Zuschriften

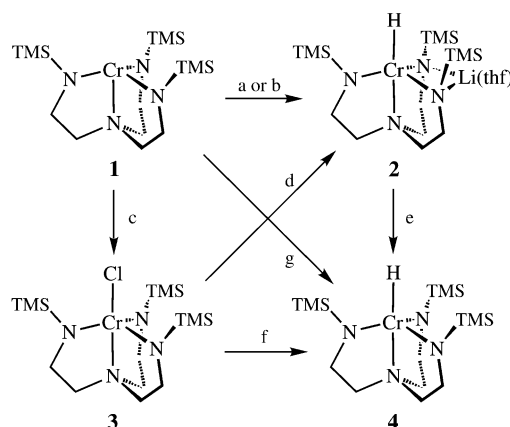## A Pair of Remarkably Stable Mononuclear Chromium(III) and Chromium(IV) Hydrides**

Alexander C. Filippou,* Sven Schneider, and Gregor Schnakenburg

Dedicated to Prof. E. O. Fischer on the occasion of his 85th birthday

The coordination and organometallic chemistry of chromium(IV) is much less developed than that of chromium in the oxidation states +II, +III, and +VI.[1] This can be traced back to the high oxidation potential of chromium(IV) complexes and their pronounced tendency to undergo valence disproportionation and reductive elimination reactions.[2] Therefore, it is not surprising that only very few reports have appeared on chromium(IV) and chromium(III) hydrides, which are suggested to be thermodynamically unstable and quite reactive compounds. In fact, CrH_4 remains elusive and its tetrahedral $^3A_2$ ground-state structure was calculated to lie 38.5 kcal mol^{-1} higher in energy than that of the dihydrogen complex isomer $[CrH_2(\eta^2\text{-}H_2)]$ ($^5A_1$) at the CCSD/TZP level of theory.[3,4] Similarly, $[Cr^{IV}H(O)(OH)]$, which was generated upon photolysis of matrix-isolated $[CrO_2(\eta^2\text{-}H_2)]$, was calculated to rearrange exothermally to its tautomer $[Cr^{II}(OH)_2]$ ($\Delta E = -22.4$ kcal mol^{-1}, B3LYP/6-311++G(d,p)),[5] and pyramidal CrH_3 ($^4A_1$) is 20.5 kcal mol^{-1} less stable than $[CrH(\eta^2\text{-}H_2)]$($^6A_1$) at the B3PW91/6-311++G(d,p)/SDD level of theory.[4c,6] To date, mononuclear chromium(III) hydrides are unknown[7] and only two chromium(IV) hydrides, $[CrH_4(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$)[8] and the *ansa*-chromocene derivative $[CrH\{C_2Me_4(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3B(C_6F_5)_3)\}(CO)]$[9] have been isolated and structurally characterized. We report herein the synthesis, characterization, and theoretical calculations of mononuclear chromium(III) and chromium(IV) hydrides stabilized by a triamidoamine ligand.

Treatment of $[Cr(N_3N)]$ ($(N_3N)^{3-}$ = $\{(Me_3SiNCH_2CH_2)_3N\}^{3-}$) (1)[10] with $Li[BEt_3H]$ or *s*BuLi in THF affords the hydridochromate(III) $[Li(thf)Cr(N_3N)H]$ (2) in 70 and 72% yields, respectively (Scheme 1).[11] Previous attempts to prepare chromium(III) hydrides by means of

[*] Prof. Dr. A. C. Filippou, Dr. S. Schneider, Dipl.-Chem. G. Schnakenburg
Institut für Chemie
Humboldt-Universität zu Berlin
Brook-Taylor-Straße 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-6939
E-mail: filippou@chemie.hu-berlin.de

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Scheme 1. Syntheses of the chromium hydrides 2 and 4 (TMS = SiMe$_3$; all reactions were started at low temperature and then warmed slowly to ambient temperature unless otherwise noted). a) Li[BEt$_3$H] in THF; b) *s*BuLi in THF; c) AgCl in THF; d) *s*BuLi (2.1 equiv) in THF; e) AgBr in THF; f) Na[BEt$_3$H] in toluene; g) H$_2$ in THF at 65 °C.

hydride-transfer reagents were unsuccessful due to reduction.[12] Addition of *s*BuLi to 1 is suggested to give the alkylchromate "[Li(thf)Cr(N$_3$N)*s*Bu]", which rapidly undergoes β-hydride elimination of butene to afford 2. Indirect evidence for the intervention of "[Li(thf)Cr(N$_3$N)*s*Bu]" is given by the selective formation of stable alkylchromate(III) complexes [Li(thf)Cr(N$_3$N)R] (R = Me, CH$_2$SiMe$_3$) from 1 and LiR, when the R group lacks β-hydrogen atoms.[13] The hydridochromate 2 can be also prepared in 46% yield by the reaction of [Cr(N$_3$N)Cl] (3) with 2.1 equiv of *s*BuLi in THF (Scheme 1). Complex 2 was isolated after crystallization from pentane as green-black, highly air-sensitive needles, which melt without decomposition at 114–115 °C. In solution, it is instantaneously oxidized by air to give the chromium(IV) hydride [Cr(N$_3$N)H] (4). Two efficient methods were employed for the synthesis of 4; these are the metathetical exchange of [Cr(N$_3$N)Cl] (3) with Na[BEt$_3$H] in toluene and the oxidation of 2 with AgBr in THF to afford 4 in 64 and 78% yield, respectively (Scheme 1). Taking advantage of the latter reaction, a one-pot synthesis of 4 from [Cr(N$_3$N)] (1) was developed, which involves addition of Na[BEt$_3$H] in THF followed by oxidation with AgBr (49% yield). Complex 4 can be also directly obtained from 1 upon hydrogenation with H$_2$ (2.5 bar) in THF at 65 °C. This reaction provides the first example for an oxidative addition of H$_2$ to a chromium(III) center.[14] The chromium(IV) hydride 4 is a brick-red, water-sensitive solid of remarkable thermal stability, which melts at 95–98 °C and can be sublimed without decomposition under vacuum ($\approx 10^{-1}$ mbar) at 80–90 °C.[15] It does not react with ethylene (1 bar) in toluene at 60 °C and is quite resistant to oxidation by pure oxygen in pentane solution at ambient temperature.

Complexes 2 and 4 have been fully characterized.[11] The IR spectra of 2 and 4 (in nujol) display a characteristic absorption band for the Cr—H stretching vibration at 1657 and 1712 cm^{-1}, respectively.[16] The effective magnetic moments of 2 (3.9 μ$_B$) and of 4 (2.9 μ$_B$) in benzene solution at room temperature compare well with the spin-only μ$_{eff}$ values

expected for high-spin d³ (3.87 μ_B) and d² (2.83 μ_B) metal complexes, respectively. Consequently, the ¹H and ¹³C{¹H} NMR spectra of **2** and **4** display at room temperature very broadened and shifted signals for the trimethylsilyl and backbone methylene protons of the triamidoamine ligand.[17] The number and relative intensities of the signals indicate threefold symmetry of complex **4** in solution. The NMR spectra of **2** in C₆D₆ and [D₈]THF are consistent with the presence of intact pseudo C_s symmetric ion-pairs in solution, as found in the solid state by X-ray diffraction. The molecular structures of **2** and **4** were determined by single-crystal X-ray diffraction (Figures 1 and 2).[18] Both five-coordinate com-
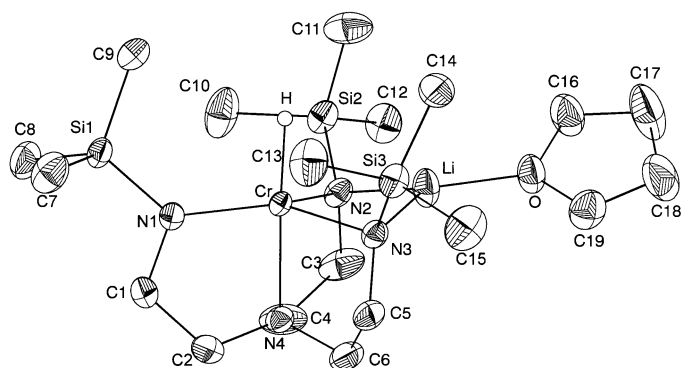

Figure 1. Diamond plot of the molecular structure of **2** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity except that bonded to the chromium atom. Selected bond lengths [Å] and bond angles [°]: Cr-H 1.58(2), Cr-N1 1.933(2), Cr-N2 2.039(2), Cr-N3 2.069(2), Cr-N4 2.138(2), Li-N2 1.999(4), Li-N3 2.006(4), Li-O 1.905(4); H-Cr-N4 177.3(8), N1-Cr-N4 84.20(7), N2-Cr-N4 84.15(7), N3-Cr-N4 82.56(6), N1-Cr-N2 125.62(8), N1-Cr-N3 136.33(7), N2-Cr-N3 94.10(7), Cr-N2-Li 81.6(1), Cr-N3-Li 80.7(1), N2-Li-N3 97.3(2), O-Li-N2 129.6(2), O-Li-N3 130.4(2).
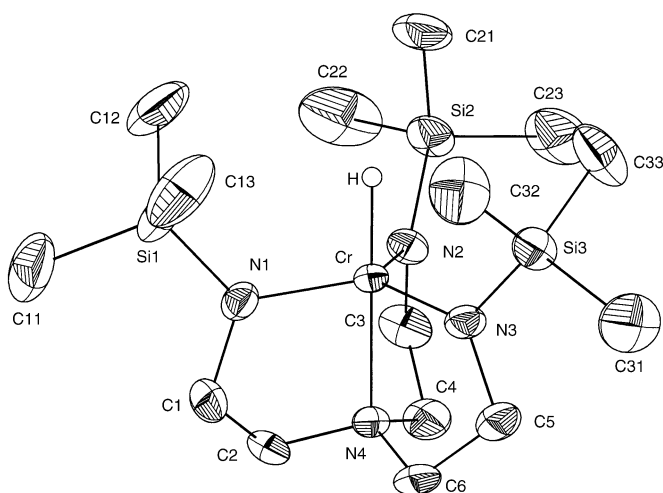

Figure 2. Diamond plot of the molecular structure of **4** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity except that bonded to the chromium atom. Selected bond lengths [Å] and bond angles [°]: Cr-H 1.56(3), Cr-N1 1.875(2), Cr-N2 1.858(2), Cr-N3 1.860(2), Cr-N4 2.140(2); H-Cr-N4 175.8(9), N1-Cr-N4 83.70(8), N2-Cr-N4 84.87(8), N3-Cr-N4 84.54(8), N1-Cr-N2 117.53(8), N1-Cr-N3 121.08(8), N2-Cr-N3 118.53(8).

plexes exhibit distorted trigonal-bipyramidal geometry, with the bridgehead amine nitrogen atom N4 of the tetradentate N₃N ligand and the hydrido ligand occupying the axial positions (**2**: N4-Cr-H 177.3(8)°; **4**: N4-Cr-H 175.8(9)°). The observed coordination geometry is uncommon for Cr^III and Cr^IV complexes.[19] The chromium atom is displaced from the equatorial plane of the three amide nitrogen atoms N1–N3 by 0.22 (**2**) and 0.183 Å (**4**) towards the hydrido ligand, which could be located on the difference Fourier map at a distance of 1.58(2) Å (**2**) and 1.56(3) Å (**4**) from the chromium center. The Cr−H bond lengths of **2** and **4** compare well with those of [CrH₄(dmpe)₂] (1.53(3)–1.60(3) Å).[8] In complex **2**, two amide nitrogen atoms are bonded to the lithium center to form a puckered Cr-N2-Li-N3 ring with a hinge angle of 28.3°. The almost trigonal-planar coordination sphere of the lithium center (sum of bond angles at Li = 357.3°) is completed by one THF molecule. The Li−N_amido (1.999(4) and 2.006(3) Å) and Li−O bond lengths (1.905(4) Å) of **2** are close to those found in [Li₃(N₃N)(thf)₂] ((Li−N)_av 1.964(6) Å; (Li−O)_av 1.938(5) Å).[20] Coordination of the nitrogen atoms N2 and N3 to Li reduces the local symmetry of the CrN₃N core in **2** from C_3 to roughly C_s, thus lifting the degeneracy of the metal d_{xy} and $d_{x^2-y^2}$ orbitals (see below). This is accompanied by a pyramidalization of the bridging amido groups, a reduction of the N2-Cr-N3 angle to 94.10(7)° (compared with N1-Cr-N2 125.62(8)°, N1-Cr-N3 136.33(7)°), and an elongation of the bridging Cr−N_amido bonds (Cr−N2 2.039(2) Å, Cr−N3 2.069(2) Å) relative to the terminal Cr−N_amido bond (Cr−N1 1.933(2) Å; sum of angles at N1 = 359.8°). In comparison, complex **4** features roughly C_3 symmetry, reminiscent of the structures of [Cr(N₃N)X] (X = Cl, Br, CN).[2,10] The amido groups are planar, all N_amido-Cr-N_amido angles are close to 120°, and the Cr−N_amido bonds ((Cr−N)_av 1.864 Å) of **4** are shorter than that of **2** suggesting, in agreement with the theoretical studies, a stronger (N_amido)_terminal→Cr π-electron donation in **4** than in **2**. The Cr−N_amine bond lengths of **2** (2.138(2) Å) and **4** (2.140(2) Å) are considerably longer than that of [Cr(N₃N)Cl] (2.043(3) Å),[2,10] which indicates the strong *trans* influence of the hydrido ligand.

Complexes **2** and **4** were calculated at different levels of theory ((RI)-BP86, B3LYP) with different basis sets (TZVPP, TZVP, LANL2DZ, 6-311G(d,p)).[11] The geometrical parameters of the optimized structures are in good agreement with the experimental values. Both molecules adopt a high-spin ground-state configuration ($\Delta E_{HS/LS}$(**2**) = −63.6 kJ mol⁻¹; $\Delta E_{HS/LS}$(**4**) = −145.7 kJ mol⁻¹; RI-BP86/TZVP) as found by the magnetic measurements.[11] The frontier orbitals of **4** form a pair of almost degenerate metal-based (d_{xz} and d_{yz}) singly occupied molecular orbitals (SOMO and SOMO + 1) and a pair of nearly degenerate LUMOs resulting from the antibonding interaction of the metal d_{xy} and $d_{x^2-y^2}$ orbitals with the p-type lone-pair orbitals of the amide ligands (Figure 3). Addition of one electron to **4** to give the anion [Cr(N₃N)H]⁻ is accompanied by a Jahn–Teller distortion, which causes a decrease of the N2-Cr-N3 angle from 119.0 to 103.3° (BP86/6-311(d,p)), lifts the degeneracy of the d_{xy} and $d_{x^2-y^2}$-based orbitals, and lowers the energy of the $d_{x^2-y^2}$-based orbital (SOMO + 2). Coordination of Li(thf)⁺ to the anion [Cr(N₃N)H]⁻ to give **2** further reduces the calculated N2-Cr-

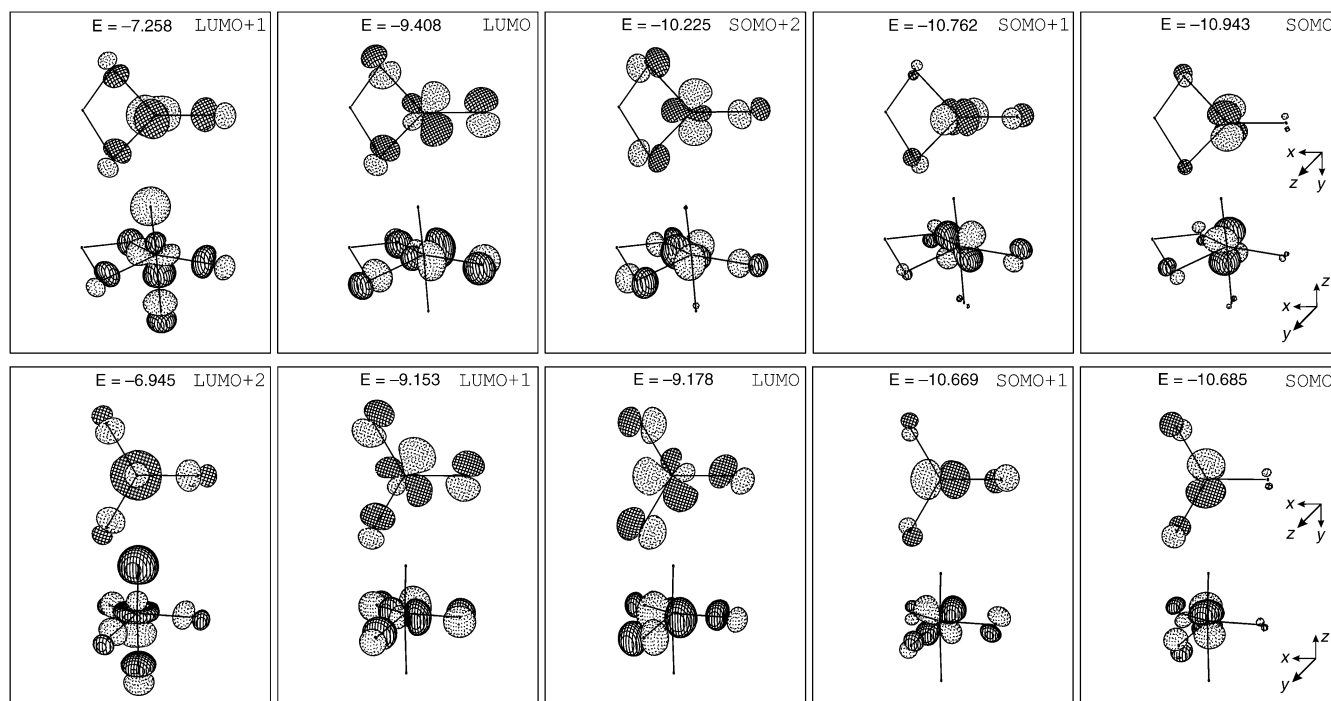| E = −7.258 LUMO+1 | E = −9.408 LUMO | E = −10.225 SOMO+2 | E = −10.762 SOMO+1 | E = −10.943 SOMO |
| E = −6.945 LUMO+2 | E = −9.153 LUMO+1 | E = −9.178 LUMO | E = −10.669 SOMO+1 | E = −10.685 SOMO |

Figure 3. Frontier orbitals of **2** (top) and **4** (bottom) from extended Hückel calculations on the BP86/6-311G(d,p) optimized structures. Si, C, and H atoms (except the hydride ligand) are omitted for clarity. The N4 atom and the hydride ligand are omitted in the top views.

N3 angle to 93.9°. The Cr−N$_{amide}$ antibonding character of the SOMO+2 orbital of **2** (Figure 3) provides an interpretation for the lower Wiberg Bond Index (WBI) values of the Cr−N$_{amide}$ bonds of **2** (Table 1). A comparison of the natural population analysis (NPA) charges reveals that oxidation of **2** to give **4** does not change the electron density at chromium (**2**: +1.34; **4**: +1.33), but is accompanied by a charge drift from the N$_{amide}$ atoms to the chromium center (Table 1). The Gibbs free bond dissociation energies (BDEs) of the Cr−H bonds (**2**: 297.1 kJmol^{-1}, **4**: 195.9 kJmol^{-1}; BP86/LANL2DZ) can be compared with those of the Cr^{II} hydrides [CpCr(CO)$_2$(L)H] (L = CO, P(OMe)$_3$, PPh$_3$, PEt$_3$) (BDE = 250.2–262.3 kJmol^{-1}) providing a rationale for the high thermodynamic stability of **2**.[21]

The present results not only illustrate the marked differences between chromium and its heavier congeners molybdenum and tungsten,[15,22] but also provide the impetus for tackling the synthetic challenge of assembling other hydrido complexes of the 3d metals in unusual oxidation states and coordination geometries.

Table 1: Atomic charges, natural electron configuration, results of the topological analyses of the electron density distribution (AIM), and Wiberg Bond Indices (WBI) of **2** and **4** (BP86/6-311G(d,p)).

| | NPA charges[a] | | | | | | | |
	Cr	H	N1	N2	N3	N4	Li	O
2	+1.34	−0.42	−1.19	−1.31	−1.31	−0.58	+0.87	−0.65
Natural electron configuration (Cr) 4s$^{0.29}$ 3d$^{4.38}$ 4d$^{0.01}$								
4	+1.33	−0.33	−1.05	−1.05	−1.05	−0.57		
Natural electron configuration (Cr) 4s$^{0.30}$ 3d$^{4.35}$ 4d$^{0.01}$								

AIM analyses and Wiberg Bond Indices

| | | **2** | | | | | **4** | | |
A−B	% A[b]	$\nabla^2\rho$[c]	ε_c[d]	WBI	A−B	% A[b]	$\nabla^2\rho$[c]	ε_c[d]	WBI
Cr−N1	48.8	9.47	0.02	0.57	Cr−N1	50.3	9.13	0.08	0.76
Cr−N2	48.7	6.86	0.17	0.38	Cr−N2	50.3	9.11	0.08	0.76
Cr−N3	50.3	6.65	0.17	0.39	Cr−N3	50.3	9.23	0.08	0.76
Cr−N4	48.0	6.34	0.02	0.16	Cr−N4	48.1	5.62	0.00	0.15
Cr−H	61.9	2.04	0.01	0.64	Cr−H	62.9	1.11	0.00	0.69
N2−Li	63.6	4.58	0.19	0.03					
N3−Li	63.6	4.49	0.18	0.04					

[a] NPA: natural population analysis. [b] Position of the bond critical point (r_c) given by $d(r_c−A)/d(A\text{-}B) \times 100$. [c] Laplacian of electron density at the bond critical point in eÅ^{-5}. [d] Ellipticity $\varepsilon_c = \lambda_1/\lambda_2 - 1$, where λ_1 and λ_2 are negative eigenvalues of the electron density Hessian.

[1] a) L. F. Larkworthy, K. B. Nolan, P. O'Brien in *Comprehensive Coordination Chemistry, Vol. 3*, 1st ed. (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, pp. 699–969; b) M. J. Winter, S. Woodward in *Comprehensive Organometallic Chemistry II, Vol. 5*, 1st ed. (Eds.: E. W. Abel,

F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 281–329.

[2] A. C. Filippou, S. Schneider, B. Ziemer, *Eur. J. Inorg. Chem.* **2002**, 2928–2935, and references therein.

[3] a) D. M. Hood, R. M. Pitzer, H. F. Schaefer III, *J. Chem. Phys.* **1979**, *71*, 705–712; b) B. Ma, C. L. Collins, H. F. Schaefer III, *J. Am. Chem. Soc.* **1996**, *118*, 870–879.

[4] For reactions of matrix-trapped chromium atoms with hydrogen atoms or H_2 to give $[CrH(\eta^2\text{-}H_2)_n]$ ($n = 0,1$) and $[CrH_2(\eta^2\text{-}H_2)_n]$ ($n = 0,1,2$) see: a) R. J. Van Zee, T. C. DeVore, W. Weltner, Jr., *J. Chem. Phys.* **1979**, *71*, 2051–2056; b) Z. L. Xiao, R. H. Hauge, J. L. Margrave, *J. Phys. Chem.* **1992**, *96*, 636–644; c) X. Wang, L. Andrews, *J. Phys. Chem. A* **2003**, *107*, 570–578.

[5] M. Zhou, L. Zhang, L. Shao, W. Wang, K. Fan, Q. Qin, *J. Phys. Chem. A* **2001**, *105*, 10747–10752.

[6] N. B. Balabanov, J. E. Boggs, *J. Phys. Chem. A* **2000**, *104*, 7370–7374.

[7] Only the mixed-valent tetranuclear chromium(II/III) hydride cluster $[(\eta^5\text{-}Cp^{**})_4Cr_4H_7]$ ($Cp^{**} = C_5Me_4Et$) has been reported so far: R. A. Heintz, T. F. Koetzle, R. L. Ostrander, A. L. Rheingold, K. H. Theopold, P. Wu, *Nature* **1995**, *378*, 359–362.

[8] a) G. S. Girolami, J. E. Salt, G. Wilkinson, M. Thornton-Pett, M. B. Hursthouse, *J. Am. Chem. Soc.* **1983**, *105*, 5954–5956; b) J. E. Salt, G. S. Girolami, G. Wilkinson, M. Motevalli, M. Thornton-Pett, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1985**, 685–692.

[9] P.-J. Sinnema, P. J. Shapiro, D. M. J. Foo, B. Twamley, *J. Am. Chem. Soc.* **2002**, *124*, 10996–10997.

[10] S. Schneider, A. C. Filippou, *Inorg. Chem.* **2001**, *40*, 4674–4677.

[11] Experimental and computational details of **2** and **4** can be found in the Supporting Information.

[12] a) R. A. Heintz, B. S. Haggerty, H. Wan, A. L. Rheingold, K. H. Theopold, *Angew. Chem.* **1992**, *104*, 1100–1102; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1077–1079; b) R. A. Heintz, R. L. Ostrander, A. L. Rheingold, K. H. Theopold, *J. Am. Chem. Soc.* **1994**, *116*, 11387–11396.

[13] The complexes $[Li(thf)Cr(N_3N)R]$ ($R = Me$, CH_2SiMe_3) were characterized by X-ray crystallography and display similar structural features with **2**: S. Schneider, dissertation, Humboldt-Universität zu Berlin, Cuvillier Verlag, Göttingen, **2003**.

[14] An appreciable amount of $(Me_3SiN(H)CH_2CH_2)_3N$ is also formed in this reaction, which is difficult to separate from **4** by repeated recrystallizations from pentane without considerable loss in yield.

[15] The isosterous molybdenum(IV) hydride $[Mo(N_3N)H]$ eliminates H_2 at 100°C to give the cyclometallation product $[Mo(CH_2SiMe_2NCH_2CH_2)N(CH_2CH_2NSiMe_3)_2]$: R. R. Schrock, S. W. Seidel, N. C. Mösch-Zanetti, K.-Y. Shih, M. B. O'Donoghue, W. M. Davis, W. M. Reiff, *J. Am. Chem. Soc.* **1997**, *119*, 11876–11893.

[16] The broad $\nu(Cr\text{—}H)$ absorption band of **4** at 1712 cm^{-1} carries a shoulder at 1754 cm^{-1}.

[17] The ^1H NMR signal of the hydrido ligand in **2** and **4** could not be detected. The ^{13}C NMR spectra of **2** and **4** displayed between ± 1000 ppm signals that were tentatively assigned to the $SiMe_3$ groups and coordinated THF (**2**).

[18] Crystal structure determination of **2**: $C_{19}H_{48}CrLiN_4OSi_3$, $M_r = 491.82$; black crystals ($0.60 \times 0.48 \times 0.20$ mm), which appear olive green in transmitted light, from a saturated pentane solution upon cooling from 20 to -25°C, $T = 180(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, monoclinic, space group $P2_1/c$, $a = 9.878(2)$, $b = 11.470(2)$, $c = 25.242(8)$ Å, $\alpha = \gamma = 90$, $\beta = 90.86(3)$°, $V = 2859.9(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.142$ g cm^{-3}, $2\theta_{max} = 50.5$°, $\mu = 0.542$ mm^{-1}, $F(000) = 1068$, 17661 reflections, 4862 unique reflections, 275 parameters, GOF = 1.019, $R_1 = 0.0330$ [$I >$

$2\sigma(I)$], $wR_2 = 0.0918$, min./max. residual electron density $-0.400/0.509$ e Å^{-3}. Crystal structure determination of **4**: $C_{15}H_{40}CrN_4Si_3$, $M_r = 412.78$; brick-red rectangular parallelepipeds ($0.40 \times 0.24 \times 0.12$ mm) from a saturated pentane solution upon cooling from 20 to -78°C, $T = 180(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, monoclinic, space group $P2_1/n$, $a = 9.618(2)$, $b = 16.662(2)$, $c = 15.316(3)$ Å, $\alpha = \gamma = 90$, $\beta = 101.78(2)$°, $V = 2402.8(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.141$ g cm^{-3}, $2\theta_{max} = 50.5$°, $\mu = 0.630$ mm^{-1}, $F(000) = 896$, 14862 reflections, 4286 unique reflections, 221 parameters, GOF = 0.907, $R_1 = 0.0337$ [$I > 2\sigma(I)$], $wR_2 = 0.0776$, min./max. residual electron density $-0.214/0.368$ e Å^{-3}. CCDC-200256 and CCDC-200257 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[19] Chromium(III) complexes usually display an octahedral and rarely a square-pyramidal, trigonal-bipyramidal, or trigonal-planar coordination sphere, and chromium(IV) complexes are in general tetrahedral: a) references [1] and [2]; b) V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, *Eur. J. Inorg. Chem.* **2001**, 1895–1903; c) L. A. MacAdams, W.-K. Kim, L. M. Liable-Sands, I. A. Guzei, A. L. Rheingold, K. H. Theopold, *Organometallics* **2002**, *21*, 952–960; d) V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **2002**, 4017–4023.

[20] Z. Duan, V. G. Young, Jr., J. G. Verkade, *Inorg. Chem.* **1995**, *34*, 2179–2185.

[21] a) G. Kiss, K. Zhang, S. L. Mukerjee, C. D. Hoff, G. C. Roper, *J. Am. Chem. Soc.* **1990**, *112*, 5657–5658.

[22] a) R. R. Schrock, K.-Y. Shih, D. A. Dobbs, W. M. Davis, *J. Am. Chem. Soc.* **1995**, *117*, 6609–6610; b) D. A. Dobbs, R. R. Schrock, W. M. Davis, *Inorg. Chim. Acta* **1997**, *263*, 171–180.