898 *Organometallics* **1996,** *15,* 898−900

A Chromium(VI) Nitrido−Silylmethyl Complex and a Chromium(V) μ-Nitrido Dimer: Synthetic and Structural Details

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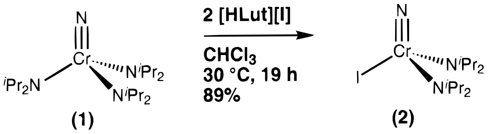
Summary: Lutidinium iodide reacts with $NCr(N^iPr_2)_3$ *(**1**) to give the nitrido−iodide* $NCr(I)(N^iPr_2)_2$ *(**2**), which provides the σ-alkyl complex* $NCr(CH_2SiMe_2Ph)(N^iPr_2)_2$ *(**3**) upon treatment with 0.5 equiv of* $Mg(CH_2SiMe_2Ph)_2$*. The thermal stability of nitrido−alkyl **3** is discussed, and its X-ray crystal structure is presented. Produced via sodium amalgam reduction of nitrido−iodide, **2** is the dimeric chromium(V) complex* $[Cr(\mu\text{-}N)(N^iPr_2)_2]_2$ *(**4**), the X-ray crystal structure of which is also described.*

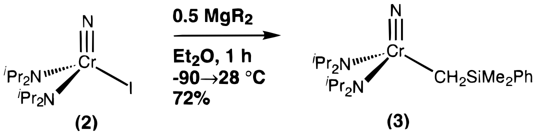
Monomeric nitrido complexes of chromium(VI) are now accessible via vanadium(III)-mediated deoxygenation of coordinated nitric oxide.[1] Since the nitrido ligand has a documented propensity to stabilize transition metals in high formal oxidation states,[2] we wished to ascertain whether chromium(VI) complexes containing both[3] the terminal nitrido function and a σ-bound alkyl[4] could be prepared. Our initial results are promising. Given here are details of the synthesis and structure of nitrido−alkyl $NCr(CH_2SiMe_2Ph)(N^iPr_2)_2$ (**3**), along with some insight on the thermal *instability* of the corresponding simple alkyls $NCr(R)(N^iPr_2)_2$ (R = Me, Et). Also given here are synthetic and structural details pertaining to the chromium(V) nitrido-bridged dimer $[Cr(\mu\text{-}N)(N^iPr_2)_2]_2$ (**4**), which was synthesized in the course of this study.

The present work originates with the nitrido−tris(amide) $NCr(N^iPr_2)_3$ (**1**), obtained[1] via deoxygenation of the known[5] nitrosyl $Cr(NO)(N^iPr_2)_3$. 2,6-Lutidinium iodide[6] proved to be the reagent of choice for selective protonolysis of a single amido substituent (eq 1).[7] A chloroform solution of beet-colored **1** underwent a color change to orange-red upon treatment with ca. 2.5 equiv of 2,6-lutidinium iodide. Run at 30 °C, the reaction was complete in ca. 19 h. Nitrido−iodide **2** was then isolated in 89% yield as an orange-red crystalline solid, soluble in common organic solvents.[8] The ^1H NMR spectrum of **2** reveals restricted rotation about the Cr−N(amido) bonds such that four clearly resolved methyl doublets are observed. The ^{13}C NMR spectrum of **2** is similarly indicative of a static structure with “upright” amido substituents (NC_2 plane parallel to the nitrido vector), as observed in the solid state for **1**[1] and **3** (vide infra). An “upright” orientation of amido substituents favorably allows for orthogonal metal−amido vis-à-vis metal−nitrido π-bonding.[9]



(1)

Conversion of nitrido−iodide **2** to an isolable nitrido−alkyl complex was achieved (eq 2) by treatment with ca. 0.5 equiv of $Mg(CH_2SiMe_2Ph)_2$.[10] Initiated in cold (ca. −90 °C) ether, the substitution reaction mixture was subsequently stirred at 28 °C for ca. 1 h, during which time a magnesium iodide precipitate appeared. After separation from MgI_2, the highly lipophilic nitrido−alkyl **3** was isolated in 72% yield by recrystallization from hexamethyldisiloxane.[11] Although stable at 28 °C both in the solid state and in solution for short periods of time (≤6−8 h), nitrido−alkyl **3** is unstable at elevated temperatures. (See below for a discussion of the thermal decomposition of **3** at elevated temperatures.)



(2)

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

[1] Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613.

[2] Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955−978.

[3] See the following and references therein: Herrmann, W. A.; Bogdanovic, S.; Poli, R.; Priermeier, T. *J. Am. Chem. Soc.* **1994**, *116*, 4989.

[4] σ-Alkyls of chromium(VI) are rare. See the following for some lead references and examples: (a) Meijboom, N.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1990**, *9*, 774. (b) Noh, S.-K.; Heintz, R. A.; Haggerty, B. S.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1992**, *114*, 1892. (c) Sullivan, A. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 53. (d) Danopoulos, A. A.; Leung, W.-H.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 2625.

[5] (a) Bradley, D. C.; Newing, C. W. *J. Chem. Soc. D* **1970**, 219. (b) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 567.

[6] Prepared in anhydrous form by reaction of 2,6-lutidine with stoichiometric amounts of $2,6\text{-}^iPr_2C_6H_3OH$ and $ISiMe_3$ in ether.

[7] Methyl iodide is also known to effect iodide-for-amide exchange: Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907.

[8] Preparation and characterization of $NCr(I)(N^iPr_2)_2$ (**2**): To a solid mixture of $Cr(N)(N^iPr_2)_3$ (**1**) (1.05 g, 2.86 mmol) and 2,6-lutidinium iodide (1.68 g, 7.16 mmol) in a 125 mL flask containing a stirbar was added $CHCl_3$ (30 mL). The mixture was stirred at 30 °C for 19 h, during which time the solution went from the beet color characteristic of **1** to red-orange. All volatile material was removed in vacuo, and the solid residue was extracted with pentane until the extract was colorless (ca. 50 mL). The extract was filtered through a sintered-glass frit. The clear orange filtrate was concentrated and cooled to −35 °C to provide **2** as orange-red crystals (1.01 g, 2.57 mmol, 89%). Mp: 151−152 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 5.31 (septet, 2H, CHMe$_2$), 3.78 (septet, 2H, CHMe$_2$), 1.85 (d, 6H, CHMe_2), 1.51 (d, 6H, CHMe_2), 1.33 (d, 6H, CHMe_2), 1.14 (d, 6H, CHMe_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 59.70 (CHMe$_2$), 58.09 ((CHMe$_2$), 30.28 (CHMe_2), 29.14 (CHMe_2), 21.19 (CHMe_2), 20.63 (CHMe_2). EIMS: m/z 393 [M$^+$]. Anal. Calcd for $C_{12}H_{28}CrIN_3$: C, 36.65; H, 7.18; N, 10.68. Found: C, 36.58; H, 7.07; N, 10.51.

[9] Cotton, F. A. *Chemical Applications of Group Theory*; Wiley: New York, 1990.

[10] Collier, M. R.; Lappert, M. F.; Pearce, R. *J. Chem. Soc., Dalton Trans.* **1973**, 445.

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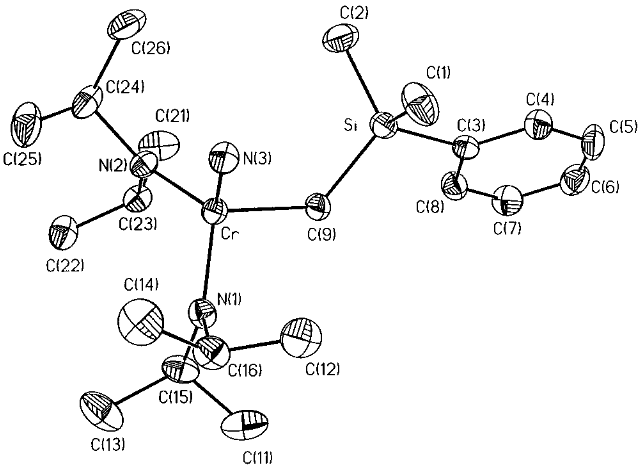
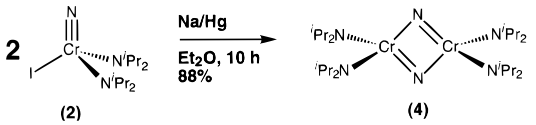


Figure 1. Drawing of the molecular structure of **3** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Cr−N(1), 1.811(3); Cr−N(2), 1.807(3); Cr−N(3), 1.535(3); Cr−C(9), 2.041(4); N(3)−Cr−N(1), 106.0(2); N(3)−Cr−N(2), 106.2(2); N(3)−Cr−C(9), 105.8(2); N(1)−Cr−N(2), 122.6(2); C(9)−Cr−N(1), 105.81(14); C(9)−Cr−N(2), 109.2(2); Cr−C(9)−Si, 121.0(2); Cr−N(1)−C(16), 128.5(3); Cr−N(2)−C(24), 130.3(2).

Solution ^{1}H and ^{13}C NMR spectra of **3** are again indicative of a static structure with "upright" amido substituents. The expected structure for crystalline **3** was confirmed via a single-crystal X-ray diffraction study.[12]

Whereas **1** evinces near-threefold symmetry about its nitrido bond axis,[1] solid-state **3** exhibits an enlarged basal N(1)−Cr−N(2) bond angle of 122.6(2)° and commensurately reduced basal N−Cr−C bond angles of 109.2(2) and 105.81(14)° (Figure 1). Given for **3** that the three N(nitrido)−Cr−(basal atom) bond angles are nearly identical (ca. 106°) and are very close to those determined previously for **1**,[1] this effect can be ascribed to the steric decompression induced upon replacement of a bulky N^iPr_2 group with a smaller CH_2SiMe_2Ph substituent. The chromium−nitrido bond distances in **3** (1.535(3) Å) and **1** (1.544(3) Å) are quite similar,[13] while the chromium−amido bond distances (1.807(3) and 1.811(3) Å) are shorter by ca. 0.033 Å for **3** than for **1**. Symmetry considerations[9] indicate that only two equatorial $N(p\pi)\rightarrow Cr(d\pi)$ bonds are permitted for pseudo-C_{3v} **1**; two π-bonds consequently are shared among the three amido ligands in that complex. Substitution of one of the three π-donor amido moieties in **1** by a σ-only alkyl ligand in **3** would therefore be expected to maximize π-bonding and lead to shorter Cr−N bonds for the two remaining amido ligands. This is observed. The Cr−C bond length of 2.041(4) Å observed for **3** is essentially identical with that reported for the other crystallographically characterized complex containing a simple chromium(VI)-bound σ-alkyl.[4b]

A limiting feature of chromium(VI) σ-alkyl chemistry could turn out to be reduction to lower oxidation states via Cr−C bond homolysis.[4] In order to explore independently the potential consequences of Cr−C homolysis for alkyls related to $NCr(CH_2SiMe_2Ph)(N^iPr_2)_2$ (**3**), we studied the reduction of nitrido−iodide **2** by sodium amalgam. Treatment of orange **2** with sodium amalgam in THF led to the high-yield production of a purple species over a 10 h period at 28 °C. Subsequent to separation from the spent amalgam and produced salt, the new complex was isolated as purple plates by recrystallization from ether (88% yield, eq 3).[14] A single-crystal X-ray diffraction study[15] (Figure 2) revealed a dimeric structure for the purple complex, $[Cr(\mu\text{-}N)(N^iPr_2)_2]_2$ (**4**), which contains chromium in the formal oxidation state +5. ^{1}H and ^{13}C NMR spectra of anti-



(2) (4) (3)

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(11) Preparation and characterization of $NCr(CH_2SiMe_2Ph)(N^iPr_2)_2$ (**3**): To a cold (ca. −90 °C) stirred solution of $NCr(I)(N^iPr_2)_2$ (**2**, 0.280 g, 0.71 mmol) in ether (10 mL) was added $Mg(CH_2SiMe_2Ph)_2$ (0.172 g, 0.53 mmol) as a solution in cold ether (5 mL) via pipet over 1 min. A colorless precipitate appeared over 1 h as the stirred reaction mixture was warmed to 28 °C. Volatile material was removed in vacuo, and the solid residue was extracted with pentane. The pentane extracts were filtered to remove white insoluble matter, and all volatile material was removed in vacuo from the filtrate. The crude product was purified by recrystallization from $(Me_3Si)_2O$ at −35 °C (0.214 g, 0.515 mmol, 72%). Mp: 75−76 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.60 (d, 2H, Ph *ortho*), 7.30 (m, 3H, Ph *meta* and *para*), 5.00 (septet, 2H, $CHMe_2$), 3.57 (septet, 2H, $CHMe_2$), 1.19 (d, 12H, $CHMe_2$), 1.15 (d, 12H, $CHMe_2$), 0.20 (s, 2H, $CrCH_2Si$). $^{13}C\{^1H$ gated-decoupled$\}$ NMR (75.43 MHz, $CDCl_3$, 25 °C): δ 144.99 (s, 1C, Ph *ipso*), 133.69 (d, 2C, Ph *ortho* or *meta*), 128.02 (d, 1C, Ph *para*), 127.53 (d, 2C, Ph *ortho* or *meta*), 56.49 (d, 2C, $CHMe_2$), 54.04 (d, 2C, $CHMe_2$), 31.10 (q, 2C, $CHMe_2$), 29.54 (q, 2C, $CHMe_2$), 25.29 (t, 1C, $CrCH_2Si$), 22.68 (q, 2C, $CHMe_2$), 20.36 (q, 2C, $CHMe_2$), 0.14 (q, 2C, $SiMe_2$). EIMS: *m/z* 415 [M^+]. Anal. Calcd for $C_{21}H_{41}CrN_3Si$: C, 60.68; H, 9.94; N, 10.11. Found: C, 61.07; H, 10.12; N, 10.01.

(12) Crystal structure data for $C_{21}H_{41}N_3SiCr$ (**3**): orange prism, 0.6 × 0.4 × 0.2 mm, monoclinic, a = 13.63(2) Å, b = 13.214(14) Å, c = 14.428(14) Å, β = 108.49(3)°, V = 2465(4) Å^3, Z = 4, space group $P2_1/c$ (No. 14), μ = 0.522 mm^{-1}, ρ_{calc} = 1.120 g/cm^3, $F(000)$ = 904. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 238 K using Mo Kα radiation (λ = 0.710 73 Å): $-15 \le h \le 14$, $-10 \le k \le 14$, $-16 \le l \le 1$; total data 8830 (3493 unique, R_{int} = 0.066). Data were corrected for Lorentz−polarization and absorption (T_{max}, T_{min}: 1.0000 and 0.7198, respectively). The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon F^2 converged with final residuals R_1 = 0.056, wR_2 = 0.129, and GOF = 1.244 based upon $I > 2\sigma(I)$. The residual electron densities were +0.29 and −0.39 e Å^{-3}.

(13) The Cr−N distance for the nitrido ligand in the structurally related $Cr(N)(O^tBu)(N^iPr_2)_2$ is 1.531(7) Å, as determined by single-crystal X-ray diffraction: Odom, A. L.; Cummins, C. C. Unpublished results.

(14) Preparation and characterization of $[Cr(N)(N^iPr_2)_2]_2$ (**4**): $NCr(I)(N^iPr_2)_2$ (**2**, 0.250 g, 0.636 mmol), a stirbar, and 15 mL of THF were loaded into a 20 mL vessel. To the solution was added 1.1 equiv of 0.5% sodium amalgam (16 mg of Na/3.2 g of Hg). The orange color of **2** gave way to the purple color of dimer **4** during 10 h of vigorous stirring. The mixture was then filtered through a pad of Celite. Removal of volatile material in vacuo provided a dark solid. Recrystallization of the solid from ether gave **4** as dark purple plates (0.149 g, 88%). Mp: 78.0−79.5 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.70 (br, 8H, $CHMe_2$), 1.51 (br, 48H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$, 25 °C): δ −23.60 (br, presumably the isopropyl methyl carbons). μ_{eff} (300 MHz, C_6D_6, 25 °C): 1.8 μ_B. EIMS: *m/z* (%) 532 (15) [M^+]. Anal. Calcd for $C_{24}H_{56}Cr_2N_6$: C, 54.11; H, 10.60; N, 15.77. Found: C, 54.22; H, 11.12; N, 15.50.

(15) Crystal data for $C_{24}H_{56}N_6Cr_2$ (**4**): purple plate, 0.6 × 0.5 × 0.15 mm, monoclinic, a = 11.3924(7) Å, b = 12.5423(8) Å, c = 21.1195(13) Å, β = 93.369(1)°, V = 3012.5(3) Å^3, Z = 4, space group $P2_1/n$ (No. 14), μ = 0.742 mm^{-1}, ρ_{calc} = 1.175 g/cm^3, $F(000)$ = 1160. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 238 K using Mo Kα radiation (λ = 0.710 73 Å). The total data collected were 11 822 reflections ($-12 \le h \le 6$, $-12 \le k \le 13$, $-22 \le l \le 23$), of which 4312 were unique (R_{int} = 0.0492). Corrections applied: Lorentz−polarization. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon F^2 converged with residuals of R_1 = 0.058, wR_2 = 0.112, and GOF = 1.292 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated (d_{C-H} = 0.96 Å) positions. The residual electron density was ±0.31 e Å^{-3}.

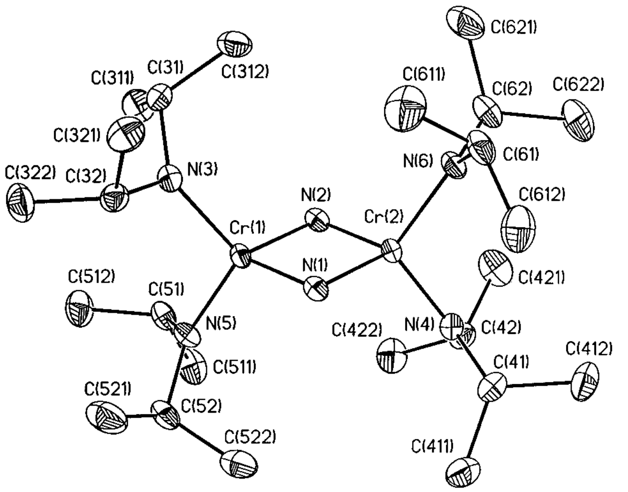

Figure 2. Drawing of the molecular structure of **4** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Cr(1)−Cr(2), 2.5251(8); Cr(1)−N(1), 1.743(3); Cr(1)−N(2), 1.730(3); Cr(1)−N(3), 1.839(3); Cr(1)−N(5), 1.845(3); Cr(2)−N(1), 1.736(3); Cr(2)−N(2), 1.735(3); Cr(2)−N(4), 1.842(3); Cr(2)−N(6), 1.845(3); N(1)−Cr(1)−N(2), 86.67(14); N(1)−Cr(1)−N(3), 114.39(14); N(1)−Cr(1)−N(5), 114.6(2); N(2)−Cr(1)−N(3), 114.9(2); N(2)−Cr(1)−N(5), 112.4(2); N(3)−Cr(1)−N(5), 111.75(14); N(1)−Cr(2)−N(2), 86.70(14); Cr(1)−N(1)−Cr(2), 93.1(2); Cr(1)−N(2)−Cr(2), 93.6(2).

ferromagnetic **4** are consistent with its formulation, as are the other characterization data.[14]

Most conspicuous in the structure of **4** are its square-planar Cr_2N_2 core (internal angles ca. 90°) and its pseudo-D_{2h} point symmetry. Although symmetry considerations permit an a_g-symmetry Cr−Cr bond along that internuclear axis, and the observed Cr−Cr distance of 2.5251(8) Å seems conducive to such an interaction, the antiferromagnetic nature of the complex argues against the presence of a Cr−Cr bond.[16] Multiple bonding in the symmetrical Cr_2N_2 core is indicated by short Cr−N bonds there, ranging between 1.735(3) and 1.743(3) Å. Precedent for the structure of **4** has recently appeared in the form of $[V(\mu\text{-}N)\{N(SiMe_3)_2\}_2]_2$, formulated as a monoanion.[17]

Thermolysis in benzene solution of the nitrido−alkyl **3** (60 °C) led to smooth first-order ($k = (2.4 \pm 0.1) \times 10^{-4}\ s^{-1}$) decomposition of this complex.[18] Dimer **4** has not been detected among the decomposition products, which include Me_3SiPh (GCMS), the imine $Me_2C{=}N^iPr$ (tentative ^1H NMR identification), and diisopropylamine (^1H NMR). We have not yet identified any of the chromium-containing materials included in the black solid deposited during this reaction, though chromium nitride would be a likely candidate. Carried out in benzene-d_6, the reaction produced $Me_3SiPh\text{-}d_0$ and not $Me_3SiPh\text{-}d_1$. The foregoing data are ostensibly inconsistent with Cr−C bond homolysis as the operative pathway for decomposition of **3**. Attack on an amido β-H by the departing alkyl seems more likely.[19] Attempts to prepare simple alkyls (e.g., R = Me, Et) analogous to **3** led only to similar decomposition. We are now attempting to prepare analogs of **3** using amido ligands that lack β-hydrogens.

In this work we have described the synthesis and X-ray crystal structure of the first chromium(VI) nitrido−alkyl complex. Though the complex, $NCr(CH_2SiMe_2Ph)(N^iPr_2)_2$ (**3**), is of only moderate thermal stability, initial indications are that Cr−C bond homolysis does not play a major role in its decomposition at elevated temperatures. Reduction of nitrido−iodide **2** led to the chromium(V) nitrido dimer **4**, not observed upon thermolysis of nitrido−alkyl **3**. We anticipate a wealth of new reaction chemistry as we extend our studies of chromium(VI) nitrido−alkyl complexes.

Acknowledgment. For funding, C.C.C. is grateful to the National Science Foundation (CAREER Award CHE-9501992), to DuPont (Young Professor Award), to the Packard Foundation, and to the MIT Department of Chemistry. A.L.O. is grateful for a Texaco fellowship.

Supporting Information Available: Tables of crystallographic data pertaining to the structural determinations for compounds **3** and **4** (12 pages). Ordering information is given on any current masthead page.

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[16] In solution at 25 °C complex **4** exhibits a μ_{eff} value of 1.8 μ_B (Evans method), and preliminary temperature-dependent solid-state magnetic data obtained using a SQUID magnetometer are indicative of antiferromagnetism.

[17] Berno, P.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 822. See also: Haddad, T. S.; Aistars, A.; Ziller, J. W.; Doherty, N. M. *Organometallics* **1993**, *12*, 2420.

[18] Kinetic data for the decomposition of **3** at 60 ± 0.5 °C were obtained by UV−vis at 333 nm; the rate constant given is the average for four runs with an error calculated on the basis of reproducibility at the 95% confidence interval.

[19] Related degradations of the N^iPr_2 ligand find recent precedent in vanadium chemistry: Song, J. I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927.