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Articles

Lithium Complexes of N-Donor-Functionalized Cyclopentadienyl—A Pyrazolate-Based Bimetallic Version

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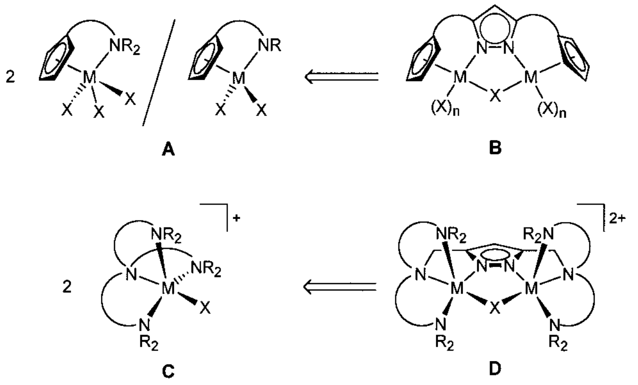
The two new pyrazole-based dinucleating ligands 3,5-bis(fluoren-9-ylmethyl)-1*H*-pyrazole (H_3L^a) and 3,5-bis(inden-3-ylmethyl)-1*H*-pyrazole (H_3L^b) have been prepared and structurally characterized in the case of H_3L^a, and their lithium complexes Li_3L^a and Li_3L^b are reported. These systems can be viewed as coupled dinucleating versions of two widely used Cp fragments bearing pendant amino or amido side chains, which is confirmed by the crystal structure of the solvent-separated ion pair $[Li_2L^a(thf)_4][Li(thf)_4]$. In solution, ^7Li NMR spectroscopy indicates the predominant presence of contact ion pairs. The crystal structure of the partially lithiated compound $[Li_2HL^a(thf)_5]$ is also presented.

Introduction

Complexes of side-chain-functionalized cyclopentadienyl (Cp) ligands (or derivatives thereof such as indenyl and fluorenyl) have received enormous attention in the past decade, which is particularly true for Cp ligands bearing pendant amino or amido side chains.[1−4] The donor substituent tethered to the Cp ligand might serve an intramolecular function, e.g. acting as a (possibly hemilabile) chelate donor in generic type **A** complexes (Scheme 1). It might also serve an intermolecular function, e.g. by coordinating to a second metal ion, anchoring to a solid support, or providing solubility.[3] Many of the complexes reported in the literature that feature linked amino−Cp or amido−Cp ligands are mononuclear type **A** compounds, and such systems are being explored with great success in both main-group (s- and p-block)[4] and transition-metal chemistry.[1−3] Synthetic applications of type **A** complexes, such as their use as catalysts for olefin polymerization,[5] are often based on the presence of (at least) two active coordination sites at the single metal center, thus suggesting an alternative bimetallic approach in which two proximate metal ions can work in concert.

Scheme 1



It is well-known from natural metalloenzymes containing di- or oligonuclear active sites that cooperativity of two adjacent metal ions might enable very particular and efficient transformations of small substrate molecules.[6] To study such cooperative reactivity in small biomimetic coordination compounds, we have been

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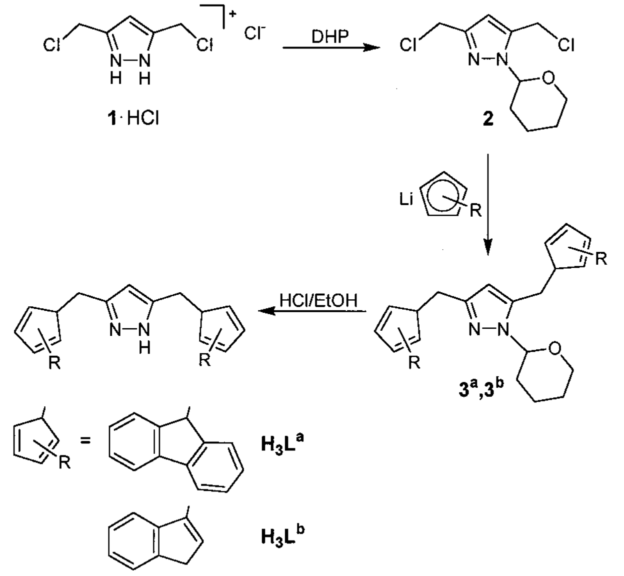
Scheme 2



investigating a series of pyrazolate-based dinuclear complexes (type **D**), in which the metal–metal separation (and hence the reactivity at the X position) can be tuned by appropriate changes of the length of the chelating sidearms attached to the pyrazole heterocycle.[7,8] These bimetallic type **D** systems can be formally viewed as a coupled version of two tran-type N-donor subunits (tran = tris(aminoalkyl)amine, type **C**),[7] which are well-established in mononuclear coordination chemistry—the additional negative charge of the pyrazolate heterocycle in **D** thereby helps to stabilize the dinuclear framework. Such a strategy, i.e., the formal coupling of two N-containing ligand compartments via a functionalized pyrazolate moiety to allow the controlled synthesis of preorganized bimetallic arrays, should be transferable to other systems, also in organometallic chemistry. Following this approach, we set out to formally combine two amino–cyclopentadienyl/amido–cyclopentadienyl mononuclear units (type **A**) in novel dinuclear type **B** complexes, where the pyrazolate group tethered to the Cp ligand (or any derivative thereof) serves both as an intramolecular N-donor function and as a bridging group spanning two metal ions. The present report describes the first synthetic access to dinucleating ligand systems for type **B** compounds and the synthesis of their "anionic synthons", including the structural characterization of two organolithium complexes.

Results and Discussion

Bis(chloromethyl)pyrazole (**1**; Scheme 2), originally reported as its hydrochloride salt by Bosnich et al.,[9] appeared to be a suitable starting material for the synthesis of multidentate ligands for type **B** complexes. The potentially nucleophilic pyrazole NH of **1**, however, had to be protected first in order to allow clean nucleophilic substitution reactions by strongly basic reagents such as Cp^- or its derivatives at the sidearms of the pyrazole heterocycle. The tetrahydropyranyl (thp) moiety, which was introduced by reacting **1** with dihydropyran, served this purpose and was easily removed later by treating with acid in the final step of the synthesis. In thp-protected **2**, the sidearm Cl atoms can be substituted by Cp equivalents: reaction with fluorenyllithium and indenyllithium gave the desired potential ligands H_3L^a and H_3L^b in good and moderate yields, respectively, after chromatographic workup. In contrast, in the case of parent Cp^- the substitution reaction proceeded less straightforwardly than expected and predominantly monosubstitution or formation of polymeric material was observed—the synthesis of the ligand system containing parent Cp groups is presently being attempted via a different route.[10]

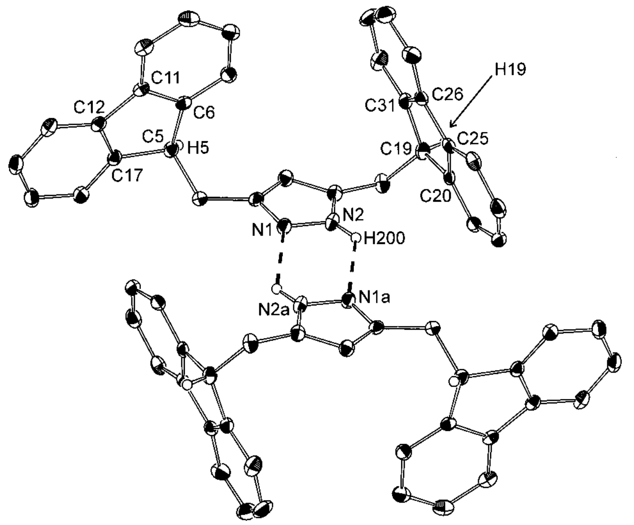


Figure 1. View of the molecular structure of H_3L^a. In the interests of clarity, most of the hydrogen atoms have been omitted. Selected atom distances (Å) and angles (deg): N1–N2, 1.365(4); N1···N2a, 3.141; H200···N1a, 2.536; N1a–H200–N2, 128.6.

The potential ligands H_3L^a and H_3L^b have been fully characterized, including an X-ray crystallographic analysis of H_3L^a. The molecular structure of H_3L^a is shown in Figure 1. The main geometrical parameters of the molecular structure are in accord with previous results for other pyrazole derivatives.[11] In the crystal lattice, the two H_3L^a molecules are arranged in face-to face pairs shielded by the bulky fluorenyl substituents (N1···N2a = 3.141 Å, H200···N1a = 2.536 Å), where the planes of the two pyrazolate heterocycles are parallel but not coplanar (distance between the planes 0.34 Å)—this is an unusual arrangement when considering that most pyrazoles form hydrogen-bonded cyclic trimers, tetramers, or catemers in the solid state.[11,12]

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Having these potential ligands H_3L^a and H_3L^b at hand, we set out to synthesize and isolate the corresponding lithiated species Li_3L^a and Li_3L^b. Interest in such lithium complexes has arisen for two reasons: first, they are expected to be valuable synthons for the subsequent preparation of a family of novel type **B** complexes, and second, there is considerable interest in the structural chemistry of compounds involving lithium atoms bonded to delocalized π-electron systems.[13−19] The latter is particularly true for Cp anion equivalents that bear pendant donor substituents, as in this case a rich structural chemistry results from the competition of the two different ligand functionalities about the lithium cation. H_3L^a and H_3L^b display the particular situation of three acidic protons (albeit with quite different pK_a values): i.e., the pyrazole NH and the two fluorenyl and indenyl subunits, respectively. Triple metalation of H_3L^a and H_3L^b turned out to require careful optimization of the reaction conditions in order to achieve clean reactions. In a typical experiment a solution of the pyrazole derivative in diethyl ether was treated with a slight excess of *n*-BuLi at −78 °C and stirred for 12 h after being warmed to room temperature. The lithium salts Li_3L^a and Li_3L^b form as bright orange and greenish precipitates, respectively, and can be isolated in good yield after appropriate workup. According to their ^{1}H NMR spectra these powders contain 1 equiv of coordinated diethyl ether per Li_3L^a or Li_3L^b. Both Li_3L^a and Li_3L^b formed in such a way show only poor solubility in aromatic solvents but are readily soluble in thf. Triple lithiation is evident from the characteristic shifts in the NMR spectra in thf-d_8, as shown for Li_3L^a in Figure 2. The bright orange color of Li_3L^a is reflected by an intense UV/vis absorption of its thf solution at 488 nm (ϵ = 2250 M^{-1} cm^{-1}; the absorption band features shoulders at 462 and 516 nm).

Single crystals of the solvent-separated ion pair $[Li_2L^a(thf)_4][Li(thf)_4]\cdot 0.5thf$ were grown from a concentrated thf solution. The molecular structure of its anion is depicted in Figure 3 together with selected atom distances and bond angles. Each of the two lithium atoms of the anion is coordinated by one of the pyrazolate N atoms, one of the tethered sidearm fluorenyl moieties, and two thf molecules. The bonding mode between the lithium atoms and the fluorenyl can be described as η^2 (Li1−C5 = 2.485(7) Å, Li1−C6 = 2.489(7) Å, Li2−C19 = 2.412(7) Å, Li2−C20 = 2.593(6) Å), where the separation with the other five-membered-ring carbon centers is substantially larger and probably outside of the bonding range (2.88−3.43 Å).[20] Organolithium compounds of fluorenyl anions have been shown to adopt a variety of structures, ranging from naked fluorenyl anions with solvent-shared or solvent-separated ion pairs[14] to η^1, η^2, η^3, and η^5 binding modes[15−18] as well as η^6 coordination to the six-membered rings,

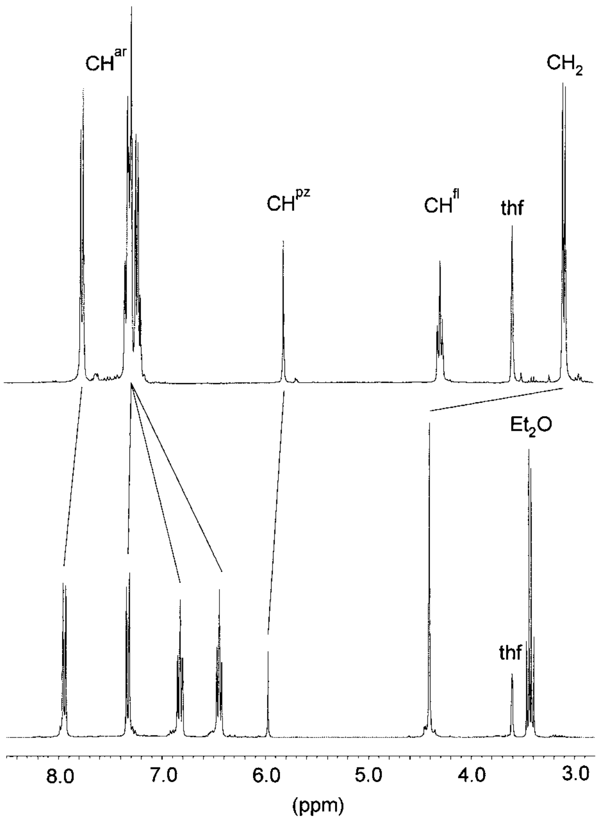

Figure 2. ^{1}H NMR spectra (300 MHz, thf-d_8) of H_3L^a (top) and Li_3L^a (bottom).

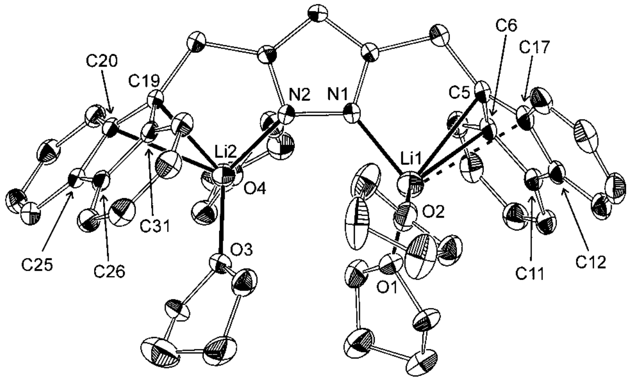

Figure 3. View of the molecular structure of the anion of $[Li_2L^a(thf)_4][Li(thf)_4]\cdot 0.5thf$. In the interests of clarity, all hydrogen atoms have been omitted. Selected atom distances (Å) and angles (deg): N1−N2, 1.392(3); N1−Li1, 1.949(7); N2−Li2, 1.937(6); Li1−O1, 1.951(7); Li1−O2, 1.938(7), Li2−O3, 1.927(6); Li2−O4, 1.953(6); Li1−C5, 2.485(7); Li1−C6, 2.489(7); Li1···C11, 2.909(7); Li1···C12, 3.130(7); Li1···C17, 2.886(7); Li2−C19, 2.412(7); Li2−C20, 2.593(6); Li2···C25, 3.231(6); Li2···C26, 3.426(7); Li2···C31, 2.963(7); N1−Li1−O1, 119.2(3); N1−Li1−O2, 107.2(3); O1−Li1−O2, 98.3(3); N2−Li2−O3, 124.4(3); N2−Li2−O4, 103.8(3); O3−Li2−O4, 106.5(3).

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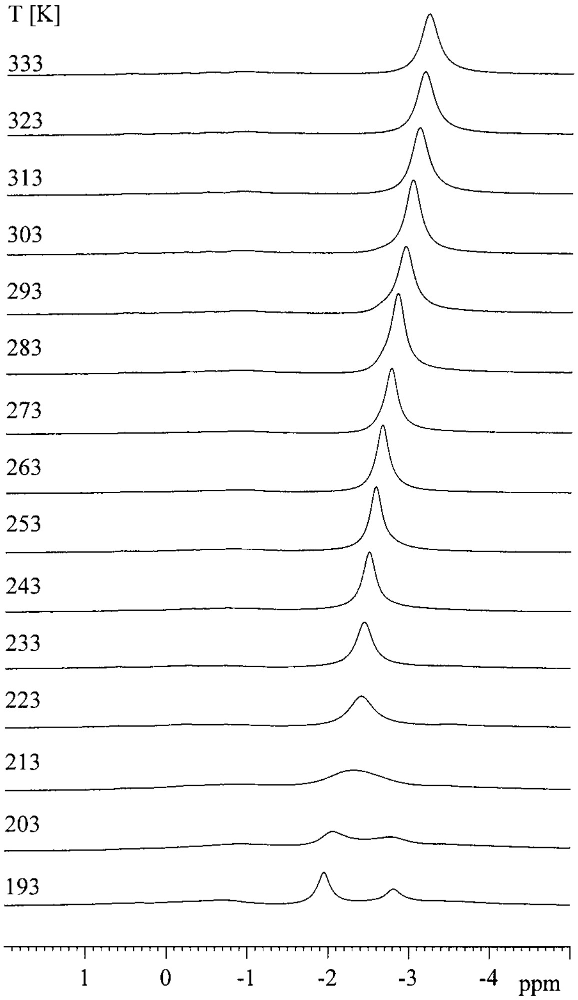
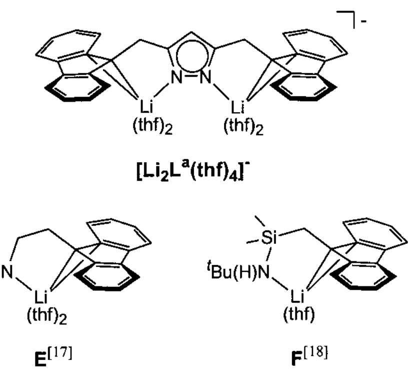


Figure 4. Temperature-dependent dynamic ^{7}Li NMR spectra (200 MHz, thf-d_8) of Li_3L^b.

as in sandwich-type base-free fluorenyllithium.[19] Considering the objective outlined in the Introduction, $[Li_2L^a(thf)_4]^-$ can be viewed as a bimetallic analogue of the mononuclear {[(dimethylamino)ethyl]fluorenyl}lithium complex **E** (Chart 1) reported by Culp and Cowley[17] and of the amino−fluorenyl complex **F** reported by Dias et al.,[18] which also feature η^2 bonding of the lithium ions in the solid state.

^{7}Li NMR spectra of Li_3L^a or Li_3L^b in thf-d_8 solutions have been recorded in order to check whether the solvent-separated ion-pair situation that is revealed for Li_3L^a in the solid state (i.e., a single $[Li(thf)_4]^+$ cation and a dinuclear $[Li_2L^a(thf)_4]^-$ anion) is also retained in solution. At 293 K, single broad signals at −1.97 ppm (Li_3L^a) and −2.94 ppm (Li_3L^b) are observed (referenced to 1.0 M LiBr in thf-d_8), indicating fast exchange between all different lithium ion positions. In the case of Li_3L^b the ^{7}Li NMR chemical shift is strongly temperature dependent (Figure 4). The downfield shift caused by decreasing the temperature is in accord with previous findings; i.e., lower temperatures favor solvent separation of the ion pairs[21] or possibly a decrease in hapticity of the indenyl moiety. Eventually decoalescence occurs upon cooling, giving rise to two signals with an approximate 2:1 intensity ratio (−1.81 and −2.44 ppm at 193 K). Decoalescence is observed at much higher temperatures for Li_3L^a, in which case the subsequent change in intensity ratio of the two separated peaks at −1.63 and −2.20 ppm upon further cooling is indicative of more complex ion pair equilibria (no pronounced temperature dependence of the mean chemical shift is observed for Li_3L^a). The absence of any signal around 0 ppm, which was to be expected for the relatively unshielded Li nucleus in $[Li(thf)_4]^+$, suggests the predominance of contact ion pairs in solution for both Li_3L^a and Li_3L^b (even though solvent-separated ion pairs might still be involved as intermediate structures in the exchange processes without being observed on the NMR time scale).[22]

Chart 1



$[Li_2L^a(thf)_4]^-$

E[17]

F[18]

In one experiment a single crystal that was picked from the thf solution of Li_3L^a and analyzed crystallographically turned out to be the dilithiated $[Li_2HL^a(thf)_5]\cdot 2thf$. The serendipitous formation of this compound might have resulted either from incomplete deprotonation of the H_3L^a starting material or from partial hydrolysis of the Li_3L^a product. Its molecular structure is shown in Figure 5 together with selected atom distances and bond angles.

In $[Li_2HL^a(thf)_5]$ the pyrazolate heterocycle again spans two lithium ions, but in this case only one of the fluorenyl sidearms is deprotonated and is bonded to Li1, while the second fluorenyl group remains dangling with the coordination sphere of the respective lithium ion Li2 replenished by three thf molecules. The lithium atom Li1 exhibits a strong bonding interaction with the central fluorenyl carbon atom (Li1−C5 = 2.42(1) Å) and additional weak interactions with the adjacent bridgehead carbon centers (Li1−C6 = 2.77(1) Å, Li1−C17 = 2.88(1) Å). In $[Li_2HL^a(thf)_5]$, the presence of both a lithiated and an untouched nondeprotonated fluorenyl group in one single compound allows a direct comparison of the geometric changes induced by the metalation of the carbocycle. As expected, the nondeprotonated fluorenyl group displays pronounced bond alternation within its five-membered-ring system (Chart 2), similar to the findings for the H_3L^a starting material, while all C−C bond lengths in the five-membered carbocycle of

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[22] In the case of Li_3L^a, a minor signal around −0.45 ppm consistently occurred in several samples prepared independently. It is presently not known whether this signal represents an impurity or has to be assigned to an equilibrium species—its intensity, however, is temperature independent, thus favoring the former explanation.

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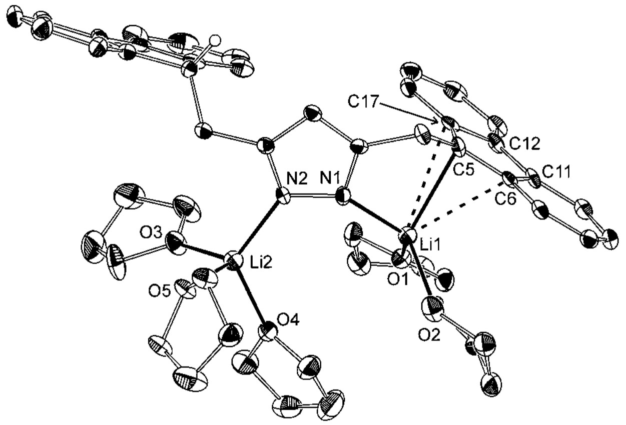
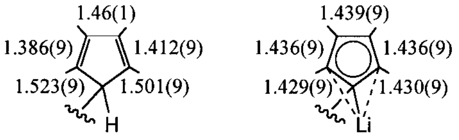


Figure 5. View of the molecular structure of [Li_2HL^a-(thf)$_5$]. In the interests of clarity, most of the hydrogen atoms have been omitted. Selected atom distances (Å) and angles (deg): N1−N2, 1.403(6); N1−Li1, 1.985(11); N2−Li2, 2.006(12); Li1−O1, 1.927(11); Li1−O2, 1.981(11); Li1−C5, 2.422(13); Li1⋯C6, 2.767(12); Li1⋯C11, 3.348(12); Li1⋯C12, 3.412(13); Li1⋯C17, 2.882(13); N1−Li1−O1, 119.9(5); N1−Li1−O2, 113.3(6); O1−Li1−O2, 106.4(5).

Chart 2



the lithiated fluorenyl group are equal within experimental error.

In conclusion, we have prepared two new dinucleating ligands that formally can be viewed as coupled versions of the widely used mononuclear amino−Cp or amido−Cp systems. The pyrazolate heterocycle, which is tethered to two fluorenyl or indenyl groups, respectively, provides a suitable bridging moiety and through its negative charge should help to stabilize a bimetallic arrangement. It is hoped that these preorganized systems provide access to a variety of dinuclear transition-metal complexes and eventually to some novel bimetallic Cp chemistry. The solid-state structure of Li_3L^a lends convincing support to such a strategy and encourages further work in this direction.

Experimental Section

General Procedures and Methods. All manipulations involving lithium compounds were carried out under an atmosphere of dry argon by employing standard Schlenk techniques or in a glovebox, and NMR tubes were flame-sealed under vacuum. Solvents were dried according to established procedures. **1** was synthesized according to the reported method;[9] all other chemicals were used as purchased. Microanalyses: Mikroanalytische Laboratorien des Organisch-Chemischen Instituts der Universität Heidelberg. IR spectra: Perkin-Elmer 983G; recorded as KBr pellets. FAB-MS spectra: Finnigan MAT 8230. NMR spectra: Bruker AC 200 at 200.13 (^{1}H) and 50.32 (^{13}C) MHz, Bruker DRX 300 at 300.13 MHz (^{1}H) and 75.47 (^{13}C) MHz, or Bruker DRX 500 at 500.13 MHz (^{1}H) and 125.77 (^{13}C) MHz; most assignments are based on a series of 2D experiments.

3,5-Bis(chloromethyl)-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (2). The hydrochloride salt **1** (9.83 g, 49 mmol) was suspended in 500 mL of dichloromethane, and 9.22 g (110 mmol) of 1,2-dihydropyran was added. The stirred suspension turned clear after 1 h. After additional stirring overnight the mixture was extracted with a solution of 25 g of sodium bicarbonate in 400 mL of water and the organic phase was dried over magnesium sulfate. The solvent was evaporated and the residue recrystallized from light petroleum to give 10.52 g (42 mmol, 86%) of **2** as colorless needles. Mp: 81 °C. MS (EI; *m*/*z* (%)): 248 (25) [M$^+$], 213 (23) [M$^+$ − Cl], 165 (25) [M$^+$ − thp], 129 (20) [M$^+$ − 2Cl − thp], 85 (100) [thp$^+$]. Anal. Calcd for $C_{10}H_{14}Cl_2N_2O$ (249.14): C, 48.21; H, 5.66; N, 11.24. Found: C, 48.12; H, 5.73; N, 11.21. IR (KBr; $\tilde{\nu}_{max}$/cm^{-1}): 2951 vs, 1846 vs, 1549 w, 1463 vs, 1253 s, 1079 vs, 1039 vs, 1001 vs, 732 s, 719 vs, 640 s. ^{1}H NMR ($CDCl_3$; δ): 1.59−1.71 (m, 3H, CH_2, H-4/H-5-thp), 1.98−2.11 (m, 2H, CH_2, H-3/H-4-thp), 2.37 (m, 1H, CH_2, H-3-thp), 3.68 (m, 1H, CH_2, H-6-thp), 4.03 (m, 1H, CH, H-6-thp), 4.58 (s, 2H, CH_2, $ClCH_2$-C-3-pyrazole), 4.66 (s, 1H, CH_2, $ClCH_2$−C-5-pyrazole), 4.68 (s, 1H, CH_2, $ClCH_2$-C-5-pyrazole), 5.46 (dd, ^3J = 9.5 Hz, ^3J = 2.3 Hz, 1H, CH, H-2-thp), 6.41 (s, 1H, CH, H-4-pyrazole). ^{13}C{^{1}H} NMR ($CDCl_3$; δ): 22.1 (CH_2, C-4-thp), 24.5 (CH_2, C-5-thp), 29.1 (CH_2, C-3-thp), 34.2 (CH_2, $ClCH_2$-C-5-pyrazole), 38.6 (CH_2, $ClCH_2$-C-3-pyrazole), 67.5 (CH_2, C-6-thp), 84.9 (CH, C-2-thp), 107.2 (CH, C-4-pyrazole), 139.4 (C, C-5-pyrazole), 148.8 (C, C-3-pyrazole).

3,5-Bis(fluoren-9-ylmethyl)-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (3^a). To a stirred solution of 7.95 g (48 mmol) of fluorene in diethyl ether was added 19.20 mL of a 2.5 M solution of *n*-butyllithium in hexane (48 mmol) at room temperature. After the mixture was stirred overnight, the diethyl ether was removed and the orange solid redissolved in thf. At −78 °C, 3 g (12 mmol) of **2** dissolved in thf (50 mL) was added through a syringe. The reaction mixture was stirred for 18 h while slowly being warmed to room temperature and was finally refluxed for an additional 3 h. After hydrolysis with aqueous ammonium chloride the organic layer was separated and dried over magnesium sulfate and the solvent evaporated. Purification was achieved by column chromatography (silica, light petroleum/diethyl ether 9:1, R_f (diethyl ether) = 0.63). A total of 3.07 g (6 mmol, 50%) of **3^a** was obtained as a colorless solid. Mp: 145−148 °C. MS (FAB; *m*/*z* (%)): 509 (35) [M + H$^+$], 425 (100) [M + H$^+$ − thp]. Anal. Calcd for $C_{36}H_{32}N_2O$ (508.66): C, 85.02; H, 6.34; N, 5.50. Found: C, 84.67; H, 6.31; N, 5.36. IR (KBr; $\tilde{\nu}_{max}$/cm^{-1}): 3056 m ($\nu_{C-H(ar)}$), 2961 m, 1541 m, 1444 vs, 1078 vs, 1041 vs, 1002 s, 933 w, 740 vs, 727 vs. ^{1}H NMR ($CDCl_3$; δ): 1.42−1.69 (m, 4H, CH_2, 3-H/4-H/5-H-thp), 1.96−2.11 (m, 1H, CH_2, 4-H-thp), 2.25−2.45 (m, 1H, CH_2, 3-H-thp), 2.82−2.94 (m, 1H, CH_2, pyrazole-CH_2-fluorene), 3.13−3.44 (m, 3H, CH_2, pyrazole-CH_2-fluorene), 3.48 (m, 1H, CH_2, H-6-thp), 3.90 (m, 1H, CH_2, H-6-thp), 4.13 (pseudo-t, ^3J = 6.9 Hz, 1H, CH, H-9-fluorene), 4.39 (pseudo-t, ^3J = 6.9 Hz, 1H, CH, H-9-fluorene), 5.01 (dd, ^3J = 9.6/2.4 Hz, 1H, CH, H-2-thp), 5.78 (s, 1H, CH, H-4-pyrazole), 6.93 (d, ^3J = 7.4 Hz, 1H, CH, H-ar), 7.18−7.40 (m, 11H, CH, H-ar), 7.70−7.73 (m, 4H, CH, H-ar). ^{13}C{^{1}H} NMR ($CDCl_3$; δ): 23.2 (CH_2, C-4-thp), 25.3 (CH_2, C-5-thp), 30.0 (CH_2, C-3-thp), 30.0 (CH_2, pyrazole-CH_2-fluorene), 32.7 (CH_2, pyrazole-CH_2-fluorene), 47.4 (CH, C-9-fluorene), 47.5 (CH, C-9-fluorene), 68.0 (CH_2, C-6-thp), 84.5 (CH, C-2-thp), 106.7 (CH, C-4-pyrazole), 120.1, 120.3, 120.4, 124.9, 125.3, 125.4, 127.1, 127.2, 127.4, 127.9 (CH, C-ar), 141.2, 141.4, 142.2, 146.5, 146.8, 147.6, 150.34 (C, C-ar).

3,5-Bis(fluoren-9-ylmethyl)-1*H*-pyrazole (H_3L^a). **3^a** (3.07 g) was dissolved in ethanol (150 mL), 15 mL of concentrated hydrochloric acid added, and the mixture refluxed for 3 h. After neutralization with aqueous sodium bicarbonate and extraction with diethyl ether, the organic layer was dried over magnesium sulfate. Removal of the solvent and purification by column chromatography (silica, light petroleum/diethyl ether 1:1, R_f (diethyl ether) = 0.45) yielded 2.20 g (5.2 mol, 86%) of **H_3L^a** as colorless crystals. Mp: 178−180 °C. MS (FAB; *m*/*z* (%)): 425 (100) [M + H$^+$], 259 (18) [M + H$^+$ − fluorene]. Anal. Calcd for $C_{31}H_{24}N_2$ (424.54): C, 87.72; H, 5.69; N, 6.59.

Table 1. Crystal Data and Refinement Details for H_3L^a, $[Li_2L^a(thf)_4][Li(thf)_4]\cdot0.5thf$, and $[Li_2HL^a(thf)_5]\cdot2thf$

	H_3L^a	$[Li_2L^a(thf)_4][Li(thf)_4]\cdot0.5thf$	$[Li_2HL^a(thf)_5]\cdot2thf$
formula	$C_{31}H_{24}N_2$	$C_{31}H_{21}N_2Li_3\cdot8.5$ thf	$C_{31}H_{22}N_2Li_2\cdot7$ thf
M_r	424.5	1055.2	941.2
cryst size (mm)	0.20 × 0.20 × 0.20	0.11 × 0.20 × 0.41	0.10 × 0.10 × 0.16
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	5.671(1)	37.328(1)	11.662(1)
b (Å)	17.244(3)	9.331(1)	18.140(2)
c (Å)	22.822(4)	35.555(1)	24.944(3)
β (deg)	90.49(1)	101.61(1)	93.87(1)
V (Å^3)	2232(1)	12131(1)	5265(1)
ρ_{calcd} (g cm^{-3})	1.263	1.156	1.187
Z	4	8	4
F(000) (e)	896	4560	2032
T (K)	200	173	173
μ(Mo Kα) (mm^{-1})	0.074	0.074	0.08
hkl range	±6, −4 to +20, ±27	−39 to +38, 0−9, 0−37	±11, 0−18, 0−24
2θ range (deg)	3.0−51.0	2.2−44.0	2.8−41.7
no. of measd rflns	4581	33 478	19 815
no. of unique rflns	4141	7421	5527
no. of obsd rflns, $I > 2\sigma(I)$	2250	5073	2661
no. of refined params	394	720	633
resid electron dens (e Å^{-3})	0.26/−0.30	0.57/−0.29	0.29/−0.27
R1	0.063	0.059	0.073
wR2 (all data)	0.179	0.171	0.223
goodness of fit	1.031	1.036	0.934

Found: C, 87.20, H, 5.65; N, 6.58. IR (KBr; $\tilde{\nu}_{max}$/cm^{-1}): 3053 m, 2933 m, 1559 s, 1472 s, 1443 vs, 1097 s, 1029 s, 987 s, 938 w, 736 vs. ^{1}H NMR (CDCl$_3$; δ): 3.11 (d, $^3J = 6.7$ Hz, 4H, CH$_2$, pyrazole-CH$_2$-fluorene), 4.18 (t, $^3J = 6.7$ Hz, 2H, CH, H-9-fluorene), 5.66 (s, 1H, CH, H-4-pyrazole), 7.18−7.42 (m, 12H, CH, H-ar), 8.14 (d, $^3J = 7.6$ Hz, 4H, CH, H-4/H-5-fluorene). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 31.3 (CH$_2$, pyrazole-CH$_2$-fluorene), 47.5 (CH, C-9-fluorene), 106.0 (CH, C-4-pyrazole), 120.3 (CH, C-4/C-5-fluorene), 125.4 (CH, C-1/C-8-fluorene), 127.4, 127.7 (CH, C-2/C-3/C-6/C-7-fluorene), 141.3 (C, C-4a/C-4b-fluorene), 146.4 (br, C, C-3/C-5-pyrazole), 147.1 (C, C-8a/C-9a-fluorene).

3,5-Bis(inden-3-ylmethyl)-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (3^b). A stirred mixture of 5.55 g (48 mmol) of indene in thf was treated with 19.20 mL of a 2.5 M solution of *n*-butyllithium in hexane (48 mmol) at −78 °C. The solution was kept at that temperature for 1 h and then warmed to room temperature. After an additional 1 h the mixture was cooled again (−78 °C) and 3 g (12 mmol) of **2** dissolved in thf (50 mL) was added through a syringe. The reaction mixture was stirred overnight while slowly being warmed to room temperature and was then refluxed for an additional 3 h. After hydrolysis with aqueous ammonium chloride the organic layer was separated and dried over magnesium sulfate and the solvent evaporated to dryness. Purification was achieved by column chromatography (silica, light petroleum/diethyl ether 9:1, R_f (diethyl ether) = 0.62). A total of 1.75 g (4.3 mmol, 36%) of **3^b** was obtained as a pale yellow oil. MS (EI; m/z (%)): 408 (20) [M$^+$], 324 (100) [M$^+$ − thp], 209 (30) [M$^+$ − thp − indene]. Anal. Calcd for $C_{28}H_{28}N_2O$ (408.53): C, 82.32; H, 6.90; N, 6.85. Found: C, 81.55; H, 6.92; N, 6.40. IR (KBr; $\tilde{\nu}_{max}$/cm^{-1}): 3065 s, 2948 vs, 1546 s, 1475 vs, 1080 vs, 1040 vs, 1002 vs, 969 s, 769 vs, 716 vs. ^{1}H NMR (CDCl$_3$; δ): 1.56−1.84 (m, 3H, CH$_2$, H-4/H-5-thp), 1.87−1.92 (m, 1H, CH$_2$, H-3-thp), 2.04−2.08 (m, 1H, CH$_2$, H-4-thp), 2.47−2.51 (m, 1H, CH$_2$,, H-3-thp), 3.40 (s, 4H, CH$_2$, H-1-indene), 3.63 (pseudo-t, $^3J = 10.9$ Hz, 1H, CH$_2$, H-6-thp), 4.01 (s, 4H, CH$_2$, pyrazole-CH$_2$-indene), 4.14 (m, 1H, CH$_2$, H-6-thp), 5.32 (dd, $^3J = 10.1/2.4$ Hz, 1H, CH, H-2-thp), 5.93 (s, 1H, CH, H-4-pyrazole), 6.19 (s, 1H, CH, H-2-indene), 6.31 (s, 1H, CH, H-2-indene), 7.22−7.53 (m, 8H, CH, ar-H). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 22.9 (CH$_2$, C-4-thp), 24.4 (CH$_2$, pyrazole-CH$_2$-indene), 24.8 (CH$_2$, C-5-thp), 27.5 (CH$_2$, pyrazole-CH$_2$-indene), 29.7 (CH$_2$, C-3-thp), 37.5 (CH$_2$, C-1-indene), 67.7 (CH$_2$, C-6-thp), 84.3 (CH, C-2-thp), 106.8 (CH, C-4-pyrazole), 119.1, 119.4, 123.5, 123.7, 124.3, 124.8, 125.8, 126.1 (CH, C-ar), 129.5, 130.1 (CH, C-2-indene), 140.6, 141.0, 142.2, 144.3, 144.4, 145.2 (C, C-ar), 150.0 (C, C-3/C-5-pyrazole).

3,5-Bis(inden-3-ylmethyl)-1*H*-pyrazole (H_3L^b). A 1.75 g amount of **3^b** was dissolved in methanol (100 mL). Then, a catalytic amount of *p*-toluenesulfonic acid was added and the solution stirred for 1 h, followed by the addition of 2 mL of water and 3 drops of concentrated hydrochloric acid. After it was stirred overnight, the reaction mixture was neutralized with aqueous ammonia and the solvent removed under reduced pressure. Aqueous sodium bicarbonate was added to the oily residue and extracted with diethyl ether. The organic layer was dried over magnesium sulfate. Removal of the solvent and purification by column chromatography (silica, light petroleum/diethyl ether 1:1, R_f (diethyl ether) = 0.36) yielded 1.05 g (3.2 mol, 75%) of **H_3L^b** as a yellowish solid. Mp: 112 °C. MS (FAB; m/z (%)): 325 (100) [M + H$^+$], 209 (10) [M + H$^+$ − indene]. Anal. Calcd for $C_{23}H_{20}N_2$ (324.42): C, 85.15; H, 6.21; N, 8.63. Found: C, 84.62; H, 6.17; N, 8.57. IR (KBr; $\tilde{\nu}_{max}$/cm^{-1}): 3189 w, 2931 w, 1566 s, 1454 vs, 1079 s, 1039 vs, 1002 vs, 967 s, 768 vs, 715 vs. ^{1}H NMR (CDCl$_3$; δ): 3.38 (s, 4H, CH$_2$, H-1-indene), 3.92 (s, 4H, CH$_2$, pyrazole-CH$_2$-indene), 6.05 (s, 1H, CH, H-4-pyrazole), 6.28 (s, 2H, CH, H-2-indene), 7.18−7.29 (m, 6H, CH, H-ar), 7.48 (d, $^3J = 6.9$ Hz, 2H, CH, H-4-indene). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 25.9 (CH$_2$, pyrazole-CH$_2$-indene), 37.5 (CH$_2$, C-1-indene), 104.1 (CH, C-4-pyrazole), 119.0 (CH, C-ar), 123.5 (CH, C-4-indene), 124.5 (CH, C-ar), 125.8 (CH, C-ar), 129.9 (CH, C-2-indene), 140.9 (C, C-3-indene), 144.3, 144.6 (C, C-3a/C-7a-indene), 146.2 (C, C-3/C-5-pyrazole).

Synthesis of Li_3L^a and Li_3L^b. A solution of 0.5 mmol of either **H_3L^a** or **H_3L^b** in 50 mL of diethyl ether was treated with 0.625 mL (1.56 mmol) of a 2.5 M solution of *n*-butyllithium in hexane at −78 °C. After it was warmed to room temperature and stirred overnight, the reaction mixture was evaporated to dryness and washed with approximately 15 mL of light petroleum. The orange (**Li_3L^a**) or green (**Li_3L^b**) residue was dried under vacuum. Single crystals of $[Li_2L^a(thf)_4][Li(thf)_4]\cdot0.5thf$ were obtained by warming a concentrated thf solution of Li_3L^a in a flame-sealed NMR tube to 70 °C followed by slow cooling to −80 °C.

Li_3L^a. Anal. Calcd for $[Li_2L^a(thf)_4][Li(thf)_4]$, $C_{63}H_{85}N_2Li_2O_8$ (1019.20): C, 74.24; H, 8.41; N, 2.74. Found: C, 74.04; H, 8.15; N, 2.99. UV/vis (thf solution; λ/nm (ϵ/M^{-1} cm^{-1})): 462 (sh, 1760), 488 (2250), 516 (sh, 1700). ^{1}H NMR (thf-d_8; δ): 4.38 (s, 4H, CH$_2$, pyrazole-CH$_2$-fluorene), 5.96 (s, 1H, CH, H-4-pyra-

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zole), 6.43 (pseudo-t, $^3J = 7.6$ Hz, 4H, CH, H-3/H-6-fluorene), 6.81 (pseudo-t, $^3J = 8.0$ Hz, 4H, CH, H-2/H-7-fluorene), 7.31 (d, $^3J = 8.0$ Hz, 4H, CH, H-1/H-8-fluorene), 7.92 (d, $^3J = 7.6$ Hz, 4H, CH, H-4/H-5-fluorene). ^{13}C{^{1}H} NMR (thf-d_8; δ): 26.1 (CH_2, pyrazole-CH_2-fluorene), 89.4 (C, C-9-fluorene), 97.0 (CH, C-4-pyrazole), 108.8 (CH, C-3/C-6-fluorene), 115.3 (CH, C-1/C-8-fluorene), 119.0 (CH, C-4/C-5-fluorene), 119.6 (CH, C-2/C-7-fluorene), 122.7 (C, C-4a/C-4b-fluorene), 136.1 (C, C-8a/C-9a-fluorene), 155.6 (C, C-3/C-5-pyrazole).

Li_3L^b. Several isomers were found. ^{1}H NMR (thf-d_8, 253 K; δ): 4.05, 4.13 (s, 4H, CH_2, pyrazole-CH_2-indene), 5.70, 5.76 (s, 1H, CH, H-4-pyrazole), 5.85 (m, 4H, CH, H-1/H-2-indene), 6.27, 6.40, 7.10, 7.18 (br, CH, H-indene). ^{13}C{^{1}H} NMR (thf-d_8, 253 K; δ): 27.7 (CH_2, pyrazole-CH_2-indene), 90.6, 91.0 (CH, C-1/C-2-indene), 96.6, 97.5 0 (CH, C-4-pyrazole), 102.3, 102.9 0 (C, C-3-indene), 111.1, 111.7, 112.5, 115.1, 115.9, 117.2, 117.5, 118.2, 119.1, (CH, C-indene), 125.2, 127.7 (C, C-3a-indene), 128.9, 130.3 (C, C-7a-indene), 155.5, 156.7 (C, C-3/C-5-pyrazole).

X-ray Crystallography. The measurements were carried out on a Siemens (Nicolet Syntex) R3m/V four-circle diffractometer (H_3L^a) or on a Bruker-AXS-CCD diffractometer ([Li_2L^a(thf)$_4$][Li(thf)$_4$] and [Li_2HL^a(thf)$_5$]) using graphite-monochromated Mo Kα radiation. For H_3L^a the intensities of 3 check reflections (measured every 100 reflections) remained constant throughout the data collection, thus indicating crystal and electronic stability. All calculations were performed using the SHELXTL PLUS software package. Structures were solved by direct methods with SHELXS-97 and refined with the SHELXL-97 program.[23] For H_3L^a an absorption correction (ψ scan, $\Delta\psi = 10°$) was applied to the data. Atomic coordinates and thermal parameters of the non-hydrogen atoms were refined in fully or partially anisotropic models by full-matrix least-squares calculation based on F^2. In general the hydrogen atoms were placed at calculated positions and allowed to ride on the atoms they are attached to. Table 1 compiles the data for the structure determinations.

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Supporting Information Available: Tables of all bond lengths and angles and atomic coordinates and thermal parameters for all structures reported in this paper and temperature-dependent dynamic ^{7}Li NMR spectra of Li_3L^b (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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