Inorganica Chimica Acta 364 (2010) 138–143

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

The synthesis, characterization, and alkylation of nacnac chromium triflate derivatives

John F. Young, Leonard A. MacAdams, Glenn P.A. Yap, Klaus H. Theopold *

Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology’, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:
Available online 12 August 2010

Dedicated to Arnie Rheingold, the fastest crystallographer in the East and (now) West.

Keywords:
Chromium
Triflates
β-Diketiminates
Lithium alkyls
Alkylation

ABSTRACT

A Cr(III) triflate coordinated by the bulky β-diketiminate $^{Me}L^{iPr}$ ($^{Me}L^{iPr}$ = 2,4-pentane *N*,*N′*-bis(2,6-diisopropylphenyl)diketiminate) was synthesized from the corresponding bridging iodide complex $[^{Me}L^{iPr}Cr(\mu\text{-}I)]_2$ by ligand substitution and subsequent oxidation with silver triflate (AgOTf). $^{Me}L^{iPr}$ $Cr^{III}(OTf)_2$ exhibits rare trigonal bipyramidal geometry about Cr(III). Attempts to alkylate this triflate synthon with 1,4-dilithiobutane ($Li(CH_2)_4Li$) led to reduction, while reaction with dimethylzinc ($ZnMe_2$) led to a mono-alkylated product; only the reaction with methyl lithium (MeLi) was successful in generating a dialkyl.

1. Introduction

β-Diketiminates have been utilized to synthesize low-[1,2] and high-valent [3] chromium compounds and they stabilize unusual coordination environments such as complexes with distorted Y-shaped geometry [4]. A homogeneous model system for the heterogeneous Phillips Catalyst has been reported using β-diketiminate ligands [5]. Synthesis of neutral Cr dialkyls provides a viable synthetic route to cationic complexes [5] and dinuclear μ-alkylidenes [6]. Cr(III) dialkyls (alkyl = CH_3, $CH_2C_6H_5$, and $CH_2Si(CH_3)_3$) with the smaller β-diketiminate $^{Me}L^{Me}$ ($^{Me}L^{Me}$ = 2,4-pentane *N*,*N′*-bis(2,6-dimethylphenyl) ketiminate) have been synthesized [1,2]; however, there is no reported synthesis using the larger $^{Me}L^{iPr}$ ligand. Alkylation of $[^{Me}L^{iPr}Cr(III)(Cl)(\mu\text{-}Cl)]_2$ with benzyl Grignard was reported to reduce the Cr(III) to a Cr(II) chloride dimer [7] Cr(III) monoalkyls featuring Cp (Cp = cyclopentadienyl) and $^{Me}L^{iPr}$ ligands have also been prepared [8]. Although precedent suggests that the synthesis of a β-diketiminato Cr(III) dialkyls bearing the bulky $^{Me}L^{iPr}$ ligand is synthetically challenging, the first example, i.e., a Cr(III) dimethyl compound is described herein.

2. Experimental

2.1. Materials and methods

All manipulations of compounds were carried out using standard Schlenk, high vacuum line, or glovebox techniques under an atmosphere of N_2. Solvents were purchased from Fisher Scientific, degassed, and dried by passing through activated alumina. THF-d_8 and C_6D_6 were purchased from Cambridge Isotopes Laboratory and stored under vacuum over Na/K alloy. All other reagents were purchased from Aldrich or Acros and dried using standard procedures when necessary. $[^{Me}L^{iPr}Cr(\mu\text{-}I)]_2$ was synthesized according to the literature procedure [1,2]. ^1H NMR spectra were taken on a Bruker DRX-400 spectrometer and were referenced to the residual protons of the solvent. FT-IR spectra were taken on a Mattson Alpha Centauri or Mattson Genesis Series spectrometers. UV–Vis spectra were taken using a HP 8453 spectrophotometer. Mass spectra were obtained by the University of Delaware Mass Spectrometry Facility. Elemental analyses were performed by Columbia Analytics and Robertson Microlit Laboratories. Room-temperature molar magnetic susceptibilities (χ_m) in the solid state were determined using a Johnson Matthey magnetic susceptibility balance. They were corrected for diamagnetism using Pascal constants [9] and converted into effective magnetic moments (μ_{eff}).

2.2. $^{Me}L^{iPr}Cr(OTf)(THF)$ (**1**)

To a solution of $[^{Me}L^{iPr}Cr(\mu\text{-}I)]_2$ (0.200 g, 0.168 mmol) in 50 mL of THF, solid AgOTf (0.084 g 0.336 mmol) was added. The reaction was stirred for 20 min and the solvent was removed under vacuum. The crude mixture was extracted with pentane, filtered through a pad of Celite, to yield a blue-green filtrate. Concentrating the solution followed by slow cooling to −30 °C yielded X-ray quality blue-green crystals (0.176 g, 76%). ^1H NMR (400 MHz, d_8-THF): 118.8 (b), 10.8 (b), 9.6 (s), 4.6 (s), 2.6 (s), 1.17 (s), −1.30 (s) ppm. IR (KBr): 3567 (m), 3060 (m), 2960 (s), 2869 (s), 1527 (s), 1437 (s),

---

* Corresponding author.
E-mail address: theopold@udel.edu (K.H. Theopold).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.08.010

1387 (s), 1317 (s), 1260 (s), 1205 (s), 1146 (m), 1101 (s), 1024 (s), 935 (w), 796 (s), 758 (m), 645 (m), 598 (w), 523 (w) cm^{-1}. UV–Vis (Pentane): λ_{max} (ε) = 602 (174 M^{-1} cm^{-1}) nm. μ_{eff} = 4.8(1) µB (294 K). Mp = 166–168 °C dec. Mass Spectrum *m/z* (%): 618 (100) [$M^+-C_4H_8O$]. *Anal.* Calc for $C_{34}H_{49}N_2O_3F_3SCr$: C, 59.15; H, 7.15; N, 4.05. Found: C, 58.68; H, 7.12; N, 4.19%.

2.3. $^{Me}L^{iPr}Cr(OTf)_2$. (**2**)

To a solution of [$^{Me}L^{iPr}Cr(\mu\text{-}I)]_2$ (0.200 g, 0.168 mmol) in 50 mL of toluene, solid AgOTf (0.169 g, 0.672 mmol) was added. The solution was stirred for 20 min and filtered through a pad of Celite. The solvent was removed under vacuum. The crude solid was recrystallized from pentane at −30 °C yielding X-ray quality brown crystals (0.190 g, 74%). ^1H NMR (400 MHz, CD_2Cl_2): 70 (vb), 23.9 (b), 1.18 (b) ppm. IR (KBr): 3063 (w), 2968 (s), 2873 (s), 1645 (m), 1525 (m), 1465 (m), 1387 (s), 1204 (s), 1106 (w), 1022 (s), 799 (m), 634 (m), 593 (w) cm^{-1}. UV–Vis (Pentane): λ_{max} (ε) = 460 (857 $M^{-1}cm^{-1}$) nm, 600 (263 $M^{-1}cm^{-1}$) nm. μ_{eff} = 3.9(1) μ_B (294 K). Mp = 246–248 °C dec. Mass Spectrum *m/z* (%): 767 (4) [M^+], 618 (100) [$M^+-SO_3CF_3$]. *Anal.* Calc for: $C_{31}H_{41}N_2S_2O_6F_6Cr$: C, 48.49; H, 5.38; N, 3.65. Found: C, 48.24; H, 5.13; N, 3.50%.

2.4. $^{Me}L^{iPr}Cr(OTf)_2(py)$ (**3**)

To a solution of **2** (0.200 g, 0.260 mmol) in 25 mL of pentane, pyridine (0.021 mL, 0.260 mmol) was added dropwise. The reaction was stirred for 20 min and the solvent was removed under vacuum. The crude solid mixture was recrystallized from pentane at −30 °C to yield a purple microcrystalline powder. X-ray quality crystals were obtained by slow evaporation of a toluene solution at ambient temperature. (0.181 g, 82%). ^1H NMR (400 MHz, CD_2Cl_2): 44.1 (vb), 36.9 (vb), 19.4 (vb), 10.5 (b), 8.55 (b), 7.3 (s), 7.1 (s), 6.3 (b), 3.1 (s), 1.18 (b) ppm. IR (KBr): 3060 (w), 2965 (s), 2930 (s), 2872 (m), 1610 (m), 1529 (s), 1447 (s), 1386 (s), 1335 (s), 1201 (s), 1108 (w), 1017 (s), 935 (m), 800 (m), 762 (m), 702 (m), 648 (s), 632 (m), 590 (w), 519 (w) cm^{-1}. UV–Vis (Pentane): λ_{max} (ε) = 441 (1837 M^{-1} cm^{-1}) nm, 522 (542 M^{-1} cm^{-1}) nm. μ_{eff} = 3.7(1) μ_B (294 K). Mp = 227–230 °C dec. Mass Spectrum *m/z* (%): 767 (5) [$M^+-C_5H_5N$], 618 (65) [$M^+-C_6H_5NSO_3F_3$]. *Anal.* Calc for $C_{36}H_{46}N_3O_6F_6S_2Cr$: C, 51.06; H, 5.47; N, 4.96. Found: C, 50.49; H, 5.94; N, 4.96%.

2.5. $^{Me}L^{iPr}Cr(OTf)(py)$ (**4**)

To a solution of **1** (0.232 g, 0.336 mmol) in 25 mL of pentane, pyridine (0.027 mL, 0.336 mmol) was added dropwise, producing a reddish orange color. Concentrating and slow cooling of the solution to −30 °C yielded a microcrystalline powder. X-ray quality crystals were grown from toluene (0.183 g, 78%). ^1H NMR (400 MHz, C_6D_6) 9.85 (b), 8.26 (b), 3.60, 2.09, 1.17, 0.28 ppm. IR (KBr): 3057 (w), 2965 (s), 2929 (s), 2869 (m), 1608 (m), 1526 (s), 1443 (s), 1410 (s), 1361 (s), 1261 (s), 1239 (s), 1213 (s), 1175 (s), 1032 (s) 933 (w), 791 (m) 754 (m), 700 (m), 629 (s), 597 (w) cm^{-1}. UV–Vis (Pentane): λ_{max} (ε) = 459 (959 M^{-1} cm^{-1}) nm. μ_{eff} = 4.9(1) μ_B (294 K). Mp = 180–182 °C dec. Mass Spectrum *m/z* (%): 618 (100) [$M^+-C_5H_5N$]. *Anal.* Calc for $C_{35}H_{46}N_3O_3F_3SCr$: C, 60.24; H, 6.64; N, 6.02. Found: C, 58.84; H, 6.89; N, 5.95%.

2.6. $^{Me}L^{iPr}CrCH_3(OTf)(THF)$ (**5a**) and $^{Me}L^{iPr}CrCH_3(OTf)$ (**5b**)

To a solution of [$^{Me}L^{iPr}Cr(\mu\text{-}Me)]_2$ [10] (0.400 g, 0.413 mmol) in 30 mL of diethyl ether solid AgOTf (0.212 g, 0.413 mmol) was added. The color of the solution immediately became dark green. After stirring for 45 min the reaction mixture was filtered. Concentration of the filtrate followed by slow cooling to −30 °C, yielded dark green crystals of marginal X-ray diffraction quality of **5b** (0.460 g, 88%). ^1H NMR (CD_2Cl_2): 14.3 (b, 6H), 8.3 (b, 4H), 4.4 (vb, 6H), 1.7 (b, 24H) ppm. IR (KBr): 3059 (w), 2965 (s), 2931 (m), 2871 (m), 1532 (s), 1466 (m), 1436 (m), 1379 (s), 1339 (s), 1312 (m), 1261 (m), 1234 (m), 1199 (s), 1138 (w), 1109 (w), 1004 (s), 935 (w), 864 (w), 796 (m), 759 (w), 632 (m) cm^{-1}. UV–Vis (Et_2O): λ_{max} (ε) = 535 (458 M^{-1} cm^{-1}), 629 (435 M^{-1} cm^{-1}) nm. μ_{eff} = 4.0(1) μ_B (294 K). Mp: 184–186 °C. Mass Spectrum, *m/z* (%): 618 (100) [M^+-CH_3]. *Anal.* Calc for $C_{34}H_{44}N_2O_3F_3SCr$: C, 58.75; H, 6.84; N, 4.42. Found: C, 58.43; H, 6.90; N, 4.67%. X-ray quality crystals of $^{Me}L^{iPr}CrCH_3(OTf)(THF)$ (**5a**) can be prepared by recrystallizing **5b** from THF.

2.7. $^{Me}L^{iPr}Cr(CH_3)_2(THF)$ (**6**)

A solution of **2** (0.322 g, 0.419 mmol) in 10 mL of diethyl ether was chilled to −30 °C. MeLi (0.600 mL, 0.839 mmol) was then added dropwise to the cold solution. The solution gradually darkened in color as it stirred for two hours at room temperature. The solvent was then removed under vacuum. The crude solid was extracted with pentane, filtered, and the pentane solvent was then removed under vacuum. The crude solid was recrystallized by slow cooling of a THF solution to −30 °C, which yielded brown crystals of marginal X-ray diffraction quality (0.203 g, 85%). ^1H NMR (400 MHz, C_6D_6): 144 (b), 46.2 (b), 13.0 (b), 5.79 (b), 4.58 (b), 3.097 (b), 1.744 (b), 1.26 (s) ppm. IR (KBr): 3056 (w), 2959 (s), 2926 (m), 2867 (m), 1521 (s), 1462 (s), 1435 (s), 1392 (s), 1310 (s), 1229 (w), 1171 (m), 1098 (m), 1054 (m), 933 (m), 868 (m), 792 (m), 760 (m), 747 (w), 643 (w), 517 (w), 450 (w) cm^{-1}. UV–Vis (Pentane): λ_{max} (ε) = nm) 668 (142 M^{-1} cm^{-1}) nm. μ_{eff} = 3.8(1) μ_B (294 K). Mp = 192–194 °C. *Anal.* Calc for $C_{31}H_{55}N_2OCr$: C, 73.52; H, 9.69; N, 4.90. Found: C, 73.85; H, 9.56; N, 4.76%.

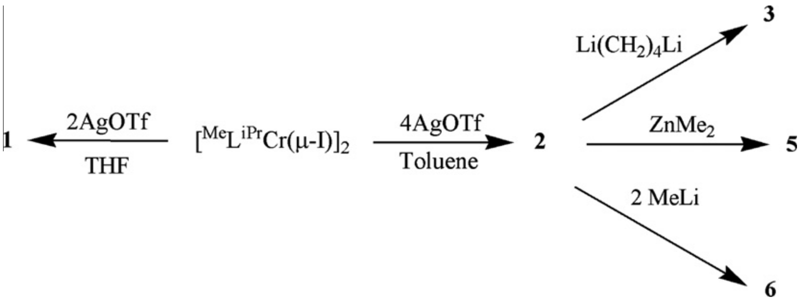
2.8. X-ray crystallography

Details of the crystallographic date collection and refinement parameters are given in Table 1. Suitable crystals were selected, mounted with viscous oil and cooled to the data collection temperature. Data were collected on a Brüker-AXS APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω, from three different sections of the Ewald sphere. The systematic absences and equivalent reflections in the diffraction data are consistent with *Cc* and *C*2/*c* for **3**, with $P2_1$ and $P2_1/m$ for **5b**, and, uniquely, with $I4_1/a$ for **6**. No symmetry higher than triclinic was observed for the other data sets. Solution in the centrosymmetric space group options yielded chemically reasonable and computationally stable results of refinement. The data-sets were treated with SADABS absorption corrections based on redundant multiscan data [11]. Compounds **5b** and **6** consistently deposited as clusters of small, multiple or cracked crystals and the data reported herein represent the best of several attempts. The data crystal for structure **4** was modeled as compound **4** co-crystallized with 3% iodide starting material. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2. A coordinated THF molecule each in **1** and **5a** was located disordered in two conformations with 53/47 and 52/48, respectively, refined site occupancy. One molecule of co-crystallized solvent molecule was located in each asymmetric unit of **2** (pentane) and **4** (toluene). Severely disordered solvent molecules in **1** (two pentane molecules per unit cell) and in **3** (12 toluene molecules per unit cell) were treated as diffused contributions [12]. Three of the isopropyl groups in **5a** were located disordered in two positions with 64/36, 57/43, and 71/29 refined site occupancies. Disordered contributions were refined with equal atomic displacement parameters and with similar 1,2 and 1,3 distances between chemically equivalent atoms. Atomic

Table 1
Crystal and experimental data for compounds **1**–**6**.

Compound	**1**	**2**	**3**	**4**	**5a**	**5b**	**6**
Formula	$C_{39}H_{61}N_2O_4F_3SCr$	$C_{36}H_{53}N_2O_6F_6S_2Cr$	$C_{64}H_{78}N_3O_6F_6S_2Cr$	$C_{41.97}H_{54}N_3O_{2.91}F_{2.91}S_{0.9}I_{0.03}Cr$	$C_{35}H_{52}N_2O_4F_3SCr$	$C_{31}H_{44}N_2O_3F_3SCr$	$C_{35}H_{55}N_2OCr$
MW	762.96	839.92	1215.41	789.28	705.85	633.74	571.81
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Tetragonal
Space group	*P*-1	*P*-1	*C*2/*c*	*P*-1	*P*-1	*P*2(1)/*m*	*I*4(1)/*a*
a (Å)	10.503(3)	11.693(2)	31.480(5)	10.396(2)	10.280(7)	9.0288(2)	27.329(3)
b (Å)	12.731(3)	12.257(2)	22.264(3)	11.703(3)	12.017(8)	20.1030(4)	27.329(3)
c (Å)	16.824(4)	14.885(2)	18.766(3)	18.772(4)	15.904(2)	10.1482(2)	17.714(4)
α (°)	82.727(4)	97.709(2)	90	77.964(3)	75.707(2)	90	90
β (°)	78.876(4)	92.878(2)	120.270(5)	81.997(3)	84.685(2)	115.262(1)	90
γ (°)	68.399(4)	96.122(2)	90	65.882(3)	70.612(2)	90	90
V ($Å^3$)	2048.5(9)	2093.4(6)	11359(3)	2034.9(8)	1796(2)	1665.8(1)	13231(4)
Z	2	2	8	2	2	2	16
T (K)	120	120	120	120	170	213	171
μ (Mo Kα) (mm^{-1})	0.383	0.443	0.352	0.408	0.431	0.455	0.373
F (0 0 0)	816	882	5128	835	750	670	4976
D_{calc} (g cm^{-3})	1.237	1.333	1.421	1.288	1.305	1.263	1.148
Data/parameters	9252/426	9381/490	13041/497	8799/493	8800/472	3485/202	8268/364
Goodness-of-fit (GOF) on F^2	1.036	1.020	1.026	1.031	1.032	1.020	1.046
R(*F*) (%)[a]	0.0632	0.0600	0.0487	0.0578	0.0480	0.0643	0.0751
R(F^2) (%)[a]	0.1200	0.1558	0.1313	0.1258	0.1303	0.2514	0.1532

[a] Quantity minimized: $R_w(F^2) = \Sigma[w(F_0{}^2 - F_c{}^2)^2]/\Sigma[wF_o{}^2)^2]1/2$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |F_o - F_c|$.



Scheme 1. Synthesis of chromium compounds.

scattering factors are contained in the SHELXTL 6.12 program library [13].

3. Results and discussion

We have reasons to be interested in mononuclear Cr(III) dialkyls featuring the sterically hindered $^{Me}L^{iPr}$ ligand; such compounds were not known heretofore. To possibly avoid reduction and the formation of a stable Cr(II) dimer, as previously reported by Gibson [7], it was hypothesized that using a monomeric Cr(III) synthon with excellent leaving groups might mitigate this problem. To generate this Cr(III) synthon it was anticipated that silver triflate (AgOTf (OTf = O_3SCF_3)) would readily oxidize [$^{Me}L^{iPr}Cr(\mu$-I)]$_2$ to yield $^{Me}L^{iPr}$CrI(OTf). However, although the reaction mixture of [$^{Me}L^{iPr}Cr(\mu$-I)]$_2$ with two equivalents of AgOTf in THF immediately changed color from green to blue, no silver mirror was observed. Characterization of the product did not reveal the anticipated oxidation product, but instead showed that ligand substitution had occurred (see Scheme 1) as confirmed by the X-ray structure (Fig. 1). ($^{Me}L^{iPr}$Cr(OTf)(THF) (**1**) has distorted square planar geometry which deviates somewhat from more prototypical Cr(II) complexes [14].

Four equivalents of AgOTf were then used to oxidize [$^{Me}L^{iPr}Cr(\mu$-I)]$_2$ in an attempt to prepare a Cr(III) bis(triflate) compound. Initial reactions in THF solvent yielded mixtures of **1** and the desired $^{Me}L^{iPr}Cr(OTf)_2$ (**2**). To avoid the coordinating effects of THF the reaction was repeated in toluene solvent. Upon addition of AgOTf, the solution immediately changed color from a dark green to brown and a distinct silver mirror was observed. The X-ray structure of **2** (see Fig. 2) confirmed the successful oxidation and the presence of two coordinated triflate ligands. Compounds containing both coordinated κ^1 and κ^2 bound triflates have been observed on other metals [15–19]; however, a search of the Cambridge Structural database showed that **2** is the first example for chromium. The triflate bonded κ^1 has a Cr–O bond distance of 1.945(2) Å and the other triflate bonded κ^2 features longer Cr–O bond distances of 2.069(2) Å and 2.117(2) Å. The coordination geometry of **2** is best described as trigonal bipyramidal and is quite rare for Cr(III), which overwhelming favors octahedral six-coordination [20]. In the reported 5-coordinate structures, trigonal bipyramidal geometry is enforced by bulky ligands or by ligands with constrained geometry as also seen in **2** (O(1)–Cr(1)–O(2) 67.57(8)°). Menjón and co-workers have reported that five-coordinate Cr(III) compounds prefer to be square pyramidal versus trigonal bipyramidal [21]. The trigonal bipyramidal geometry in **2** is defined by the O(4)–Cr–O(2) axis (angle = 159.51(9)°) and the trigonal plane (N1,N2,O1) (sum of the bonding angles around the Cr center is 357.2(2)°).

As our interest in Cr(III) dialkyls was sparked by the potential preparation of metallacycles, alkylation of **2** was initially attempted with Li(CH_2)$_4$Li [22]. The product of this reaction was

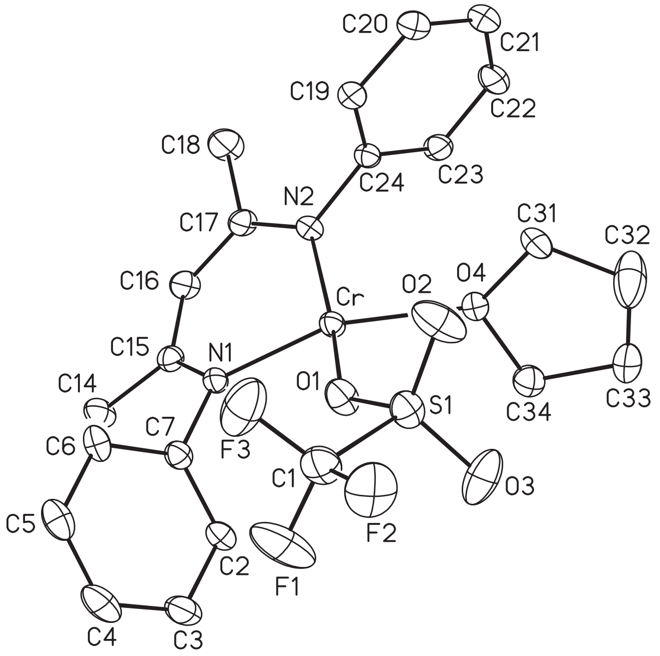


Fig. 1. The molecular structure of **1**. 2,6-Diisopropyl groups and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Cr–N(1) 2.005(3) Å, Cr–N(2) 2.015(3) Å, Cr–0(4) 2.096(2) Å Cr–O(1) 2.039(2) Å, N(1)–Cr(1)–O(4) 156.93(10)°, N(2)–Cr(1)–O(1) 159.99(11)°.

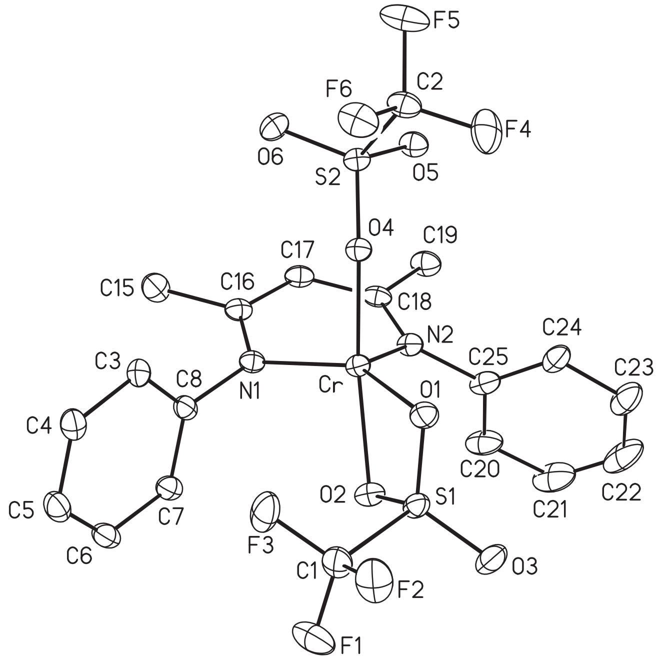


Fig. 2. The molecular structure of **2**. 2,6-Diisopropyl groups, hydrogen atoms, and solvent are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Cr–N(1) 1.924 (2) Å, Cr–N(2) 1.921(2) Å, O(4)–Cr(1)–O(2) 159.51(9)°.

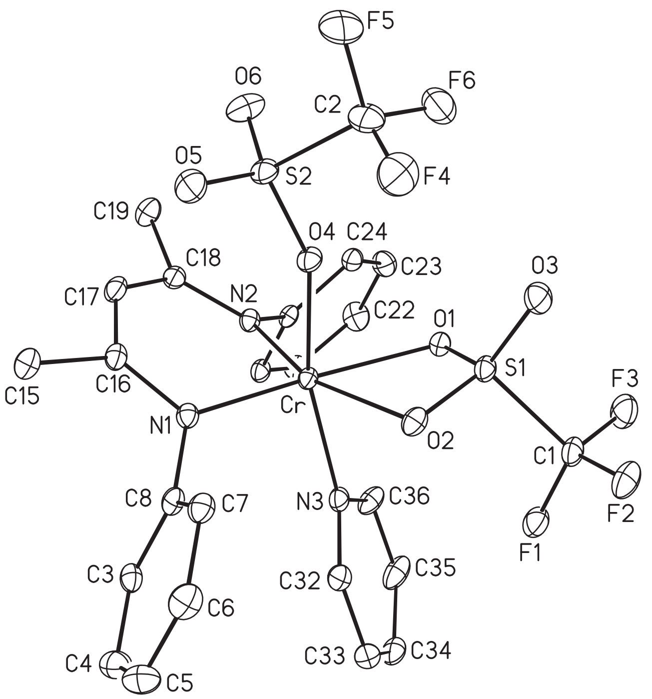


Fig. 3. The molecular structure of **3**. 2,6-Diisopropyl groups and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Cr–N(1) 1.979(2) Å, Cr–N(2) 2.001(2) Å, Cr–N(3) 2.001(2) Å.

determined to be reduced, namely $[^{Me}L^{iPr}Cr(\mu\text{-}I)]_2$. Mechanistically, it is envisioned that **2** is first reduced to a Cr(II) triflate intermediate either via homolysis or electron transfer, which then undergoes ligand substitution with lithium iodide. $Li(CH_2)_4Li$ was synthesized by lithium/halogen exchange of 1,4-diiodobutane, thus two equivalents of inseparable lithium iodide are present with each equivalent of $Li(CH_2)_4Li$.

To disfavor reduction, **2** was treated with pyridine to make the Cr more electron rich. The change in the coordination environment around Cr was apparent from the solution's instant color change from brown to purple, to form the octahedral $^{Me}L^{iPr}Cr(OTf)_2(py)$ (**3**). The crystal structure of **3** (Fig. 3) confirmed the presence of a coordinated pyridine. As a result of **3** being a crowded octahedral complex the Cr-atom bond distances all increase compared to less crowded five-coordinate **2**. The κ^2-triflate Cr–O bond distances increased by 0.046(2) Å and 0.080(1) Å, the κ^1 triflate Cr–O bond distance is longer by 0.047(2) Å. Finally, the Cr–N bond distances of the β-diketiminate moiety increased in length by 0.071(2) Å and 0.077(2) Å, respectively.

Unfortunately, the reaction of **3** with $Li(CH_2)_4Li$ also resulted in reduction. X-ray crystallography revealed that the product of this reaction was the pyridine adduct of the Cr(II) triflate, i.e., $^{Me}L^{iPr}Cr(OTf)(py)$ **(4)** (see Fig. 4). In contrast to the reaction of **2** with $Li(CH_2)_4Li$, $[^{Me}L^{iPr}Cr(\mu\text{-}I)]_2$ was not obtained, but the crystal structure of **4** did contain 3% of an iodide species. Compound **4** differs from **1** only in the coordinated donor ligand; however, the Cr–O bond distance of 2.026(2) Å indicated that the triflate is bound with similar strength in both complexes. Compound **4** can also be prepared independently by treating **1** with one equivalent of pyridine.

Attempts were made to avoid the facile reduction by using less reducing alkylating agent. Thus, **2** was reacted with one equivalent of $ZnMe_2$. X-ray quality crystals grown in THF revealed that although reduction was averted, **2** only underwent mono-alkylation to form $^{Me}L^{iPr}CrCH_3(OTf)(THF)$ (**5a**) (see Fig. 5). Compound **5a** is a square pyramidal Cr(III) species containing a κ^1-triflate with an apically positioned methyl group (the basal plane is defined by N(1), N(2), O(1), and O(4)). Compound **5a** can also be isolated without coordinated THF **(5b)** by oxidizing $[^{Me}L^{iPr}Cr(\mu\text{-}CH_3)]_2$ with two equivalents of AgOTf in ether [10]. The coordination of THF caused the triflate to be bound κ^1 in **5a**, whereas, without THF the triflate is bound κ^2.[1]

---

[1] See supplementary material for structure.

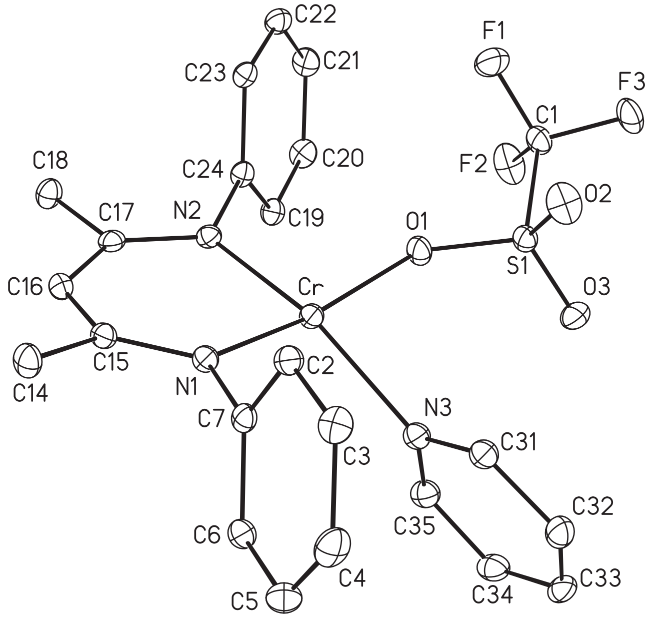


Fig. 4. The molecular structure of **4**. 2,6-Diisopropyl groups, hydrogen atoms, and solvent are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Cr–N(1) 2.016(2) Å, Cr–N(2) 2.034(2) Å, Cr–N(3) 2.133(2) Å, N(1)–Cr(1)–O(1) 165.23(9)°, N(2)–Cr(1)–N(3) 158.52(9)°.

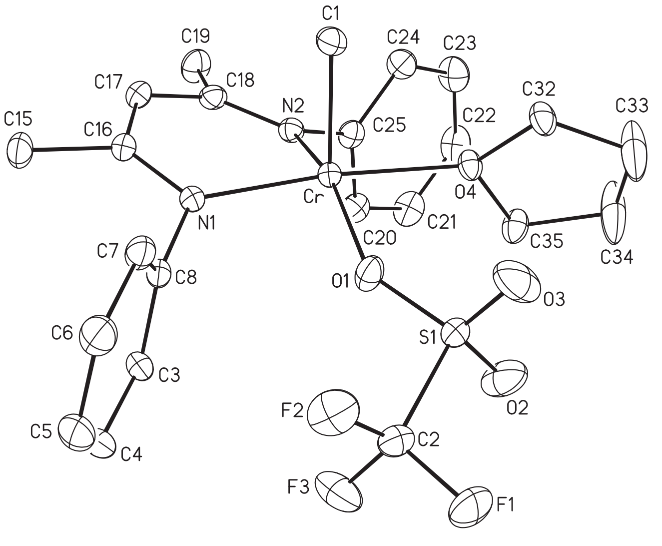


Fig. 5. Structure of **5a**. 2,6-Diisopropyl groups and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Cr–N(1) 2.025(2) Å, Cr–N(2) 2.018(2) Å, Cr–O(1) 2.045(2) Å, Cr–O(4) 2.010(2) Å, Cr–C(1) 2.049(3) Å, N(2)–Cr–O(1) 158.70(8)°, C(1)–Cr–O(1) 105.22(9)°.

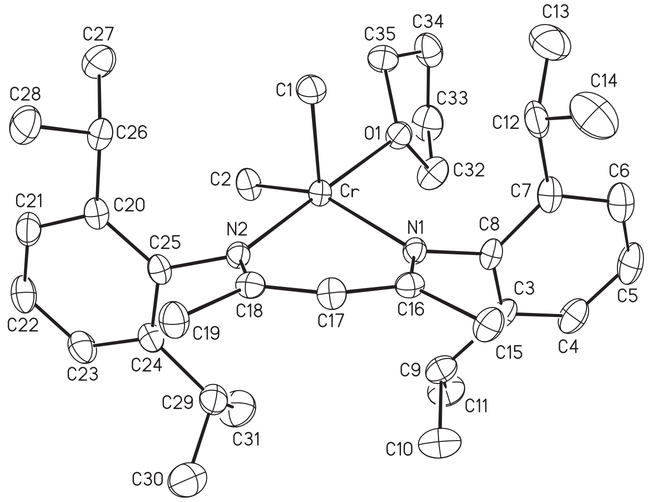


Fig. 6. The molecular structure of **6**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. N(1)–Cr–N(1) 89.5(2)°, N(1)–Cr–O(1) 90.7(2)°, O(1)–Cr–C(2) 85.5(2)°, C(2)–Cr–N(2) 93.6(2)°, N(1)–Cr–C(1) 98.8(2)°, N(2)–Cr–C(1) 93.4(2)°, O(1)–Cr–C(1) 88.1(2)°, C(1)–Cr–C(2) 109.2(2)°.

The reduction potential of $Li(CH_2)_4Li$ is not known; however, lithium aryls and alkyls (LiR) have estimated E° values which vary widely depending on the identity of R (e.g., R = ^{t}Bu, *ca.* −2.7 V; R = Cp, *ca.* −0.8 V) [23–25]. Accordingly, **2** was then reacted with two equivalents of MeLi. The use of MeLi was auspicious in yielding the desired bis(methyl) species ${}^{Me}L^{iPr}Cr(CH_3)_2$ **(6)** (see Scheme 1). The molecular structure of **6** (see Fig. 6) was determined by X-ray diffraction and confirmed the presence of two methyl groups. Compound **6** is a square pyramidal complex with a coordinated molecule of THF and also is the first reported Cr dialkyl coordinated by ${}^{Me}L^{iPr}$. The methyl group (C1), located in the apical site of the pyramid, has a Cr–C bond distance of 2.045(4) Å, which is similar to the apical methyl carbon to Cr bond distance in **5a**. The methyl group (C2) in the basal plane (defined by N(1), N(2), O(1), and C(2)) is located 2.084(4) Å from the Cr. The longer Cr–C bond distance in the basal plane is presumably a result of the *trans* influence of the nitrogen atom (N1) from the β-diketiminate ligand. This *trans* influence is also evident in the Cr–N bond distances. The Cr–N(2) has a bond distance of 2.032(2) Å, while the *trans* nitrogen atom (N1) has a Cr–N(1) bond distance of 2.104(3) Å. Thus **2** suffered reduction when reacted with $Li(CH_2)_4Li$, but the analogous reaction with two equivalents of MeLi produced the dialkyl species. It is, of course, difficult to predict *a priori* the outcome of such reactions, since there are various factors that could affect the reduction potential. It is well documented that organolithium compounds can vary in their reactivity as they exist as aggregates and these aggregation states can change with coordinating ligands [26]. Methyllithium is known to exist as a tetramer in ether [27–29]; however, the state of $Li(CH_2)_4Li$ in ether is unknown.

4. Conclusions

This work surveys the synthesis and reactivity of several chromium triflate compounds supported by the sterically extremely encumbering β-diketiminate ligand ${}^{Me}L^{iPr}$. As expected based on previous results, these β-diketiminato Cr(III) complexes are easily susceptible to reduction by alkylating reagents. However, the supreme lability of the triflate ligands has allowed for the synthesis of MeLiPrCr(Me)$_2$THF, the first example of a neutral Cr(III) dialkyl featuring this particular diketiminate ligand.

5. Supplementary material

CCDC 764574 – 764580 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5a**, **5b**, and **6**, respectively. These data can be obtained free of charge from the The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We thank the National Science Foundation (Grants CHE-0616375 and CHE-0911081) for financial support.

References

[1] W.H. Monillas, G.P.A. Yap, L.A. MacAdams, K.H. Theopold, J. Am. Chem. Soc. 129 (2007) 8090.

[2] W.H. Monillas, G.P.A. Yap, K.H. Theopold, Angew. Chem., Int. Ed. 46 (2007) 6692.

[3] Y.C. Tsai, P.Y. Wang, S.A. Chen, J.M. Chen, J. Am. Chem. Soc. 129 (2007) 8066.

[4] H. Fan, D. Adhikari, A.A. Saleh, R.L. Clark, F.J. Zuno-Cruz, G.S. Cabrera, J.C. Hoffman, M. Pink, D.J. Mindiola, M.H. Baik, J. Am. Chem. Soc. 130 (2008) 17351.

[5] L.A. MacAdams, G.P. Buffone, C.D. Incarvito, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 127 (2005) 1082.

[6] R.A. Heintz, S. Leelasubcharoen, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 5477.

[7] V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Eur. J. Inorg. Chem. (2001) 1895.

[8] J.C. Doherty, K.H.D. Ballern, B.O. Patrick, K.M. Smith, Organometallics 23 (2004) 1487.

[9] K.H. Hellwege, A.M. Hellwege (Eds.), Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Landolt-Börnstein Series, vol. 11, Springer-Verlag, Berlin, 1981.

[10] L.A. MacAdams, Ph. D. thesis, University of Delaware, Newark, DE, 2005.

[11] G.M. Sheldrick, AXS-Bruker Inc, Madison, WI, 2001.

[12] Squeeze, Platon: A.L. Spek, Appl. Cryst. 36 (2003) 7.

[13] G.M. Sheldrick, Acta Cryst. A64 (2008) 112A.

[14] A.R. Hermes, R.J. Morris, G.S. Girolami, Organometallics 7 (1988) 2372.

[15] F. Basuli, U.J. Kligore, D. Brown, J.C. Hoffman, D.J. Mindiola, Organometallics 23 (2004) 6166.

[16] J. Fawcett, A.W.G. Platt, D.R. Russell, Polyhedron 21 (2002) 287.

[17] L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamelloti, J. Am. Chem. Soc. 119 (1997) 9198.

[18] J.G. Donkervoort, J.T.B.H. Jastrzebski, B.J. Deelman, H. Kooijman, N. Veldman, A.L. Spek, G. van Koten, Organometallics 16 (1997) 4174.

[19] T. Imamoto, M. Nishiura, Y. Yamanoi, H. Tsuruta, K. Yamaguchi, Chem. Lett. (1996) 875.

[20] (a) L.A. MacAdams, W.K. Kim, L.M. Liable-Sands, I.A. Guzel, A.L. Rheingold, K.H. Theopold, Organometallics 21 (2002) 952;
(b) I.R. Beattle, G.A. Ozin, H.E. Blayden, J. Chem. Soc. A (1969) 2535;
(c) P.T. Greeene, B.J. Russ, J.S. Wood, J. Chem. Soc. A (1971) 3636;
(d) N.C. Smythe, R.R. Schrock, P. Muller, W.W. Weare, Inorg. Chem. 45 (2006) 7111;
(e) A. Ciborska, J. Cholnacki, W. Wojnoski, Acta Crystallogr., Sect. E: Struct. Rep. Online 63 (2007) m1103.

[21] P.J. Alonso, J. Forniés, M.A. Garcia-Monforte, A. Martín, B. Menjón, Organometallics 24 (2005) 1269.

[22] E. Neghisi, D. Swanson, C.J. Rousset, J. Org. Chem. 55 (1990) 5406.

[23] H.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.

[24] L. Eberson, Acta Chem. Scand., Ser. B 38 (1984) 439.

[25] B. Jaun, J. Schwarz, R.J. Breslow, J. Am. Chem. Soc. 102 (1980) 5471.

[26] H. Yakamoto, K. Oshima (Eds.), Main Group Metals in Organic Synthesis, vol. 1, Wiley-VCH, Weinheim, 2004, p. 4.

[27] H. Dietrich, Acta. Crystallogr. 16 (1963) 681.

[28] E. Weiss, E.A.C. Lucken, J. Organomet. Chem. 2 (1964) 197.

[29] E. Weiss, G. Sauermann, G. Thirase, Chem. Ber. 116 (1983) 74.