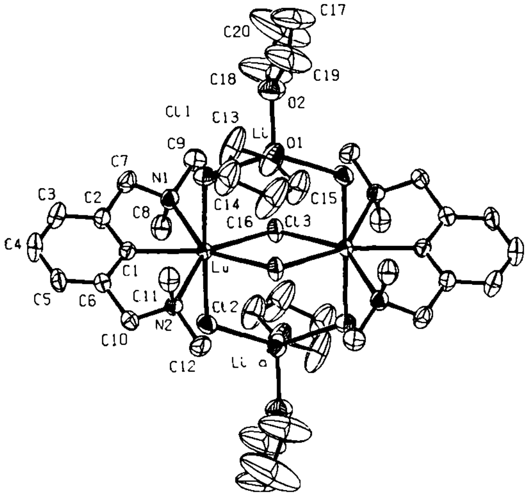

Fig. 2. ORTEP plot (ellipsoids at 30% probability level) of **1a** with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic data for **1a** and **2**.

Complex	**1a**	**2**
formula	$C_{40}H_{70}N_4O_4Lu_2Li_2Cl_6$	$C_{32}H_{60}N_4Lu_2Si_2Cl_2$
molecular weight	1247.55	977.86
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (no. 14)	$P1$ (no. 2)
a/Å	10.4559(4)	9.8575(7)
b/Å	21.6150(9)	10.0171(7)
c/Å	12.1700(7)	11.1460(14)
α/°	–	75.096(8)
β/°	105.294(4)	78.092(8)
γ/°	–	77.474(6)
V/Å^3	2653.1(2)	1024.95(18)
D_{calcd}/g cm^{-3}	1.562	1.584
Z	2	1
$F(000)$/e	1240	484
μ/cm^{-1}	40.5	108.0
crystal size/mm	0.12 × 0.45 × 0.45	0.2 × 0.2 × 0.6
T/K	298	293
radiation, λ/Å	$Mo_{K\alpha}$, 0.71073 (Zr-filtered)	$Cu_{K\alpha}$, 1.54184 (Ni-filtered)
$\Delta\omega$/°	$0.53 + 0.35\tan\theta$	$1.03 + 0.14\tan\theta$
horiz., vert. aperture/mm	3.00, 4.00	4.57, 6.00
lineair decay/%	1.5	21
reference reflections	232, 322, 322	241, 320, 222
data set, hkl	−13:13, 0:28, −15:15	−12:12, 0:12, −13:13
total unique data	6077	4230
observed data	3695 ($I > 2.5\sigma(I)$)	4230
no. of refined param.	278	190
final R [a]	0.039	0.11 [1361 $F_0 > 4\sigma(F_0)$]
final $wR2$ [b]	–	0.27
final R_w [c]	0.032	–
weighting scheme [d]	$[\sigma^2(F)]^{-1}$	$[\sigma^2(F^2) + (0.095P)^2]^{-1}$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.03, 0.4	0.000, 0.001
min. and max. resid. density/e Å^{-3}	−1.12, 0.64	−2.03, 1.81

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $R_w = [\sum[w(||F_0| - |F_c||)^2/\sum[w(F_o^2)]]^{1/2}$. [d] $P = (\max(F_o^2,0) + 2F_c^2)/3$.

Editorial Board Member:[*] *Gerard van Koten obtained his Ph.D. from Utrecht University under the supervision of Professor G. J. M. van der Kerk. After a period in the Inorganic Chemistry Department at the University of Amsterdam, where he was promoted to Professor in 1984, he went back to Utrecht University (Debye Institute) in 1986 to become Professor of Organic Chemistry. He has been Visiting Professor in Strasbourg (France), Heidelberg (Germany), and Sassari (Italy). His research interests include the organometallic chemistry of late (Ni, Pd, Pt, Ru) and early (Ta, La, Lu) transition metals as well as of Cu, Li, and Zn, and the development and use of organometallic complexes of chelating arylamines ("pincer") and aminoarenethiolates as homogeneous catalysts, in particular, for the synthesis of fine chemicals. He also works on supramolecular systems with catalytically active (organometallic) functionalities and has published the first examples of homogeneous dendrimer catalysts.*

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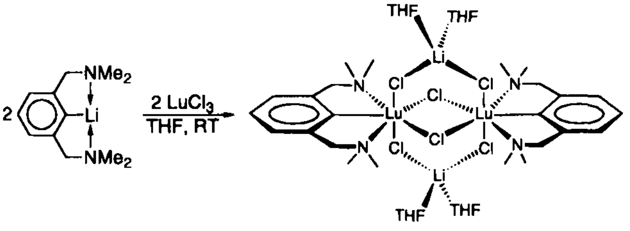
[*] Members of the Editorial Board will be introduced to the readers with their first manuscript.

Table 2. Selected bond lengths (Å) and angles (°) for **1a** (Esd in parentheses).

Lu–C(1)	2.351(7)	Lu–Cl(3)	2.712(2)
Lu–N(1)	2.623(6)	Li–Cl(1)	2.350(13)
Lu–N(2)	2.623(6)	Li–Cl(2)	2.349(13)
Lu–Cl(1)	2.600(2)	Li–O(1)	1.929(15)
Lu–Cl(2)	2.589(2)	Li–O(2)	1.967(15)
N(1)-Lu-N(2)	135.8(2)	Cl(1)-Lu-Cl(2)	177.19(7)
N(1)-Lu-Cl(3)	77.86(15)	Cl(3)-Lu-Cl(3a)	75.04(6)
N(2)-Lu-Cl(3a)	75.76(15)	Cl(1)-Li-O(1)	107.6(6)
C(1)-Lu-N(1)	68.0(2)	Cl(1)-Li-Cl(2)	129.4(6)
C(1)-Lu-N(2)	67.8(2)	Cl(2)-Li-O(2)	105.0(6)
C(1)-Lu-Cl(1)	89.20(17)		

Structure of 1a in the solid state: Crystals of **1a** suitable for an X-ray analysis were obtained by slow diffusion of pentane into a THF solution. The structure determination shows **1a** to be a dimeric lutetiate species, $[(NCN)LuCl_2(\mu\text{-}Cl)(\mu\text{-}Li(thf)_2)]_2$, in which each NCN moiety functions as a terdentate N,C,N′ ligand to one lutetium center (see Fig. 2). Each lutetium center is heptacoordinate. The best geometrical description is of a highly distorted pentagonal bipyramid (see Scheme 1) in which the pentagonal plane contains the N- and C-donor atoms of terdentate coordinated NCN and two bridging chlorine atoms [Cl(3) and Cl(3a)]. The latter produce a flat $Lu(\mu\text{-}Cl)_2Lu$ unit ($\sphericalangle$ClLuCl = 75.04(6), $\sphericalangle$LuClLu = 104.96(7)°) that is twisted by 21.1° with respect to the aromatic plane of the aryldiamine ligand (Fig. 3). It is clear from the projection in Figure 3 that the molecule has approximate C_2 symmetry, and that the N- and C-donor atoms do not define a mirror plane for the molecule. Consequently the two methyl groups on each nitrogen and the two protons of each benzyl group are nonequivalent. The coordination sphere of each lutetium center is completed by two axially positioned (*trans*) chlorine atoms to provide a formally dianionic dilutetate system, $[Cl_2(NCN)Lu(\mu\text{-}Cl)_2Lu(NCN)Cl_2]^{2-}$. The two lithium cations are each bound to two of the axial chlorine atoms (one from each lutetium center) in such a way that they "bridge" above and below the $Lu(\mu\text{-}Cl)_2Lu$ unit; this structural feature is new to early transition metal chemistry. The tetrahedral coordination sphere of each lithium is completed by two O-bound THF molecules.



1a

Scheme 1. Synthesis and schematic representation of the lutetiate **1a**.

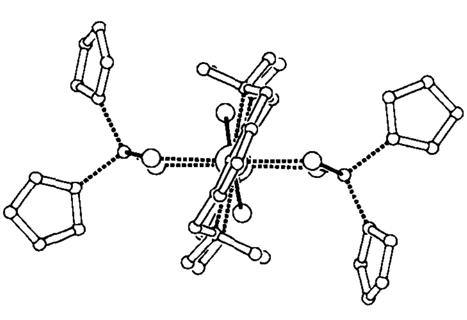


Fig. 3. PLUTON view of **1a** showing the angle of 21.1° between the aromatic plane and the four-membered $Lu(\mu\text{-}Cl)_2Lu$ bridging unit. Hydrogen atoms have been omitted for clarity.

Spectroscopic characterization of 1: Complexes **1** are very soluble in THF, but only slightly soluble in apolar solvents like benzene. The ^1H and ^{13}C NMR data of **1a** and **1b** in THF are temperature-dependent, and these data provide interesting information regarding the solution structure and behavior of these species.

Lutetium complex **1a** in [D$_8$]THF at 297 K (the highest temperature employed) shows characteristic singlet ^1H NMR resonances for the NMe_2 and CH_2 groups of NCN (δ = 2.50 and 3.75, respectively) that are significantly downfield of those of the parent aryldiamine (δ = 2.15 and 3.34, respectively). This pattern shows that the *ortho*-CH_2NMe_2 substituents are equivalent on the NMR time scale, and the chemical shifts indicate that the N-donor atoms are probably involved in coordination to a metal center. When this solution is cooled to 245 K, the singlet NMe_2 resonance splits into two singlets at δ = 2.50 and 2.45. Although further cooling to 190 K leads to severe line broadening, probably as a result of the viscosity of the sample, decoalescence of the benzylic proton resonance is also observed. These data are consistent with a molecule in which the N- and C-donor atoms do not lie in a molecular mirror plane, as was observed for the overall molecular geometry of **1a** in the solid state.

The ^1H NMR data for **1b**, including the temperature dependence, closely resemble those of **1a**. The ^{13}C NMR spectra of the two complexes at room temperature are also similar. From this we conclude that the two complexes are isostructural. However, the NMR data of yttrium complex **1b** show additional features arising from coupling to yttrium (^{89}Y 100% abundance, $I = {}^1/_2$), and in the ^{13}C spectra this affords extra information regarding the fluxional behavior of complexes **1** in solution. The ^{13}C NMR spectrum of **1b** in [D$_8$]THF at 297 K is simple and shows a set of four aryl resonances and a single resonance for both the benzylic and NMe_2 carbon atoms of the NCN ligand. Furthermore, all the resonances are sharp and the C_{ipso} resonance appears as a doublet due to coupling with ^{89}Y, with J_{YC} = 42.3 Hz. This coupling is comparable to those reported for other yttrium–aryl compounds.[18, 19] Surprisingly, the spectrum at 200 K and below shows two sets of signals for the aromatic carbons, including C_{ipso} (both show an ^{89}Y coupling), while the signals for the benzylic and aminomethyl carbons are broad. These data are consistent with the existence of an equilibrium between two species (**A** and **B** in the rest of the discussion) that is fast on the NMR time scale at 300 K and becomes slow at 200 K.

The coalescence behavior of these two sets of aryl resonances of **1b**, as monitored by the two C_{ipso} signals at different temperatures, affords information with respect to the nature of the two species **A** and **B** present in solution. Whereas one doublet (A_1/A_2) shows only a small downfield shift of 0.37 ppm over the temperature range 297–225 K, the other doublet (B_1/B_2) shows a greater temperature dependency with a shift of 1.65 ppm to low field over this temperature range (see Fig. 4). In addition to the strong temperature dependence of the B_1/B_2 doublet, the $^1J_{YC}$ of 39.8 Hz for this doublet is smaller than that for the A_1/A_2 doublet (42.3 Hz) (Fig. 4). This smaller coupling to ^{89}Y of C_{ipso} in **B** suggests a lower electron density between yttrium and the C_{ipso} atom. On the basis of this evidence we believe that species **B** corresponds to a dinuclear structure like that found for **1a** in the solid state and that the equilibrium involves a cation/anion association/dissociation process between this neutral spe-

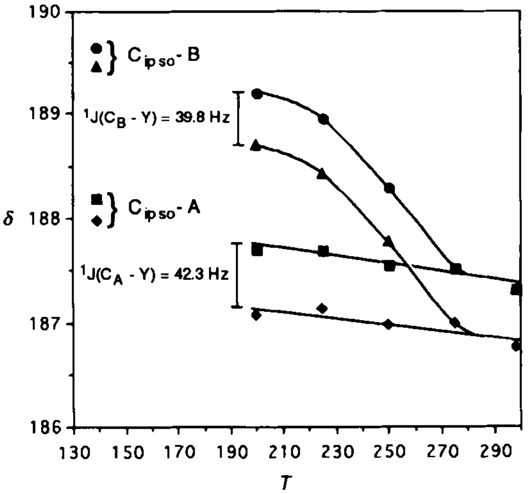


Fig. 4. Temperature dependence of the chemical shifts of the C_{ipso} doublets for **1b**. T = 275 K is taken as the coalescence temperature.

cies **B** on the one hand and the separate THF-solvated lithium cations and the $[(NCN)YCl_3]_2^{2-}$ anion on the other [Eq. (1)].

$$[(NCN)YCl_3]_2^{2-} + 2\,Li(thf)_4^+ \rightleftharpoons [(NCN)YCl_2(\mu\text{-}Cl)Li(thf)_2]_2 \qquad (1)$$
$$\qquad\mathbf{A} \qquad\qquad\qquad\qquad\qquad \mathbf{B}$$

Additional support for this view is given by the observation that the percentage of **B** increases at lower temperatures; this is consistent with the expected shift in Equilibrium (1) towards the neutral species **B** with decreasing temperature. Furthermore, a ^{13}C NMR spectrum of a dilute solution of **1b** at 200 K shows only resonances for species **B**. Although the NMR data could theoretically be interpreted in terms of mononuclear species, we think this unlikely. Unfortunately attempts to determine the degree of association of **1b** in THF by means of cryoscopy were unsuccessful.

Synthesis of the monoalkyl complex 2: Reaction of **1a** with one molar equivalent of trimethylsilylmethyl (neosilyl) lithium in THF at −78 °C led to substitution of the chloride and formation of a 1:1 mixture of the monoalkyl complex $[LuCl(NCN)(CH_2SiMe_3)]$ (**2**) and the bisalkyl complex $[Lu(NCN)(CH_2SiMe_3)_2]$ (**3**). When this reaction was carried out at room temperature, a 1:3 mixture was obtained with **3** as the main product. In contrast, reaction of the yttrium complex **1b** with neosilyllithium led to instantaneous decomposition of the mixture, with formation of the parent aryldiamine and tetramethylsilane (TMS).

Complex **2** was obtained pure from the 1:1 reaction mixture of **2** and **3** by first removing all volatiles, followed by extraction into hexane (LiCl removed by filtration) and cooling at −30 °C. This complex is a colorless crystalline material, which is moisture-sensitive (the parent aryldiamine and TMS are produced upon hydrolysis) and extremely soluble in both polar and nonpolar organic solvents. Its NMR and elemental microanalysis data are consistent with the formulation $[(NCN)LuCl(CH_2SiMe_3)]_n$. To obtain direct proof for the apparent low coordination number of the metal center suggested by the composition of the complex, the molecular structure of complex **2** was determined by X-ray diffraction (Fig. 5, Table 3).

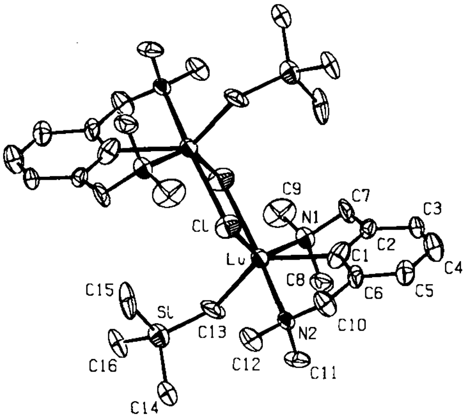


Fig. 5. ORTEP plot (ellipsoids at 30% probability level) of **2** with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

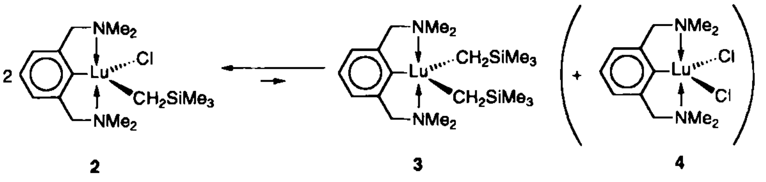
Table 3. Selected bond lengths (Å) and angles (°) for **2** (Esd in parentheses).

Lu-C(1)	2.32(3)	Lu-C(13)	2.39(3)
Lu-N(1)	2.60(2)	Lu-Cl	2.646(8)
Lu-N(2)	2.541(19)	Si-C(13)	1.82(3)
N(1)-Lu-N(2)	123.1(6)	C(1)-Lu-N(1)	65.2(9)
N(1)-Lu-Cl(a)	79.2(5)	C(1)-Lu-N(2)	70.2(9)
N(2)-Lu-Cl	78.1(4)	C(1)-Lu-C(13)	131.0(11)
Lu-C(13)-Si	126.0(15)	Cl-Lu-Cl(a)	75.8(2)

Structure of the monoalkyl complex 2 in the solid state: Crystals of **2** for an X-ray analysis were grown as described above from a 1:1 mixture of **2** and **3** at −30 °C, but were of relatively poor quality. Consequently, the final structure obtained (Fig. 5) is not particularly good and is included here only to show the global geometry around the metal center. One of the most significant features of this structure is the dimeric nature of **2** with a central $Lu(\mu\text{-}Cl)_2Lu$ unit as in complex **1a**. The two chloride ligands and the two carbon donor atoms of NCN and CH_2SiMe_3 are arranged in a distorted tetrahedral geometry around the metal center. The two amino substituents coordinate to the lutetium on two faces of this tetrahedron; the terdentate ligand ($\sphericalangle$NLuN = 123.1(6)°) thus coordinates in a pseudo-facial manner, which resembles the well-known facial coordination mode of the cyclopentadienyl ligand. The two neosilyl ligands are bound to the lutetium centers on opposite sides of the $Lu(\mu\text{-}Cl)_2Lu$ unit, and their steric bulk effectively shields the metal centers in the dinuclear arrangement. The presence of the sterically bulky neosilyl group on one side of each metal center could be a reason for the change from the meridional coordination of NCN in **1a** to the facial coordination of NCN in **2**.

Spectroscopic characterization of 2: The stability of **2** in solution is very dependent on the solvent used. In solution in hexane at −30 °C, pure **2** decomposed within 16 hours to form an as yet unidentified precipitate, and $1,3\text{-}(Me_2NCH_2)_2C_6H_4$ and TMS as the only organic products. In contrast, a solution of **2** in benzene remained essentially unchanged for days; in the ^1H NMR spectrum of **2** in C_6D_6, a TMS signal was observed, but its intensity increased only slightly during one hour at 75 °C.

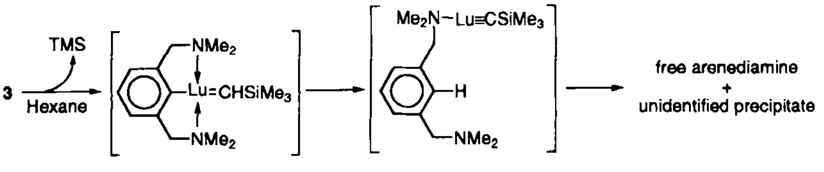
The ^1H NMR spectrum of pure **2**[20] in C_6D_6 at 297 K shows an AB pattern for the benzylic protons and two singlets for the NMe_2 protons. Since both the benzylic protons and the methyl groups on nitrogen are diastereotopic, we can conclude that the amino-N donor atoms are coordinated to the metal center with a pseudo-facial coordination mode of NCN found for **2** in the solid state. This spectrum of **2** is complicated by the presence of low-intensity signals due to bisalkyl complex **3** and a new species **4** (Scheme 2); the ratio for the benzylic signals of the organometallic species **2**, **3**, and **4** is approximately 9:1:1 (in addition there are also signals corresponding to decomposition products, namely, 1,3-$(Me_2NCH_2)_2C_6H_4$ and TMS (vide infra)). We believe that **4** may be a new species $[LuCl_2(NCN)]$, which is present in solution together with **3** as a result of the disproportionation equilibrium shown in Scheme 2. Support for the presence of this equilibrium comes from the fact that **4** is not observed in a 1:1 mixture of **2** and **3** (resulting from the reaction of **1a** with one equivalent of neosilyllithium).



Scheme 2. Equilibrium between mono- and bisneosilyl lutetium complexes.

Synthesis and spectroscopic characterization of the bisalkyl complex 3: Complex **3** was first identified as a secondary product in the synthesis of **2** from **1a** with one equivalent of neosilyllithium, but could not be obtained pure by using two equivalents of neosilyllithium. This unique bisalkyl complex could, however, be obtained in pure form by treating **2** with one equivalent of neosilyllithium in benzene at room temperature and has been isolated as a yellow moisture-sensitive oil.

The ^1H NMR spectrum of **3** in C_6D_6 at room temperature shows singlets for both the benzylic and NMe_2 protons of the aryldiamine, as well as singlets for the CH_2 and CH_3 groups of the neosilyl substituents. These data indicate the presence of apparent planes of molecular symmetry both perpendicular to and coplanar with the aryl skeleton, with the lutetium center positioned on the resulting C_2 axis and the neosilyl groups positioned symmetrically with respect to one of these planes. On the basis of these data we assume **3** to be monomeric, with the trigonal-bypyramidal structure shown in Scheme 2 and with the three carbon donor atoms in the trigonal plane. This five-coordinate, coordinatively unsaturated bisalkyl complex is suprisingly stable in benzene and has been characterized spectroscopically. However, it decomposes within one or two days, both in the pure state (oil) and when dissolved in hexane, with the liberation of TMS and the parent aryldiamine. The proposed decomposition route, summarized in Scheme 3, involves α-hydrogen transfer from the neosilyl groups. This route implies the formation, by loss of TMS from **3**, of an unstable carbene species $[(NCN)Lu{=}CHSiMe_3]$ (Scheme 3), which has neither been isolated nor detected. Further decomposition of this species then affords the neutral aryldiamine (see Discussion). Attempts to stabilize the anticipated carbene species by the use of coordinating solvents like THF were unsuccessful and, furthermore, decomposition of **3** in hexane in the presence of C_2H_4 did not lead to metathesis or to metallacyclobutanes.



Scheme 3. Proposed decomposition route for the bisneosilyl complex **3**.

Discussion

Syntheses: The synthetic results show that NCN is an interesting alternative to C_5H_5 (= Cp) and its derivatives in yttrium and lutetium chemistry. For example, the preparation of the NCN/metal chloride complexes **1a** and **1b** is achieved under milder conditions and in higher yields than reported for the closely related C_5Me_5 (= Cp*) complex $[Na(thf)(OEt_2)][Lu(\eta^5\text{-}Cp^*)Cl_3]$ (**5**),[10] which also incorporates the salt formed during its preparation. Our failure to prepare the corresponding NCN complex of the larger early lanthanide lanthanum is in accord with the observation by Wayda et al. that the homoleptic complexes $[Ln\{2\text{-}(Me_2NCH_2)C_6H_4\}_3]$ (Ln = Er, Yb, Lu) could not be obtained from the early and middle lanthanide chlorides.[12]

The versatility of NCN is shown in the reaction of **1a** with $LiCH_2SiMe_3$ to form the salt- and solvent-free monoalkyl complex **2**, which, owing to the absence of salt retention, has a dimeric structure. In contrast, reaction of Cp* complex **5** with $LiCH(SiMe_3)_2$ leads to the formation of a monomeric salt-containing complex $[LiL_2][Lu(\eta^5\text{-}Cp^*)\{CH(SiMe_3)_2\}(\mu\text{-}Cl)_2]$ (L_2 = $(thf)_2$, tetramethylethylenediamine) (**6**),[10] which has a monomeric structure containing a six-coordinate lutetium center as in dimeric **2**.

The bisalkyl NCN complex **3** is a salt- and solvent-free material that can be synthesized under very mild conditions from **2**. This facile conversion contrasts sharply with a report that monoalkyl complex **6** does not react with $LiCH(SiMe_3)_2$ and that its reaction with $KCH(SiMe_3)_2$ results in decomposition (vide infra).[10] This difference between the chemistry of NCN and cyclopentadienyl-type ligands can in this instance be attributed to the reduction in steric crowding at the metal center on going from $CH(SiMe_3)_2$ to CH_2SiMe_3. This is illustrated by the fact that Cp* complex **6** reacts with $LiCH_2SiMe_3$ to give a mixed bisalkyl complex $[Lu(\eta^5\text{-}Cp^*)\{CH(SiMe_3)_2\}(CH_2SiMe_3)(thf)]$, which is a mononuclear solvent-containing species.[10] Removal of coordinated THF from this complex, to produce a solvent-free bisalkyl complex like **3**, could not be achieved. Apparently, the NCN ligand is more effective in shielding and stabilizing a five-coordinate lutetium center than the Cp* ligand.

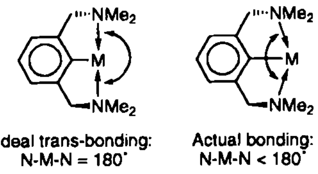
Stability of the alkyl complexes: The stability of solutions of both **2** and **3** in benzene contrasts with the low stability of hexane solutions (vide infra) and indicates that both **2** and **3** are most probably stabilized by π-complexation with the solvent in benzene solution, a type of stabilization that is also present in an intramolecular fashion in $[Yb\{OC_6H_3\text{-}2,6\text{-}(C_6H_5)_2\}_3]$.[21] The observed instability of monoalkyl complex **2** in hexane solution is not, however, intrinsic, but rather a direct consequence of the disproportionation equilibrium (Scheme 2), which affords the unstable bisalkyl complex **3**. It is because of this equilibrium and the connected decomposition of **3** (see Scheme 3) that isolated **2** can not be *re*crystallized from hexane. The thermal stability of the solvent-free NCN complex **3** is comparable to that of the bisalkyl complexes $[Lu(\eta^5\text{-}Cp^*)R'R''(thf)]$ (R', R'' = CH_2CMe_3,[10] CMe_3;[22] R' = CH_2SiMe_3, R'' = $CH(SiMe_3)_2$[10]); these complexes also decompose when attempts are made to remove coordinated THF.[10]

Our proposed decomposition route for the bis(neosilyl) complex **3**, in which a bisalkyl species undergoes an α-hydrogen transfer with the formation of an unstable carbene species, can be used to explain other results from the literature. For example, the reaction of the monoalkyl complex [Li(thf)(OEt$_2$)][Lu(η^5-Cp*){CH(SiMe$_3$)$_2$}Cl$_2$] with one equivalent of KCH(SiMe$_3$)$_2$ leads to decomposition—presumably via an intermediate bisalkyl species—and the liberation of approximately one equivalent of CH$_2$(SiMe$_3$)$_2$.[10] In addition, there is a report that lanthanide complexes containing more than one neosilyl substituent at the metal center decompose by loss of TMS with concomitant formation of carbene species.[23] The formation of the parent aryldiamine from the decomposition of **3** could be due to a σ-bond metathesis process between the Lu–C(aryl) and the alkylidene C–H bonds (of M=CH(SiMe$_3$)); the inorganic product would be a yet more unstable Lu≡CSiMe$_3$ alkylidyne species. A similar bond metathesis reaction in [TaX(O*t*Bu){2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(=CH*t*Bu)] is believed to be responsible for the formation of the rearranged product [TaX(O*t*Bu){2,4-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(=CH*t*Bu)].[24] In this rearrangement a neutral aryldiamine remains coordinated to tantalum and metalates intramolecularly at the outer *ortho* position of one CH$_2$NMe$_2$ group, rather than at the inner *ortho* position where metalation would regenerate the starting material. In the present case, the aryldiamine does not remain coordinated to the Lu center.

The immediate decomposition of the yttriate **1b** on reaction with neosilyllithium, with formation of both the parent aryldiamine and TMS, indicates that the disproportionation equilibrium and the decomposition route(s) available for the lutetium neosilyl complexes **2** and **3** are also operative for the yttrium analogues. The lower stability of the latter complexes compared to the former is in accord with the general trend in the transition metal triads that the heavier elements usually form more stable, isolable complexes, and the lighter elements form the more reactive complexes.[25]

Structure of 1a in the solid state: The type of lithium coordination found in the solid state structure of **1a** is similar to that of the Li cations in [Li(thf)$_4$][Li(thf)$_2$(μ-Cl)$_4${CdC(SiMe$_3$)$_3$}$_2$].[26] Since the parent aryldiamine 1,3-(Me$_2$NCH$_2$)$_2$C$_6$H$_4$ can serve as a bidentate N-donor ligand it can displace two THF ligands from the lithium ions, and it is therefore not surprising that small amounts of this diamine are difficult to remove from **1a** even by recrystallization.

The puckering of the two five-membered LuCCCN rings in **1a** is of the "twofold axis" type, which has previously been described for many *mer*-bound late transition metal complexes of the NCN ligand (see Fig. 1).[1] So far, this *mer*-bonding of the NCN ligand has afforded N-M-N bond angles ranging from 145.0(2) to 166.59(6)°.[1] An interesting feature in the structure of **1a** is the rather acute N-Lu-N angle of 135.8(2)° combined with the Lu–C bond length of 2.351(7) Å. This complex represents an extreme example of the trend found in transition metal/NCN complexes that smaller N-M-N bond angles are associated with longer M–C bond lengths. This can be easily rationalized in terms of the size of the pocket between the two nitrogen atoms (see Fig. 6), which is too small for the nitrogen atoms to coordinate to any transition metal in a pure *trans* geometry (N-M-N = 180°).



Ideal trans-bonding: N-M-N = 180°
Actual bonding: N-M-N < 180°

Fig. 6. Deviation from ideal *trans* bonding in NCN, leading to smaller N-M-N angles.

The Lu–C bond length in **1a** (2.351(7) Å) is substantially shorter than those reported for lutetium complexes of the mono(*ortho*)-chelating ligand [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$^-$ (2.395(6)–2.455(7) Å)[12, 13] and for [Li(thf)$_4$][Lu(C$_6$H$_3$-2,6-(Me)$_2$)$_4$] (2.425–2.501 Å).[27] The short bond in **1a** is probably the result of a strong Lu–C interaction; this can be explained by the additional presence of four chloride ligands, which are more strongly ionic than the ligands in the other lutetium complexes. In contrast to the short Lu–C bond, the Lu–N bond in **1a** is substantially longer (2.623(6) Å) than those found in the lutetium complexes of mono(*ortho*)-chelating [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$^-$ (2.468(6)–2.588(5) Å).[12, 13] It is, however, of comparable length to that in [(η^5-Cp*)Lu{CH$_2$CH(Me)CH$_2$NMe$_2$}(Cl)] (2.637(8) Å).[15] The Lu–Cl bond lengths for the two axial chloride ligands in **1a** (2.589(2) and 2.600(2) Å) are also similar to that found in the latter Cp* complex (2.608(2) Å).

Structure of 2 in the solid state: As shown in Figure 1, the pseudo-facial type of bonding found for NCN in the solid state structure of **2** has recently also been encountered in several transition metals complexes, for example, [Ru(NCN)X(nbd)] (X = Cl, η^1-OSO$_2$CF$_3$, nbd = norbornadiene),[6] [TiCl$_2$(O*i*Pr)(NCN)],[7] and [TaCl$_2$(NCN)(CH*t*Bu)].[5] In this way, the NCN monoanion accommodates N-M-N bond angles in these complexes ranging from 109.35(6) to 118.63(14)°. The structures show a trend towards larger N-M-N bond angles with increasing M–C bond lengths.[28] The Lu–C(1) bond length of 2.32(3) Å and N-Lu-N bond angle of 123.1(6)° in **2** fit in with this trend.

Conclusions

With the potentially terdentate NCN, we have introduced a new ligand in lanthanide chemistry. It has proven to be very flexible in shielding the lanthanide ion by displaying different coordination modes (either meridional or pseudo-facial; Fig. 1), depending on the metal center and the steric requirements of the other ligands. Using this ligand we have been able to synthesize and (crystallographically) characterize solvent- and salt-free mono- and bisalkyl lutetium complexes, which are difficult to prepare with cyclopentadienyl-type ligands.[10]

The ate complexes **1** are readily accessible and an excellent starting point for the synthesis of (mixed) bisalkyl complexes [Ln(NCN)R′R″], which may be of interest with respect to their reactivity towards simple alkenes[10, 18] and the formation of catalytically active lanthanide carbenes. The ready accessibility of the NCN complexes, the expected low transferability of NCN compared to that of Cp ligands,[18] and other parallels and differences between NCN and Cp-type ligands warrant further research into aryldiamine lanthanide chemistry. One of our first goals in this respect was recently achieved with the synthesis of [(NCN)La(η^5-C$_5$H$_5$)$_2$] (Fig. 7),[28] which provides a perfect example for the interchangability of NCN and cyclopentadienyl ligands.

The mono- and bisalkyl complexes **2** and **3** are organolutetium complexes with suprisingly low coordination numbers, whose low thermal stability can be attributed to the coordinative unsaturation of the metal center and the presence of α-hydrogen atoms. The decomposition pathway of complexes such as **3** provides new indications for the existence (as intermediates) of lutetium and yttrium carbene species, a class of complexes that is of great interest with respect to olefin metathesis reactions.

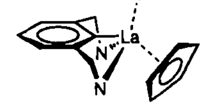


Fig. 7. Schematic representation of [(NCN)La(Cp)$_2$].

Experimental Section

General: The reactions were performed using standard Schlenk techniques in an atmosphere of dry, oxygen-free dinitrogen. All solvents were carefully dried and distilled prior to use. Anhydrous $LuCl_3$ and YCl_3 were purchased from Strem Chemicals. Trimethylsilylmethyllithium [29] and salt- and solvent-free 2,6-bis[(dimethylamino)methyl]phenyllithium [30] were synthesized according to literature procedures. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim, Germany. ^1H and ^{13}C NMR data were collected on Bruker AC200 and AC300 instruments.

[$LuCl_2\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(\mu\text{-}Li(thf)_2)]_2$ (**1a**): To a suspension of lutetium trichloride (2.11 g, 7.50 mmol) in THF (60 mL) was added dropwise over a period of 0.5 h a solution of 2,6-bis[(dimethylamino)methyl]phenyllithium (1.49 g, 7.50 mmol) in THF (30 mL). The metal salt dissolved rapidly. The slightly cloudy solution was allowed to stir for 1 h. It was then filtered, and the filtrate concentrated in vacuo to 20 mL. The product was precipitated by the addition of pentane (75 mL) and obtained as a white powder by centrifugation and subsequent drying in vacuo. Yield: 3.75 g (80%). ^1H NMR ([D_8]THF, 300 MHz, 298 K): $\delta = 6.75$ (m, 1H, $p\text{-}H^a$); 6.66 (d, 2H, $^3J(H^b,H^a) = 7.1$ Hz, $m\text{-}H^b$); 3.75 (s, 4H, CH_2N); 2.50 (s, 12H, NMe_2). ^{13}C NMR ([D_8]THF, 75 MHz, 298 K): $\delta = 193.20$ (C_{ipso}); 148.56 ($o\text{-}C$); 125.23 ($p\text{-}C$); 121.39 ($m\text{-}C$); 71.95 (CH_2N); 47.71 (NMe_2). Anal. calcd for $C_{20}H_{35}N_2O_2LuLiCl_3$: C, 38.51; H, 5.66; N, 4.49. Found: C, 38.32; H, 5.62; N, 4.50.

[$YCl_2\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(\mu\text{-}Li(thf)_2)]_2$ (**1b**): Synthetic procedure is identical to that for **1a** employing yttrium trichloride (1.46 g, 7.50 mmol) with 2,6-bis[(dimethylamino)methyl]phenyllithium (1.49 g, 7.50 mmol) in THF (90 mL). After workup, the product was obtained as a white powder. Yield: 4.03 g (quantitative). ^1H NMR ([D_8]THF, 200 MHz, 298 K): $\delta = 6.75$ (m, 1H, $p\text{-}H^a$); 6.62 (d, 2H, $^3J(H^b,H^a) = 6.6$ Hz, $m\text{-}H^b$); 3.73 (s, 4H, CH_2N); 2.50 (s, 12H, NMe_2). ^{13}C NMR ([D_8]THF, 75 MHz, 298 K): $\delta = 187.04$ (C_{ipso}, $J_{YC} = 42.3$ Hz); 148.09 ($o\text{-}C$); 125.41 ($p\text{-}C$); 121.19 ($m\text{-}C$); 72.01 (CH_2N); 47.51 (NMe_2). Anal. calcd for $C_{20}H_{35}N_2O_2YLiCl_3$: C, 44.67; H, 6.56; N, 5.21. Found: C, 44.55; H, 6.52; N, 5.08.

[$Lu(\mu\text{-}Cl)\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(CH_2SiMe_3)]_2$ (**2**): A solution of **1a** (2.33 g, 3.74 mmol) in THF (75 mL) was cooled to −78 °C, and a solution of trimethylsilylmethyllithium (0.35 g, 3.72 mmol) in THF (15 mL) added dropwise over 0.5 h. The clear solution was then allowed to warm to room temperature. After an additional hour of stirring, the solvent was removed in vacuo and the residue extracted with hexane (80 mL). The hexane extract was concentrated in vacuo to 25 mL and cooled to −30 °C. After 3 d **2** was isolated as colorless crystals by decantation of the supernatant hexane solution and washing of the crystals with small amounts (2 × 5 mL) of cold pentane. Yield: 0.55 g (30%). ^1H NMR (C_6D_6, 200 MHz, 298 K): $\delta = 7.11$ (m, 1H, $^3J(H^a,H^b) = 7.4$ Hz, $p\text{-}H^a$); 6.85 (d, 2H, $^3J(H^b,H^a) = 7.4$ Hz, $m\text{-}H^b$); 3.92 (d, 1H, $^2J(H^c,H^d) = 13.3$ Hz, $C(H^c)(H^d)N$); 3.19 (d, 1H, $^2J(H^c,H^d) = 13.3$ Hz, $C(H^c)(H^d)N$); 2.30 (s, 6H, $N(Me^e)(Me^f)$); 2.24 (s, 6H, $N(Me^e)(Me^f)$); 0.37 (s, 9H, $SiMe_3$); −0.64 (s, 2H, CH_2). ^{13}C NMR (C_6D_6, 50 MHz, 298 K): $\delta = 193.95$ (C_{ipso}); 174.40 ($p\text{-}C$); 122.00 ($m\text{-}C$); 70.03 (CH_2N); 46.66 (NMe_2); 45.65 (CH_2Si); 4.79 ($SiMe_3$). Anal. calcd for $LuC_{16}H_{30}N_2SiCl$: C, 39.30; H, 6.18; N, 5.73; Cl, 7.25. Found: C, 39.14; H, 6.21; N, 5.74; Cl, 7.31.

[$Lu\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(CH_2SiMe_3)_2$] (**3**): To a solution of **2** (0.39 g, 0.80 mmol) in C_6H_6 (25 mL) was added dropwise a solution of trimethylsilylmethyllithium (0.075 g, 0.80 mmol) in C_6H_6 (10 mL) at room temperature over a period of 0.5 h. A white precipitate formed during the addition, and the reaction mixture was stirred for an additional hour, after which the precipitate was removed by centrifugation. The solvent was removed in vacuo to afford **3** as a yellow oil in quantitative yield (0.43g). ^1H NMR (C_6D_6, 200 MHz, 298 K): $\delta = 7.15$ (m, 1H, $p\text{-}H^a$); 6.87 (d, 2H, $^3J(H^b,H^a) = 7.5$ Hz, $m\text{-}H^b$); 3.52 (s, 4H, CH_2N); 2.20 (s, 12H, NMe_2); 0.26 (s, 18H, $SiMe_3$); −0.78 (s, 4H, CH_2Si). ^{13}C NMR (C_6D_6, 50 MHz, 298 K): $\delta = 196.64$ (C_{ipso}); 146.90 ($p\text{-}C$); 121.74 ($m\text{-}C$); 70.65 (CH_2N); 47.12 (CH_2Si); 45.63 (NMe_2); 4.76 ($SiMe_3$). The instability of the complex prevented an elemental microanalysis.

X-ray data collection and structure refinement for the Complexes 1a and 2 [31]: Colorless crystals of **1a** and **2**, sealed in Lindemann glass capillaries, were transferred to an Enraf-Nonius CAD4 diffractometer for data collection. Accurate unit-cell parameters were derived from the setting angles (SET4) of 25 well-centered reflections in the range $10 < \theta < 14°$ and $8 < \theta < 30°$ for **1a** and **2**, respectively. All data were collected with $\omega/2\theta$ scan mode. Crystal data and details on data collection and refinement are collected in Table 1. Data were corrected for Lp effects, for the observed linear decay of the reference reflections and for absorption (DIFABS [32]; correction range 0.867–1.250 and 0.536–1.434 for **1a** and **2**, respectively). The structures were solved by using heavy-atom methods (**1a**: SHELXS86 [33]; **2**: DIRDIF-92 [34]) and subsequent difference Fourier techniques. Refinement on F was carried out by full-matrix least-squares techniques (SHELX76 [35]) for **1a**. Complex **2** was refined on F^2 by full-matrix least-squares techniques (SHELXL-93 [36]). Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of **1a** were refined with four common isotropic thermal parameters with values of 0.098(16), 0.072(12), 0.093(8) and 0.039(3) for the aromatic, benzylic, methyl, and THF protons, respectively. The hydrogen atoms of **2** were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor of 1.5 and 1.2 for the methyl hydrogen atoms and the other hydrogen atoms, respectively. No effort was made to model the disorder in the THF molecules in **1a**. Neutral atom scattering factors were taken from Cromer and Mann [37] and corrected for anomalous dispersion [38] for **1a**. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography for **2** [39]. All calculations were carried out on a DEC5000 cluster. Geometrical calculations and illustrations were generated with PLATON [40].

Acknowledgement: This work was supported (M. P. H.) by the Innovation-Oriented Research Program on Catalysis (IOP-Katalyse), and in part (A. L. S.) by the Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for Scientific Research (NWO).

Received: January 2, 1995 [F47]

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