Notes

Synthesis and Structure of Li[$(C_5H_4)CH_2CH_2$(TACN-^{i}Pr$_2$)]. A Lithium Complex Supported by a Cp/TACN-^{i}Pr$_2$ Ligand

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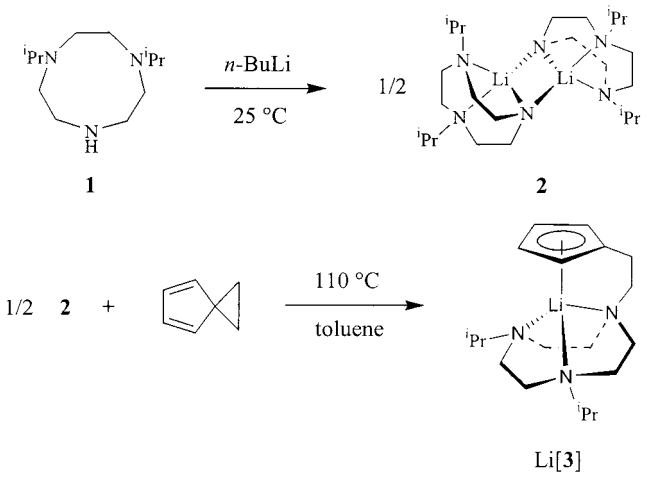
Summary: The new ligand $(C_5H_5)CH_2CH_2$(TACN-^{i}Pr$_2$) (TACN-^{i}Pr$_2$ = *4,7-diisopropyl-1,4,7-triaza-1-cyclononyl) has been prepared and structurally characterized as its lithium complex,* Li[$(C_5H_4)CH_2CH_2$(TACN-^{i}Pr$_2$)]. *The method of preparation employed nucleophilic addition of the lithium amide complex* [Li(TACN-^{i}Pr$_2$)]$_2$ *to spiro-[2.4]hepta-4,6-diene. The crystal structure of* [Li(TACN-^{i}Pr$_2$)]$_2$ *is also presented.*

Introduction

The synthesis and study of reactive, potentially low-valent metal complexes of early transition elements,[1−5] in addition to their lanthanide[6−8] and actinide[9−13] counterparts, continues to be an active and fruitful area for exploratory research. To this end, our research group is interested in the design and preparation of a family of uni-negative, multidentate ligands that satiate the requirements of large, electropositive metal centers. Tethering of neutral, *tridonor* functionalities to an anionic anchor provides one avenue into this regime. This report presents one such ligand, featured as its lithium complex Li[$(C_5H_4)CH_2CH_2$(TACN-^{i}Pr$_2$)], Li[**3**], whereby the macrocyclic tridonor functionality 1,4-diisopropyl-1,4,7-triazacyclononane has been linked to an anionic cyclopentadienyl anchor.[14,15] Our primary interest in this and related ligands stems from their potential utility in stabilizing low-valent, reactive metal synthons well poised for the activation of small molecule substrates.[16−18]

Scheme 1



Results and Discussion

1,4-Diisopropyl-1,4,7-triazacyclononane (TACN-^{i}Pr$_2$) (**1**), originally reported by Tolman and co-workers,[19,20] provides an essential building block for the construction of the target ligand [**3**]. Deprotonation of **1** by *n*-BuLi in petroleum ether yields its lithio derivative [Li(TACN-^{i}Pr$_2$)]$_2$ (**2**) in good yield, as shown in Scheme 1. An X-ray structural investigation was carried out on a single crystal of **2** isolated from a petroleum ether solution. Two chemically identical dimers of [Li(TACN-^{i}Pr$_2$)]$_2$ are present in the unit cell, each dimer residing on a center of symmetry as shown in Figure 1. The lithium cations are coordinated by four nitrogen atoms and sit asym-

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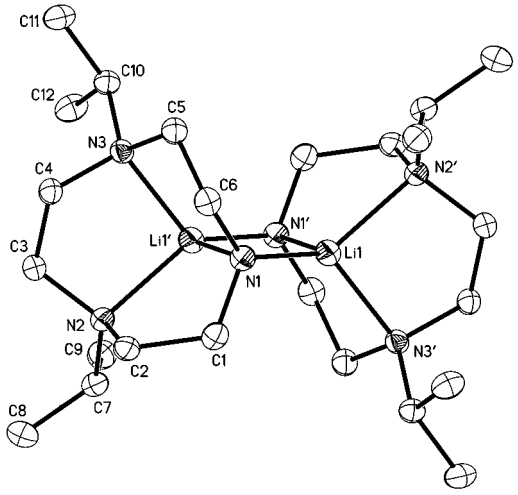

Figure 1. 50% thermal ellipsoid representation of [Li(TACN-^{i}Pr$_2$)]$_2$ (**2**). Selected bond distances (Å) and angles (deg): Li1′−N1, 2.047(3); Li1′ −N2, 2.100(3); Li1′ −N3, 2.102(2); Li1′−N1′, 1.995(3); Li1′−N1−Li1, 73.26(12); N1−Li1′−N1′, 106.74(12); N1′−Li1′−N2, 136.43(13); N1−Li1′−N2, 89.74(10); N1′−Li1′−N3, 130.38(12); N1−Li1′−N3, 89.71(10); N2−Li1′−N3, 88.49(10).

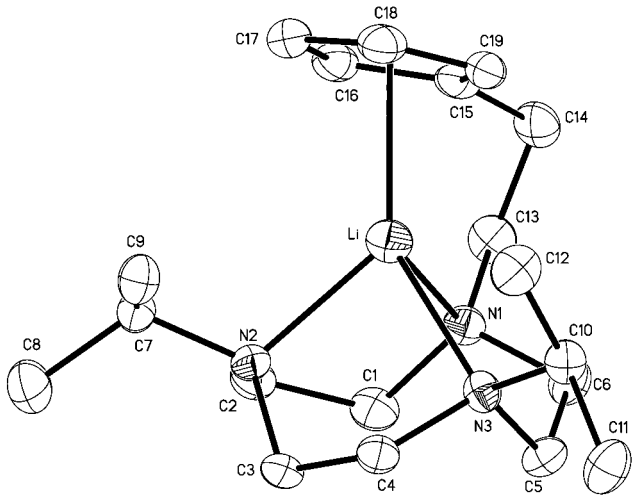

Figure 2. 50% thermal ellipsoid representation of Li[(C$_5$H$_4$)CH$_2$CH$_2$(TACN-^{i}Pr$_2$)], Li[**3**]. Selected bond distances (Å) and angles (deg): Li−N1, 2.151(3); Li−N2, 2.112(3); Li−N3, 2.296(3); Li−C19, 2.263(3); Li−C15, 2.277(3); Li−C18, 2.461(3); Li−C16, 2.464(3); Li−C17, 2.586(3); N2−Li−N1, 85.77(11); N2−Li−N3, 83.53(10); N1−Li−N3, 82.07(10).

metrically within the pocket of one of the two TACN-^{i}Pr$_2$ macrocycles that comprise the dimeric unit. The immediate coordination sphere of Li1′ consists of two neutral donors groups, N2 and N3 (av Li1′−N2/3 = 2.101(3) Å) in Figure 1; one amido nitrogen linkage, N1, from the macrocycle that encompasses it (Li1′−N1 = 2.047(3) Å); and a second amido nitrogen, N1′, provided by the symmetry-related macrocycle of the dimer (Li1′−N1′ = 1.955(3) Å). Importantly, the structure of **2** shows that a metal cation is accommodated by the macrocyclic framework of a monoanionic derivative of triazacyclononane and suggests that precursor **2** may yield an interesting class of amido ligands in its own right. Surprisingly, relatively few structural examples of lithiated triazacyclonane derivatives have been previously reported.[21−23]

The lithium amide **2** is sufficiently nucleophilic to open strained ring systems under relatively mild conditions. Hence, **2** was functionalized at the amido nitrogen position by direct reaction with spiro[2.4]hepta-4,6-diene in toluene solution at 110 °C to produce the key target complex, Li[**3**] (Scheme 1). A ^{1}H NMR spectrum of Li[**3**] suggests that its molecular structure in solution possesses a mirror plane bisecting the macrocyclic ring and passing through the central nitrogen donor atom that is tethered to the cyclopentadienyl unit. A single set of resonances is observed for the two N-isopropyl groups, and one corresponding set of resonances is observed for each of the diastereotopic methylene units of the macrocyclic ring. As expected, only two resonances are observed for the anionic cyclopentadienyl ring protons. An X-ray structural investigation of a single crystal of Li[**3**] confirms this suggested structure in the solid state, as seen in Figure 2. The lithium cation sits within a well-defined pocket of the coordinating anionic ligand, consisting of one cyclopentadienyl linkage and three tertiary amine donors derived from the macrocyclic ring. The central donor amine N1 fastens the cyclopentadienyl ring, which is coordinated in an η^5-fashion to the lithium cation, to the bulky tridonor macrocycle that saturates the opposite face of the cation. The Li−N3 distance of 2.296 Å is considerably longer than the 2.112(3) Å distance to the chemically equivalent N2 donor and the 2.151(3) Å distance to N1; the difference presumably results from a steric interaction between the isopropyl group bound to N3 and the cyclopentadienyl ring.

The lithium salt Li[**3**] was conveniently quenched by the addition of water. Extraction of the organic product with chloroform afforded the neutral derivative (C$_5$H$_5$)CH$_2$CH$_2$(TACN-^{i}Pr$_2$) (**4**), which was present as a mixture of two isomers distinguishable by ^{1}H NMR spectroscopy. The neutral ligand derivative **4** should provide a convenient precursor for the preparation of metal complexes bearing anionic [**3**] by way of soft, protolytic strategies.

In conclusion, we have prepared a new ligand consisting of two ubiquitous fragments, that of the anionic cyclopentadienide unit and the neutral triazacyclononane macrocycle. As an ancillary ligand, [**3**] may be contrasted to its bis(cyclopentadienyl) counterpart. While both ligand sets are nominally 12-electron donors, [**3**] is mono- rather than dianionic and may provide access to the chemistry of low-valent, reactive metal fragments. Our hope is that the central N-donor group in [**3**], serving to fasten the multidentate ligand together, is a design feature that will yield to structurally predictable, well-defined metal complexes. The satisfying solid-state structure of Li[**3**] lends initial support to this strategy.

Experimental Section

All manipulations were carried out using standard Schlenk or glovebox techniques. Unless otherwise noted, solvents were

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(23) During the course of this work we became aware that John Arnold and co-workers recently solved the X-ray structure of Li(TACN-^{i}Pr$_2$) and also found it to be dimeric in nature: Personal communication.

deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Nonhalogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. Spiro[2.4]hepta-4,6-diene was prepared as previously described.[24] Triethylammonium chloride was prepared by slow addition of 2 M HCl to an ethereal solution of triethylamine at 0 °C. The hydrochloride salt was recrystallized from ethanol/ether. Elemental analyses were carried out at Desert Analytics, Tucson, AZ, and/or at the Caltech Elemental Analysis Facility. A Varian Mercury-300 NMR spectrometer was used to record ^{1}H (300.080 MHz) and ^{13}C (75.462 MHz) NMR spectra at room temperature. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. MS data for samples were obtained by injection of an acetonitrile solution into a Hewlett-Packard 1100MSD mass spectrometer. Deuterated benzene was degassed and dried over activated 3-Å molecular sieves prior to use.

[Li(TACN-^{i}Pr$_2$)]$_2$, 2. A solution of ^{n}BuLi in hexanes (1.6 M, 31 mL, 49 mmol) was added over a period of 20 min to a solution of 1,4-diisopropyl-1,4,7-triazacyclononane (10.5 g, 49.2 mmol) in petroleum ether (100 mL) at 25 °C. After stirring for 2 h, a white precipitate had formed. The resulting mixture was then concentrated to 20 mL, and the colorless product was collected by suction filtration on a sintered-glass frit, washed thoroughly with petroleum ether, and dried in vacuo, affording the product as a white powder (9.43 g, 87%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ 3.51−3.42 (m, 4H), 3.27−3.18 (m, 4H), 2.96 (septet, J = 6.6 Hz, 4H), 2.78−2.70 (m, 4H), 2.44−2.30 (m, 4H), 2.24−2.14 (m, 4H), 1.23 (d, J = 6.6 Hz, 12H), 0.88 (d, J = 6.3 Hz, 12H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 56.0, 54.4, 53.9, 45.8, 22.0, 15.2. Anal. Calcd for $C_{24}H_{52}Li_2N_6$: C, 65.72; H, 11.95; N, 19.16. Found: C, 65.93; H, 12.07; N, 19.31.

Li[(C$_5$H$_4$)CH$_2$CH$_2$(TACN-^{i}Pr$_2$)], Li[3]. A solution of spiro-[2.4]hepta-4,6-diene (2.2 g, 24 mmol) and **2** (2.6 g, 5.9 mmol) in toluene (50 mL) was heated at 110 °C for 1 h in a thick-walled glass reaction vessel sealed with a Teflon stopcock. The resulting mixture was cooled to room temperature and then concentrated until precipitation ensued. Petroleum ether (5 mL) was added to effect complete precipitation. The precipitate was collected by filtration, washed with petroleum ether, and dried in vacuo, affording the compound as an off-white solid (2.6 g, 71%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ 6.39 (pseudo-triplet, J = 2.4 Hz, 2H), 6.03 (pseudo-triplet, J = 2.4 Hz, 2H), 2.95 (t, J = 6.2 Hz, 2H), 2.68 (septet, J = 6.6 Hz, 2H), 2.56 (t, J = 6.2 Hz, 2H), 2.08−1.96 (m, 4H), 1.94−1.82 (m, 2H), 1.76−1.59 (m, 4H), 1.45−1.36 (m, 2H), 0.98 (d, J = 6.6 Hz, 6H), 0.66 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 114.6, 105.4, 101.8, 61.0, 54.2, 51.0, 50.1, 45.5, 29.1, 21.5, 15.0. Anal. Calcd for $C_{19}H_{34}LiN_3$: C, 73.27; H, 11.00; N, 13.49. Found: C, 73.24; H, 11.02; N, 13.28.

(C$_5$H$_5$)CH$_2$CH$_2$(TACN-^{i}Pr$_2$), 4. A solution of Li[**3**] (565 mg, 1.81 mmol) was prepared in toluene/ether (8 mL, ca. 2:1). To this solution was added 5 mL of distilled water, followed by vigorous shaking and subsequent extraction with chloroform (3 × 15 mL). The combined organic phase was washed thoroughly with water, ensuring complete removal of LiCl, and then dried over magnesium sulfate. The volatiles were removed in vacuo, and the resulting oil was extracted with petroleum ether and filtered through Celite. The filtrate was again dried in vacuo, affording a pale yellow oil (481 mg, 74%). A lithium flame test established that lithium had been effectively removed from the ligand. The NMR spectra (^{1}H and ^{13}C) of this oil were consistent with the presence of two substitutional isomers at the vinylic positions of the cyclopentadienyl group. Due to overlapping resonances in the aliphatic region, full assignments for each distinct isomer cannot be made. However, the vinylic region in both the ^{1}H (δ = 6.0−7.0 ppm) and ^{13}C NMR (δ = 127−149 ppm) were resolved well enough to establish the presence of the two isomers in ca. 1:1 ratio. ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ 6.54−6.52 (m, 1H), 6.50−6.46 (m, 1H), 6.35−6.32 (m, 1H), 6.25−6.23 (m, 2H), 6.04−6.02 (m, 1H), 2.90−2.51 (m, 40H), 0.95 (d, J = 6.6 Hz, 24H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): vinylic resonances δ 148.34, 146.05, 135.39, 133.49, 132.82, 130.63, 127.29, 126.65; distinct aliphatic resonances 59.27, 58.55, 56.56, 54.97, 54.95, 53.40, 53.06, 43.93, 41.61, 30.18, 29.53, 18.75. LR-MS (electrospray): calcd for $C_{19}H_{35}N_3$ (M^+) m/z 305.3, found (M^+) m/z 306.4.

X-ray Crystal Structure Analysis of 2. Crystals suitable for an X-ray diffraction study were obtained from a concentrated solution of **2** in petroleum ether at −30 °C. A rough cube was excised from a larger crystal and mounted on a glass fiber with Paratone-N oil. Three runs of data were collected with 35 s, −0.25° wide ω-scans at three values of φ (0°, 120°, 240°) with the detector 5 cm (nominal) distant at a θ of −28°. The three runs consisted of 740, 740, and 353 frames, respectively. The initial cell for data reduction was calculated from approximately 1000 reflections chosen from throughout the data frames. For data processing with SAINT v6.02, all defaults were used except (i) the box size optimization was enabled; (ii) periodic orientation matrix updating was disabled; (iii) no Laue class integration restraints were used; (iv) the model profiles from all nine areas were blended; and (v) for the post-integration global least-squares refinement, no constraints were applied. SADABS manipulations were *not* performed, nor was a decay correction applied.

Crystal data for 2: colorless cube, $C_{24}H_{52}Li_2N_6$, triclinic space group $P\bar{1}$ (#2), a = 10.5137(7) Å, b = 10.6736(7) Å, c = 13.6436(9) Å, α = 87.6270(10)°, β = 87.8950(10)°, γ = 61.1110(10)°, V = 1339.15(15) Å^3, Z = 2, fw = 438.60, D_{calcd} = 1.088 g/cm^3, abs coefficient = 0.064 mm^{-1}, Mo Kα λ = 0.71073 Å, T = 98 K, Bruker SMART 1000 CCD, crystal size 0.23 × 0.22 × 0.21 mm^3, θ_{max} 28.87°, R1 = 0.0449, wR2 = 0.0676 for $I > 2\sigma(I)$, R1 = 0.0710, wR2 = 0.0722 for all observed reflections, number of reflections collected 10 546, number of independent reflections 5925, number of parameters 445.

X-ray Crystal Structure Analysis of Li[3]. X-ray quality crystals were obtained from a concentrated solution of Li[**3**] in toluene at −30 °C. A thin trapezoidal crystal was mounted on a glass fiber with Paratone-N oil. Six runs of data were collected with 35 s, −0.25° wide ω-scans at six values of φ (0°, 120°, 240°, 0°, 180°, 300°) with the detector 5 cm (nominal) distant at a θ of −28°. The initial cell for data reduction was calculated from just under 1000 reflections chosen from throughout the data frames. For data processing with SAINT v6.02, all defaults were used, except (i) the box size optimization was enabled; (ii) periodic orientation matrix updating was disabled; (iii) no Laue class integration restraints were used; (iv) the model profiles from all nine areas were blended; (v) For the post-integration global least-squares refinement, no constraints were applied. SADABS manipulations were *not* performed, nor was a decay correction applied.

Crystal data for Li[3]: colorless trapezoid, $C_{19}H_{34}LiN_3$, monoclinic space group $P2_1/n$ (#14), a = 9.5920(8) Å, b = 15.0892(12) Å, c = 12.8676(10) Å, β = 91.661(2)°, V = 1861.6(3) Å^3, Z = 4, fw = 311.43, D_{calcd} = 1.111 g/cm^3, abs coefficient = 0.065 mm^{-1}, Mo Kα λ = 0.71073 Å, T = 98 K, Bruker SMART 1000 CCD, crystal size 0.41 × 0.14 × 0.044 mm^3, θ_{max} 24.9°, R1 = 0.0443, wR2 = 0.0590 for $I > 2\sigma(I)$, R1 = 0.1225, wR2 = 0.0668 for all observed reflections, number of reflections collected 34 200, number of independent reflections 4447, number of parameters 310.

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cussing related results with us prior to publication. Finally, Mr. Matthew Allen is acknowledged for his assistance with the preparation of TACN-$^{i}Pr_2$.

Supporting Information Available: Full details for the X-ray structures of **2** and Li[**3**], including tables of positional parameters, displacement parameters, and bond lengths and angles, are available free of charge via the Internet at http://pubs.acs.org.

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