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Imidazolin-2-iminato Complexes of Rare Earth Metals with Very Short Metal−Nitrogen Bonds: Experimental and Theoretical Studies

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The reactions of 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imine ($\mathrm{Im^{Dipp}NH}$, **1**-H) with trimethylsilylmethyl lithium ($LiCH_2SiMe_3$) and anhydrous rare earth metal trichlorides MCl_3 afforded the imidazolin-2-iminato complexes [(**1**)$MCl_2(THF)_3$] (**2a**, M = Sc; **2b**, M = Y; **2c**, M = Lu) and [(**1**)$GdCl_2(THF)_2$]·[$LiCl(THF)_2$] (**2d**). Treatment of complexes **2** with dipotassium cyclooctatetradienide, $K_2(C_8H_8)$ resulted in the formation of two- or three-legged piano-stool complexes of the type [(η^8-C_8H_8)M(**1**)$(THF)_n$] (**3a**, M = Sc, *n* = 1; **3b**, M = Y, *n* = 2; **3c**, M = Lu, *n* = 2; **3d**, M = Gd, *n* = 2). X-ray diffraction analyses of all eight complexes **2** and **3** revealed the presence of very short metal−nitrogen bonds, which are among the shortest ever observed for these elements. [(η^8-C_8H_8)Sc(**1**)(THF)] (**3a**) reacted with 2,6-dimethylphenyl isothiocyanate (Xy-NCS) to form the [2 + 2]-cycloaddition product **4**, which contains a thioureato-*N*,*N*′ moiety. The related COT-titanium complex [(η^8-C_8H_8)TiCl(**1**)] (**6**) could be obtained from [(**1**)$TiCl_3$] (**5**) by reaction with $K_2(C_8H_8)$ and was structurally characterized. As a theoretical analysis of the nature of the metal−nitrogen bond, density functional theory (DFT) calculations have been carried out for complexes **3a** and **6** and also for the model complexes [(η^8-C_8H_8)Sc($\mathrm{NIm^{Me}}$)] (**7**), $[(\eta^8\text{-}C_8H_8)Ti(\mathrm{NIm^{Me}})]^+$ (**8**), and [(η^8-C_8H_8)Ti(NXy)] (**9**), revealing a marked similarity of the bonding in imidazolin-2-iminato and conventional imido metal complexes.

Introduction

Organoimido complexes of the transition metals have been extensively studied because of their important role in a number of biological, industrial, and catalytic processes.[1] This interest is primarily stimulated by the ability of the metal-imido group (M = NR) to undergo a wide range of metathesis, cycloaddition, C−H bond activation, and hydroamination reactions.[2] In addition, imido ligands are also widely used as ancillary ligands in organotransition metal chemistry, for instance in olefin metathesis and polymerization catalysts.[3,4] In stark contrast to the large number of imido complexes containing d-block elements, the imido chemistry of the f-elements is much less developed,[5,6] Nevertheless, a considerable number of actinide, and in particular uranium, complexes containing terminal or bridging imido

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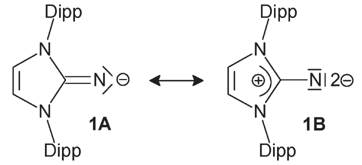
ligands are known,[7] whereas reports on well-defined lanthanide imido complexes are scarce.[8] More specifically, structurally characterized lanthanide complexes containing terminal imido groups are unknown to date, since the imido group is generally found to bind in a capping or bridging fashion.[9] The situation is similar in organogroup 3 metal chemistry[10] despite several efforts to isolate terminal scandium imido complexes.[11] Only recently, however, evidence has been presented for the existence of a transient Sc=NR species.[12]

Coordination of the formally dianionic imido ligand $(NR)^{2-}$ as a terminal ligand involves a metal−nitrogen multiple bond consisting of one σ and either one or two π interactions.[13] This resembles the bonding in transition metal complexes containing monoanionic imidazolin-2-iminato ligands such as $\mathrm{Im^{Dipp}N}$ (**1**), which can be described by the two limiting resonance structures **1A** and **1B** (Scheme 1), indicating that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands[14] with a strong electron donating capacity toward early transition metals.[15,16] Because of their ability to act as $2\sigma,4\pi$-electron donors, these ligands can be regarded as monodentate analogues of cyclopentadienyls, C_5R_5, and also as monoanionic imido ligands in a similar fashion to that described for related phosphoraneiminato ligands.[17] Therefore, lanthanide complexes with terminal imidazolin-2-iminato ligands, as presented in this paper, might serve as models for elusive mononuclear lanthanide imido complexes, and their structural investigation could lead to a better understanding of lanthanide-nitrogen multiple bonding.[5,18] A preliminary account on imidazolin-2-iminato lutetium complexes was previously published,[19] and this chemistry has now been extended to cover the rare earth metals scandium, yttrium, lutetium, and gadolinium.

Scheme 1. Mesomeric Structures for the Imidazolin-2-imide **1** (Dipp = 2,6-Diisopropylphenyl)



Results and Discussion

Structural Characterization of the Imine 1-H. The protonated ligand 1,3-bis(diisopropylphenyl)imidazolin-2-imine ($\mathrm{Im^{Dipp}NH}$, **1**-H) was obtained as a white crystalline solid from the reaction of the corresponding *N*-heterocyclic carbene 1,3-bis(diisopropylphenyl)imidazolin-2-ylidene[20] with trimethylsilyl azide (Me_3SiN_3), followed by desilylation of the intermediate **1**-$SiMe_3$ in methanol.[14] Single crystals of **1**-H were obtained at −30 °C from pentane solution, and the molecular structure of **1**-H was determined by X-ray diffraction analysis (Figure 1a) for comparison with the structures of the complexes containing its conjugate base **1** (vide infra). Perhaps surprisingly, the hydrogen H1 is not symmetrically disordered to both sides of the C1−N1 vector, but instead is well localized in the ring plane. This is explained by an investigation of the crystal packing, revealing intermolecular N1···H−C3 hydrogen bonds ($d_{N\cdots H}$ = 2.36 Å), connecting molecules by **b** translation

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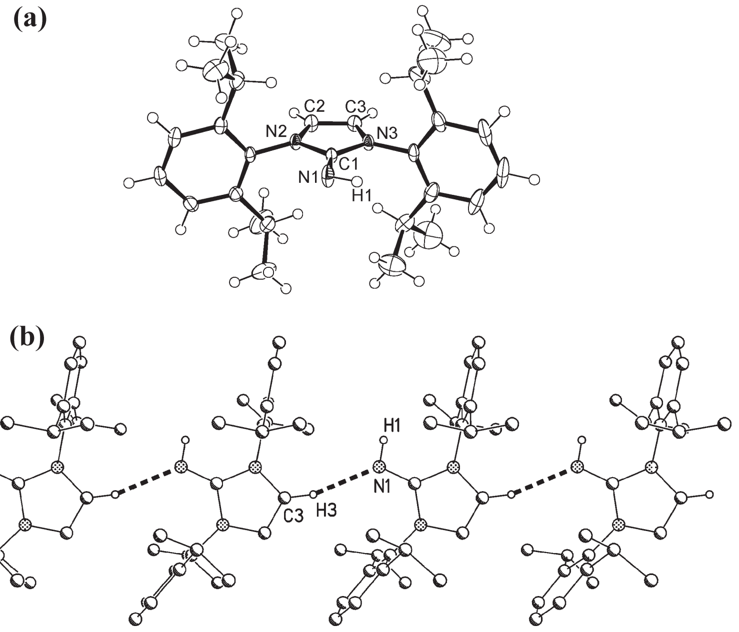
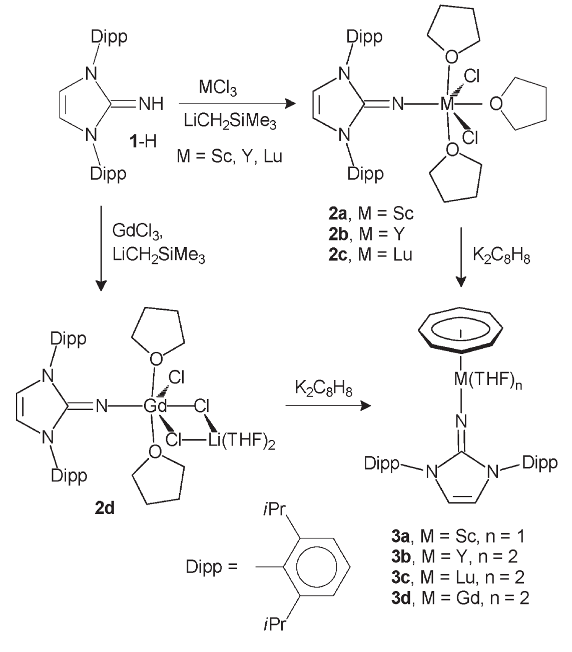


Figure 1. (a) ORTEP diagram of **1**-H with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: N1−C1 1.2888(17), C1−N2 1.3815(15), C1−N3 1.4004(16); N1−C1−N2 124.05(11), N1−C1−N3 131.75(11), N2−C1−N3 104.19(10). (b) C−H···N hydrogen bonds in **1**-H.

(Figure 1b); the chains thus formed lie in layers parallel to the *xy* plane and are further linked by additional C−H···π and π-stacking interactions. The structural parameters are in good agreement with those reported for other imidazolin-2-imines;[14,21] and the slight shortening of the C1−N1 bond distance [1.2888(17) Å] with respect to the corresponding silyl derivative **1**-SiMe$_3$ [1.263(3)/1.265(3) Å for two independent molecules] is also in agreement with the trend observed for related imines.[14]

Preparation and Structural Characterization of Imidazolin-2-iminato Rare Earth Metal Dichlorides. The reactions of the imine **1**-H with trimethylsilylmethyl lithium (Me$_3$SiCH$_2$Li) and the anhydrous rare earth metal halides MCl$_3$ (M = Sc, Y, Lu) in THF solution afforded the imidazolin-2-iminato complexes [(**1**)MCl$_2$(THF)$_3$] (**2a**, M = Sc; **2b**, M = Y; **2c**, M = Lu) M as colorless crystalline solids in good yield after extraction with pentane and crystallization from THF/pentane solution (1:2) (Scheme 2). **2a**−**2c** could be fully characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. In general, coordination to the rare earth metals does not have a significant impact on the resonances observed for the hydrogen and carbon atoms of the heterocyclic imidazoline moiety; the ^{1}H NMR spectra at room temperature exhibit two doublet resonances as expected for one set of diastereotopic isopropyl CH$_3$ groups, indicating the presence of equivalent 2,6-diisopropylphenyl groups. The molecular structures of **2a**−**2c** were also established by X-ray diffraction analyses; the three complexes are isostructural and crystallize as THF solvates in the space group $P2_1/n$. Their overall structural parameters are very similar, and pertinent data are summarized in Table 1. The representative molecular structure of the scandium complex **2a** is shown in Figure 2.

Scheme 2. Preparation of Imidazolin-2-iminato Rare Earth Metal Complexes



In all cases, the metal (M) is hexacoordinated with the two chlorine atoms in *trans*-position, and the three THF ligands adopt a meridional arrangement. The Cl1−M−Cl2 and O2−M−O3 angles deviate significantly from 180°, whereas the N1−M−O1 axes are close to linearity. Thus, the coordination geometries about the metal atoms can be described as distorted octahedra or, since the M−O1 bond in each complex is considerably longer than the other two M−O bonds, this THF ligand can be regarded as being *trans*-coordinated to a square-pyramid with the imido N1 atom at the apex. Presumably, the elongation of the M−O1 bonds is a result of the strong N1−M interactions, revealed by very short M−N bond lengths of

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Table 1. Selected Bond Lengths [Å] and Angles [deg] in Complexes **2a**−**2d**

	2a·THF	**2b**·THF	**2c**·THF	**2d**
	(M = Sc)	(M = Y)	(M = Lu)	(M = Gd)
M−N1	1.963(2)	2.1278(18)	2.091(3)	2.153(3)
M−O1	2.3776(19)	2.4937(16)	2.459(2)	2.396(3)
M−O2	2.2053(18)	2.3440(15)	2.303(2)	2.384(3)
M−O3	2.1937(18)	2.3328(14)	2.287(2)	
M−Cl1	2.4676(10)	2.6120(7)	2.5589(8)	2.7299(9)
M−Cl2	2.4758(10)	2.6176(7)	2.5668(9)	2.8430(10)
M−Cl3				2.6229(10)
N1−C1	1.264(3)	1.254(3)	1.251(4)	1.266(5)
M−N1−C1	174.5(2)	174.35(16)	174.2(2)	175.5(3)
N1−M−O1	178.38(8)	177.63(6)	177.86(9)	98.94(11)
Cl1−M−Cl2	163.65(3)	160.47(2)	161.66(3)	80.50(3)
O2−M−O3	157.14(7)	157.43(5)	157.54(8)	
N2−C1−N3	101.7(2)	101.59(16)	101.5(2)	102.0(3)
N1−M−Cl1				91.29(8)
N1−M−Cl2				171.41(8)
O1−M−O2				163.38(9)
Cl1−M−Cl3				166.39(3)

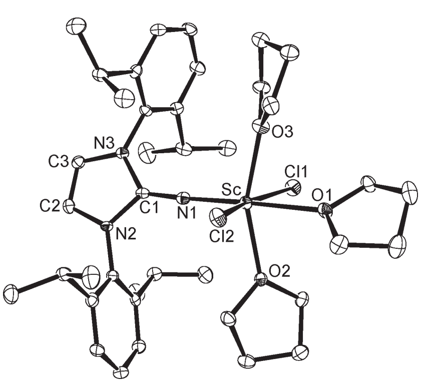

Figure 2. ORTEP diagram of **2a** in **2a**·THF with thermal displacement parameters drawn at 50% probability.

1.963(2) Å (**2a**), 2.1278(18) Å (**2b**), and 2.091(3) Å (**2c**) together with almost linear M−N1−C1 angles. For scandium, there is only one complex featuring a shorter Sc−N bond length of 1.9366(14) Å, and that is the $AlMe_3$ adduct of the recently reported transient scandium-imido complex [(PNP)Sc(N-Dipp)] containing the PNP pincer ligand bis (2-diisopropylphosphino-4-methylphenyl)amide.[12] The only other Sc−N bond lengths that also lie below 2 Å have been observed in the β-diketiminato complexes [(nacnac)ScCl(NH*t*Bu)] [1.986(2) Å] and [(nacnac)Sc (CH_3)(NH*t*Bu)]·$B(C_6F_5)_3$ [1.969(3) Å] with nacnac = [Dipp-NC(tBu)CHC(tBu)N-Dipp].[11b,11c] The metal−nitrogen bond length in **2b** is also the second shortest reported for yttrium complexes to date; and the shortest value [2.116(6) Å] was observed in a tetranuclear cyclopentadienyl-yttrium complex containing μ_3-ethylimido ligands.[22] Short Y−N distances have also been reported for yttrium-phosphoraneiminato complexes.[23] In contrast, the Lu−N bond length in **2c** is still the shortest ever observed for lutetium complexes,[19] and the previous shortest Lu−N distances of 2.145(2) and 2.149(4) Å were found in benzamidinate and amido complexes, respectively.[22,24]

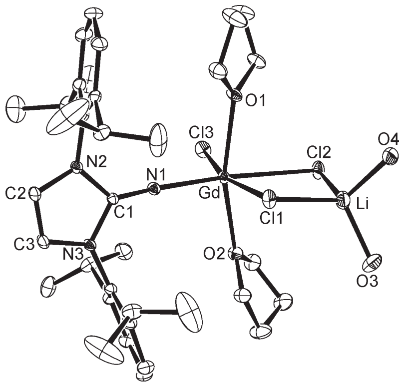

Figure 3. ORTEP diagram of **2d** with thermal displacement parameters drawn at 50% probability, the two THF ligands coordinated to lithium are disordered; the respective carbon atoms have been omitted for clarity.

Following the conditions for the preparation of complexes **2a**−**2c**, the use of $GdCl_3$ resulted in the formation of the gadolinium complex [(**1**)$GdCl_2(THF)_2$]·[LiCl $(THF)_2$] (**2d**), which was isolated as a colorless crystalline solid after extraction with pentane and crystallization from THF/pentane (1:2) solution (Scheme 2). The molecular structure of **2d** was determined by an X-ray diffraction analysis, and its presentation in Figure 3 reveals that the *trans*-coordinated THF ligand in **2a**−**2c** has been formally replaced by a chlorine atom (Cl2). The resulting negative charge is neutralized by a $[Li(THF)_2]^+$ moiety, capping the chlorine atoms Cl1 and Cl2. The *trans*-influence of the imidazolin-2-iminato results in a weakening of the Gd−Cl2 bond [2.8430(10) Å], which is significantly longer than the other two Gd−Cl distances [Gd−Cl1 = 2.7299(9) Å, Gd−Cl3 = 2.6229(10) Å]; as expected, the shortest bond is observed between gadolinium and the terminal chlorine atom. Again the Gd−N1 distance is very short, with 2.153(3) Å being the shortest value ever reported for gadolinium−nitrogen systems. The previous shortest Gd−N distances ranging from 2.190(3) to 2.240(3) Å were observed for five-membered amidolanthanide heterocycles.[25]

Preparation and Structural Characterization of Cyclooctatetraenyl Rare Earth Metal Complexes. For most of its history, organolanthanide chemistry has been dominated by cyclopentadienyl (Cp) ligands or by ligands that can be regarded as Cp analogues.[26] As mentioned above, the imidazolin-2-iminato ligand **1** represents such a monodentate Cp analogue because of its ability to act as a 2σ,4π-electron donor. The second most important carbocyclic ligand in organo-f-element chemistry is the 10-π-electron aromatic cyclooctatetraene dianion $C_8H_8^{2-}$, which is well suited to forming stable mononuclear

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Table 2. Selected Bond Lengths [Å] and Angles [deg] in the COT Complexes **3a**−**3d**, and **6**

	3a·THF[a]	**3b**·THF	**3c**·THF	**3d**·THF	**6**·THF
	(M = Sc)	(M = Y)	(M = Lu)	(M = Gd)	(M = Ti)
M−N1	1.982(2)/1.965(2)	2.163(2)	2.122(2)	2.191(2)	1.7905(15)
M−O1	2.241(2)/2.271(2)	2.4329(18)	2.380(2)	2.4501(19)	
M−O2		2.407(2)	2.380(2)	2.4718(18)	
M−C(COT)	2.377(2)−2.507(3)/2.380(3)−2.507(3)	2.577(3)−2.700(3)	2.544(3)−2.643(3)	2.619(3)−2.735(3)	2.292(2)−2.540(2)
M−Cl					2.4305(5)
N1−C1	1.254(4)/1.263(4)	1.255(3)	1.244(4)	1.258(3)	1.303(2)
M−N1−C1	166.6(2)/168.1(2)	163.51(19)	166.7(2)	162.89(19)	149.48(13)
N1−M−O1	87.20(9)/86.44(9)	86.92(7)	89.76(8)	87.17(7)	
N1−M−O2		87.57(7)	84.90(8)	86.75(7)	
O1−M−O2		76.93(7)	74.47(8)	77.04(6)	
N1−M−Cl					86.17(5)
N2−C1−N3	102.3(2)/102.4(2)	101.4(2)	101.5(2)	101.7(2)	105.06(14)

[a] Two independent molecules in the asymmetric unit.

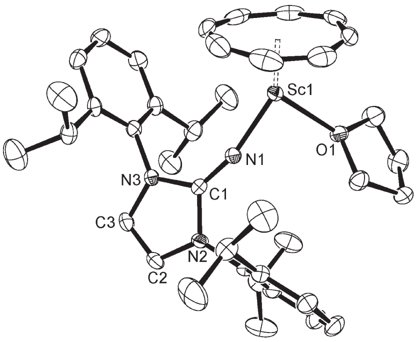

Figure 4. ORTEP diagram of one of the two independent molecules **3a** in **3a**·THF with thermal displacement parameters drawn at 50% probability.

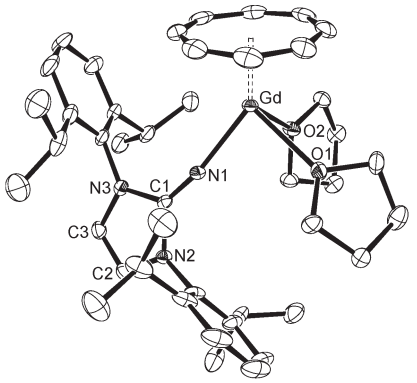

Figure 5. ORTEP diagram of **3d** in **3d**·THF with thermal displacement parameters drawn at 50% probability.

complexes with the lanthanide elements.[26,27] Accordingly, the substitution of the two chloride ligands in complexes **2a**−**2d** by $C_8H_8^{2-}$ could afford cyclooctatetraenyl (COT) complexes of the type $[(\eta^8\text{-}C_8H_8)M(\mathbf{1})(THF)_n]$ that are related to mixed sandwich COT-Cp rare earth metal complexes.[27] Indeed, the COT complexes **3a**−**3d** were isolated in satisfactory yield by treatment of the dichlorides **2a**−**2d** with the dipotassium cyclooctatetraenide salt $K_2(C_8H_8)$, followed by extraction with pentane and crystallization from THF/pentane mixtures (Scheme 2).[28] The ^1H NMR spectra (in C_6D_6) of the diamagnetic complexes **3a**, **3b**, and **3c** exhibit a singlet resonance for the C_8H_8 hydrogen atoms at 6.49, 6.29, and 6.28 ppm, respectively, and, similarly to complexes **2a**−**2c**, two doublet resonances are observed for the diasterotopic isopropyl CH_3 groups, indicating that rotation around the C−N-metal axes is fast on the NMR time scale. In contrast, the paramagnetic nature of the gadolinium complex **3d** does not allow NMR spectroscopic characterization.

The molecular structures of **3a**−**3d** could be established by X-ray diffraction analyses; all four COT complexes crystallize as THF solvates. The scandium complex **3a** crystallizes in the triclinic space group $P\bar{1}$ with two structurally closely similar molecules in the asymmetric unit; the structure of one molecule is shown in Figure 4. It should be noted that reports on COT-scandium complexes are extremely scarce,[29−31] and we are only aware of one other structurally authenticated scandium complex containing a η^8-C_8H_8 ligand, namely $[(\eta^8\text{-}C_8H_8)Sc\{\mu\text{-}(\eta^4{:}\eta^4\text{-}C_8H_8)Li(THF)_2\}]$.[31] The COT ligand in **3a** is essentially η^8-bound but in a slightly distorted fashion with the Sc−C distances ranging from 2.377(2) to 2.507(3) Å (molecule 1) and from 2.380(3) to 2.507(3) Å (molecule 2). The coordination spheres at scandium are both completed by the imido ligand **1** and by one THF ligand to afford a two-legged piano-stool geometry. The scandium−nitrogen bond lengths of 1.982(2) Å (Sc1−N1) and 1.965(2) Å (Sc2−N4) are very short and only slightly longer than in **2a** (see Tables 2 and 3 for comparison).

In agreement with the previously reported structure of the lutetium complex **3c**, the yttrium and gadolinium complexes **3b** and **3d** contain two coordinated THF ligands resulting in three-legged piano-stool geometries around the metal atoms. The complexes are isostructural and crystallize in the monoclinic space group $P2_1/n$; the

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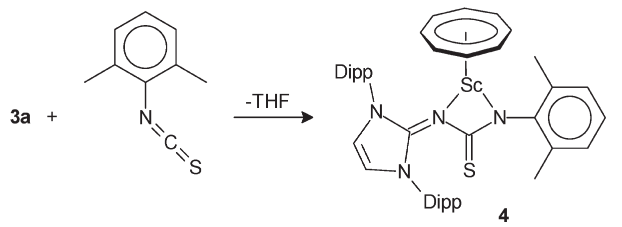
Table 3. Crystallographic Data

	1-H	**2a**·THF	**2b**·THF	**2d**	**3a**·THF	**3b**·THF	**3d**·THF	**4**·2THF·0.5 hexane	**6**·THF
Empirical formula	$C_{27}H_{37}N_3$	$C_{43}H_{68}Cl_2N_3O_4Sc$	$C_{43}H_{68}Cl_2N_3O_4Y$	$C_{43}H_{68}Cl_3GdLiN_3O_4$	$C_{43}H_{60}N_3O_2Sc$	$C_{47}H_{68}N_3O_3Y$	$C_{47}H_{68}GdN_3O_3$	$C_{55}H_{75}N_4O_2SSc$	$C_{39}H_{52}ClN_3OTi$
a (Å)	19.7270(14)	17.975(2)	18.1725(16)	10.7373(8)	10.4088(14)	12.2941(11)	12.2615(6)	11.5604(14)	28.1598(14)
b (Å)	6.5185(6)	12.2576(16)	12.3217(12)	12.3656(9)	10.7170(14)	12.1767(12)	12.1517(6)	12.4633(14)	14.3409(6)
c (Å)	20.1008(16)	19.817(2)	19.9922(18)	35.321(3)	37.471(2)	29.395(3)	29.4262(14)	18.806(2)	22.3609(10)
α (deg)	90	90	90	90	92.590(3)	90	90	104.876(3)	90
β (deg)	106.755(4)	96.139(6)	96.103(3)	90	92.633(3)	94.233(3)	94.096(3)	105.057(3)	125.210(3)
γ (deg)	90	90	90	90	107.290(3)	90	90	96.412(3)	90
V (Å^3)	2475.0(3)	4341.3(9)	4451.2(7)	4689.7(6)	3979.2(8)	4388.5(7)	4373.2(4)	2482.3(5)	7378.0(6)
Z	4	4	4	4	4	4	4	2	8
formula weight	403.60	806.86	850.81	961.54	695.90	811.95	880.29	877.02	662.19
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/c$
T (°C)	−173	−173	−140	−173	−140	−140	−173	−140	−173
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.083	1.234	1.270	1.362	1.162	1.229	1.337	0.957	1.192
μ (mm^{-1})	0.063	0.336	1.472	1.626	0.223	1.371	1.558	0.218	0.337
R(F_o or F_o^2)	0.0513	0.0496	0.0359	0.0443	0.0600	0.0457	0.0306	0.0465	0.0421
R$_w$(F_o or F_o^2)	0.1340	0.1107	0.0908	0.0947	0.1658	0.1307	0.0721	0.1286	0.1068

molecular structure of **3d** is shown in Figure 5, and pertinent structural data are summarized in Table 3. In all cases, the metal−nitrogen bond lengths are marginally elongated in comparison with complexes **2**. This is accompanied by a greater deviation from linearity at N1, and the M−N1−C1 angles range from 162.89(19)° (**3d**) to 166.7(2)° (**3c**). The C_8H_8 ligands in **3b**−**3d** are η^8-bound, albeit in slightly distorted fashions. On average the metal−carbon distances are relatively long in comparison with other COT complexes containing Y, Lu, and Gd metal atoms,[32] which might be a consequence of the sterically demanding Dipp-substituents of the imidazolin-2-imide **1**.

Reactivity of the Imidazolin-2-iminato Scandium Complex 3a. In view of the isolobal relationship between mononegative imidazolin-2-imides such as **1** and dinegative imido ligands,[17,19] the [(η^8-C_8H_8)Sc(**1**)] fragment in **3a** can be regarded as isolobal and isoelectronic with 16-electron titanium imido complexes of the type [(η^8-C_8H_8)Ti(NR)] (R = *t*Bu, Dipp).[33−35] The reactivity of these unique one-legged piano-stool ("pogo stick") imido complexes toward a variety of organic substrates such as CO_2, CS_2, isocyanates, and isothiocyanates was studied, and the Ti(NR) unit was shown to be reasonably reactive, undergoing cycloaddition or cycloaddition−elimination reactions.[34] Therefore, the reaction of **3a** with similar substrates was studied, since the 16-electron [(η^8-C_8H_8)Sc(**1**)] fragment, provided by elimination of the THF ligand, could be expected to exhibit similar reactivity. Whereas the reaction of **3a** with 2,6-dimethylphenyl isocyanate (Xy-NCO) did not result in the formation of a clean product, addition of the corresponding isothiocyanate Xy-NCS afforded a white powder in high yield, which could be recrystallized from THF/pentane solution at −35 °C (Scheme 3).

Scheme 3. Reaction of the Scandium-COT Complex **3a** with 2,6-Dimethylphenyl Isothiocyanate (XyNCS)



X-ray diffraction analysis revealed the formation of the [2 + 2] cycloaddition product **4**, in which the N=C bond has added across the scandium−nitrogen bond in [(η^8-C_8H_8)Sc(**1**)] to give a thioureato-*N*,*N*′ moiety (Figure 6). This result is in contrast to the observation made for the reaction of [(η^8-C_8H_8)Ti(NDipp)] with Xy-NCS, which was reported to result in the formation of an N,S-bound cycloaddition product, in agreement with its decomposition to afford the carbodiimide Dipp-N=C=N=Xy.[34] Similar behavior has been reported for [Cp_2Zr=N*t*Bu (THF)],[36] whereas the reaction of Ph-NCS with the diimido complex [$(DippN)_2Mo(OtBu)_2$] afforded the structurally characterized complex [(DippN)MoL(O*t*Bu)$_2$] (L = Dipp−N-C(S)-N-Ph) as the only example in which a dianionic *N*,*N*′-bound thioureato ligand is bound to a

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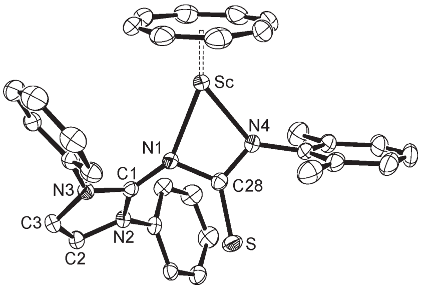


Figure 6. ORTEP diagram of **4** with thermal displacement parameters drawn at 50% probability. The Dipp-isopropyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Sc−N1 2.2505(10), Sc−N4 2.1413(10), Sc−C(COT) 2.2638(15)−2.4101(14), C1−N1 1.3384 (15), N1−C28 1.4184(15), N4−C28 1.3360(15), C28−S 1.6753(12); N1−Sc−N4 60.90(4), Sc−N1−C28 91.51(7), Sc−N4−C28 98.79(7), N1−C28−N4 107.91(10), Sc−N1−C1 147.57(8), Sc−N4−C29 137.05(8), N4−C28−S 127.48(9), N1−C28−S 124.46(9).

transition metal.[37] The *N*-(imidazolin-2-ylidene)-*N*′-(2,6-dimethylphenyl)thioureato(−1) ligand in **4** is unsymmetrically coordinated to the scandium atom, with the Sc−N4 bond length of 2.1413(10) Å being shorter than the Sc−N1 bond lengths of 2.2505(10) Å. This might be a result of the stronger donating properties of the amido N4 nitrogen atom in comparison with those of the iminoimidazole-nitrogen atom N1; however, the steric impact of the large Dipp-substituents must also be taken into account. Steric overcrowding can also be held responsible for the observation that the thioureato plane containing the atoms N1, N4, C28, and S is tilted with respect to the plane containing Sc, N1, and N4 (dihedral angle = 12.2°). The C1−N1 distance of 1.3384(15) Å is significantly longer than the corresponding exocyclic C−N bonds in the imidazolin-2-iminato complexes **2** and **3** (see Tables 2 and 3 for comparison), which indicates an increase of charge separation and pronounced ylidic imidazolium-amido-type characteristics of the ligand.

Preparation and Structural Characterization of a Cyclooctatetraenyl Titanium Complex. For comparison, we aimed toward the synthesis of the COT-titanium complex [(η^8-C_8H_8)TiCl(**1**)] (**6**), which can be regarded as being isoelectronic with [(η^8-C_8H_8)Sc(**1**)(THF)] or, after abstraction of the chloride anion, could form the cation [(η^8-C_8H_8)Ti(**1**)]$^+$ as an isoelectronic and isostructural analogue of [(η^8-C_8H_8)Sc(**1**)]. Dropwise addition of $TiCl_4$ to a solution of the silylated imine **1**-$SiMe_3$ in hexane at room temperature afforded [(**1**)$TiCl_3$] (**5**) as an orange precipitate, which can be isolated in good yield by filtration. The COT ligand can be conveniently introduced by reaction of **5** with $K_2(C_8H_8)$ in THF, and dark red crystals of complex **6** were obtained by extraction with toluene and crystallization from THF/pentane mixtures (Scheme 4). The NMR spectroscopic data of **6** are very similar to those of the COT-scandium complex **3a**; for instance, the ^{1}H and ^{13}C NMR resonances (in C_6D_6) for the C_8H_8 hydrogen and carbon atoms in **6** are observed at 6.41 and 101.4 ppm, respectively, as compared to 6.49 and 96.0 ppm in **3a**. Unfortunately, all attempts to remove the chloride atom from the Ti atom in **6**, for example, by treatment with sodium or silver triflates, have hitherto proved unsuccessful and lead to decomposition.

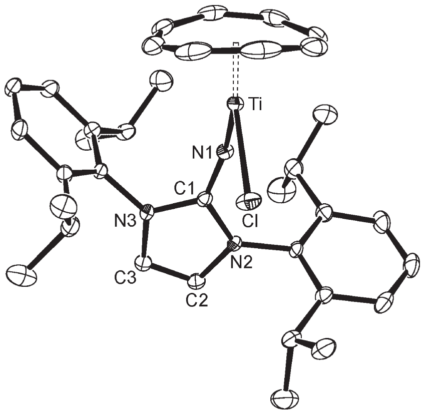
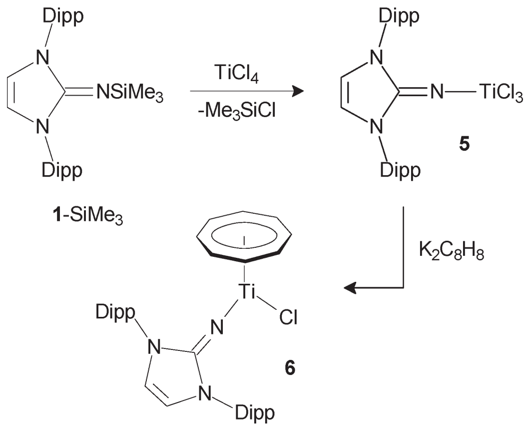


Figure 7. ORTEP diagram of **6** in **6**·THF with thermal displacement parameters drawn at 50% probability.

Scheme 4. Preparation of Imidazolin-2-iminato Titanium Complexes



Complex **6** crystallizes as a THF solvate in the monoclinic space group *C*2/*c*, and the solid-state structure of **6**·THF was established by X-ray diffraction (Figure 7); selected bond lengths and angles are presented in Table 2. As expected from the trend of the metal radii, all metal-element distances in **6** are shorter than those found for the COT complex **3a**, which contains the neighboring group 3 metal scandium.[38] As also observed for complexes **3a**−**3d**, the geometry of the COT ligand in **6** is appreciably distorted; the Ti−C bond lengths vary from 2.292(2)−2.540(2) Å, with the longest distances being those *trans* to the imidazolin-2-iminato ligand. The same puckering of the COT ligand has been observed for the pyridine (py) adduct of the imido complex [(η^8-C_8H_8)Ti(N*t*Bu)] and has been ascribed to the strong *trans* influence of the imido ligand.[34] Furthermore, the coordination sphere in this adduct, [(η^8-C_8H_8)Ti(N*t*Bu)(py)], is very similar to that in **6**, and both complexes adopt two-legged piano-stool geometries with acute N−Ti−N and N1−Ti−Cl angles, respectively; the average N−Ti−N value for the four independent molecules in the imido-pyridine complex is 86.4°,[34] which is almost identical with the corresponding N1−Ti−Cl angle of 86.17(5)°. As expected, the Ti−N1 bond length in **6** [1.7905(15) Å] is longer than the Ti−N distances observed for the COT-imido complexes

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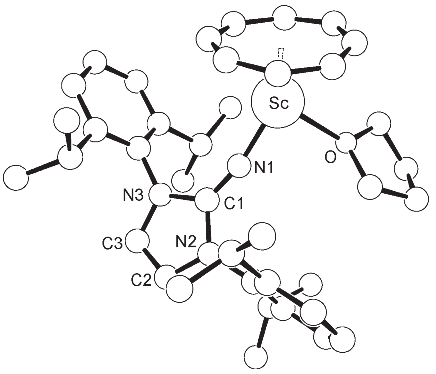

Figure 8. PLUTO drawing of the calculated structure **3a**. Selected bond lengths [Å] and angles [deg]; for comparison, experimental values are given in parentheses: Sc−N1 1.975 [1.982(2)/1.965(2)], Sc−O 2.355 [2.241 (2)/2.271(2)], C1−N1 1.262 [1.254(4)/1.263(4)]; Sc−N1−C1 168.4 [166.6 (2)/168.1(2)], N1−Sc−O 85.3 [87.20(9)/86.44(9)].

[(η^8-C_8H_8)Ti(N*t*Bu)(py)] (1.72 Å on average),[34] [(η^8-C_8H_8)Ti(N*t*Bu)] [1.699(6) Å], and [(η^8-C_8H_8)Ti(NDipp)] [1.7217(18) Å];[33] it is also slightly longer than the Ti−N distance reported for [(η^5-C_5H_5)TiCl_2(**1**)] [1.778(2) Å].[15c] It should be noted that the shorter Ti−N distance in the latter complex is accompanied by an almost linear Ti−N1−C1 angle of 175.8(1)°, whereas the corresponding angle in **6** [149.48(13)°] indicates a strong deviation from linearity; this bending is probably due to steric factors, since it allows a decrease in the interaction between the Dipp-substituents and the large C_8H_8 ring. In addition, one should refer to previous studies, which have shown that the potential energy surface of imido species is rather shallow with respect to changes of the M−N−C angle.[15b,34,39]

Theoretical Investigation of the Bonding in Cyclooctatetraenyl Scandium and Titanium Imido Complexes. For comparison of the metal−nitrogen bonding in COT scandium and titanium complexes, we performed density functional theory (DFT) calculations on the Sc and Ti complexes **3a** and **6**. Both structures were freely optimized with no geometric constraints, and the resulting calculated geometries (Figures 8 and 9) are in very good agreement with those established by X-ray diffraction (vide supra). In **3a**, the calculated Sc−N1 distance of 1.975 Å perfectly matches the average of the Sc−N1 bond lengths [1.965(2) and 1.982(2) Å], which have been experimentally determined for two crystallographically independent molecules of **3a**. The two-legged piano-stool geometry with a comparatively small N1−Sc−O angle of 85.5° has also been well reproduced. The same is true for **6**, which shows excellent correlation between theoretically and experimentally derived values, for example, Ti−N1 = 1.795 versus 1.7905(15) Å; Ti−Cl = 2.415 versus 2.4305(5) Å; N1−Ti−Cl = 87.5° versus 86.17(5)°. The marked deviation of the Ti−N1−C1 angle from linearity (157.3°) was confirmed, albeit to a smaller extent than found by X-ray diffraction analysis of **6** [149.48(13)°]. Visual inspection of the canonical orbitals in **3a** and **6** reveals the existence of ligand−metal π-bonding (see Supporting Information); however, comparison between the two systems is complicated by the low symmetry and by the presence of the THF ligand in **3a** or the chlorine ligand in **6**, respectively. Therefore, we performed computations on the isoelectronic model complexes [(η^8-C_8H_8)Sc(NIm^{Me})] (**7**) and [(η^8-C_8H_8)Ti(NIm^{Me})]$^+$ (**8**) ($Im^{Me}N$ = 1,3-dimethylimidazolin-2-imide), assuming C_{2v} symmetry (Figure 10). For comparison, the "true" titanium imido complex [(η^8-C_8H_8)Ti(NXy)] (**9**) (Xy = 2,6-dimethylphenyl) was calculated, which also allows us to make reference to the 16-electron titanium imido complexes of the type [(η^8-C_8H_8)Ti(NR)] (R = *t*Bu, Dipp).[33−35]

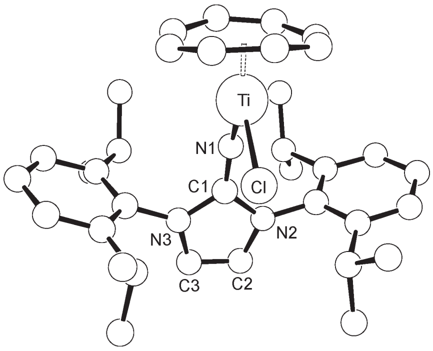

Figure 9. PLUTO drawing of the calculated structure **6**. Selected bond lengths [Å] and angles [deg]; for comparison, experimental values are given in parentheses: Ti−N1 1.795 [1.7905(15)], Ti−Cl 2.415 [2.4305(5)], C1−N1 1.287 [1.303(2)]; Ti−N1−C1 157.3 [149.48(13)], N1−Ti−Cl 87.5 [86.17(5)].

The metal−nitrogen distances in **7** (1.925 Å) and **8** (1.745 Å) are shorter than those established for **3a** and **6**, which is in agreement with the expected increase in bond strength upon dissociation of the THF or chloride ligand, respectively. In contrast, the Ti−N distance in **9** (1.691 Å) is almost identical with the bond lengths that have been established experimentally [1.7217(18) Å] and theoretically (1.70 Å) for [(η^8-C_8H_8)Ti(NDipp)].[33] An analysis of the canonical orbitals in **7**, **8**, and **9** reveals the presence of two orthogonal orbitals in each complex that are clearly associated with metal−ligand π-bonding. Figure 10 shows the isosurfaces of these orbitals: HOMO and HOMO-3 in the imidazolin-2-iminato complexes **7** and **8**, HOMO and HOMO-4 in the 2,6-dimethylphenyl imido complex **9**, respectively (see also Supporting Information for the presentation of an extended set of frontier orbitals). Visual inspection of these orbitals clearly indicates that the orbital shapes are very similar and that the three complexes are in an isolobal relationship. The energies of the π-orbitals in the neutral complexes **7** and **9** are very similar, whereas the cationic charge of complex **7** naturally leads to a significantly higher stabilization of these frontier orbitals.

A bonding analysis of the π-orbitals in the scandium complex **7** reveals 5% and 9% orbital contribution from the metal center (Figure 10), which is in agreement with the expected predominantly ionic character of the Sc−N bond; for similar considerations concerning the Lu−N bond in the corresponding lutetium complex, see ref 19. Replacing trivalent scandium in **7** by tetravalent titanium affords cationic **8** and an increase of the metal orbital contribution (11%, 15%), in line with a decrease of the

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[39] (a) Jørgensen, K. A. *Inorg. Chem.* **1993**, *32*, 1521. (b) Antiñolo, A.; Espinosa, P.; Fajardo, M.; Gómez-Sal, P.; López-Mardomingo, C.; Martin-Alonso, A.; Otero, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1007. (c) Ciszewski, J. T.; Harrison, J. F.; Odom, A. L. *Inorg. Chem.* **2004**, *43*, 3605.

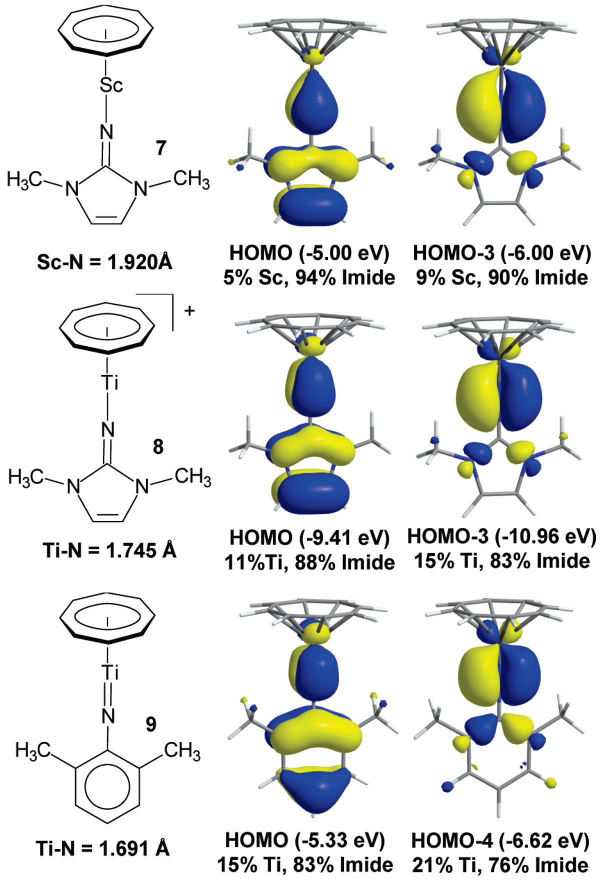

Figure 10. Isosurfaces and eigenvalues of the metal−ligand π-bonding orbitals in complexes **7**, **8**, and **9**.

orbital energies as the valence state of the metal increases.[40] An additional increase of the metal orbital contribution (15%, 21%) is observed for [(η^8-C_8H_8)Ti(NXy)] (**9**), in which the mononegative imidazolin-2-iminato ligand in **8** has been replaced by a "true" dinegative imido ligand with a stronger π-donating ability toward the metal center. Despite these differences, comparison of the bonding in complexes **7**, **8**, and **9** clearly indicates that both imidazolin-2-iminato and imido ligands can be regarded as 2σ,4π-electron donors, capable of forming highly polarized triple bonds with the early transition metals. For imidazolin-2-iminato ligands, this behavior can be mainly attributed to the ability of the imidazolium ring to stabilize a positive charge as indicated by resonance structure **1B** in Scheme 1, and the contribution from this structure to the overall electronic ground state can be expected to increase significantly upon metal−nitrogen interaction.

Conclusions

The present study gives further evidence for the suitability of imidazolin-2-iminato ligands to form particularly strong metal−nitrogen bonds. The reactivity of the polarized Sc−N bond in complex **3a** toward 2,6-dimethylphenyl isothiocyanate and also the theoretical study reveal a strong analogy between imidazolin-2-iminato and conventional imido complexes. In view of the imidazolin-2-iminato complexes **2** and **3** presented in this paper, this implies that mononuclear rare earth metal imido complexes should be isolable under the right conditions, although a higher tendency to form clusters must certainly be conceded because of the higher charge of the imido species. Future studies will continue to exploit the reactivity along the metal−nitrogen bond in these imidazolin-2-iminato complexes, and preliminary studies reveal that these systems are highly active in the catalytic ring-opening polymerization of lactones.

Experimental Section

General Information. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled glovebox (MBraun 200B). All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. Deuterated solvents were obtained from Sigma Aldrich (all ≥99 atom % D) and were degassed, dried, and stored in the argon-filled glovebox. NMR spectra were recorded on Bruker DPX 200, Bruker DRX 400, and Bruker DPX 600 devices. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard (^{1}H, ^{13}C). Elemental analysis (C, H, N) succeeded by combustion and gas chromatographical analysis with an Elementar vario MICRO. 1,3-Bis (2,6-diisopropylphenyl)imidazolin-2-imine (Im$^{\mathrm{Dipp}}$NH, **1**-H),[14] the corresponding silylated imine Im$^{\mathrm{Dipp}}$NSiMe$_3$ (**1**-SiMe$_3$),[14] [$LiCH_2SiMe_3$],[41] and $K_2(C_8H_8)$[42] were prepared according to published procedures. The anhydrous trichlorides $LnCl_3$ (Ln = Sc, Y, Lu, Gd) were purchased from Sigma-Aldrich and used as received.

General Procedure for the Preparation of Complexes [(1)MCl$_2$(THF)$_3$] (2a, M = Sc; 2b, M = Y; 2c, M = Lu) and [(1)GdCl$_2$(THF)$_2$]·[LiCl(THF)$_2$] (2d). A mixture of anhydrous MCl_3 (0.5 mmol, M = Sc, Y, Lu, or Gd) and $LiCH_2SiMe_3$ (47 mg, 0.5 mmol) was treated with THF (10 mL). After stirring for 2 h, a solution of **1**-H (202 mg, 0.5 mmol) in THF (5 mL) was added. The reaction mixture was allowed to stir for another 12 h. The solvent was evaporated, and the compound was repeatedly extracted with 30 mL (3 × 10 mL) of pentane. The complexes were recrystallized from THF/pentane (1:2) at −30 °C to obtain colorless crystals.

Analytical Data for [(1)ScCl$_2$(THF)$_3$] (2a). Yield: 301 mg (75%). Anal. Calcd for $C_{43}H_{68}Cl_2N_3O_4Sc$ (**2a**·THF): C, 64.00; H, 8.49; N, 5.20. Found: C, 63.80; H, 7.96; N, 5.35. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 7.36−7.24 (m, 6 H, Ph), 5.93 (s, 2 H, NC*H*), 3.57 (br, 4 H, THF), 3.31 (sept., 4 H, C*H*Me$_2$), 1.55 (d, 12 H, C*H*$_3$), 1.25 (br, 4 H, THF), 1.20 (d, 12 H, C*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 159.2 (N*C*N), 149.2 (*ipso-C*), 137.1 (*o-C*), 129.5 (*p-C*), 124.4 (*m-C*), 113.8 (N*C*H), 67.5 (THF), 29.5 (*C*HMe$_2$), 25.5 (THF), 24.9 (CH*C*H$_3$), 24.6 (CH*C*H$_3$) ppm.

Analytical Data for [(1)YCl$_2$(THF)$_3$] (2b). Yield: 255 mg (60%). Anal. Calcd for $C_{39}H_{60}Cl_2N_3O_3Y$ (**2b**): C, 60.15; H, 7.76; N, 5.39. Found: C, 59.54; H, 7.59; N, 5.17. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 7.17 (br, 6 H, Ph), 5.95 (s, 2 H, NC*H*), 3.57 (br, 4 H, THF), 3.42 (sept., 4H, C*H*Me), 1.55 (d, 12 H, C*H*$_3$), 1.4 (br, 4 H, THF), 1.34 (d, 12 H, C*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 159.3 (N*C*N), 154.1 (*ipso-C*), 148.3 (*o-C*), 128.2 (*p-C*), 123.8 (*m-C*), 113.7 (N*C*H), 67.4 (THF), 28.6 (*C*HMe$_2$), 25.4 (THF), 23.8 (CH*C*H$_3$), 23.7 (CH*C*H$_3$) ppm.

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Analytical Data for [(1)LuCl$_2$(THF)$_3$] (2c). Yield: 300 mg (69%). Anal. Calcd for $C_{39}H_{60}Cl_2N_3O_3Lu$ (**2c**): C, 54.16; H, 6.99; N, 4.85. Found: C, 54.81; H, 6.95; N, 4.70. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 7.18 (br, 6H, Ph), 5.91 (s, 2 H, NC*H*), 3.70 (br., 4 H, C*H*Me), 3.52 (br, 4 H, THF), 1.53 (d, 12H, C*H*$_3$), 1.37 (br, 4 H, THF), 1.26 (d, 12H, C*H*$_3$) ppm; ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 159.2 (N*C*N), 154.2 (*ipso-C*), 148.1 (*o-C*), 128.4 (*p-C*), 123.6 (*m-C*), 113.5 (N*C*H), 67.4 (THF), 28.7 (*C*HMe$_2$), 25.1 (THF), 23.8 (CH*C*H$_3$), 23.7 (CH*C*H$_3$) ppm.

Analytical Data for [(1)GdCl$_2$(THF)$_2$]·[LiCl(THF)$_2$] (2d). Yield: 350 mg (73%). Anal. Calcd for $C_{43}H_{68}Cl_3GdLiN_3O_4$ (**2d**): C, 53.71; H, 7.12; N, 4.37. Found: C, 53.58; H, 6.85; N, 4.20. Because of the highly paramagnetic nature of the compound, no NMR spectra were recorded.

General Procedure for the Preparation of Complexes [(η^8-C$_8$H$_8$)M(1)(THF)$_n$] (3a, M = Sc, *n* = 1; 3b, M = Y, n = 2; 3c, M = Lu, n = 2; 3d, M = Gd, n = 2). A solution of the respective complex **2** (0.5 mmol) in THF (5 mL) was treated with freshly prepared $K_2(C_8H_8)$ (from 39 mg of potassium and 0.055 mL of cyclooctatetraene). After stirring for 12 h, the solvent was evaporated, and the residue was extracted with 30 mL (3 × 10 mL) of pentane. After filtration and evaporation, the complexes were recrystallized from THF/pentane (1:2) at −30 °C.

Analytical Data for [(η^8-C$_8$H$_8$)Sc(1)(THF)] (3a). Yield: 250 mg (72%). Anal. Calcd for $C_{43}H_{60}N_3O_2Sc$ (**3a**·THF): C, 74.21; H, 8.69; N, 6.03. Found: C, 73.99; H, 8.20; N, 6.28. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 7.28−7.20 (m, 4 H, *m*-C*H*), 7.12−7.08 (m, 2 H, *p*-C*H*), 6.49 (s, 8 H, C$_8$*H*$_8$), 5.67 (s, 2 H, NC*H*), 3.49−3.43 (m, THF), 2.75 (sept., 4 H, C*H*Me), 1.4−1.3 (m, THF), 1.25 (d, 12 H, C*H*$_3$), 1.09 (d, 12 H, C*H*$_3$) ppm; ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 148.2 (*ipso-C*), 137.2 (*o-C*), 129.6 (*p-C*), 124.3 (*m-C*), 112.6 (N*C*H), 96.5 (*C*$_8$H$_8$), 67.2 (THF), 29.1 (*C*HMe$_2$), 26.2 (THF), 25.1 (CH*C*H$_3$), 24.9 (CH*C*H$_3$) ppm; the N*C*N resonance was not observed.

Analytical Data for [(η^8-C$_8$H$_8$)Y(1)(THF)$_2$] (3b). Yield: 210 mg (57%). Anal. Calcd for $C_{43}H_{60}N_3O_2Y$ (**3b**): C, 69.80; H, 8.17; N, 5.67. Found: C, 69.47; H, 7.91; N, 5.42. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 7.28−7.21 (m, 4 H, *m*-C*H*), 7.12−7.11 (m, 2 H, *p*-C*H*), 6.29 (s, 8 H, C$_8$*H*$_8$), 5.85 (s, 2 H, NC*H*), 3.12 (sept., 4 H, C*H*Me), 1.31 (d, 12 H, C*H*$_3$), 1.17 (d, 12 H, C*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 148.3 (*ipso-C*), 137.3 (*o-C*), 128.5 (*p-C*), 123.7 (*m-C*), 113.1 (N*C*H), 93.4 (*C*$_8$H$_8$), 67.1 (THF), 28.6 (*C*HMe$_2$), 25.1 (THF), 24.5 (CH*C*H$_3$), 23.7 (CH*C*H$_3$) ppm; the N*C*N resonance was not observed.

Analytical Data for [(η^8-C$_8$H$_8$)Lu(1)(THF)$_2$] (3c). Yield: 300 mg (62%). Anal. Calcd for $C_{47}H_{68}N_3O_3Lu$ (**3c**·THF): C, 62.86, H 7.63, N 4.67; Found: C 62.15, H 7.04, N 4.12. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 7.27−7.20 (m, 4 H, *m*-C*H*), 7.11−7.10 (m, 2 H, *p*-C*H*), 6.28 (s, 8 H, C$_8$*H*$_8$), 5.86 (s, 2 H, NC*H*), 3.25−3.18 (m, THF), 3.09 (sept., 4 H, C*H*Me), 1.30 (d, 12H, C*H*$_3$), 1.24−1.19 (m, THF), 1.16 (d, 12H, C*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 148.3 (*ipso-C*), 137.2 (*o-C*), 128.5 (*p-C*), 123.7 (*m-C*), 113.2 (N*C*H), 92.8 (*C*$_8$H$_8$), 68.1 (THF), 28.6 (*C*HMe$_2$), 25.2 (THF), 24.4 (CH*C*H$_3$), 23.7 (CH*C*H$_3$) ppm; the N*C*N resonance was not observed.

Analytical Data for [(η^8-C$_8$H$_8$)Gd(1)(THF)$_2$] (3d). Yield: 350 mg (79%). Anal. Calcd for $C_{47}H_{68}GdN_3O_3$ (**3d**·THF): C, 64.12; H, 7.78; N, 4.77. Found: C, 63.92; H, 7.51; N, 4.47. Because of the highly paramagnetic nature of the compound, no NMR spectra were recorded.

Reaction of 3a with 2,6-Dimethylphenyl Isothiocyanate. A solution of XyNCS (13.34 mg, 0.08 mmol) in toluene (2 mL) was added to a solution of **3a** (51 mg, 0.08 mmol) in toluene (2 mL), and the reaction mixture was stirred at room temperature for 1 h. After the solvent was removed under reduced pressure, the residue was washed with 2 mL of pentane. A white powder was obtained after removing the solvent under reduced pressure in >95% yield (56 mg, 0.08 mmol). Colorless crystals of complex **4** were isolated from THF/pentane solution at −35 °C. Anal. Calcd for $C_{44}H_{53}N_4SSc$: C, 73.92; H, 7.47; N, 7.84. Found: C, 74.45; H, 7.48; N, 8.70. ^{1}H NMR (toluene d$_8$, 400 MHz, 25 °C): δ 7.24−7.28 (2H, m, *p*-Dipp-C*H*), 7.09−7.14 (4H, m, *m*-Dipp-C*H*), 6.89−6.91 (2H, m, *m*-Xy-C*H*), 6.79−6.83 (1H, m, p-Xy-C*H*), 6.42 (8H, s, C$_8$*H*$_8$), 6.26 (2H, s, NCH), 3.48 (2H, sept., C*H*Me$_2$), 2.73 (2H, sept., C*H*Me$_2$), 1.83 (6H, s, Xy-C*H*$_3$), 1.50 (6H, d, Dipp-C*H*$_3$), 1.29 (6H, d, Dipp-C*H*$_3$), 0.92 (6H, d, Dipp-C*H*$_3$), 0.90 (6H, d, Dipp-C*H*$_3$). ^{13}C NMR (toluene d$_8$, 400 MHz, 25 °C): δ 190.5 (*C*S), 151.8 (*i*-Xy-*C*N), 148.1 (N*C*N), 146.8 (*o*-Dipp-*C*), 133.2 (*i*-Dipp), 132.2 (*o*-Xy-*C*H), 130.6 (*p*-Dipp-*C*H), 128.1 (*m*-Xy-*C*H), 127.7 (*m*-Dipp-*C*H), 123.6 (*p*-Xy-*C*H), 118.8 (N*C*H), 97.3 (*C*$_8$H$_8$), 28.8 (*C*HMe$_2$), 28.6 (*C*HMe$_2$), 26.1 (Dipp-*C*H$_3$), 25.6 (Dipp-*C*H$_3$), 23.3 (Dipp-*C*H$_3$), 23.1 (Dipp-*C*H$_3$), 20.1 (Xy-*C*H$_3$) ppm.

Synthesis and Characterization of [(1)TiCl$_3$] (5). $TiCl_4$ (199.3 mg, 1.05 mmol) was added dropwise to a solution of **1**-SiMe$_3$ (500 mg, 1.05 mmol) in hexane (20 mL) at ambient temperature, and the resulting reaction mixture was stirred for 12 h. The orange precipitate was isolated by filtration, washed with hexane (3 × 5 mL) and dried in vacuo. The product was obtained as an orange solid in 95% yield (526 mg). Anal. Calcd for $C_{27}H_{36}Cl_3N_3Ti$: C, 58.24; H, 6.52; N, 7.55. Found: C, 58.63; H, 6.61; N, 7.08. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.73−7.65 (m, 4 H, *m*-C*H*), 7.53−7.49 (m, 2 H, *p*-C*H*), 6.85 (s, 2 H, NC*H*), 2.89 (sept., 4 H, C*H*Me), 1.59 (d, 12 H, C*H*$_3$), 1.30 (d, 12 H, C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 25 °C): δ 146.2 (*ipso-C*), 131.3 (*o-C*), 130.3 (*p-C*), 124.5 (*m-C*), 116.2 (N*C*H), 29.2 (*C*HMe$_2$), 24.4 (CH*C*H$_3$), 23.4 (CH*C*H$_3$) ppm; the N*C*N resonance was not observed.

Synthesis and Characterization of [(η^8-C$_8$H$_8$)TiCl(1)] (6). A solution of [(**1**)TiCl$_3$] (**6**) (278.4 mg, 0.5 mmol) in THF (20 mL) was treated with 10 mL of a THF solution of freshly prepared $K_2(C_8H_8)$ (from 39 mg of potassium and 0.055 mL of cyclooctatetraene). After stirring for 12 h, the solvent was evaporated, and the residue was extracted with 25 mL of toluene. After filtration and evaporation, ruby-colored crystals of complex **6** were isolated from THF/pentane solution (1:2) at −30 °C. Yield: 190 mg (64%). Anal. Calcd for $C_{35}H_{44}ClN_3Ti$: C, 71.24; H, 7.52; N, 7.12. Found: C, 70.29; H, 8.28; N, 6.56; low %C analyses were also consistently found for related COT-titanium complexes.[33,34] ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 7.30−7.23 (m, 4 H, *m*-C*H*), 7.12−7.11 (m, 2 H, *p*-C*H*), 6.41 (s, 8 H, C$_8$*H*$_8$), 5.72 (s, 2 H, NC*H*), 2.82 (sept., 4 H, C*H*Me), 1.41 (d, 12 H, C*H*$_3$), 1.00 (d, 12 H, C*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz, 25 °C): δ 147.6 (*o-C*), 133.1 (*ipso-C*), 131.4 (*p-C*), 124.0 (*m-C*), 115.0 (N*C*H), 101.4 (*C*$_8$H$_8$), 28.8 (*C*HMe$_2$), 25.1 (CH*C*H$_3$), 23.6 (CH*C*H$_3$) ppm; the N*C*N resonance was not observed.

Electronic Structure Calculations. The calculations were performed using the Gaussian03 package.[43] All structures were

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fully optimized at the DFT level employing the B3PW91 hybrid functional[44] which has been frequently employed for calculations on rare earth metal complexes.[45] For all main-group elements (C, H, N, O, and Cl) and for the 3d transition metals titanium (Ti) and scandium (Sc) the all-electron triple-ζ basis set (6-311G**) was used as implemented in the Gaussian03 program package. The bonding analysis was performed employing the program GaussSum 2.1.[46] Further details together with presentations and coordinates in *x*,*y*,*z* format of all optimized structures and isosurfaces of selected frontier orbitals can be found in the Supporting Information.

X-ray Crystal Structure Determinations. Data were recorded on various area detectors (Bruker, Oxford Diffraction) at low temperature. Structures were refined anisotropically using the program SHELXL-97.[47] Hydrogen atoms were included using rigid methyl groups or a riding model. Pertinent data are summarized in Table 3 (data for compound **2c** were reported earlier[19]). *Special features and exceptions*: Compound **1**-H: The NH hydrogen was refined freely. Compound **2d**: The THF molecules at lithium are each disordered over two positions. Compound **3a**: One isopropyl group is disordered over two positions. Compound **3d**: The uncoordinated THF is poorly defined. For compound **4**, a poorly defined region of residual electron density was tentatively identified as two THF molecules and half a hexane, but could not be refined satisfactorily. The program SQUEEZE (A.L. Spek, University of Utrecht, Netherlands) was therefore used to remove mathematically the effects of the solvent.

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Supporting Information Available: Details of the electronic structure calculations together with presentations and coordinates in *x*,*y*,*z* format of all optimized structures; isosurfaces of selected frontier orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

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