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# Notes

## Structural Characterization of [(2,6-$Pr^i_2C_6H_3$)-NC(Me)C(H)C(Me)N(2,6-$Pr^i_2C_6H_3$)K·$PhCH_3$]$_\infty$: A Heavy Alkali Metal Diazapentadienyl Complex

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### Introduction

A recent report highlighted the current interest in early main-group metal coordination chemistry of pentadienyl-type ligands,[1] including those with p-block heteroatoms. The geometry of such ligands is amenable to fine-tuning to give close control of the coordination environment of the metal. This is relevant to the design of homogeneous catalysts[2] and low molecular weight precursors for metal−organic chemical vapor deposition.[3] As an extension to our previous work on lithium diazapentadienyl complexes,[4] we present this preliminary account of our synthetic and structural studies on potassium salts of this versatile ligand class. It describes a simple, two-step reaction from commercially available reagents to the toluene-soluble potassium salt of the [(2,6-$Pr^i_2C_6H_3$)NC(Me)C(H)C(Me)N(2,6-$Pr^i_2C_6H_3$)]$^-$ ion. The salt is a potentially versatile metathesis transfer agent for the synthesis of new metal complexes with this useful bidentate "spectator" ligand, a possible alternative to $C_5Me_5$ and the more recent bulky amidinate anions $[RC(NR')_2]^-$ (R = Me, Ph; R′ = $Me_3Si$) gaining wide use in this capacity.[5] As this Note was being prepared, a further use for the diazapentadienyl ligand class came to light, in the novel nickel and palladium diimine complex-catalyzed polymerization of alkenes.[6]

Though diazapentadienyl complexes (also known as $\beta$-iminoamine complexes or $\beta$-diketiminato complexes) were first reported in 1968,[7] and sporadic reports of structural characterizations have appeared since,[4,8] sustained attention to their structural chemistry is quite recent, notably from Magull[9] and from Lappert and co-workers,[10] who rely on a lithium-mediated nitrile-addition/silyl-migration sequence, reminiscent of previous scandium-[11] and chromium-mediated[12] nitrile-addition/hydrogen-migration reactions as their synthetic entry. That route restricts the nitrogen substituents to be silyl groups and requires the presynthesis of the $(Me_3Si)_2CHLi$ reagent.[13] Potassium salts were prepared by subsequent metathesis with $Bu^tOK$, but the only fully structurally characterized alkali metal salts reported at present remain those of lithium.[4,10] As interest from coordination chemists turns from lithium to the heavier alkali metals in general, we present the results of our direct synthesis of $K^+$[(2,6-$Pr^i_2C_6H_3$)NC(Me)C(H)C(Me)N(2,6-$Pr^i_2C_6H_3$)]$^-$, **1**, by direct metalation, using commercially available $(Me_3Si)_2NK$, of the parent iminoamine ligand 2-(2,6-diisopropylphenyl)aminopent-2-en-4-(2,6-diisopropylphenyl)imine, **2**, prepared by simple condensation.

### Experimental Section

All manipulations were carried out under a protective argon blanket, either in a double-manifold argon/vacuum line or argon-filled recirculating glovebox. Solvents were purified using standard procedures. NMR shifts are quoted relative to TMS and were referenced using peaks from residual protons in the deuterated solvent. Potassium bis(trimethylsilyl)amide was synthesized by metathesis of lithium bis(trimethylsilyl)amide with potassium *tert*-butyl oxide in hexane solvent, and recrystallized from hexane. All other reagents were obtained from standard commercial vendors and used as received. Melting points were recorded in sealed capillaries and are uncorrected.

**Synthesis of 2**. Using a Dean and Stark apparatus, approximately 1.5 mL of $H_2O$ was removed as a toluene azeotrope over 2.5 h from a solution of acetylacetone (15 mL, 0.146 mol), diisopropylaniline (30 mL, 0.159 mol), and *p*-toluenesulfonic acid (ca. 0.1 g) in toluene (150 mL) heated to reflux in a round-bottomed flask. Vacuum distillation yielded 2-(2,6-diisopropylphenyl)aminopent-2-en-4-one (22.23 g, 0.086 mol, 58.7% after recrystallization from hexane based on initial amount of acetylacetone), mp 43−46 °C. Trituration of the residual tar with methanol yielded solid 2-(2,6-diisopropylphenyl)aminopent-2-en-4-(2,6-diisopropylphenyl)imine, **2**, 5.34 g (0.013 mol, 21% based on residual acetyl acetone) after recrystallization from hexane. Where only aminoimine is required, the synthesis may be performed with 2 molar equiv of amine per acetylacetone, giving a yield of 25% of purified **2**; mp from methanol, 142 °C (lit. 142 °C). Satisfactory elemental analyses were obtained, and spectral parameters were consistent with those published. The yield was lower than that in the procedure reported in the Supporting Information of ref 6 but was considered satisfactory given the inexpensiveness of the starting materials and the savings in time over the previously published procedure.

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(1) Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2136.

(2) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

(3) Schulz, D. L.; Hinds, B. J.; Neumayer, D. A.; Stern, C. L.; Marks, T. J. *Chem. Mater.* **1993**, 1605.

(4) Mair, F. S.; Scully, D.; Edwards, A. J.; Raithby, P. R.; Snaith, R. *Polyhedron* **1995**, *14*, 2397.

(5) (a) Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1982. (b) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (c) Edelman, F. T. *Coord. Chem. Ref.* **1994**, *137*, 403.

(6) Feldman, J.; McLaine, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514.

(7) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408.

(8) (a) Healy, P. C.; Bendall, M. R.; Doderell, D. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 727. (b) Filipou, A. C.; Völkl, C.; Rogers, R. D. *J. Organomet. Chem.* **1993**, *463*, 135.

(9) (a) Drees, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 814. (b) Drees, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 984.

(10) (a) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699. (b) Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *500*, 203. (c) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M.; Liu, D.-S.; Severn, J. R.; Shu, T. *An. Quim. Int. Ed.* **1996**, *92*, 186.

(11) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1989**, *8*, 2570.

(12) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868.

(13) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P.; Liu, D.-S.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1386.

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**Table 1.** Crystallographic Data for 1

| | |
|---|---|
| empirical formula | $C_{36}H_{49}N_2K$ |
| fw | 548.87 |
| temp/°C | −113(2) |
| wavelength/Å | 0.710 73 |
| space group | $P2_1/c$ (No. 14) |
| unit cell dimens | |
| *a*/Å | 10.6537(9) |
| *b*/Å | 26.200(2) |
| *c*/Å | 11.9055(10) |
| *β*/deg | 99.137(2) |
| $V$/Å$^3$ | 3280.9(5) |
| *Z* | 4 |
| *D*(calcd)/g cm$^{-3}$ | 1.111 |
| $\mu$/mm$^{-1}$ | 0.0187 |
| $R_1$[a] | 0.0639 |
| $wR_2$[b] | 0.1604 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ (observed reflections). [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (all data).

**Synthesis and Characterization of 1**. Potassium bis(trimethylsilyl)amide (0.449 g, 1.07 mmol) and **2** (0.213 g, 1.07 mmol) were placed in a dry Schlenk tube under an atmosphere of argon. Toluene (7 mL, freshly distilled from sodium benzophenone ketyl) was added to produce a yellow solution. A crop of colorless crystals, mp 320−322 °C, deposited after overnight refrigeration at −15 °C and were isolated by vacuum filtration (0.13 g, 0.285 mmol, 27%). Anal. Calcd for $C_{29}H_{41}N_2K$: C, 76.32; H, 8.99; N, 6.14. Found: C, 77.2; H, 10.3, N, 5.9. The discrepancy is ascribed to the toluene of crystallization, which was only partially removed upon vacuum filtration. IR: shift from 1564.5 to 1622.3 cm$^{-1}$ on exposure to air (C═N str.). $^1$H NMR (200 MHz, benzene-$d_6$): $\delta$ 1.32 (12H, d, $J$ = 6 Hz, *Me*CHMe); 1.52 (12H, d, $J$ = 6 Hz, MeCH*Me*); 2.15 (6H, s, NC*Me*CHC*Me*N); 3.62 (4H, septet, $J$ = 6 Hz, MeC*H*Me); 5.08 (1H, s, NCMeC*H*CMeN); 7.25−7.44 (6H, second-order multiplet, aromatic protons).

**Crystal Structure Determination of 1**. A single crystal of **1** grown from toluene was mounted on a glass fiber in a drop of perfluoropolyether oil and transferred to a goniometer head on a Siemens SMART CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. Diffraction intensities were measured using the $\omega$ rotation method with narrow frames. Data collection and processing parameters are given in Table 1. The structure was solved by direct methods using SHELXS-90[14] and refined on $F^2$ using SHELXL-97[15] with all heavy atoms anisotropic and all hydrogens in calculated positions.

## Results and Discussion

The condensation route employed by Parks and Holm[7] provides access to a wide variety of ligand substituent variations, and in our hands it could be simplified to a rapid one-step procedure quickly yielding both enaminone (the coordination chemistry of which will be reported elsewhere) and iminoamine **2** in acceptable yields. Metalation of **2** using $(Me_3Si)_2NK$ in a toluene solution produced a good yield of **1** as large colorless blocks from a chilled toluene solution. Crystallographic analysis (Table 1) revealed the molecular structure depicted in Figure 1. Most notable is the essentially monomeric nature of the material, polymerized only by a single $\eta^5$ contact to a 2,6-diisopropylphenyl group of a neighboring monomer. This fact underlines the potential of this diazapentadienyl ligand as a bulky spectator ligand, offering control of the coordination environment of the metal to an extent that challenges substituted cyclopentadienyls, most of which so far crystallized as potassium salts having done so as Lewis base solvates, and even in the presence of such ancillary donors, often still having more than one cation contacting that part of the ligand bearing the negative charge.[16] There are however, some isolated examples of donor-free potassium cyclopentadienyls.[16d] Though the crystal of **1** was a toluene solvate, in this instance the toluene remained uncoordinated (see Figure 2). The $\eta^5$ interaction which generates the pseudo one-dimensional zigzag polymeric structure presumably is replaced by toluene solvation when crystals of **1** are dissolved. It is noteworthy how frequently a potassium ion is found with solvation from aryl rings. In fact, this type of solvation has recently been suggested to have great importance in biochemistry, where the selectivity of potassium ion channels has in part been ascribed to the fact that arene solvation is most competitive with aqueous solvation for potassium of all the alkali

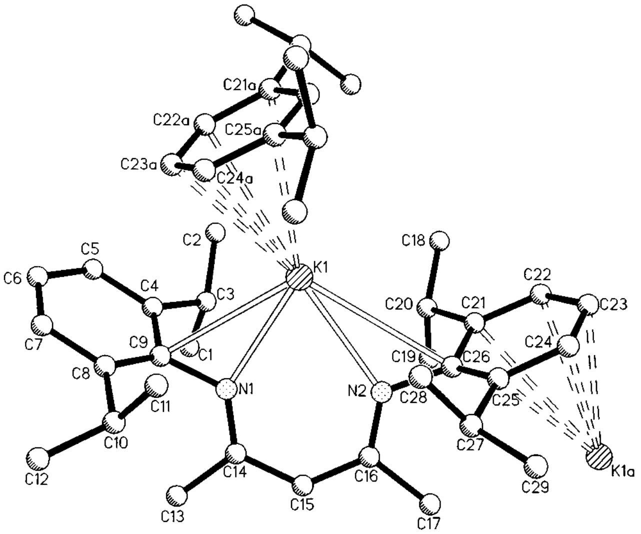

**Figure 1.** Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): K(1)−N(1) = 2.6387(19), K(1)−N(2) = 2.7398(19), K(1)−C(26) = 3.369(2), K(1)−C(9) = 3.135(2), K(1)−C(21a) = 3.538(2), K(1)−C(22a) = 3.351(3), K(1)−C(23a) = 3.214(3), K(1)−C(24a) = 3.276(3), K(1)−C(25a) = 3.459(2), N(1)−C(14) = 1.317(3); N(2)−C(16) = 1.323(3); C(14)−C(15) = 1.414(3), C(15)−C(16) = 1.400(3), N(1)−C(9) = 1.412(3), N(2)−C(26) = 1.406(3); N(1)−K(1)−N(2) = 66.01(6), K(1)−N(1)−C(14) = 141.28(15); K(1)−N(1)−C(9) = 96.73(12), C(9)−N(1)−C(14) = 121.76(19), K(1)−N(2)−C(16) = 135.78(15), K(1)−N(2)−C(26) = 104.08(13), C(16)−N(2)−C(26) = 120.11(19), N(1)−C(14)−C(15) = 122.4(2), C(14)−C15)−C(16) = 129.3(2), C(15)−C(16)−N(2) = 124.9(2).

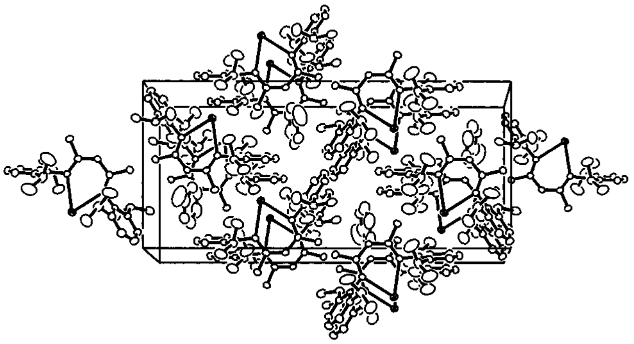

**Figure 2.** Unit cell contents of **1** viewed normal to the [100] plane. Hydrogen atoms omitted for clarity.

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(14) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(15) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(16) (a) Schaefer, W. P.; Cotter, W. D.; Bercaw, J. D. *Acta Crystallogr., Sect. C* **1993**, *49*, 1489. (b) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11. (c) Lorberth, J.; Shin, S.-H.; Mocadlo, S.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735.

metals.[17] In particular, the $\eta^5$ coordination of a 2,6-diisopropylphenyl ring has precedent in the pseudo two-dimensional polymeric structure of K[La(O-2,6-$Pr^i_2C_6H_3)_4$] (**3**), where the average K−C distance for the $\eta^5$-contacted ring was 3.332(9) Å.[18] In **1**, the average is at 3.368(9) Å, only slightly longer than the $\eta^5$-ring in **3**, but significantly longer than another $\eta^6$-contacted 2,6-diisopropylphenyl ring in the same two-dimensional polymer **3**, where the average K−C distance was 3.199(35) Å, the shortest such mean distance yet found for a six-membered ring coordinating to potassium.[18] Furthermore, the precise manner of $\eta^5$ contact in **1** and in **3** is different. In **3**, one of the carbons lying ortho to the phenoxide oxygen is deemed unbonded [K−C = 3.562(3) Å], whereas in **1** it is the ipso carbon itself which lies farthest from potassium [K(1)−C(26a) = 3.557(3) Å]. This is perhaps due to the fact that the same carbon seems to be engaging in an intramolecular bonding contact [K(1)−C(26) = 3.369(2) Å ] on the opposite face of the aryl ring, a contact which is even shorter to the non-multihapto phenyl group on the other side of the molecule [K(1)−C(9) = 3.135(2) Å]. Consequently, the diazapentadienyl ligand in **1** behaves as a *C,N,C,N*-$\eta^4$ ligand within a monomer. Without doubt, the strongest of these interactions are the K−N dative bonds [2.639(2) and 2.740(2) Å], their existence being the reason for the weaker intermolecular contacts in **1** relative to **3**, where the only bonding contacts to potassium are from aryl groups. These K−N distances are quite short (median from 1913 cases in the Cambridge Crystallographic Database = 2.816 Å), though a similar distance of 2.745(4) Å was observed in the shortest K−N contact in a benzotriazolepotassium−hexamethylphosphoric triamide complex.[19] Their asymmetry is not reflected in the C−C and C−N distances within the anion ring, which are indicative of full delocalization. In this respect **1** is compatible with its light-metal analogue [{PhN(CH)$_3$NPh}Li·OP(NMe$_2$)$_3$]$_2$, in which each nitrogen atom engages in terminal bonding to one lithium ion, two of which are bridged by the phosphine oxide ligand.[4] In the only other structurally characterized alkali metal diazapentadienyl complex known, [{Me$_3$SiNC(Ph)C(H)C(Bu$^t$)NSiMe$_3$}Li]$_2$, the dimerization occurs via bridging nitrogens, and this in turn seems to partially localize charge on the bridging atom as judged by relative bond lengths within the metallacycle.[10]

Turning to the structural details of the KNCCCN ring itself, it is notable that metallacycle is almost fully planar (rms deviation = 0.0201(2) Å), showing no sign of $\eta^5$ behavior of the NCCCN diazapentadienyl fragment. This is in stark contrast to the related 2,4-dimethylpentadienylpotassium tetramethylethylenediamine complex in which each side of the delocalized anionic ring is closely $\eta^5$-bound to potassium ions.[20] It is in further contrast to recently characterized diazapentadienyl complexes of other metals, e.g. [{Me$_3$SiNC(Ph)C(H)C(Bu$^t$)NSiMe$_3$}ZrCl$_3$],[10] and related Sm, Gd, Ce, Nd, U, and Th complexes[9b,10,21] in which angles of approximately 100° are made between the NCCCN plane and the NMN plane. Similarly significant $\eta^5$ binding has been seen in {Me$_3$SiNC(Ph)C(H)C(Ph)NSiMe$_3$}SnClMe$_2$,[10] though the fact that the removal of the bulky silyl groups from nitrogen resulted in ring-flattening supports our computational arguments[4] that such distortions are sterically promoted. Where both substituents on nitrogen are aromatic, the metallacyles are never far from planarity,[8a,9a,c] with the exception of [PhN(CH)$_3$NPhLi·OP(NMe$_2$)$_3$]$_2$, where the slight distortion was ascribed to packing effects from the bulky hexamethylphosphoramide ligands.[4] Further apparent exceptions to this trend appeared in the very recent paper[6] on nickel and palladium complexes of ligand **2**, which had boat conformations, but in these cases the ligand was bound as a neutral, C-protonated (or palladated) fragment and so are not directly comparable.

It remains slightly puzzling, however, that a metal ion with such a pronounced tendency for polymerization via multihapto $\pi$ interaction and ionic bonding[22] prefers to do this via a neutral aryl group over an anionic diazapentadienyl group. It is perhaps the diisopropylamino substitution of the phenyl groups which prevents this (note here the contrast with solvent-free substituted cyclopentadienyls: in those cases the anionic centers are coordinated to more than one metal, unlike the situation in **1**). The effectiveness of encapsulation that this ligand topology offers promises rich rewards in wide areas of chemistry. Indeed, silyl-subsituted variants have already shown their effectiveness in Ziegler−Natta chemistry,[23] and nickel and palladium complexes have very recently shown effectiveness in ethene polymerization also.[6] We are pursuing the synthesis of further sterically encapsulated metal ion complexes from our starting material, and also are examining its reactivity with carbon electrophiles, in the search for highly substituted neutral $\beta$-diimines for the aforementioned[6] Ni-catalyzed polymerization regime.

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**Supporting Information Available:** An X-ray crystallographic file for **1**, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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[17] (a) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708. (b) Dougherty, D. A. *Science* **1996**, *271*, 163.

[18] Clark. D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903.

[19] Andrews, P. C.; Clegg, W.; Mulvey, R. E.; O'Neil, P. A.; Wilson, H. M. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1142.

[20] Gong, L.; Hu, N.; Jin, Z.; Cheng, W. *J. Organomet. Chem.* **1988**, *352*, 67.

[21] Hitchcock, P. B.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Dalton Trans.* **1997**, 1945.

[22] Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

[23] Lappert, M. F.; Liu, D.-S. Netherlands Pat. PCT/NL 95.00202.